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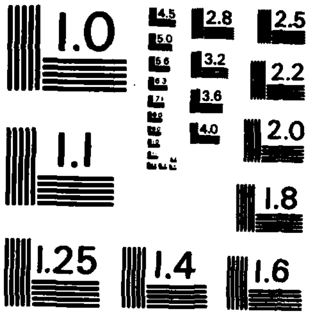

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Synthesis and Properties of Hexachloromolybdates(V) and Related Species

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20. Abstract The general objective of this research program was to prepare complexes of the general type $A[MoCl_6]$ (A = monopositive cation), for use as cathode materials in chemical batteries with the specific aim of developing techniques for large scale preparation of the lithium and sodium salts. The various complexes were studied by a wide range of spectrochemical and electrochemical techniques such as epr, ir, Raman and solution electronic absorption spectroscopy and cyclic voltametry. The work and results have been closely evaluated with personnel at the USAF FJ Seiler Research Laboratories. 84 03 28 076	

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This report has been reviewed by the EOARD Information Office and is releasable to the National Technical Information Service (NTIS). At NTIS it will be releasable to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

JOHN C. GOWAN
Major, USAF
Chief, Materials & Chemistry

FOR THE COMMANDER

JERRY R. BETTIS
Lt Colonel, USAF
Deputy Commander

INTRODUCTION

As the predominant concern of this report is chloromolybdenum complexes, this chapter briefly details the relevant chemistry of these systems.

1.1 MOLYBDENUM(VI) OXOCHLORIDES

Molybdenum(VI) forms two oxohalides $[MoOCl_4]$ and $[MoO_2Cl_2]$. The oxotetrachloride is most conveniently prepared by heating thionyl chloride with molybdenum(VI) oxide under reflux and isolating the solid product by evaporation of solvent [1]. Purification is by vacuum sublimation. $[MoOCl_4]$ forms green crystals which appear red in thin films. It is hydrolysed rapidly in moist air to molybdate(VI). It has a high solubility in dry chlorinated organic solvents. $[MoOCl_4]$ melts at 102 $^{\circ}$C and boils at 159 $^{\circ}$C to give a dense brown monomeric vapour.

$[MoOCl_4]$ dissolves in concentrated hydrochloric acid to give the $[MoOCl_5]^{2-}$. Infrared studies have been made in tetrachloromethane and thionyl chloride solution.

Molybdenum(VI) dioxide dichloride, MoO_2Cl_2, may be prepared by a number of methods involving chlorine-oxygen mixtures on molybdenum metal or molybdenum(IV) sulphide, or by reaction of molybdenum(V) chloride with molybdenum(VI) oxide, or by chlorine on molybdenum(VI) oxide, either by direct heating or in flow systems.

MoO_2Cl_2 is a white crystalline solid, volatile and very sensitive to moisture, although it is stable in solutions of concentrated hydrochloric acid. It is soluble in many organic solvents.

Studies reveal MoO_2Cl_2 to crystallise in an orthorhombic lattice, and infrared studies show an absence of molybdenum-oxygen double bonds: the proposed structure is shown in Figure 1.1.

It is thought that in solution it may exist as dimers although in the vapour it is predominantly monomeric [2].

1.2 MOLYBDENUM(VI) CHLORIDE COMPLEXES

Molybdenum(VI) oxide dissolves in aqueous hydrochloric acid to give oxochloride anions. In 12 <u>M</u> acid, the $[MoO_2Cl_4]^{2-}$ ion predominates, but in 6 <u>M</u> acid a species formulated as $[MoO_2Cl_2(H_2O)_2]$ is thought to be the main one [3]. A series of salts of the dioxotetrachloromolybdate(VI)

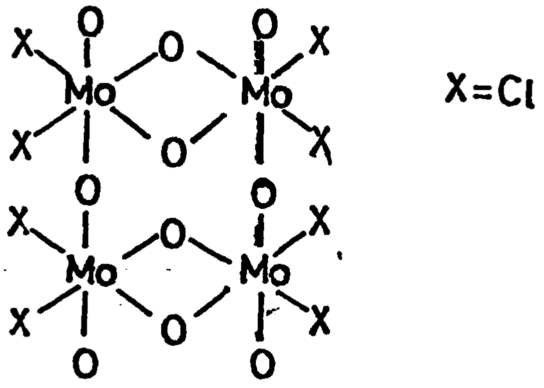


Fig 1.1 The Structure of MoO_2Cl_2

anion has been prepared, and also some examples of the oxoperoxotetrachloromolybdate(VI) anion, $[MoO(O_2)Cl_4]$ are known. These salts are yellow in colour, but are rapidly hydrolysed by water. Spectral properties of Mo(VI) solutions have been studied by Wendling [4].

There is a claim of $[MoCl_6]$, which is discussed in detail later in this report.

1.3 MOLYBDENUM(V) OXYCHLORIDES AND CHLORIDES

1.3.1 Molybdenum(V) oxide trichloride

$MoOCl_3$ is prepared by reaction of MoO_3 and $[Mo_2Cl_{10}]$ or reduction of $[MoOCl_4]$ in chlorobenzene at reflux. The slow reaction of $[Mo_2Cl_{10}]$ in liquid SO_2 or $SOCl_2$ in a sealed tube also produces $MoOCl_3$ [5].

It is a black crystalline solid, instantly hydrolysed in the presence of moisture; in HCl solution, the oxopentachloromolybdate(V) anion, $[MoOCl_5]^{2-}$, is formed. $MoOCl_3$ is isostructural with $NbOCl_3$ (Fig. 1.2).

$MoOCl_3$ is thermally unstable and disproportionates at 215 $^{\circ}C$ according to

$$3MoOCl_3 \longrightarrow MoCl_3 + MoOCl_4 + MoO_2Cl_2$$

It forms many adducts with donor molecules.

1.3.2 Molybdenum(V) chloride

$[Mo_2Cl_{10}]$ is prepared by the direct chlorination of the metal at

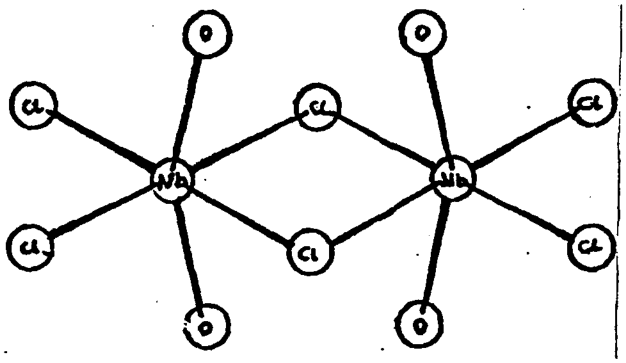


Fig 1.2 The Structure of $NbOCl_3$

400°C. $[MoOCl_4]$ is produced as an impurity, and may be removed by vacuum sublimation at a temperature below the melting point of $[Mo_2Cl_{10}]$.

$[Mo_2Cl_{10}]$ is black, shiny, crystalline compound which melts at 194.4 °C. The vapour is reddish-brown. It is slowly oxidised in air, but rapidly hydrolysed by the presence of moisture. It has a marked solubility in benzene and the more polar organic solvents, especially chlorinated ones. It shows a marked propensity for the extraction of oxygen from oxygenated solvents to form oxo-species and occupies a central rôle in in synthesis of molybdenum complexes (Figs. 1.3 and 1.4).

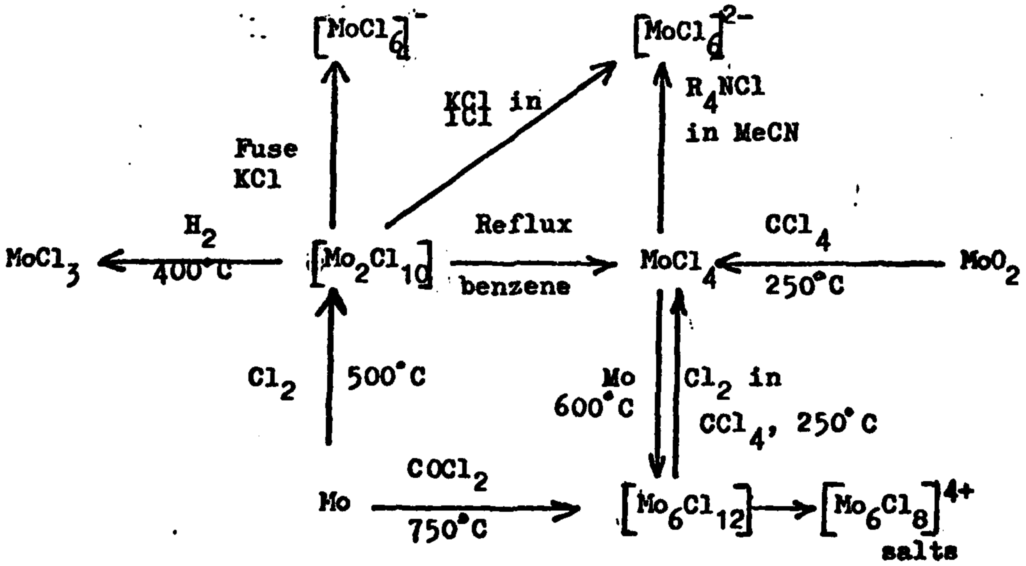


Fig 1.3 Synthesis of molybdenum chlorides

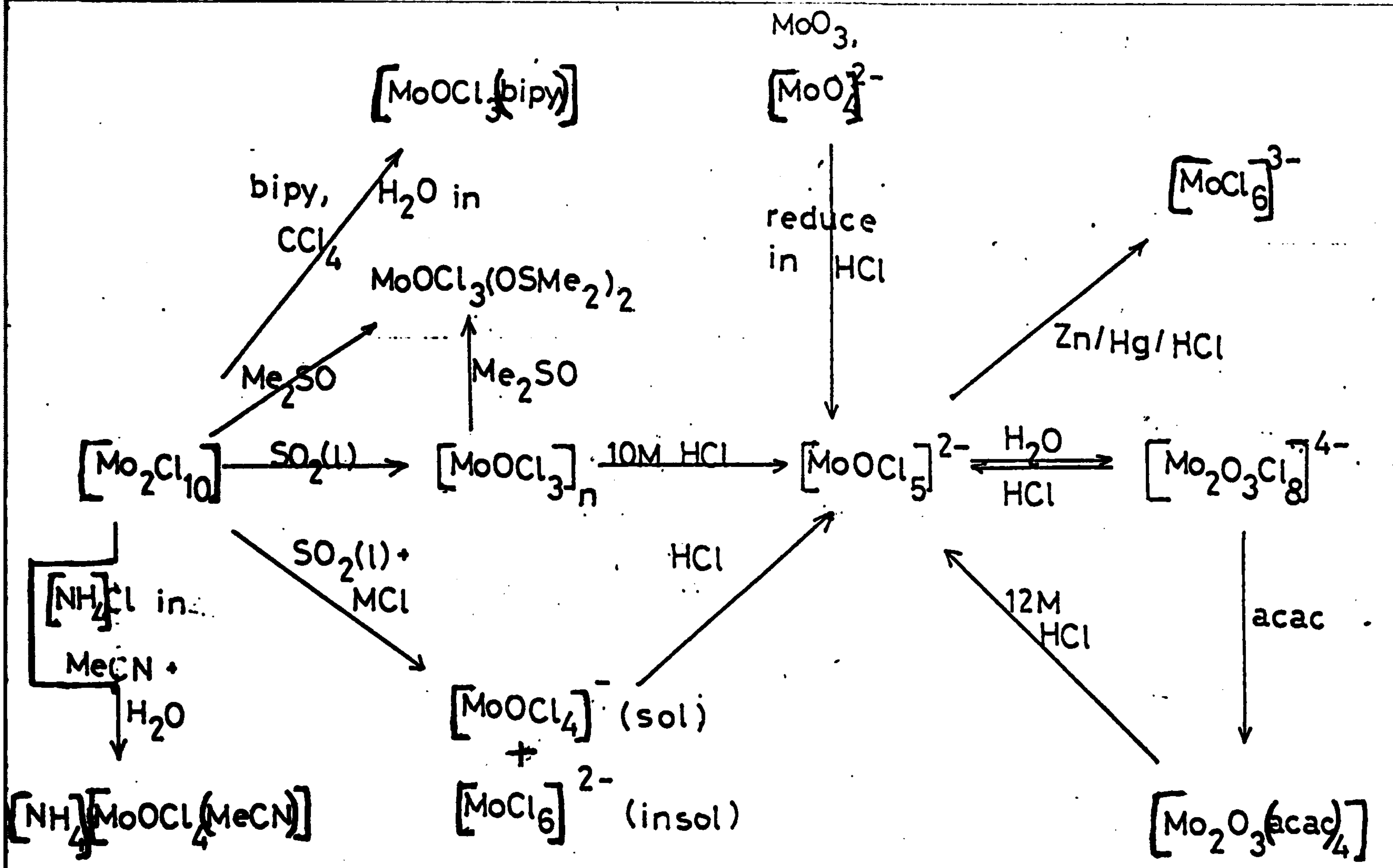


Fig. 1.4 Synthesis of oxochloromolybdenum complexes

In the vapour it is monomeric, exhibiting a trigonal bipyramidal structure, but in the crystal, chlorine-bridged dimers are formed so that each molybdenum atom is six coordinate. Magnetic studies indicate negligible coupling of electron spins on the two molybdenum atoms.

1.4 MOLYBDENUM(V) CHLORIDE AND OXOCHLORIDE COMPLEXES

1.4.1 Hexachloromolybdates(V)

The only well substantiated preparation of hexachloromolybdate(V) compounds is by reaction of tetraethylammonium or tetraphenylarsonium chloride with molybdenum(V) chloride in dichloromethane in a sealed tube at 70 °C [6].

The salts are black crystalline solids, soluble in the more polar organic solvents (e.g. dichloromethane or ethanenitrile) and have conductivities typical of 1:1 electrolytes in ethanenitrile.

Horner and Tyree [7] have reported the presence of the $[MoCl_6]^-$ ion in solidified KCl-$MoCl_5$ melts, but later studies [8] could not confirm their results.

The salts are highly moisture sensitive, and are rapidly hydrolysed to a yellow compound on exposure to air.

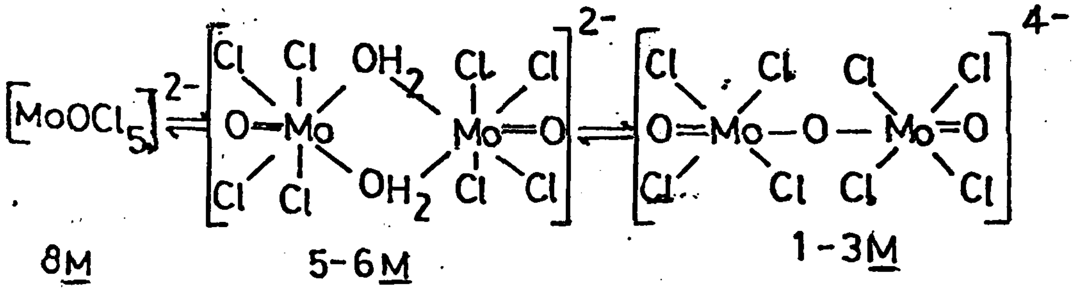
1.4.2 Oxochloromolybdates(V)

There are two oxochlorocomplexes of molybdenum(V), the oxopentachloromolybdate(V), $[MoOCl_5]^{2-}$ anion, and the oxotetrachloromolybdate(V), $[MoOCl_4]^-$ anion.

The $[MoOCl_5]^{2-}$ species is the stable form of molybdenum(V) in chloride media. There are two methods of preparing this anion; by reduction of molybdenum(VI) species (either chemically [9], or electrolytically [10]), or by mixture of solutions of molybdenum(V) chloride and an alkali-metal chloride in hydrochloric acid solution [11]. The second method allows for the preparation of organic salts if an amine hydrochloride is used in place of the metal chloride. The products are filtered under dinitrogen and washed with ether thionyl mixtures (9:1), and then with dry ether. The salts are emerald green in colour and stable for long periods in dry air. The caesium salt, $Cs_2[MoOCl_5]$, has been reported [12] as cubic with the $K_2[PtCl_6]$ structure, but the rubidium and ammonium salts are rhombohedral [13].

Much interest has been centered on the behaviour of molybdenum(V) in solutions of varying HCl concentration. In concentrated acid (8 M HCl) the solutions are green and are assumed to contain the monomeric species $[MoOCl_5]^{2-}$. In less concentrated acid solution (5-6 M HCl) the solution darkens, becomes opaque and the magnetic susceptibility of the molybdenum species in solution decreases. Finally, the colour of the solution turns to dark red-brown and the magnetic susceptibility falls to zero in acid concentrations less that 3 M. Haight [14] studied this phenomenon spectrophotometrically and concluded that two dimers were present in the system. An EPR study by Hare and co-workers [15] confirmed that a paramagnetic species exists at the 5-6 M HCl concentration, whilst a diamagnetic species is formed at low acidities.

A diamagnetic salt, $Cs_4[Mo_2O_3Cl_8]$ was isolated [16], with spectral properties identical to those of solutions studied by Haight in 1 M acid. It now appears that the species present are



Oxotetrachloromolybdate(IV) compounds, $A[MoOCl_4]$ may be prepared by the reaction of molybdenum(V) chloride and an alkali-metal chloride or amine hydrochloride in liquid SO_2 in sealed ampoules [11]. When RbCl and CsCl are used, the hexachloromolybdate(IV) salts are precipitated. The reaction scheme is thought to be

$$(1)\quad MoCl_5 + SO_2 \longrightarrow MoOCl_3 + SOCl_2$$
$$MoOCl_3 + Cl^- \longrightarrow [MoOCl_4]^-$$
$$(2)\quad MoCl_5 + 2Cl^- \longrightarrow [MoCl_6]^{2-} + \tfrac{1}{2}Cl_2$$

where (1) is the solvolytic reaction and (2) the competing redox reaction. A possible explanation of this effect assumes that the insolubility of rubidium and caesium salts in liquid SO_2 is a contributing factor.

Pyridium and quinolinium salts have been prepared by the reaction

$$M'_2[MoOCl_5] \xrightarrow{SO_2} M'Cl + M'[MoOCl_4]$$

Decomposition takes place over several days.

The salts of the $[MoOCl_4]^-$ ion are also green and relatively stable in dry air.

Piovesana and Furlani [17] report that the formation of $[MoOCl_5]^{2-}$ or $[MoOCl_4]^-$ salts depends strongly on the nature of the cation rather than the preparatory method. Large organic cations invariably precipitated $A[MoOCl_4]$ species { such as $A=[(C_4H_9)_4N]$, $[(CH_3)_4N]$ or $[(C_6H_5)_4As]$ } even from different preparative methods:

(1) $MoCl_5$ + MCl in conc. HCl after saturation with gaseous HCl

(2) by electrolytic reduction of MoO_3 in HCl in presence of MCl

(3) by oxidation of $A_3[MoCl_6]$ in CH_3OH.

The last method involves spontaneous quantitative oxidation of $A_3[MoCl_6]$ to $[MoOCl_4]$ even at room-temperature.

1.5 MOLYBDENUM(IV) CHLORIDES

$MoCl_4$ is prepared by reaction of $MoCl_3$ and a slight excess of Mo_2Cl_{10} in a sealed tube at 250 °C. It is very sensitive to oxidation and hydrolysis, and exists in two forms. The α-form may be prepared by the reaction:

$$MoCl_5 + C_2Cl_4 \longrightarrow \alpha\text{-}MoCl_4$$

α-$MoCl_4$ is isomorphous with $NbCl_4$.

Heating the α-form with $MoCl_5$ produces the β-form of $MoCl_4$. The α-form has partial spin pairing through Mo-Mo interactions, whereas the β-form has no Mo-Mo bond.

1.6 MOLYBDENUM(IV) CHLORIDE COMPLEXES

1.6.1 Hexachloromolybdates(IV)

The hexachloromolybdates(IV) are generally prepared either by reaction of alkali-metal chloride and molybdenum(V) chloride in the melt [8] or by reaction in liquid SO_2 in the case of rubidium and caesium [11].

A particularly useful synthesis of this anion is afforded by reaction of MCl and [Mo_2Cl_{10}] in a sealed tube at 150 °C in the presence of iodine monochloride solution (three-fold excess) for three days (where M = K, Rb, or Cs) [19].

A useful reaction for the preparation of organic salts of the anion is provided by an amine hydrochloride and tetrachlorodi(butanenitrile)-molybdenum(IV) in trichloromethane.[11]

$$[MoCl_4(PrCN)_2] + 2\ [AH]Cl \longrightarrow AH_2[MoCl_6] + 2PrCN$$

Prepared salts include those of $[C_5H_5NH]^+$, $[C_9H_9NH]^+$ and $[(C_2H_5)_2NH_2]^+$. Tetrachlorodi(butanenitrile)molybdenum(IV) is readily prepared by reaction of $Mo_2Cl_{10}]$ with PrCN.

Horner and Tyree reported [7] the preparation of the solvated tetramethylammonium salt;

$$[Me_4N]Cl + MoCl_5 \xrightarrow{MeCN} [Me_4N]_2[MoCl_6].0.5MeCN$$

It has been shown that MeCN reduces $[Mo_2Cl_{10}]$ to $[MoCl_4(MeCN)_2]$, so it is this adduct which reacts.

The caesium salt has also been prepared by reduction of molybdenum(V) chloride with red phosphorus [20] according to the reaction:

$$P + 6CsCl + 3MoCl_5 \longrightarrow PCl_3 + 3Cs_2[MoCl_6]$$

by grinding and heating the reactants to 200 °C for several days.

The alkali-metal salts are dark to olive-green, whilst the organic salts are bright yellow in colour. They are extremely sensitive to moisture and dissolve in water or aqueous acids with decomposition, although they are less readily hydrolysed than the oxochloride complexes of the $[MoOCl_4]^-$ ion.

The salts crystallise in the cubic system, with a $K_2[PtCl_6]$ structure.

In liquid ammonia, the complex $[MoCl_6]^{2-}$ disproportionates and salts of the $[Mo_2Cl_9]^{3-}$ ion are precipitated [19].

1.7 MOLYBDENUM(III) CHLORIDES

Molybdenum(III) chloride is prepared by dihydrogen reduction of $MoCl_5$ in a bomb at 125 °C. One polymorph forms a stratified lattice with layers parallel to the (001) plane. It crystallises in the monoclinic system: this form is diamagnetic.

The form obtained by thermal decomposition of $[Mo_2Cl_{10}]$ is paramagnetic, and is proposed to contain trinuclear clusters of molybdenum atoms.

1.8 MOLYBDENUM(III) CHLORIDE AND OXOCHLORIDE COMPLEXES

Salts of these anions are generally prepared by electrolytic reduction of hydrochloric acid solutions of MoO_3 [21]. The colourless solutions become red upon electrolysis and then a solution of MCl is added and HCl gas passed into the solution. The red $A_3[MoCl_5(H_2O)]$ salt precipitates. The filtrate of the solution is collected and treated with ethanol and the $A_3[MoCl_6]$ salt is precipitated. The ammonium, rubidium and caesium salts may also be prepared [22] by mixing solutions of tetrakis(ethanoato)dimolybdenum and the appropriate cation chloride in 12 M HCl and heating to evaporate solvent. Finally, when the concentrated solution is placed in an ice-bath for at least 6 hours, the aquapentachloromolybdate(III) salt precipitates. The $[MoCl_5(H_2O)]^{2-}$ salt is then dissolved with heating in 12 M HCl, and cation chloride is added. Gaseous hydrogen chloride is passed into the solution, and ethanol is added. When this solution is saturated with HCl and cooled in an ice-bath $A_3[MoCl_6]$ is precipitated.

$$[Mo_2(O_2CCH_3)_4] + HCl(aq) + O_2 \longrightarrow [MoCl_5(H_2O)]^{2-} + [MoCl_6]^{3-}$$

The salts are brick-red to pink, the pentachloro- salts being the darker. The salts are stable indefinitely in air, but undergo hydrolysis and oxidation in water, the red colour fades and colloidal substances are formed.

There have been many studies on the hydrolysis of the hexachloro-salts [23-25]. Kinetic studies by Andruchow and DeLiddo[26] reveal that aquation of this ion occurs rapidly even in 6 M HCl and that the $[MoCl_6]^{3-}$ ion is really only stable in acid concentrations greater than 9 M.

The first aquation step:

$$[MoCl_6]^{3-} + H_2O \longrightarrow [MoCl_5(H_2O)]^{2-} + Cl^-$$

occurs readily, but the second:

$$[MoCl_5(H_2O)]^{2-} + H_2O \longrightarrow [MoCl_4(H_2O)_2]^- + Cl^-$$

is slow at 0 °C.

Nyholm et al. [27] state that if the molybdenum concentration is high, in hydrochloric acid, then salts of the binuclear complex $[Mo_2Cl_9]^{3-}$

may be isolated. The binuclear species is not particularly stable, and dilution with acid produces the mononuclear species.

The caesium, methylammonium and tetraethylammonium salts of the $[Mo_2Cl_9]^{3-}$ ion have been isolated. Molybdenum(III) solution is produced from electrolytic reduction of Mo(VI) species in hydrochloric acid. The solution is evaporated to near dryness and then a solution of CsCl in HCl is added, producing a pink precipitate. The salts are all dark pink or red and are stable in air. Organic salts are made by treatment of the Mo(III) solution with amine hydrochloride and are soluble in dmf, dmso and pyridine. The ion has the same structure as that of $[W_2Cl_9]^{3-}$, that of two confacial octahedra, with a weak Mo-Mo bond.

Delphin and Wentworth [28] have prepared the $[Mo_2Cl_9]^{3-}$ and the $[Mo_2Cl_9]^{2-}$ ions in an elegant procedure using hexachloromolybdate species. $[MoCl_6]^{\underline{n}-}$ ($\underline{n}$ = 0, 1 or 2) ions can serve as easily reduced tridentate ligands which can displace CO ligands on the trigonal face of a metal carbonyl halide.

The following preparations have been carried out:

$$[MoCl_6]^{2-} + [Mo(CO)_4Cl_3]^{-} \longrightarrow [Mo_2Cl_9]^{3-} + 4CO$$

$$[MoCl_6]^{-} + [Mo(CO)_4Cl_3]^{-} \longrightarrow [Mo_2Cl_9]^{2-} + 4CO$$

The $[Mo_2Cl_9]^{2-}$ salt reacts with most donor solvents; it is instantly reduced to $[Mo_2Cl_9]^{3-}$ in ethanenitrile.

1.9 MOLYBDENUM(II) CHLORIDE CLUSTER COMPOUNDS

Molybdenum(II) chloride may be prepared by passing carbonyl chloride, $COCl_2$, over the metal at 600 °C.

All the molybdenum chloro- cluster compounds consist of the $[Mo_6Cl_8]^{4+}$ hexameric unit, containing an octahedron of molybdenum atoms with chloride atoms situated above each face of the metal octahedron. There is one octahedral coordination site vacant and available for additional ligand coordination on each metal atom.

Molybdenum(II) chloride is soluble in HCl, and a number of derivatives of $[Mo_6Cl_8]^{4+}$ have been prepared. The anion $[(Mo_6Cl_8)Cl_6]^{2-}$ can be isolated from the solutions of $[Mo_6Cl_{12}]$ in HCl. All derivatives show only six ligands coordinated to the $[Mo_6Cl_8]^{4+}$ unit.

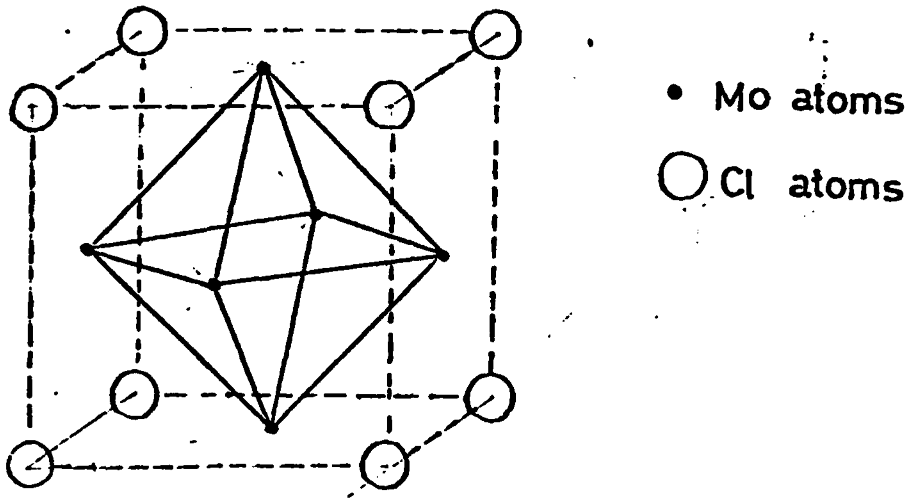


Fig 1.5 The Structure of the $[Mo_6Cl_8]^{4+}$ Unit

1.10 IONIC LIQUIDS

The background and development of room temperature ionic liquids is well-known to the U.S.A.F., much of the important work having been performed by Capt. L. Vaughn, Dr. J. S. Wilkes and Prof. C. L. Hussey at the Frank J. Seilar Laboratories, Colorado. For this reason, no further discussion of this extremely important area is included here. It is pertinent to note that the contents of this report have been communicated to Seilar, in significantly more detail, in two units: the first part in July, 1981, the second part in July, 1982. Collaborative work with Seilar is continuing.

2.1. PURIFICATION OF SOLIDS

2.1.1 Molybdenum(V) Chloride

Commercial molybdenum(V) chloride (ex Aldrich) contains a small quantity of molybdenum oxotetrachloride, $MoOCl_4$, and was used as supplied for chemical reactions. For spectroscopic measurements commercial molybdenum(V) chloride was purified by fractional sublimation *in vacuo*. The impurity oxotetrachloride was removed at 70 °C by sublimation.

2.1.2 Tetraethylammonium Chloride and Tetraphenylarsonium Chloride

Anhydrous tetraethylammonium chloride was prepared from commercial tetraethylammonium chloride monohydrate (ex Aldrich) by continuous evacuation at 110 °C for 24 hours. Similarly anhydrous tetraphenylarsonium chloride was prepared by continuous evacuation of the monohydrate (ex Aldrich) at 100 °C.

2.1.3 Tetrakis(ethanoato)dimolybdenum(II)

Hexacarbonylmolybdenum(0) (10g) was heated at reflux for twenty hours with ethanoic acid ($550cm^3$) containing 10% by volume of ethanoic anhydride. The solvent had previously been deoxygenated by heating at reflux in a dinitrogen atmosphere for fifteen minutes. Yellow crystals were formed as the reaction mixture cooled. These were separated from the supernatant liquid and washed with two portions of absolute ethanol ($100cm^3$) and then with two portions of diethyl ether ($50cm^3$). The pure crystals were dried *in vacuo* and stored under a dinitrogen atmosphere.

2.1.4 Other Solids

K_3MoCl_6 (*ex* Climax Molybdenum Co.) $[NH_4]_2[MoO_4]$(*ex* Aldrich Gold Label), aluminium metal (*ex* Harringtons), sodium chloride (*ex* BDH), $CoCl_2.6H_2O$ (*ex* Fisons), $NiCl_2.6H_2O$ (*ex* Harringtons), $CuCl_2.2H_2O$ (*ex* BDH), $FeCl_3.6H_2O$ (*ex* Harringtons), anhydrous chromium(III) chloride (*ex* Alfa Products), $CrCl_3.6H_2O$ (*ex* BDH), $MnCl_2.4H_2O$ (*ex* BDH), $FeCl_2.6H_2O$ (*ex* East Anglia Chemicals), vanadium(V) oxide (*ex* BDH), tetraethylammonium chloride hydrate (*ex* Aldrich), tetraphenylarsonium chloride (*ex* Aldrich), potassium chloride (*ex* BDH) and ammonium chloride (*ex* Fisons) were used without further purification.

Pyridinium chloride was prepared as follows:

Hydrogen chloride gas was passed into a flask containing pyridine ($80cm^3$) and ethoxyethane ($100cm^3$) until hydrogen chloride was seen to be escaping from the top of the flask. The off-white solid was collected and washed with ethoxyethane, and the product dried in vacuo for 24 h.

2.2 PURIFICATION OF LIQUIDS

Sulphur monochloride (ex BDH), ethanol (ex Burroughs), dichloromethane (ex Aldrich), 1-chlorobutane (ex Aldrich), hydrochloric acid (ex East Anglia Chemicals) and concentrated ammonia (ex East Anglia Chemicals) were used without further purification.

The following solvents were dried as indicated:

Pyridine (ex BDH) dried over P_2O_5
Ethanenitrile (ex BDH) dried over P_2O_5
Ethyl Ethanoate (ex BDH) dried over K_2CO_3
Dichloromethane (ex BDH) dried over P_2O_5
1-Chlorobutane and thionyl chloride were used as supplied.

Thionyl chloride (ex Aldrich) was freshly distilled in an all glass standard distillation apparatus before use.

Benzene (ex East Anglia Chemicals) and carbon disulphide (ex BDH) were dried by heating under reflux with calcium hydride (ex BDH) for at least 24 h.

Ethoxyethane (ex East Anglia Chemicals) was dried by prolonged contact with sodium wire.

The following routine was used for drying MeCN and CH_2Cl_2 for spectroscopic studies:

Dichloromethane (ex Aldrich Gold Label) or ethanenitrile were heated under reflux over calcium hydride for two days and then collected into a flask containing phosphorous pentoxide. The solvent was then triply distilled from phosphorus pentoxide in vacuo and then transferred in a sealed apparatus to the dry-box, where it was stored in dark glass bottle over Linde 4A molecular sieves.

2.3 PURIFICATION OF GASES

Dinitrogen (ex BOC 'white spot' containing only 1 ppm dioxygen) was dried by passage through a silica gel column and a column containing phosphorus (V) oxide suspended on glass wool.

2.4 ANALYSIS

Analysis for carbon, hydrogen, nitrogen and halogens was performed by the micro-analytical department of the Inorganic Chemistry Laboratory Oxford. This department lacks a dry box and consequently all the moisture sensitive compounds are expected to have slightly low analyses for chloride, carbon and nitrogen and slightly high hydrogen figures.

2.5 DRY-BOX

The vast majority of compounds handled were either air or moisture-sensitive and an effective dry-box was essential. A balance and magnetic stirring apparatus present in the dry-box allowed quantitative work to be carried out under a dinitrogen atmosphere. The dry-box was continually flushed with dry dinitrogen (silica-gel and phosphorus pentoxide, as described earlier in Section 2.3) and contained an open tray of phosphorus pentoxide as a dessicant. The moisture content of the box was quantitatively determined by exposing a small quantity of titanium(IV) chloride to the dry-box atmosphere and observing for fuming. All common operations (eg. mull preparations, filling of sample tubes, reflectance cells and solution preparation) were carried out in the dry-box.

2.6 INFRARED SPECTROSCOPY

Infrared absorption spectra were recorded on a Unicam SP-2000 spectrometer. The range of the instrument is from 4000 to 200 wavenumbers. Spectra were calibrated by recording the standard absorption frequencies for a thin polystyrene film at 2924 cm^{-1}, 1601 cm^{-1}, 1029 cm^{-1} and 907 cm^{-1} and for indene at 591 cm^{-1} and 381 cm^{-1}.

All measurements were performed using mulls of the various compounds in nujol (liquid paraffin, absorption at 2900, 1460, and 725cm^{-1}) between caesium iodide plates (cut-off at 180 cm^{-1})

2.7 ELECTRONIC SPECTROSCOPY

Electronic spectra were recorded on a Perkin-Elmer 330 spectrophotometer (range 2600-185 nm) : 1cm silica cells were used. Diffuse reflectance electronic spectra were recorded using the standard diffuse reflectance attachment on the above mentioned equipment in cells with vitrosil windows, using magnesium oxide as reference.

2.8 MASS SPECTROMETRY

Samples were submitted to the mass spectrometric service in the Inorganic Chemistry department, Oxford.

2.9 CYCLIC VOLTAMMETRY

Cyclic voltammetry is an electrochemical technique akin to polarography, but employing a stationary electrode in an unstirred solution, the applied voltage being varied at a constant rate using a triangular waveform generator. The theory and practical details of the technique have been described by Salmon [29].

The cell used was constructed in the Inorganic Chemistry Laboratory, Oxford. Cyclic voltammograms run in melts were conducted with an aluminium (ex Goodfellow metals, 5N) auxiliary electrode and a 2mm tungsten (Goodfellow metals, high purity) rod sealed in glass, with the end polished by alumina, as a working electrode. The reference electrode in the case of aluminium chloride-N-butylpyridinium chloride melts was an aluminium wire (Goodfellow metals 5N) immersed in a 2:1 melt. The cell design is shown in the figure.

2.10 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance spectra were recorded on a JEOL FX-90Q machine located at Bedford College, University of London.

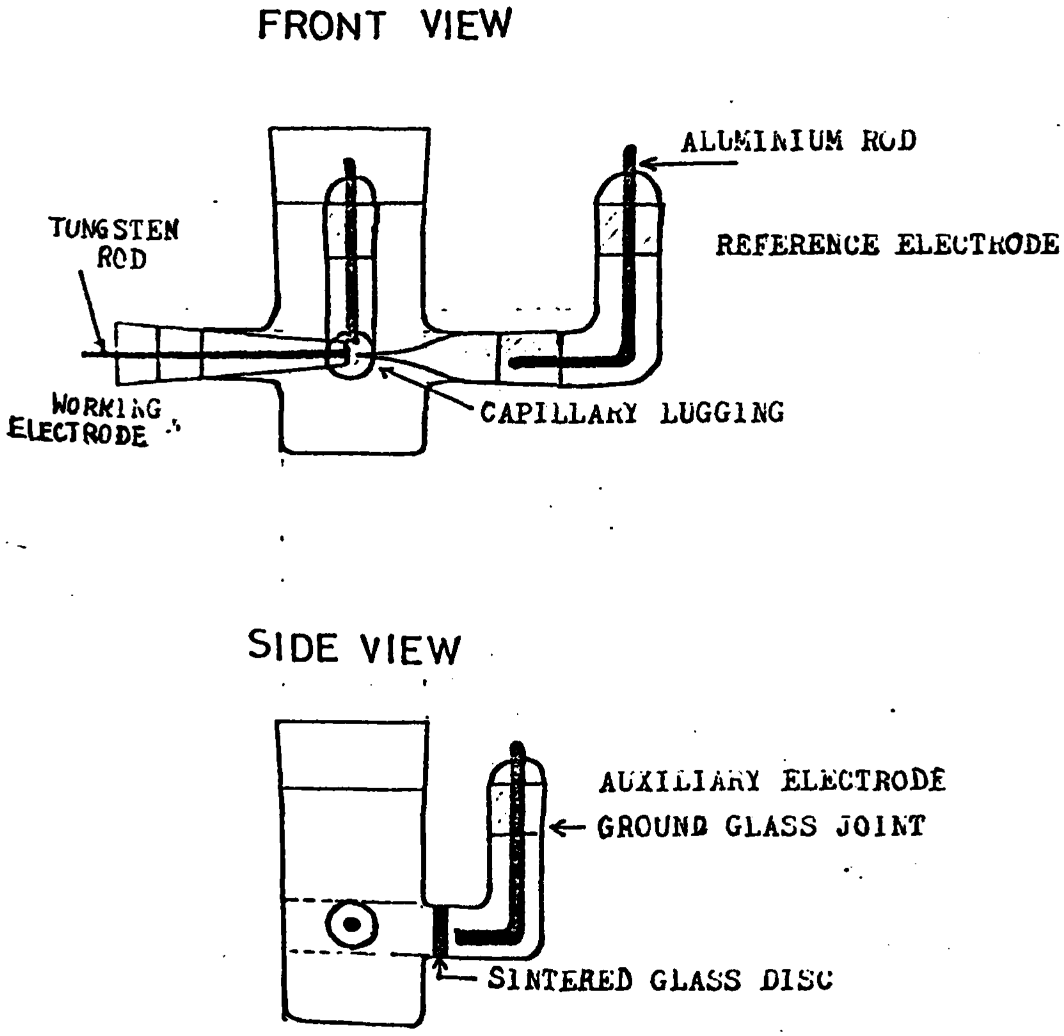


Fig 2.1 Cyclic voltommetry cell

3.1 PREPARATION OF ROOM TEMPERATURE MELTS

3.1.1 Preparation of N-butylpyridinium chloride (BPC)

Equimolar quantities of pyridine (238 cm^3) and 1-chlorobutane (321 cm^3) were mixed together and heated under reflux at 115 °C in the dark for about 36 h. A dense dark yellow-brown oil was visible in the bottom of the flask at this stage and on cooling to room temperature, off-white crystals were precipitated. The unreacted starting materials were decanted from the solid, which was then broken up and dissolved in the minimum amount of boiling ethanenitrile (ca 160 cm^3). Activated charcoal (10g) was added and the mixture heated under reflux for 20 min. The solution was filtered whilst still hot and approximately 10% (by volume) of boiling ethyl ethanoate was added to the filtrate before leaving it to cool, with a silica gel drying tube isolating it from atmospheric moisture.

On cooling to room temperature, white crystals of N-butylpyridinium chloride precipitated. These were filtered under suction, washed with ethyl ethanoate and transferred as quickly as possible to a vacuum desiccator whilst still moist with solvent (crystals of N-butylpyridinium chloride are very hygroscopic). Excess solvent was then removed under vacuum. The recrystallisation and decolourising processes were repeated twice more. The crystals were finally recrystallised from a 10:1 ethanenitrile-ethyl ethanoate mixture, filtered, and the final traces of solvent were removed by continuous evacuation at 70 °C for 24 h. The flask was transferred to the dry box and the solid stored in dark glass bottles.

3.1.2 Sublimation of aluminium chloride

Aluminium chloride (50 g), aluminium metal (1 g) and sodium chloride (0.5 g) were placed in a round-bottomed flask (the aluminium and sodium chloride serve to eliminate the major impurity iron (III) chloride, probably initially present as volatile $[FeAlCl_6]$, by reduction to iron(II) and complexation as $[FeCl_4]^{2-}$, which is much less volatile than aluminium chloride). An air condenser was fitted to the flask and the system evacuated, then flushed with dry dinitrogen. This was repeated several times, leaving the apparatus filled with dinitrogen. The flask was then heated to 180 °C on an oil bath to ensure melting. The system was evacuated slowly, and the aluminium chloride started to condense on the walls of the condenser, which was cooled by a fan-blower. When only 10% of the original contents of the flask remained, the system was filled with dry dinitrogen, taken from the oil bath and allowed to cool. The condenser was sealed at both ends and transferred to the dry box. The sublimed aluminium chloride was removed by scraping the condenser walls. Sodium chloride (0.5 g) was then added to the sublimate and the sublimation process repeated as before. Again, when only 10% of the original contents remained, the sublimation was stopped. The condenser was transferred to the dry box and the aluminium chloride, which was now white, scraped out and stored in a suitable container.

3.1.3 Preparation of aluminium chloride-N-butylpyridinium chloride melts

All preparations and weighings were performed in the dry box simply by adding appropriate amounts of N-butylpyridinium chloride to aluminium chloride (the basic melt, 0.8:1 $AlCl_3$:BPC, typically requires $AlCl_3$ (4.00 g) and BPC (6.44 g), and the acid melt, 2:1 $AlCl_3$:BPC, typically requires $AlCl_3$ (6.22 g) and BPC (4.00 g)).

The N-butylpyridinium chloride was added very slowly to the aluminium chloride, with stirring by glass rod, until the mixture was fluid enough to be stirred by a glass coated magnetic stirrer bar. A crucial stage in the preparation occurs just as the mixture is becoming "pasty", and great care must be taken at this point to avoid overheating and charring due to the exothermic nature of the reaction. The melts produced were colourless to straw-yellow in colour if prepared correctly, but much darker if the addition had been performed too quickly, or if the dry box was not sufficiently dry. The colouration is due to oxidised organic species (probably colloidal charcoal).

The total addition occurred over a time period of three to six hours, depending on the quantity of liquid prepared. The liquids were used without further purification. The acid melt was very fluid and remained liquid at ambient temperatures, whereas the basic melt solidified on standing for several hours (melting occurred on very gently heating). The basic melt was also generally less susceptible to hydrolysis.

It should be stated unambiguously that figures given in the melt ratios refer to the $AlCl_3$ species and not the Al_2Cl_6 dimer. Furthermore, in this thesis the term 'basic melt' will be reserved for the 0.8:1,

$AlCl_3$:BPC composition, whilst the term 'acid melt' will indicate the melt composition to be 2:1, $AlCl_3$:BPC.

3.2 DISCUSSION OF MELT PROPERTIES AND PROCEDURES

All preparations of melts were conducted in the dry-box, the melts being unstable in the presence of moisture. The basic melt (0.8:1; $AlCl_3$:BPC) was more stable to hydrolysis than the acid melt (2:1; $AlCl_3$:BPC).

The addition of aluminium chloride to the N-butylpyridinium chloride was conducted with great care, ensuring that the melt temperature did not exceed 100 °C (which would result in thermal decomposition). Slight colouration of the melts was occasionally encountered, and this is due to charring of the organic component of the melt.

During the preparation of the melt components, it is essential to ensure purity. The presence of sodium chloride in the sublimation of aluminium is an important step in ensuring there is no contamination from iron compounds (see section 3.3).

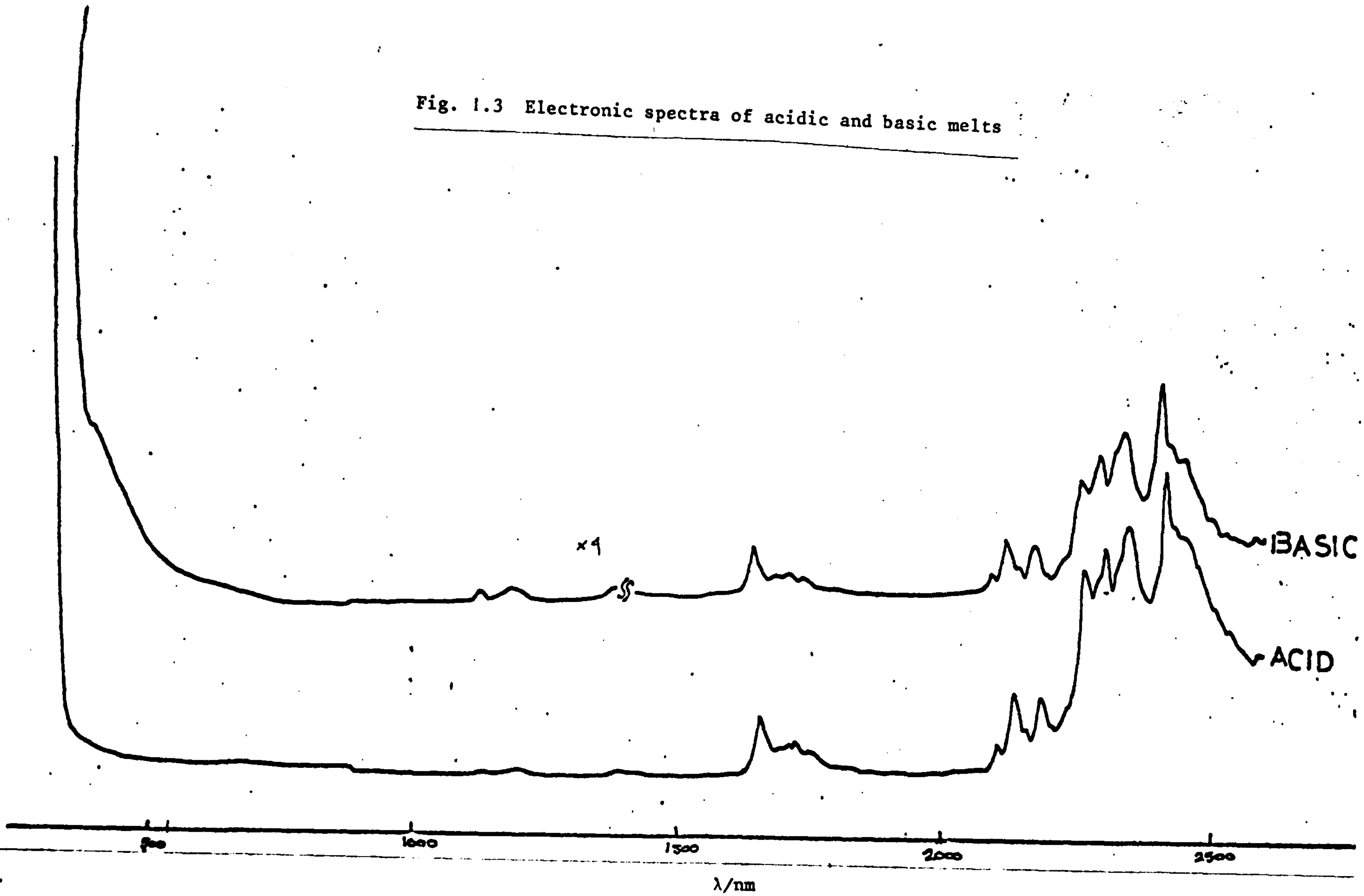
3.3 ELECTRONIC SPECTRAL STUDIES OF THE ALUMINIUM CHLORIDE-N-BUTYLPYRIDINIUM CHLORIDE MELT

Electronic spectra were recorded for the acid and basic melts in 1mm silica cells. The results are shown in Figure 3.1.

The spectra reveal an essentially absorbance free region at frequencies higher than $10000cm^{-1}$ (<1000nm). There are some quite strong absorbance peaks at lower frequencies, but it is well within the ability of the PE 330 spectrphotometer to internally correct for the absorbances and produce a flat baseline.

The bands present are of unknown origin, but if they had been due to an inorganic species it was possible that the impurity may have interfered with results obtained in the melts. On the other hand, if the species is organic in nature, it is unlikely to produce extraneous results. If of inorganic nature, the sharpness of the peaks on the spectra would indicate forbidden transitions, the most likely cause being the high-spin tetrahedral iron species (d^5), $[FeCl_4]^-$. If this ion were present, it would be in high concentration, because the spin-forbidden transitions of this species are necessarily very weak. The $[FeCl_4]^-$ ion is well documented and if sodium chloride were not present in the purification step of aluminium chloride, it would be expected to be

Fig. 1.3 Electronic spectra of acidic and basic melts



present. The predominant band in $[FeCl_4]^-$ is at 18800cm^{-1} (≡530nm). This portion of the melt spectra is remarkably clear in both the acidic and basic melt cases and hence confirms that the impurities are likely to be organic in nature.

The cut-off region is measured according to the definition of Gillarn and Stern; cut-off is the point at which the absorbance is approximately 1 unit (or the transmittance 10%) for a 10 mm cell.

The UV window (for both the basic and acidic melts) is

2600 to 350 nm
3900 to 28500 cm^{-1}

In this respect it is a better solvent than, for example:

Nitromethane (cut-off 26300cm^{-1})
Carbon Disulphide (cut-off 26300cm^{-1})

The melts thus make ideal solvents for the study of the transition metal complexes.

3.4 CYCLIC VOLTAMMETRY STUDIES

Cyclic voltammograms were recorded (Figures 3.2 and 3.3) for both the acidic and basic melts in the cell described in Section 2.9. The backgrounds are essentially featureless, except for a small impurity peak in each case, with the cathodic and anodic limits being the deposition of aluminium and the evolution of chlorine, respectively.

The detected impurity (see figures 3.2 and 3.3) was considered to be small enough to be acceptable, and did not interfere with any of the measurements recorded in this work.

The redox ranges for the two melts used, relative to the reference (Al wire in 2:1 melt) are:

Basic melt	-1.1	to	+0.65V
Acidic melt	+0.2	to	+2.4V

Robinson and Osteryoung [30], determined the potential of the Al^{3+}/Al (2:1 melt) couple by calibrating with the ferricinium ion/ ferrocene couple which is known to be constant for all melt acidities. They concluded that the potential of the Al^{3+}/Al electrode lies approximately 60 mV anodic of the SCE (Saturated Calomel Electrode).

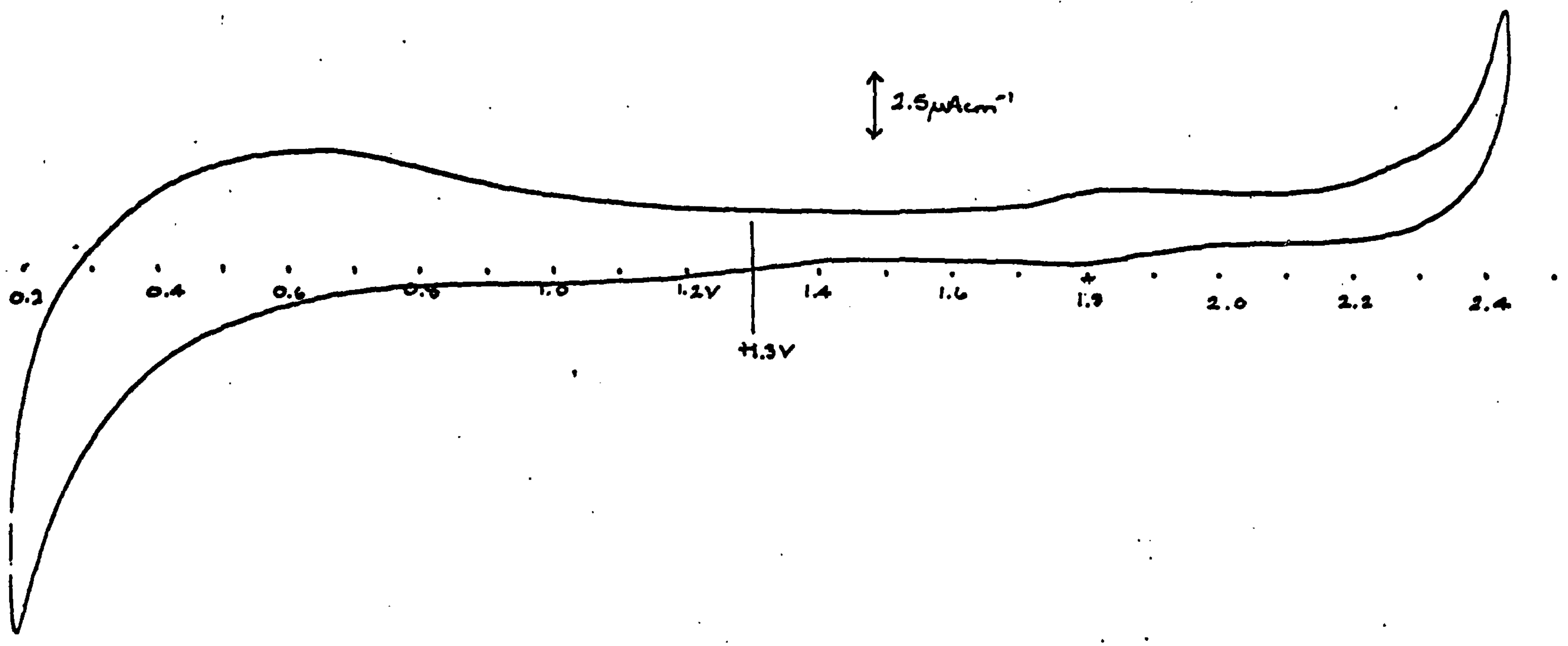


Fig. 3.2 C.V. of acid melt

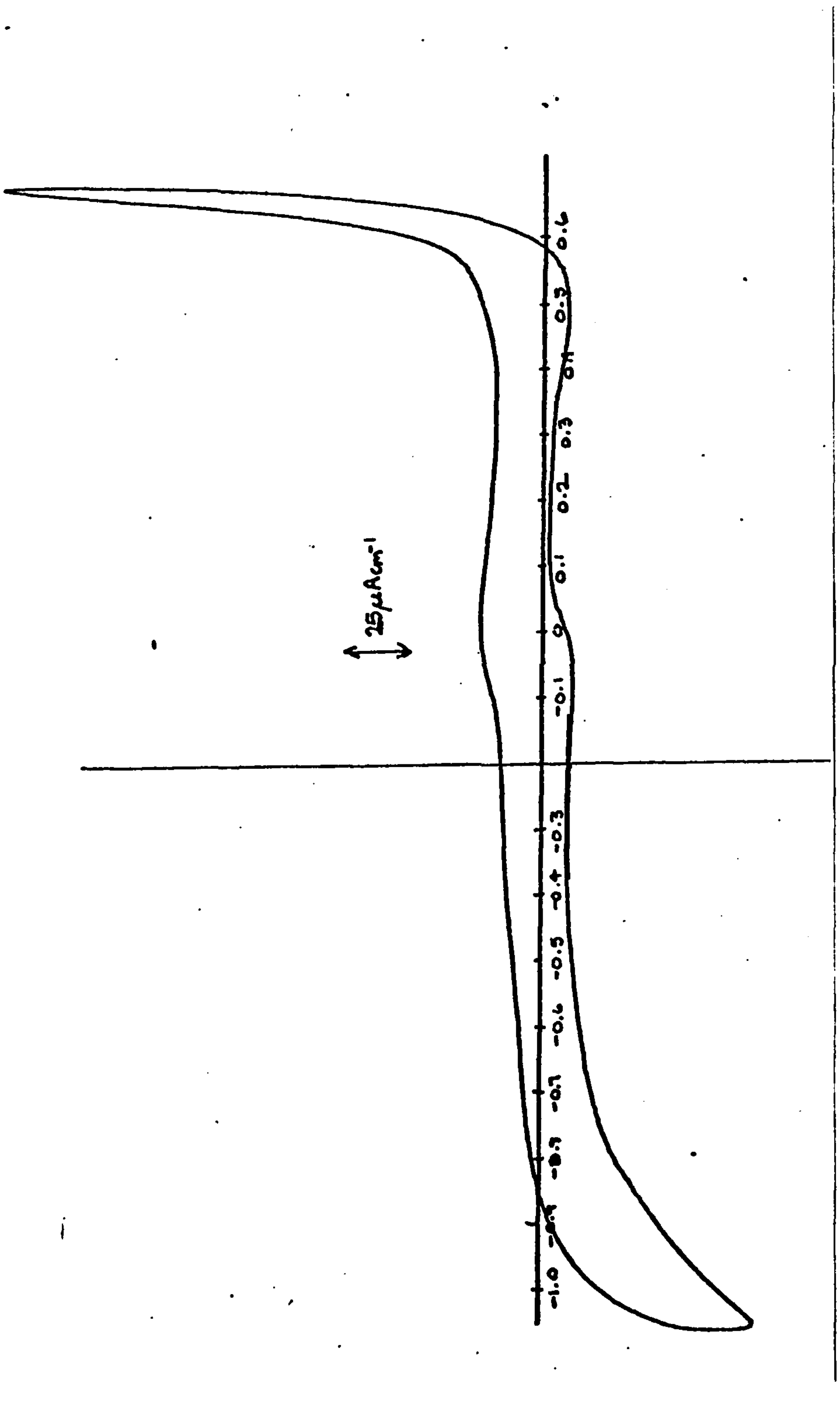
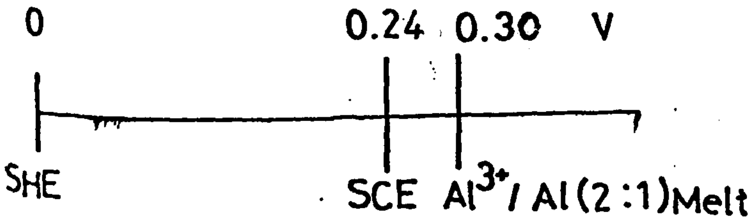


Fig. 3.3 C.V. of basic melt

The situation may be shown schematically



The redox ranges of the melt may therefore be stated with respect to the SHE by the addition of 0.3V to the values found with respect to the aluminium electrode. Hence

	Cathodic Limit/V vs.SHE	Anodic Limit/V vs.SHE
Basic melt	-0.8	+0.95
Acidic melt	+0.5	+2.7

The melts are therefore ideal for redox studies, being easily comparable in range to organic solvents.

4.1 EXPERIMENTAL

4.1.1 Attempted Preparation of Molybdenum(VI) Chloride

The preparation of molybdenum(VI) chloride has been the subject of a preliminary report [31], but has never been substantiated. An attempt was made here to confirm the preparation.

A small quantity of ammonium molybdate, $[NH_4]_2[MoO_4]$ (2.5 g) was heated under reflux with thionyl chloride (40 cm^3) in a standard reflux apparatus fitted with a silica gel drying tube. The faint yellow solution turned deep red as the boiling point of the solvent was approached. Heating was continued for approximately seven hours. The apparatus was then transferred to the vacuum line and the solvent removed under reduced pressure. The solid remaining in the flask had the appearance of an intimately mixed brown and green powder, and was very moisture sensitive.

No evidence for the formation of molybdenum(VI) chloride was found in the mass spectrum of the product, the predominant volatile species appearing to be $MoCl_2$.

4.1.2 Preparation of Tetraethylammonium Hexachloromolybdate(V)

$[Et_4N][MoCl_6]$ was prepared by the method of Brisdon and Walton [6].

Equimolar quantities of anhydrous tetraethylammonium chloride (0.91 g) and molybdenum(V) chloride (1.5 g) were mixed into a Carius tube in the dry-box. The tube was then placed on the vacuum line and evacuated. Dichloromethane was doubly distilled from phosphorus pentoxide in vacuo and then distilled (15 cm^3) onto the solid reactants at -196 °C. The Carius tube was then sealed in vacuo. The sealed ampoule was then placed in a metal casing (fitted with a safety valve) and allowed to gradually warm to room temperature. The reactants were then heated in an oven at 70 °C for 7 hours.

The product, $[Et_4N][MoCl_6]$, formed shiny, black acicular crystals which were suspended in a dark-yellow solution. The ampoule was then opened in the dry-box and filtered on the Schlenk-line. The product was washed sparingly with dried dichloromethane (2 cm^3) and sodium-dried ether (2 cm^3) to remove unreacted starting materials. The black solid was dried on the vacuum line.

Analysis figures.

	C%	H%	Cl%	N%
Obtained (avg.)	20.99	4.76	43.72	2.95
Calculated for $C_8H_{20}Cl_6MoN$	21.89	4.59	48.46	3.19

The salt was extremely air-sensitive, forming bright green crystals on exposure. The presence of any moisture during reaction causes reduction of the product with the formation of the characteristic yellow colour of hexachloromolybdate(IV) salts.

4.1.3 Attempted Preparation of Lithium Hexachloromolybdate(V)

Anhydrous lithium chloride (0.24 g) and molybdenum(V) chloride (1.55 g) were sealed in a tube with dichloromethane (15 cm^3). The reaction mixture was prepared as described in Section 4.1.2. The reactants were heated for 7 hours in an oven maintained at 70 °C.

The resultant solution was a deep red colour with a dark solid and particles of a white solid suspended in it. Molybdenum(V) chloride solutions in dichloromethane are red in colour and it was assumed that the white particles were unreacted lithium chloride. Obviously, dichloromethane is an inappropriate solvent for lithium chloride.

4.1.4 Preparation of Tetraphenylarsonium Hexachloromolybdate(V)

Tetraphenylarsonium hexachloromolybdate(V), $[Ph_4As][MoCl_6]$, was prepared in an analogous procedure to that used in the preparation of the tetraethylammonium salt.

Anhydrous tetraphenylarsonium chloride (1 g) and molybdenum(V) chloride (0.7 g) (1:1 mole ratio) in dichloromethane (9 cm^3) were heated at 70 °C for seven hours. The reaction mixture was prepared as described in Section 4.1.2.

The precipitated salt, $[Ph_4As][MoCl_6]$, formed large prismatic crystals, black to dark blue in colour. The salt was very sensitive to moisture, but comparably stable in air when compared to its tetraethylammonium analogue.

Analysis figures.

	C%	H%	Cl%
Obtained (avg.)	41.42	2.96	29.00
Calculated for $C_{24}H_{20}AsCl_6Mo$	41.66	2.91	30.74

4.1.5 Preparation of Tetraethylammonium Hexachloromolybdate(IV)

Horner and Tyree's method [7], modified by using $[Et_4N]Cl$ instead of $[Me_4N]Cl$, was used for the preparation of $[Et_4N]_2[MoCl_6]$.

Anhydrous tetraethylammonium chloride (2.7 g; 1.6mmol) was added to warm ethanenitrile (50 cm^3) which was immediately purged with dinitrogen. Sublimed molybdenum(V) chloride (3.0 g; 11.0mmol) was added and more dinitrogen was passed through the reaction mixture, which had the appearance of a red solution containing a suspended solid. The suspension was decanted from unreacted molbdenum(V) chloride in the reaction vessel, filtered and the solid remaining washed with absolute ethanol (50 cm^3), dichloromethane (20 cm^3) and diethyl ether (20 cm^3). Solvent was removed from the bright yellow product on the vacuum line over a period of 12 hours.

Analysis figures.

	C%	H%	N%	Cl%
Obtained (avg.)	33.7	8.1	4.8	36.7
Calculated for $C_{16}H_{40}N_2MoCl_6$	33.8	7.1	4.9	37.4

4.1.6 Preparation of Potassium Octachlorodimolybdenum(II)

Tetrakis(ethanoato)dimolybdenum(II) (2.0 g; 4.7mmol) and potassium chloride (2.8 g; 37.6mmol) were added to a saturated aqueous hydrogen chloride solution (100 cm^3) at 0 °C. Stirring this slurry at 25 °C for one hour produced a purple suspension which was filtered in air and washed with two portions of absolute ethanol (20 cm^3) before being dried at 25 °C for 8 hours.

Analysis Figures.

	Cl%
Obtained (avg.)	43.9
Calculated for $K_4Mo_2Cl_8$	44.9

The product, a bright red/purple powder appeared to be unaffected by short term exposure to laboratory air, but with water it formed a dark brown solid.

4.1.7 Preparation of Caesium Hexachloro-μ-Dichloro-μ-Hydridodimolybdenum(II)

$[Mo_2(OAc)_4]$ (2.0 g; 4.7mmol) was dissolved in hydrochloric acid (100 cm^3; 12M) at 60 °C, producing a red solution. Addition of CsCl (3.0 g; 17.8mmol) caused the immediate precipitation of a yellow solid. The product was filtered in air, washed several times with absolute ethanol and then with diethyl ether and was dried *in vacuo* at 25 °C

Analysis Figures.

	H%	Cl%
Obtained (avg.)	0.1(5)	32.1
Calculated for $Cs_3Mo_2Cl_8H$	0.1	32.4

$Cs_3[Mo_2Cl_8H]$ is a yellow powder stable to the atmosphere over a period of hours.

4.1.8 Discussion of Experimental Detail

The quality and yield of desired product in the sealed tube reactions described earlier was found to vary a great deal with different preparations. Attention to minute detail was necessary to ensure a 'clean' sample. In particular, it was found that shaking the reactants together prior to heating ensured a good environment for reaction and it was found important to lay the tubes horizontally in the oven, otherwise a 'plug' of solid material formed in the end of the tube, preventing complete reaction of all starting materials.

Brisdon and Walton [8] reported a very low yield in their preparation of tetraphenylarsonium hexachloromolybdate(V). It was found that reducing the amount of solvent present in the ampoule, due to the known high solubility of salts of the tetraphenylarsonium cation in dichloromethane, produced large yields, comparable to those in the tetraethylammonium analogue.

It was observed that if the sealed ampoule was left standing for a long period of time, the resultant product was degraded, reduction occurring and producing the hexachloromolybdate(IV) salt.

The samples were checked for purity by recording infrared and electronic spectra. The infrared spectra were particularly instructive. The most likely impurity in the chloro- complexes is an oxo- species. The molybdenum-oxygen double bond stretch is observed between 900 and 1000 cm^{-1} in the oxo- complexes and hence shows up any impurity in the infrared spectra. The tetraethylammonium and tetraphenylarsonium hexachloromolybdate(V) salts were remarkably clear of peaks in this area. The tetraethylammonium hexachloromolybdate(IV) exhibited a band at 950 cm^{-1} (see Figure 4.1). The most likely impurity is the tetraethylammonium salt of the oxopentachloromolybdate(V) anion, $[Et_4N]_2[MoOCl_5]$. The infrared spectra of rubidium and caesium oxopentachloromolybdates(V) have been studied in detail [32]. The results show that the M=0 stretch frequency for salts of this anion depend on the cation size and fall in the range 950-975 cm^{-1}, the band intensity being described as very strong. This tends to confirm the presence of some $[Et_4N]_2[MoOCl_5]$ in the sample of $[Et_4N]_2[MoCl_6]$, even though analytically pure samples were obtained.

Far-infrared spectra were recorded for the $[MoCl_6]^-$ ion, $[MoCl_6]^{2-}$ and $[MoCl_6]^{3-}$ ion to compare the positions of the Mo-Cl stretch (Figure 4.2). Creighton and Sinclair [33] report the positions of these peaks (see Table 4.1).

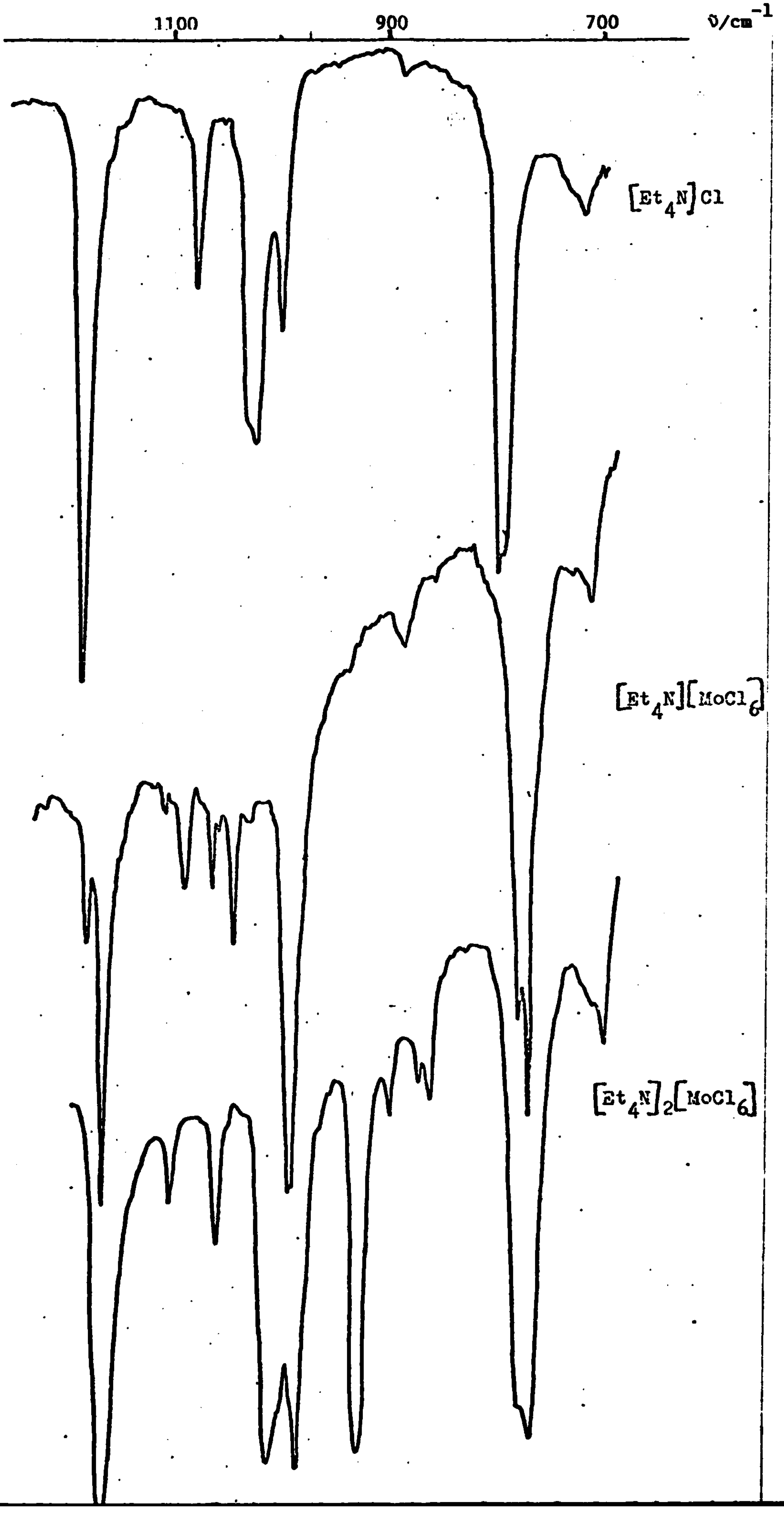
TABLE 4.1 IR Data for $[MoCl_6]^{n-}$ Salts

Compound	This work (Mo-Cl)/cm^{-1}	[6] (Mo-Cl)/cm^{-1}
$[Et_4N][MoCl_6]$	330 vs	327 vs
$[Et_4N]_2[MoCl_6]$	310 vs	308 vs
$Cs_2[MoOCl_5]$	-	329 s 320 sh
$K_3[MoCl_6]$	318,302,290,265	302 vs, 286 s, 268 m

4.2 ELECTRONIC SPECTROSCOPY

4.2.1 Introduction

There have been four studies of the electronic spectra of the hexachloromolybdate(V) anion (see Table 4.2), showing no real correlation to each other.


1100
900
700
ṽ/cm^{-1}
[Et$_4$N]Cl
[Et$_4$N][MoCl$_6$]
[Et$_4$N]$_2$[MoCl$_6$]

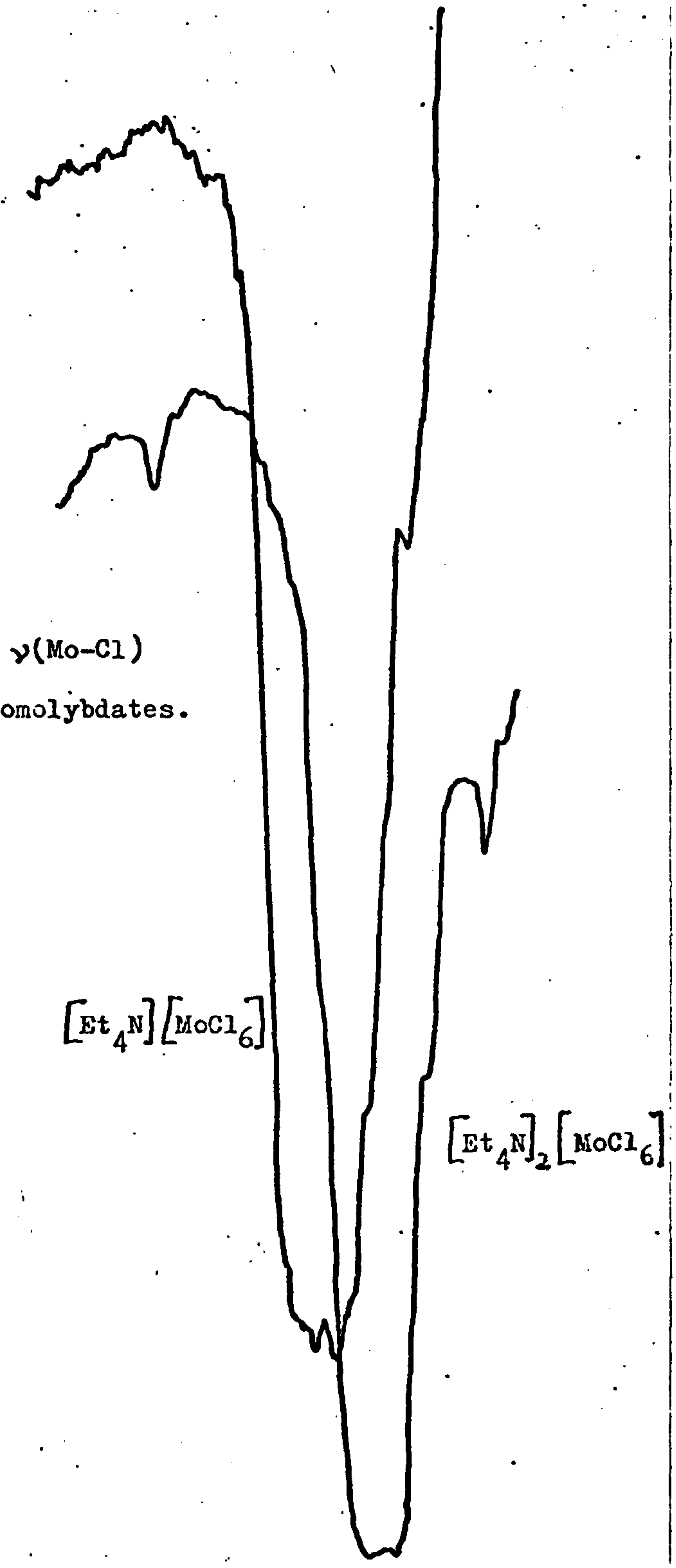


Fig.4.2
Comparison of ν(Mo-Cl) for hexachloromolybdates.

TABLE 4.2 Literature Electronic Spectra for some $MoCl_6^-$ Salts

Compound	Phase	γ/cm^{-1} ($\varepsilon_{max.}/lmol^{-1}cm^{-1}$)			Ref
$[Et_4N][MoCl_6]$	solid	26 700	20 500	15 200	6
	MeCN	25 600(2 100)			
$[Et_4N][MoCl_6]$	solid		21 700	15 400	8
	MeCN	27 000(2 300)	21 700(950)	16 700(300)	
	CH_2Cl_2	27 000(1 000)	21 900(700)	16 800(200)	
$[Ph_4As][MoCl_6]$	solid	27 000	22 100	16 900 sh	8
$K[MoCl_6]$	solid		24 100		7
$Cs[MoCl_6]$	solid	25 697 - 23 830			34

Brisdon and Walton concluded that Horner and Tyree [7] had actually been measuring the spectra of a molybdenum(IV) species.

The electronic spectra of $MoCl_5$, $[MoCl_6]^{2-}$, $[MoCl_6]^{3-}$ and $[MoOCl_5]^{2-}$ have also been determined and results are tabulated here (table 4.3).

TABLE 4.3 Literature Electronic Spectra for $[MoCl_6]^{n-}$, $MoCl_5$ and $[MoOCl_5]^{2-}$

Compound	Phase	γ/cm^{-1} ($\varepsilon_{max.}/lmol^{-1}cm^{-1}$)		
$[Me_4N]_2[MoCl_6]$	solid [7]	41 300	36 760	33 900
		28 400	25 800	22 260
$K_3[MoCl_6]$	solid [48]	45 000	42 500	36 800
		24 000	19 200	14 800
$[NH_4]_2[MoOCl_5]$	10M HCl[49]	41 700 (3 600)	32 200 (5 300)	28 200
		22 500 (10)	14 100 (11)	
$MoCl_5$	CCl_4 [50]	42 600 (10 000)	35 700 (2 000)	27 800
		21 300 (20 000)	15 200 (4 000)	1 009(1 000)
	solid [8]	25 000	18 500	14 300

4.2.2 Electronic Spectra of some Molybdenum Chloride Species

The diffuse reflectance spectra of the species $[Et_4N][MoCl_6]$, $[Ph_4As][MoCl_6]$, $[Et_4N]_2[MoCl_6]$ and $K_3[MoCl_6]$ were measured (Figures 4.3 and 4.4). In addition the solution spectra of $MoCl_5$, $[Et_4N][MoCl_6]$, and $[Ph_4As][MoCl_6]$ in dichloromethane were recorded (Figure 4.3), and the spectrum of $K_3[MoCl_6]$ was measured in the 10<u>M</u> HCl (Table 4.5).

The spectra of the hexachloromolybdate(V) anion (Table 4.4) show a good correlation with each other (see Figure 4.3), and with the results presented by Brisdon and Walton (cf. Tables 4.2 and 4.4).

Fig.4.3 Comparison of the spectra of hexachloromolybdates

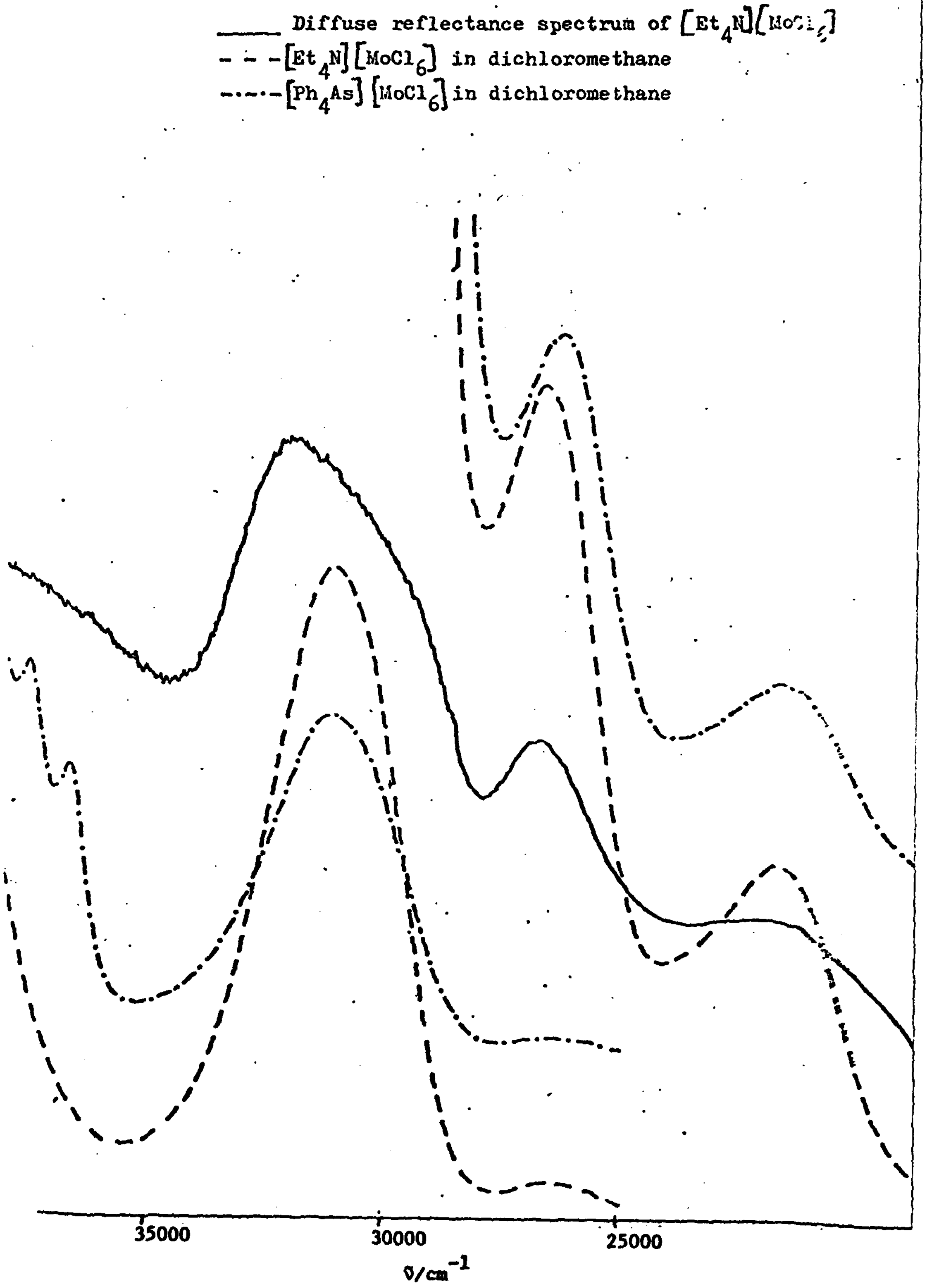


TABLE 4.4 Electronic Spectra of A[$MoCl_6$] (A=Et_4N or Ph_4As)

Compound	Medium	γ/cm^{-1}	($\varepsilon_{max.}/lmol^{-1}cm^{-1}$)	
[Et_4N][$MoCl_6$]	D/R			32 000 s
		26 800	22 000 sh	16 000 sh
	CH_2Cl_2		46 300(13 100)	31 200 (13 400)
		26 700	21 800	
[Ph_4As][$MoCl_6$]	CH_2Cl_2	37 800(18 500)	36 800(16 000)	31 200 (11 000)
		26 000(1 400)	21 700(800)	

The diffuse reflectance spectra of [Et_4N]$_2$[$MoCl_6$] is very poorly resolved, probably due to impurity bands present from the [Et_4N]$_2$[$MoOCl_5$] (Figure 4.4).

TABLE 4.5 Electronic Spectra of some Molybdenum Chloride Complexes

Compound	Phase		$\tilde{\gamma}/cm^{-1}$		
[Ph_4As][$MoCl_6$]	D/R	37 000 s,b	31 000 sh	22 000	16 000 sh
		8 800 w	6 000		
$MoCl_5$	D/R	35 000 s	31 000 sh	21 000 b	
		7 300			
[Et_4N]$_2$[$MoCl_6$]	D/R	37 000	33 000	22 000	13 000
		8 700	5 800		
K_3[$MoCl_6$]	D/R	37 000 s		24 000	19 400
		15 000	9 500		
	10 M HCl	32 500	28 000 sh	24 000	19 000

These spectra were used to fingerprint the species, for characterisation of the species present when these complexes were dissolved in both acidic and basic melts.

4.3 SPECTROSCOPIC AND ELECTROCHEMICAL MEASUREMENTS IN A BASIC MELT

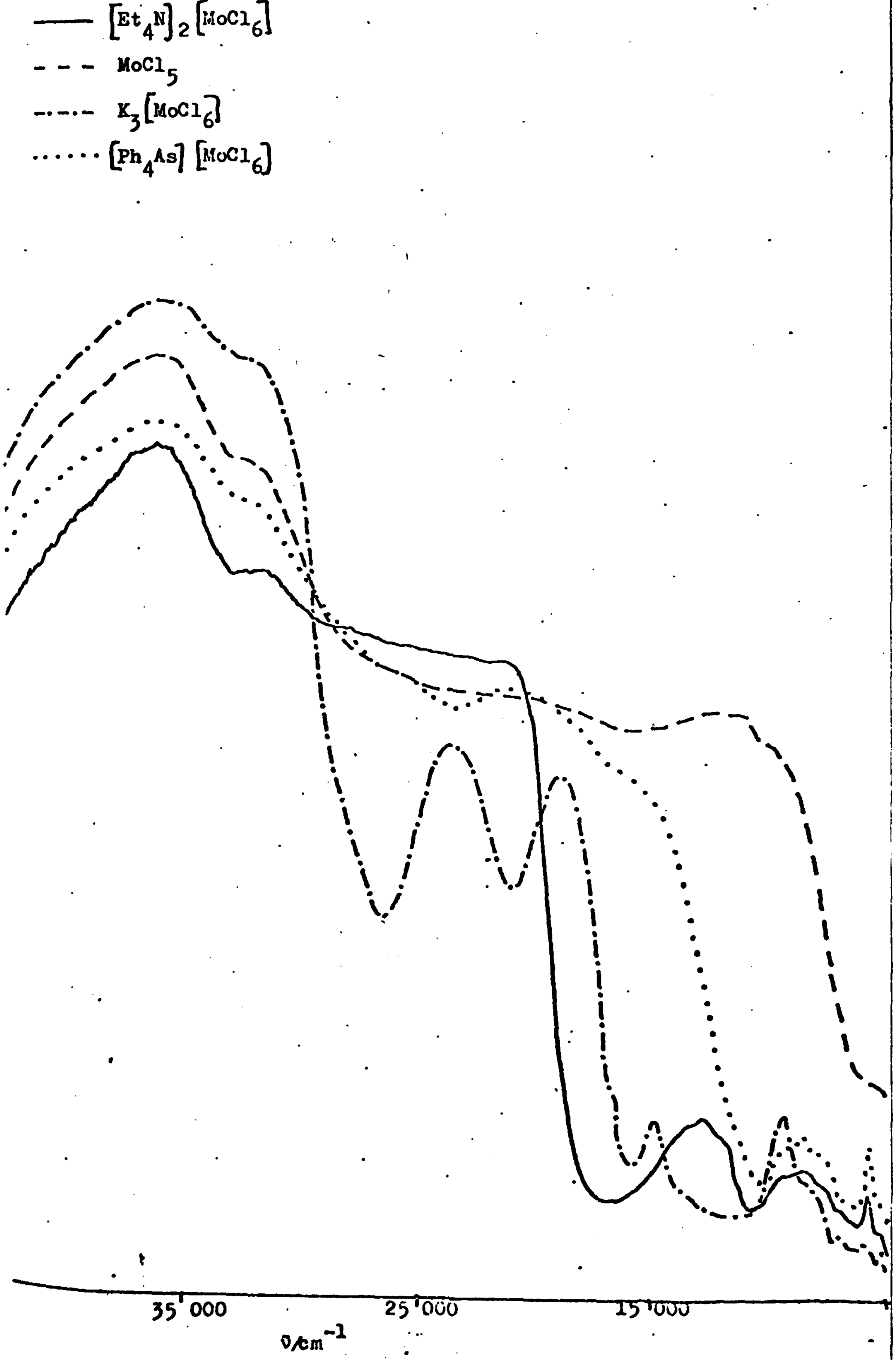
4.3.1 Electronic Spectroscopy

The electronic spectra of [Et_4N][$MoCl_6$], [Et_4N]$_2$[$MoCl_6$], K_3[$MoCl_6$] and $MoCl_5$ were obtained in the basic melt (see Figure 4.5 and Table 4.6)

TABLE 4.6 Electronic Spectra in the Basic Melt

Compound		$\tilde{\gamma}/cm^{-1}$	
$MoCl_5$	27 700	24 700	22 000 sh
[Et_4N][$MoCl_6$]	27 600	25 200 sh	22 000 sh
[Et_4N]$_2$[$MoCl_6$]	27 700	24 700	22 000
K_3[$MoCl_6$]	31 000		23 300

Fig.4.4 Comparison of diffuse reflectance spectra



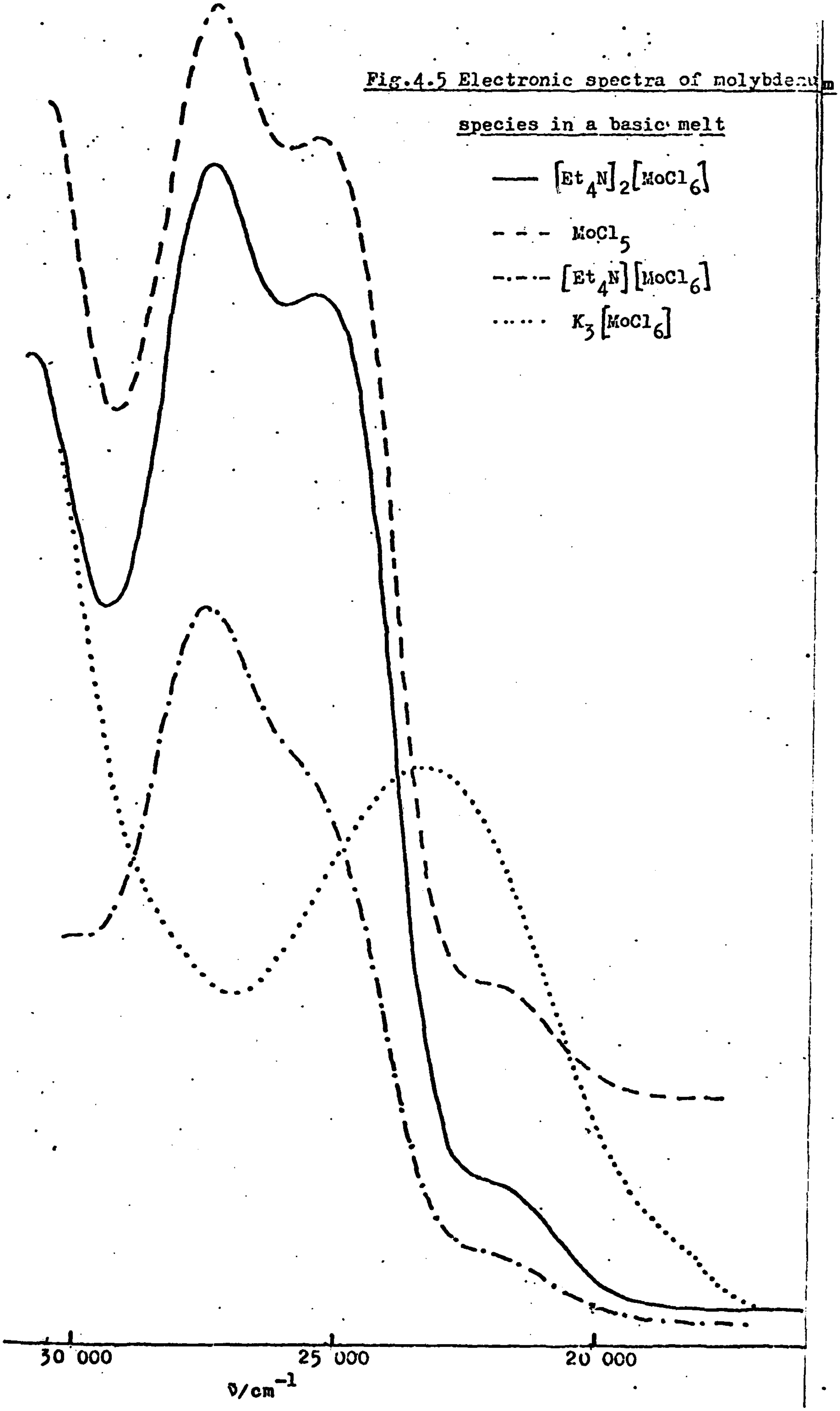


Fig.4.5 Electronic spectra of molybdenum species in a basic melt

The spectra are likely to be due to $[MoCl_6]^{n-}$ species, as there is no evidence of increasing the chloride ion co-ordination sphere beyond six in molybdenum chemistry.

The most striking observation is the equivalence of the spectra obtained from the dissolution of both of the molybdenum(V) and the molybdenum(IV) species. However, a comparison of the spectrum of the Mo(V) species in the melt with that obtained in dichloromethane (Figure 4.6) reveals no significant correlation. The spectra obtained of the Mo(V) complexes in the melt do, however, resemble the diffuse reflectance spectrum recorded for the hexachloromolybdate(IV) anion (see Figure 4.4).

This work indicates that in the basic melt $[MoCl_6]^-$ is spontaneously reduced according to:

$$[MoCl_6]^- + Cl^- \longrightarrow [MoCl_6]^{2-} + \tfrac{1}{2}Cl_2$$

This is borne out by the observation (Section 4.1.6) that prolonged contact of $[MoCl_6]^-$ with dichloromethane and excess chloride ions also leads to reduction to $[MoCl_6]^{2-}$. Moreover, the strong band in the region 24 000 to 25 000cm^{-1} corresponds well with the band recorded by both Horner and Tyree [7] and Paterson and Nims [34], in a crushed KCl-MoCl$_5$ melt and caesium hexachlorozirconate(IV) matrix, respectively, which are in similar chloride environments. Hence it is likely that the spectra recorded by Horner and Tyree and Paterson and Nims were also of the $[MoCl_6]^{2-}$ ion, and not the reported $[MoCl_6]^-$ species.

The spectrum of $[MoCl_6]^{3-}$ is essentially unchanged from that in HCl solution, indicating the stability of this ion in the basic melt; its spectrum is very different from that of $[MoCl_6]^{2-}$.

If this assumption, concerning Mo(V) reduction is correct, the electrochemical studies should reveal no Mo(IV)/Mo(V) oxidation wave in the melt range as it must lie above the Cl^-/Cl_2 potential.

This work represents the first recorded spectrum of $[MoCl_6]^{2-}$ in solution, as it has previously decomposed in all solvents in which it dissolved.

4.3.2 Electrochemical Studies in a Basic Melt

The cyclic voltammograms of $[Et_4N][MoCl_6]$, MoCl$_5$ and $K_3[MoCl_6]$ were recorded in the basic melt (Figures 4.7-4.9; Table 4.7). The cv's are all

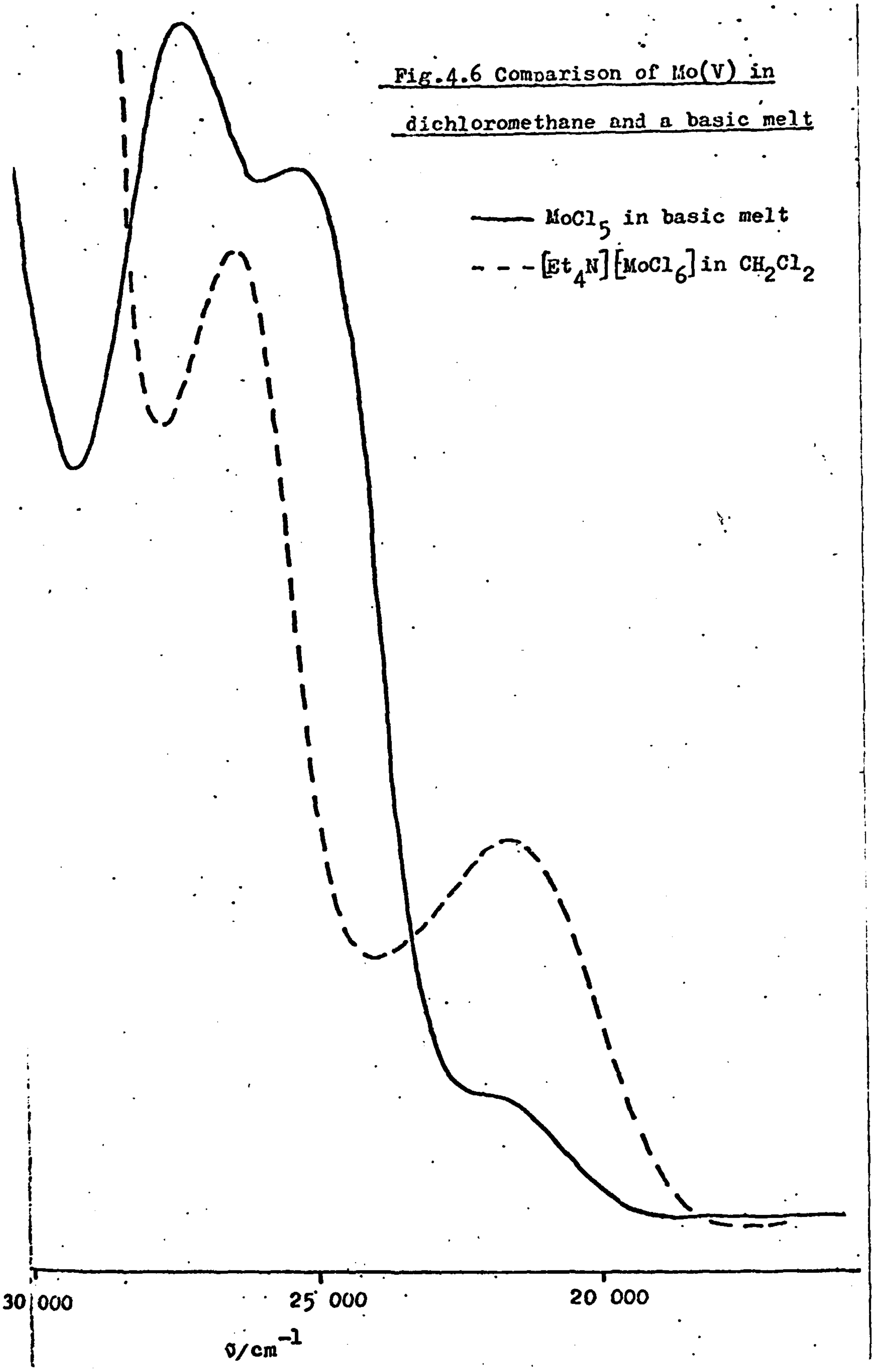


Fig.4.6 Comparison of Mo(V) in dichloromethane and a basic melt

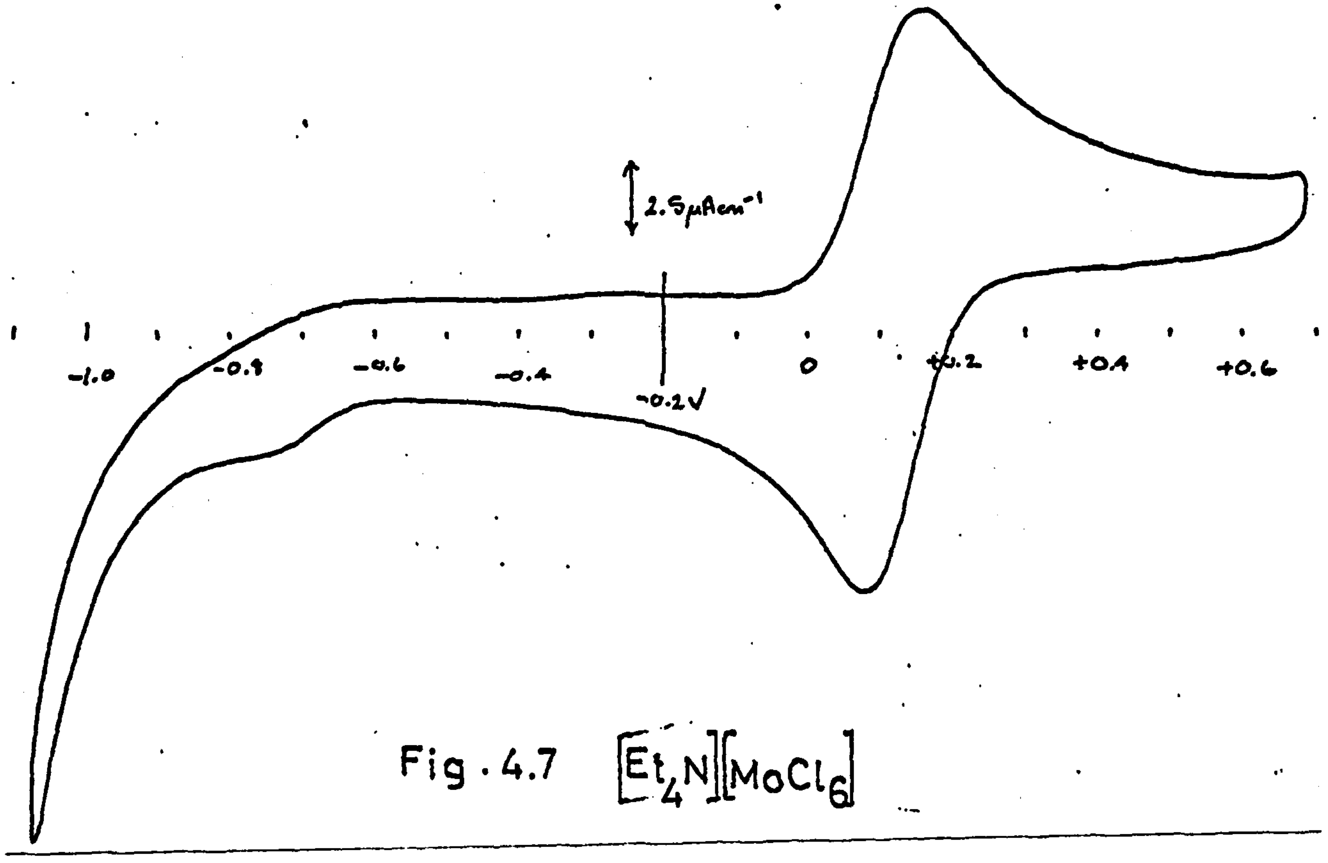


Fig. 4.7 $[Et_4N][MoCl_6]$

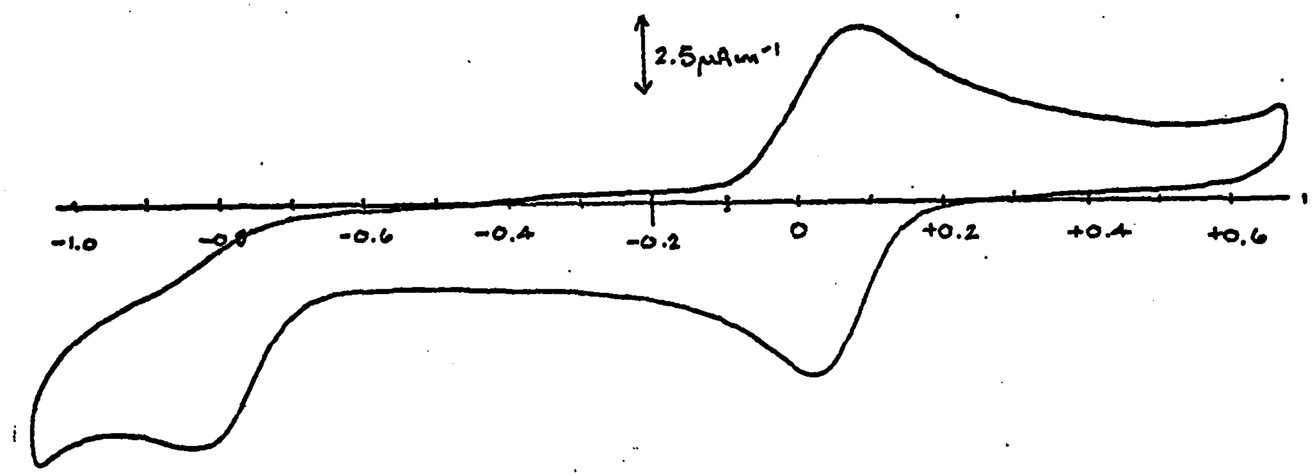


Fig 4.8 $MoCl_5$

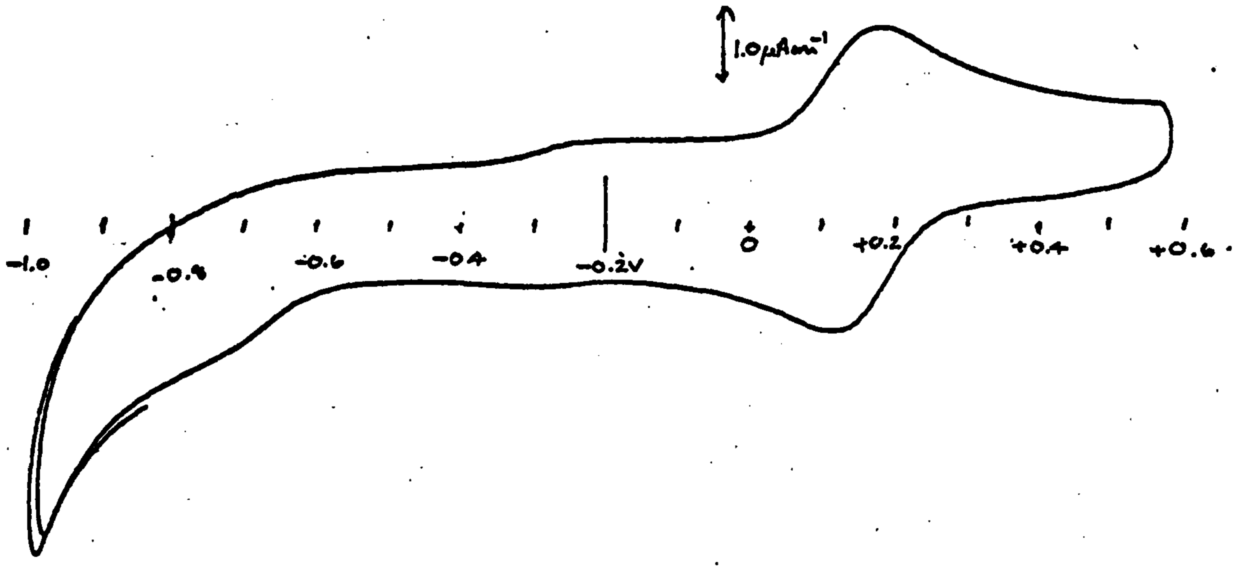


Fig.4.9 K_3MoCl_6

essentially similar, showing a single reversible and a more cathodic irreversible wave.

This fits in well with the electronic spectra recorded in the basic melt if the reversible peak is assigned to the Mo(IV)/Mo(III) couple, as both these species are stable. The irreversible reduction wave must then be due to a Mo(III)/Mo(II) reduction, resulting in the formation of cluster compounds.

TABLE 4.7 Redox Data for $[MoCl_6]^{n-}$ in a Basic Melt

Compound	E(III/II) vs SHE	$E_{\frac{1}{2}}$(IV/III) vs SHE	E_{pp}/V(IV/III)
$MoCl_5$	-0.5	+0.34	
$[MoCl_6]^-$	-0.4	+0.41	60-70mV
$[MoCl_6]^{3-}$	a	+0.39	-

[a] poorly defined

There is a shift in position of all the peaks from one cv relative to another, but as all peaks are shifted a similar distance it is likely that the potentials of peaks are moved by changing conditions. The basic melt is near to its freezing point at room temperature and it is probable that junction potential effects should be considered; the reference electrode lugging would be a likely place for any solidification to take place and this could well cause an error. From these data, the value for the average redox couple Mo^{4+}/Mo^{3+} of +0.38V (vs SHE) was determined. This assignment is endorsed by the cv of $K_3[MoCl_6]$ in 10M HCl (Figure 4.10). The irreversible wave is at a comparable position (+0.63V vs SHE) to the reversible peak in the melt cv. The $[MoCl_6]^{2-}$ is known to hydrolyse in acid and hence the Mo(III)/Mo(IV) oxidation is completely irreversible.

4.4 SPECTROSCOPIC AND ELECTROCHEMICAL MEASUREMENTS IN THE ACID MELT

4.4.1 Electronic Spectroscopy

The electronic spectra of $MoCl_5$, $[Et_4N][MoCl_6]$, $[Et_4N]_2[MoCl_6]$ and $K_3[MoCl_6]$ were recorded in an acidic melt (see Figure 4.11). The spectra of the Mo(V) species in the acid melt are very similar to the spectrum of $[Et_4N][MoCl_6]$ in dichloromethane and tend to indicate that the Mo(V) species is stable in the melt (Figure 4.12).

This would be consistent with a species of the form $[Mo(Al_2Cl_7)_3]^{2+}$. If this is so a Mo(V) reduction wave should be seen in the cyclic

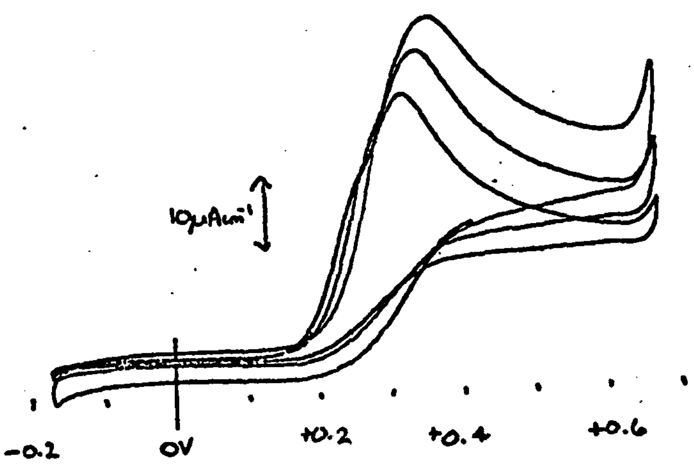


Fig. 4.10 K_3MoCl_6 in 10M HCl

Fig.4.12 Comparison of Mo(V) in the acid melt and dichloromethane

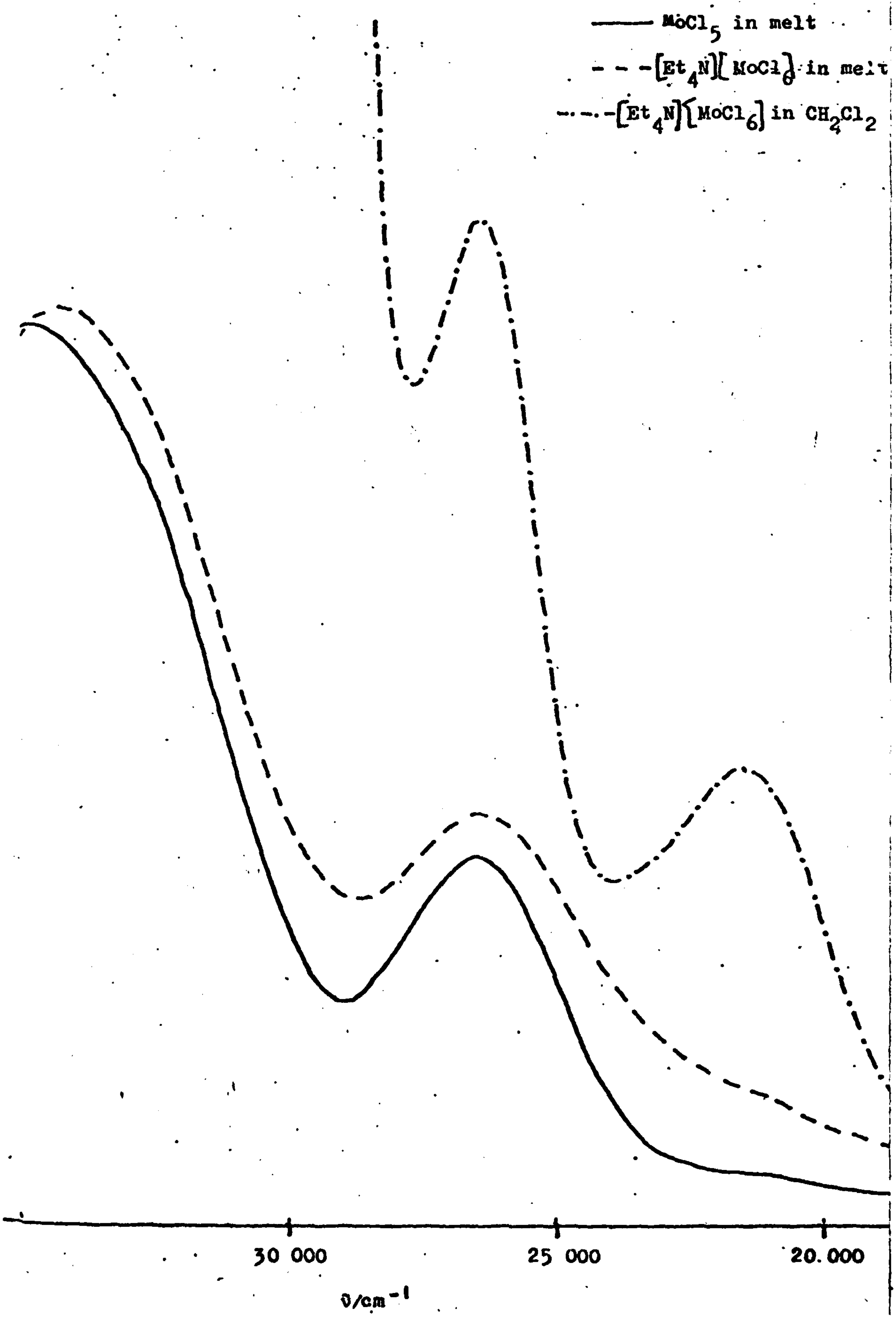
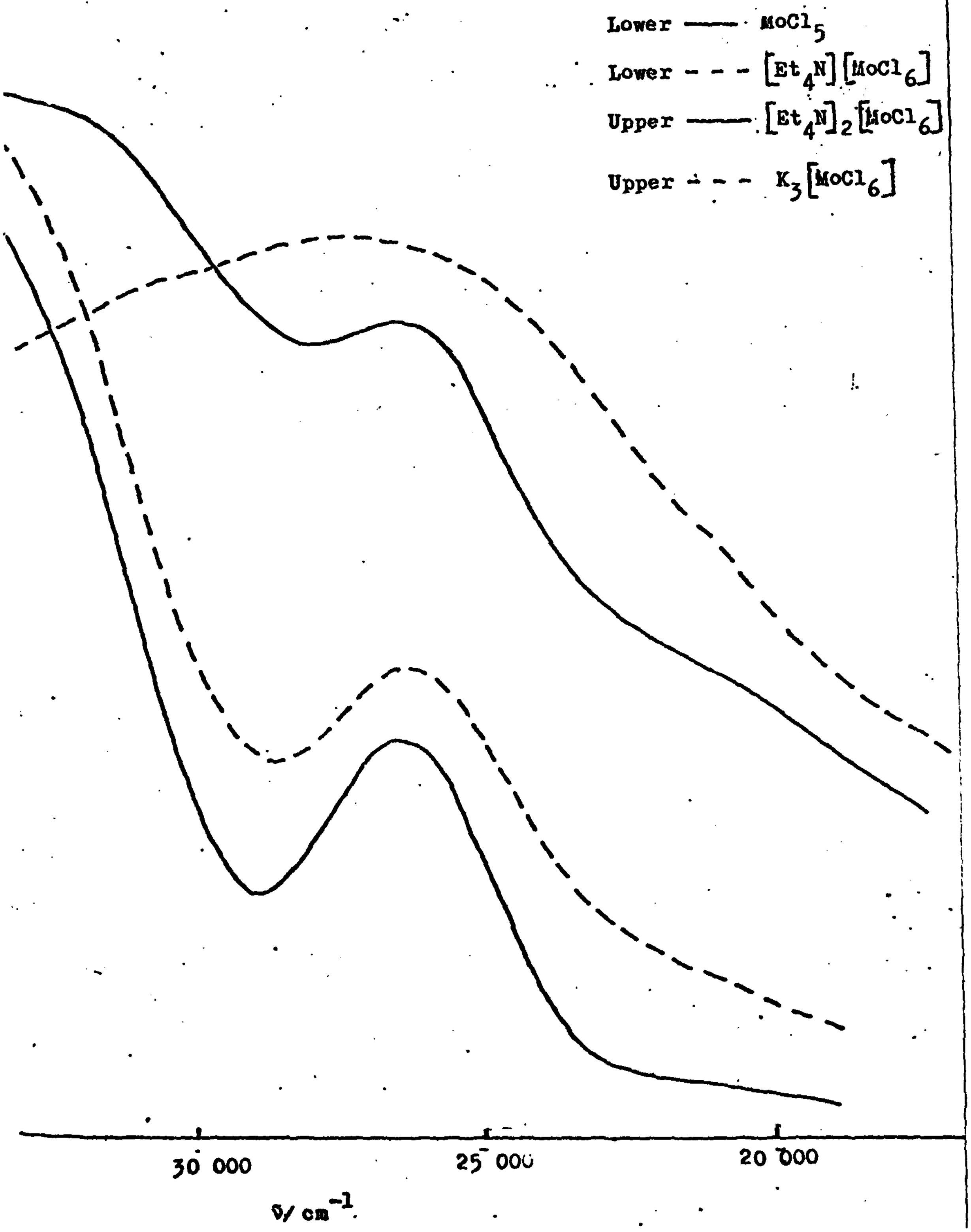


Fig.4.11 Comparison of spectra in the acidic melt



voltammograms in the acid melt.

However, this could well be an idealistic argument based on a coincidence. The same argument should apply to the $[MoCl_6]^-$ species in both acidic and basic melts, but examination of Figure 4.13 reveals very little similarity between the spectra. However, there is some evidence for a time-dependent decomposition of $[MoCl_6]^{3-}$ in the acidic melt, causing precipitation of a dark solid and spectral changes. Further investigation of this phenomena is clearly required before any meaningful conclusions can be drawn.

Comparison of the diffuse reflection spectrum of $[MoCl_6]^{2-}$ and that of $[MoCl_6]^{2-}$ in the acidic melt (Figure 4.14) is complicated by the presence of the $[MoOCl_5]^{2-}$ impurity (unstable in basic melts, but possibly stable in acidic conditions). Again, further work is required to clarify this situation.

4.4.2 Electrochemical Studies

The cyclic voltammograms of $MoCl_5$, $[Et_4N][MoCl_6]$ and $K_3[MoCl_6]$ were recorded in the acidic melt (Figures 4.15-4.17). The waves are tabulated in Table 4.8.

TABLE 4.8 Redox Data for $[MoCl_6]^{n-}$ in Acidic Melts

	MoCl	$[Et_4N][MoCl_6]$	$K_3[MoCl_6]$
Wave	$E_{1/2}$/V vs SHE	$E_{1/2}$/V vs SHE	$E_{1/2}$/V vs SHE
A	+2.5	+2.57	+2.61
B	+2.22	+2.16	+2.21
C	+1.97	+1.96	+1.88
D	+1.35	+1.4	INDETERMINATE

There may be a drift in the positions of waves, in a similar manner to the cyclic voltammograms conducted in the basic melt. There seems reasonable correlation between the cv's derived from the three species in the acid melt, but (in contrast to the situation in the basic melts) there are also some significant changes. The major difference between the cv's occurs between Mo_2Cl_{10} in the acid melt, and the other molybdenum species. The ratio of the peak heights of wave B in the former case to those of the latter case leads to the conclusion that in the $MoCl_5$ case, dimers are present, possibly of the form:

Fig.4.13 Comparison of $K_3[MoCl_6]$ spectra in (a) basic & (b) acid melt

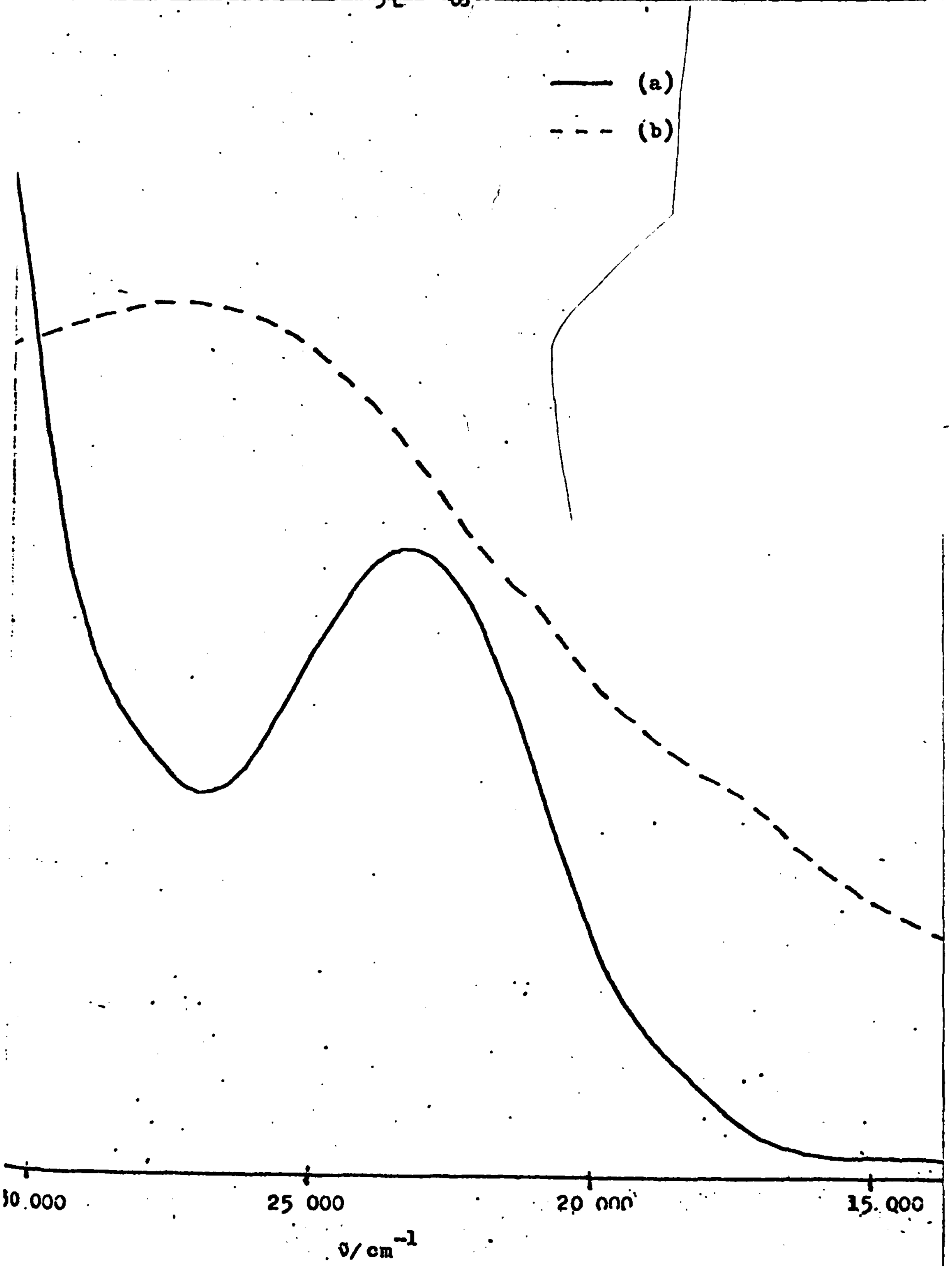
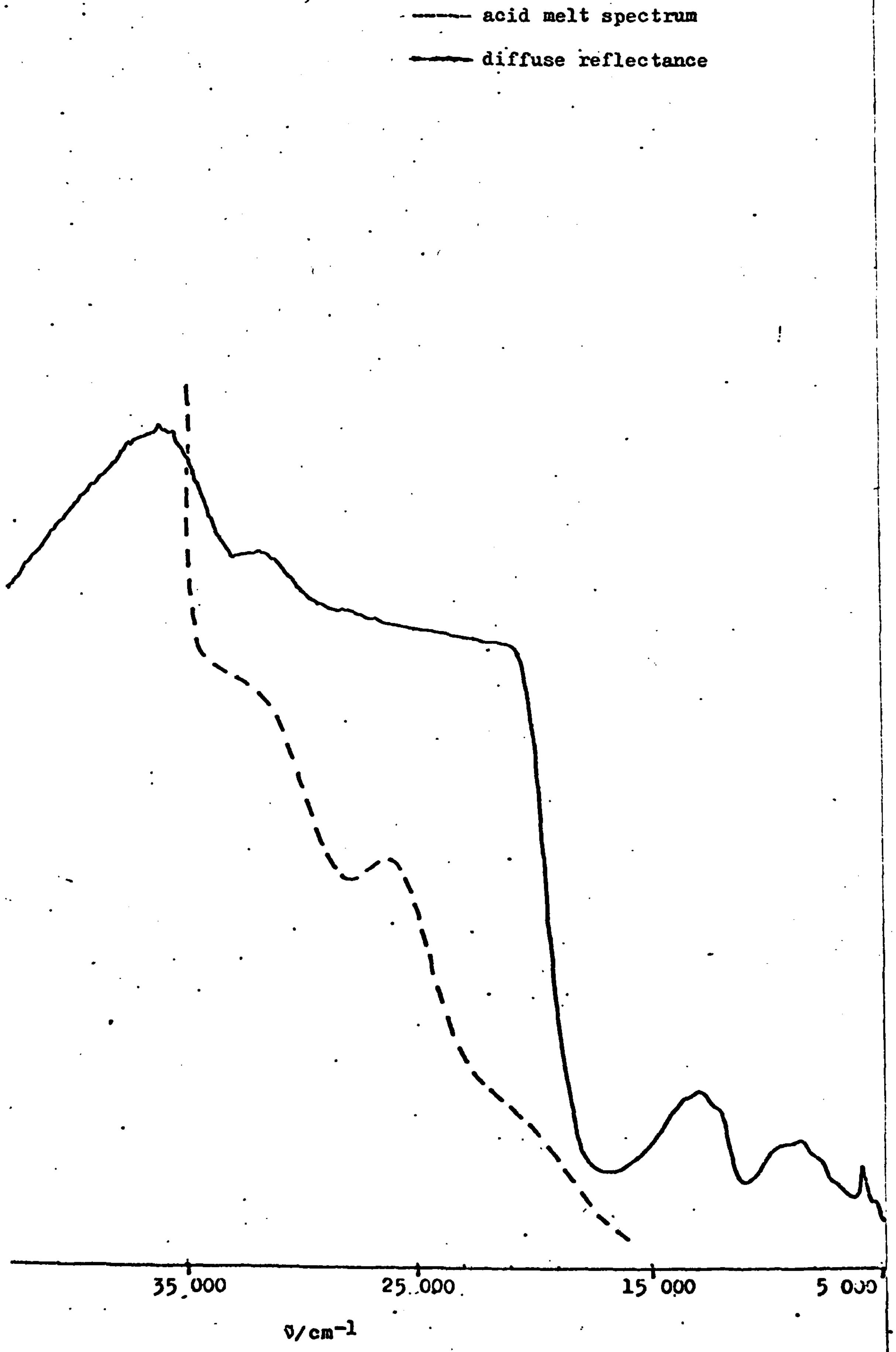


Fig.4.14 Comparison of the diffuse reflectance and acid melt spectra of$[Et_4N]_2[MoCl_6]$



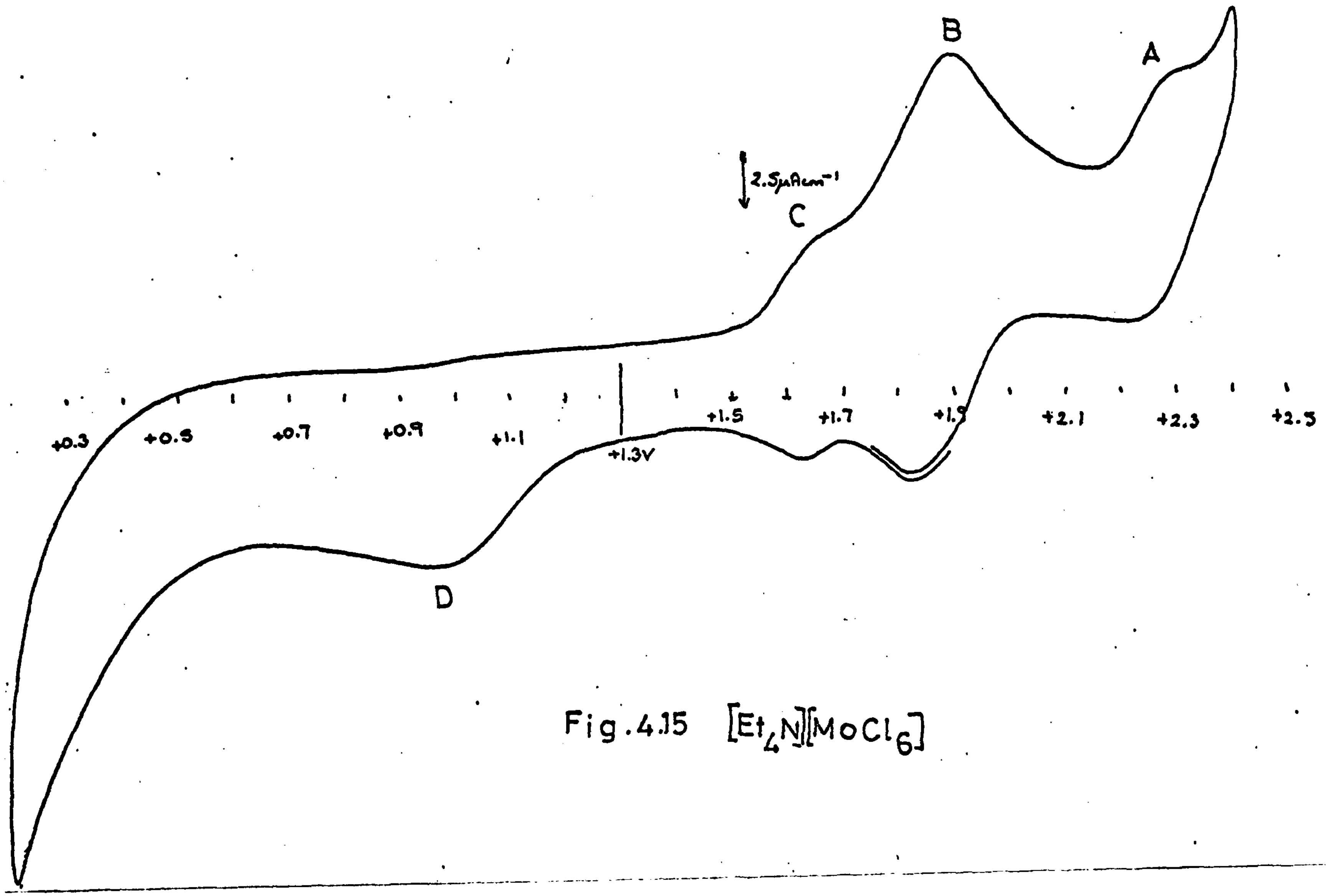


Fig. 4.15 $[Et_4N][MoCl_6]$

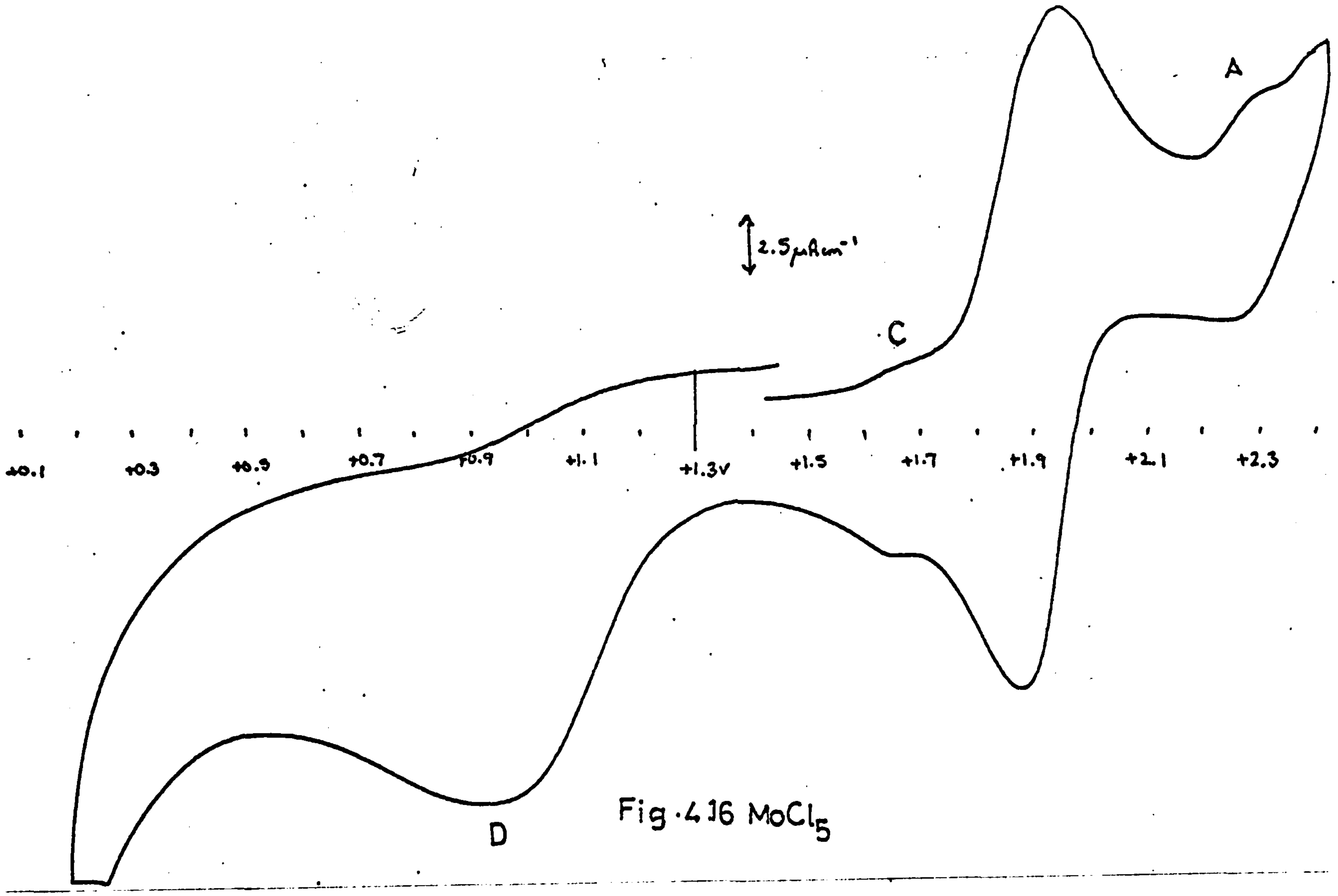


Fig. 4.16 $MoCl_5$

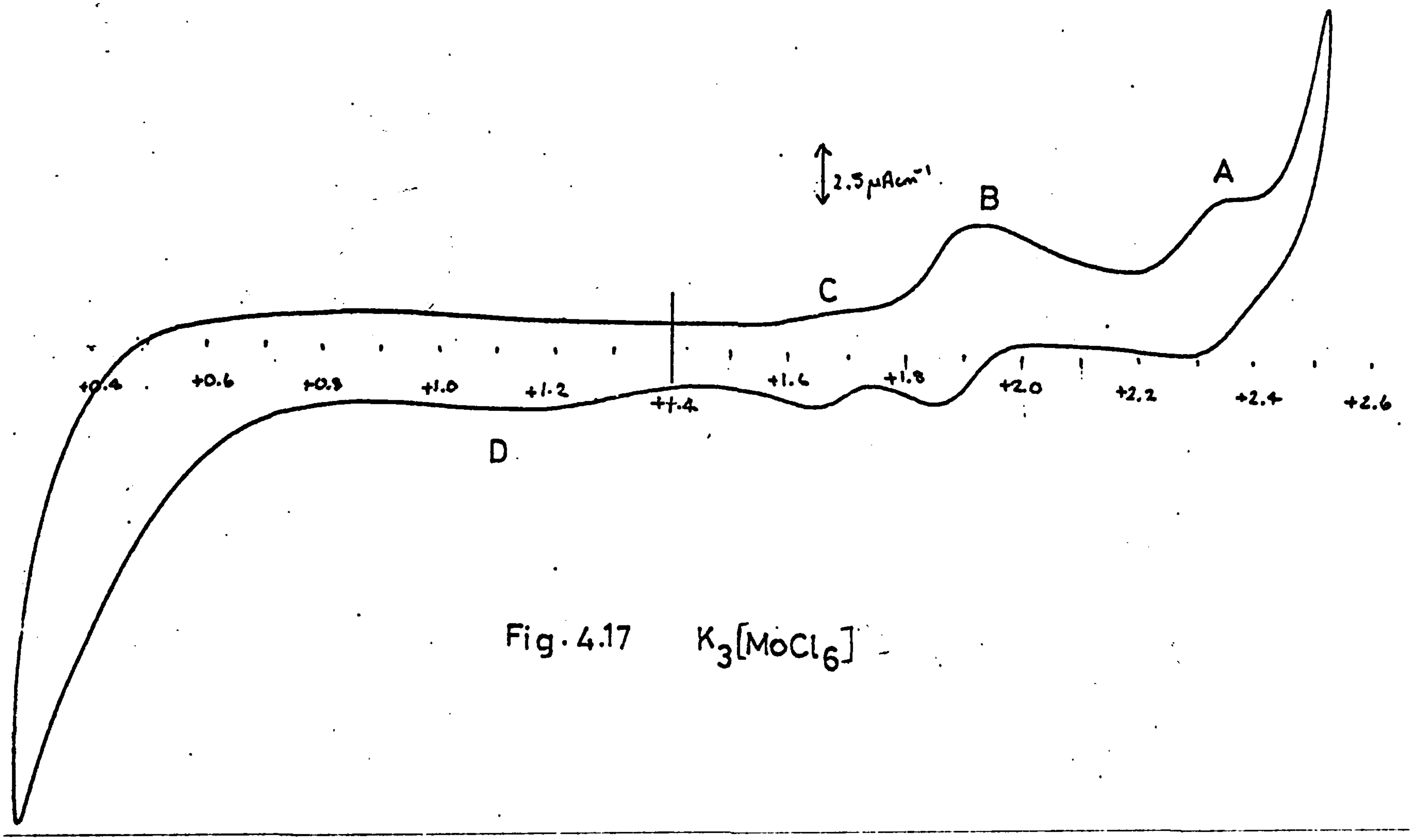
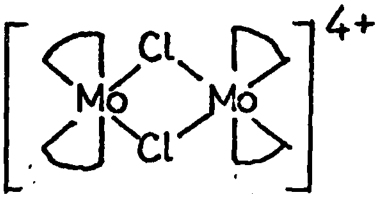


Fig. 4.17 $K_3[MoCl_6]$



$[Mo_2Cl_2(Al_2Cl_7)_4]^{4+}$

Examination of the data in Table 4.8 and Figures 4.15-4.17 leads to the conclusion that waves A and C are correlated, and that there must be a contribution to B which is related to A and C. This, together with chemical and spectroscopic considerations leads to the following tentative assignments of the data:

Wave A	:	Mo(VI)/Mo(V)	
Wave B	:	Mo(V)/Mo(IV) +	Mo_2(V)/Mo_2(III)
Wave C	:	Mo(IV)/Mo(III)	
Wave D	:		Mo_2(III)/$Mo_{cluster}$(II)

These results must remain tentative until further studies are performed. Of particular interest would be a study of $K_3[Mo_2Cl_9]$.

4.5 DIMERIC MOLYBDENUM SPECIES

Dimeric molybdenum species containing a metal-metal quadruple bond have been the subject of a number of electronic spectral studies, mainly in attempts to verify the calculated energies of electronic transitions in these species. A solution study of the related $[Mo_2Cl_8H]^{3-}$ anion has also been published [83]. Data from a number of literature studies is presented in Table 4.9.

TABLE 4.9 Literature Electronic Spectra of Some Molybdenum Dimers

Species	Phase	max./kK			
$K_4[Mo_2Cl_8]2H_2O$	solid [82]		31.4	24.0	18.8
$K_4[Mo_2Cl_8]$	3<u>M</u> HCl[83]			26.3	19.4
$Rb_3[Mo_2Cl_8H]$	3<u>M</u> HCl[83]			23.7	16br
$[Mo_2(OAc)_4]$	ethanol [81]	34.0	32.8sh	23.0	
$[Mo_2(OAc)_4]$	solid [81]			23.1	

The basic melt electronic spectra of the molybdenum dimers prepared in this work were measured, in addition to electronic spectra in other solvents and in the solid state. These measurements are presented in Table 4.10.

TABLE 4.10 Electronic Spectra of Molybdenum Dimers Prepared in this Work

Species	Phase	$_{max.}$/kK					
$K_4[Mo_2Cl_8]$	solid	41.8	32.0	29.2	23.2	19.3	13.6
	basic melt				23.2	18.9	13.3
	$3\underline{M}$ HCl				24.7	19.6	
$Cs_3[Mo_2Cl_8H]$	solid		42.0	37.0	22.7	14.4	13.5sh
	basic melt(a)				23.3	19.5	13.5
	$3\underline{M}$ HCl				24.3		13.6
$[Mo_2(OAc)_4]$	basic melt				22.8	19.3	13.6
	solid	41.2sh	35.4	29.8sh	22.8		
	ethanol		34.4	29.8	20.6		

(a) the orange coloured solution of $[Mo_2(OAc)_4]$.

Most of the dimers prepared were sparingly soluble in basic melt, but the yellow $[Mo_2(OAc)_4]$ was readily soluble, yielding a bright red solution. Interestingly, the initial colouration rapidly changed to orange. From observing the colour changes in the basic melt solution and by comparison of the basic melt and ethanol electronic spectra of $[Mo_2(OAc)_4]$ (Fig. 4.18) it was clear that the compound had undergone chemical reaction upon dissolution. This was not surprising because the reaction of $[Mo_2(OAc)_4]$ with hydrochloric acid is the main route to the other molybdenum dimers prepared in this work and basic melt has a very large effective concentration of chloride ion.

The diffuse reflectance spectrum of each of the dimers studied (Fig. 4.19) was quite distinct and also different from that of $K_3[MoCl_6]$. However, the coincidence of a number of absorption energies complicated the determination of the solution species present, and the criteria of band profile and band width were required to elucidate the nature of the species present in basic melt.

Even though there were coincidental band energies between $Cs_3[Mo_2Cl_8H]$ and $K_4[Mo_2Cl_8]$ melt spectra, the occurrence of groups of bands was used to distinguish between the species present in these two solutions. Comparison of the diffuse reflectance and hydrochloric acid

Fig 4.18 Comparison of $[Mo_2(OAc)_4]$ in ethanol and basic melt

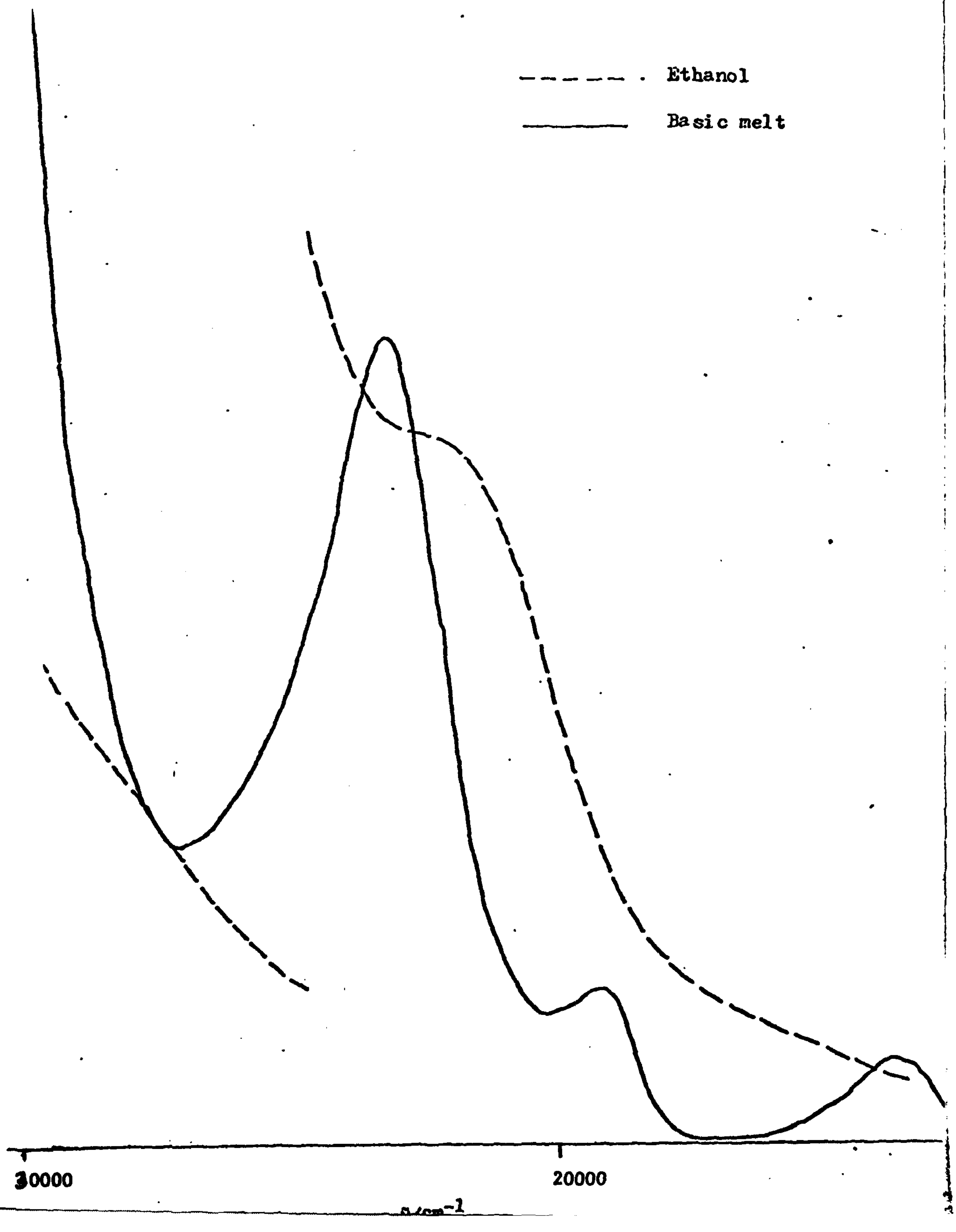
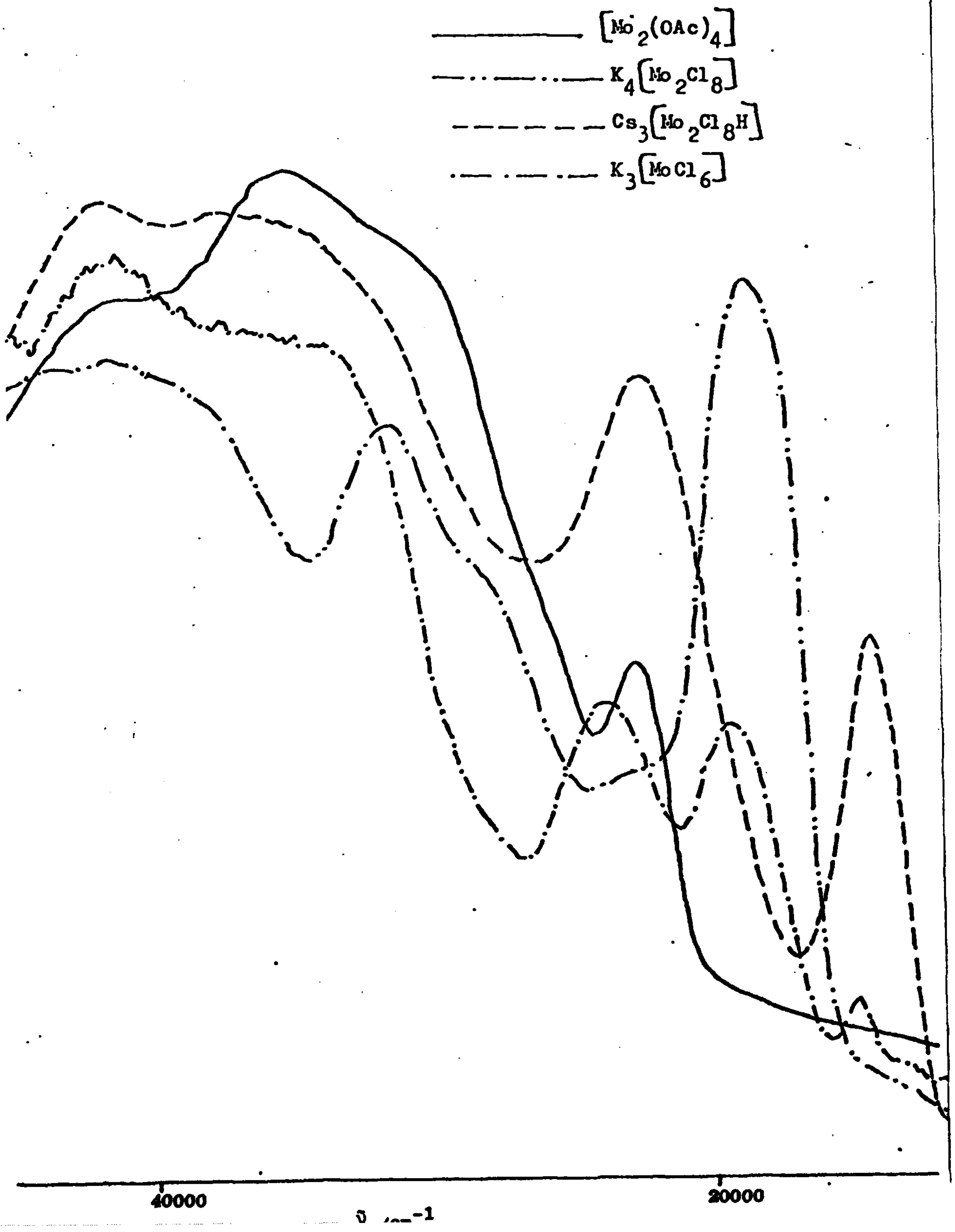


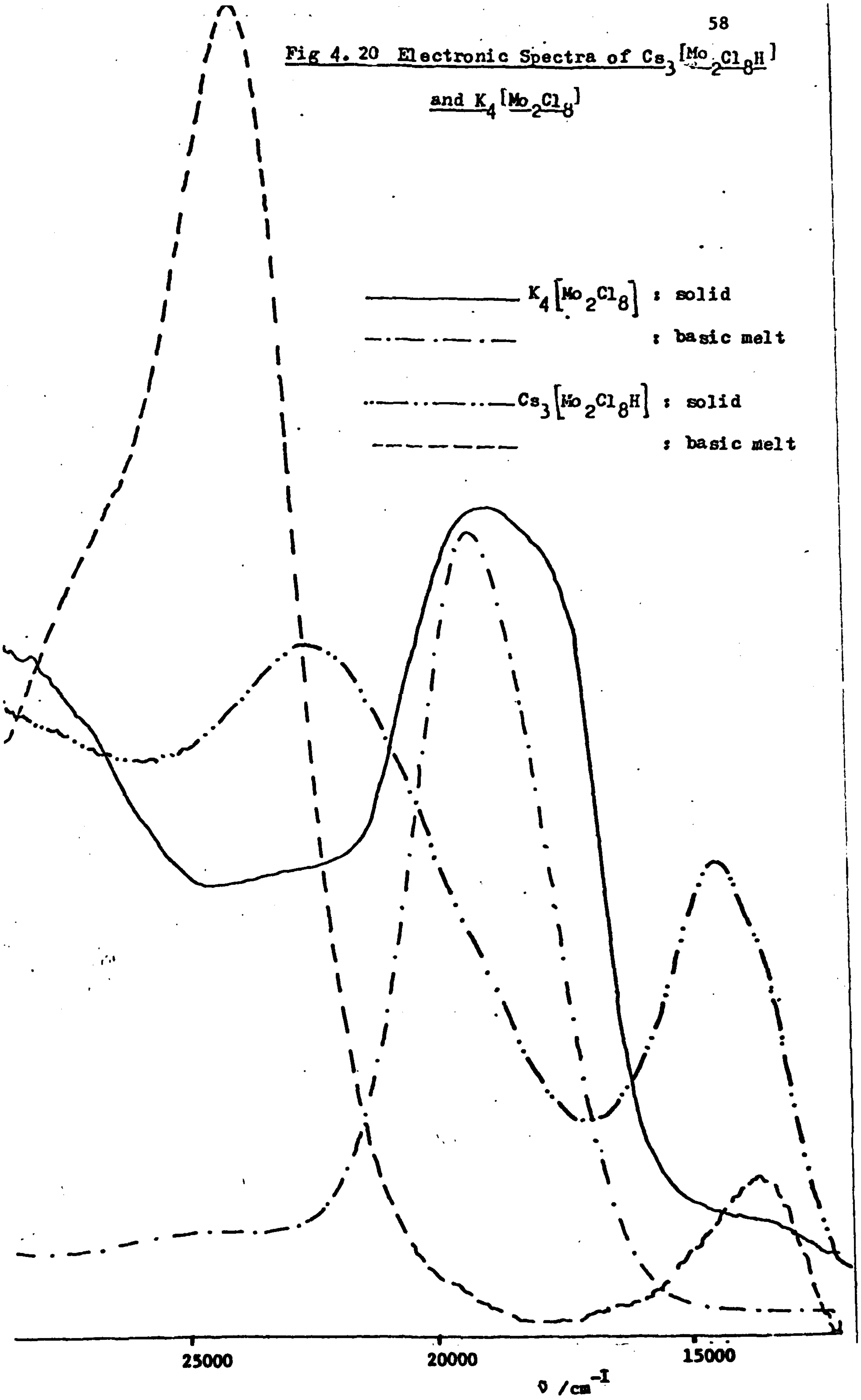
Fig 4.19 Diffuse Reflection Spectra of Molybdenum Dimers and $K_3[MoCl_6]$



electronic spectra of $K_4[Mo_2Cl_8]$ and $Cs_3[Mo_2Cl_8H]$ (Fig. 4.20) indicated that these compounds dissolved in 3M HCl to give $[Mo_2Cl_8]^{4-}$ and $[Mo_2Cl_8H]^{3-}$ respectively as the initial solution species formed. Trogler and co-workers [83] have studied the photochemically induced oxidation of $[Mo_2Cl_8H]^{3-}$ in 3M HCl. Irradiation of such a solution at 254nm (39.4kK) produces $[Mo_2Cl_8H]^{3-}$, which is then hydrolysed to form dihydrogen and an hydroxy bridged molybdenum dimer containing the $\{Mo(OH)_2Mo\}^{4+}$ entity. In this work, the hydrolysis of $[Mo_2Cl_8H]^{3-}$, as detected by the electronic spectra of solutions in hydrochloric acid was rapid (Fig. 4.21). This is thought to be the cause of the shift in energy (relative to the solid state) of the strongest band in the electronic spectra of $Cs_3[Mo_2Cl_8H]$ in hydrochloric acid. The fact that basic melts were themselves extremely moisture sensitive, requires that no hydrolysis of dissolved species was possible. No shift was observed between the basic melt spectrum and the solid state spectrum of $Cs_3[Mo_2Cl_8H]$, and moreover, basic melt solutions of $Cs_3[Mo_2Cl_8H]$ gave unchanged electronic spectra over a period of months. The strongest band in $Cs_3[Mo_2Cl_8H]$ spectra in various media was always sharp, a particularly important point because all the dimers studied, as well as $K_3[MoCl_6]$ gave basic melt spectra with an intense absorption at approximately 23kK. (Fig. 4.22). Whereas $[Mo_2(OAc)_4]$ and $Cs_3[Mo_2Cl_8H]$ solutions in basic melt produced electronic spectra with sharp absorption at 23 KK, the band at this wavenumber in $K_3[MoCl_6]$ or $K_4[Mo_2Cl_8]$ basic melt solutions was broad. In addition, the $K_4[Mo_2Cl_8]$ spectrum had a shoulder on this band to high energy which was not seen in any other melt spectrum. This shoulder and the absorption at 19.2kK were assigned to the $[Mo_2Cl_8]^{4-}$ anion by comparison with the hydrochloric acid and diffuse reflectance spectra of $K_4[Mo_2Cl_8]$ (Fig. 4.23). The peak at 23.2kK was attributed to the $[MoCl_6]^{3-}$ anion (Fig. 4.23). Hence it appears that $K_4[Mo_2Cl_8]$ dissolves in basic melt to form a mixture of $[MoCl_6]^{3-}$ and $[Mo_2Cl_8]^{4-}$.

Apart from the sharp feature at 23.2kK observed in basic melt solutions of both $[Mo_2(OAc)_4]$ and $Cs_3[Mo_2Cl_8H]$, another important absorption is the asymmetrical band at 13.6kK, seen also in the hydrochloric acid spectrum of $Cs_3[Mo_2Cl_8H]$, and as a shoulder in the diffuse reflectance spectrum of $Cs_3[Mo_2Cl_8H]$. The similarity between the electronic spectra of these three solutions and the diffuse reflectance spectrum of $Cs_3[Mo_2Cl_8H]$ (Fig. 4.24) suggests that the solutions all contain the $[Mo_2Cl_8H]^{3-}$ anion as the only molybdenum containing species.

Fig 4.20 Electronic Spectra of $Cs_3[Mo_2Cl_8H]$ and $K_4[Mo_2Cl_8]$



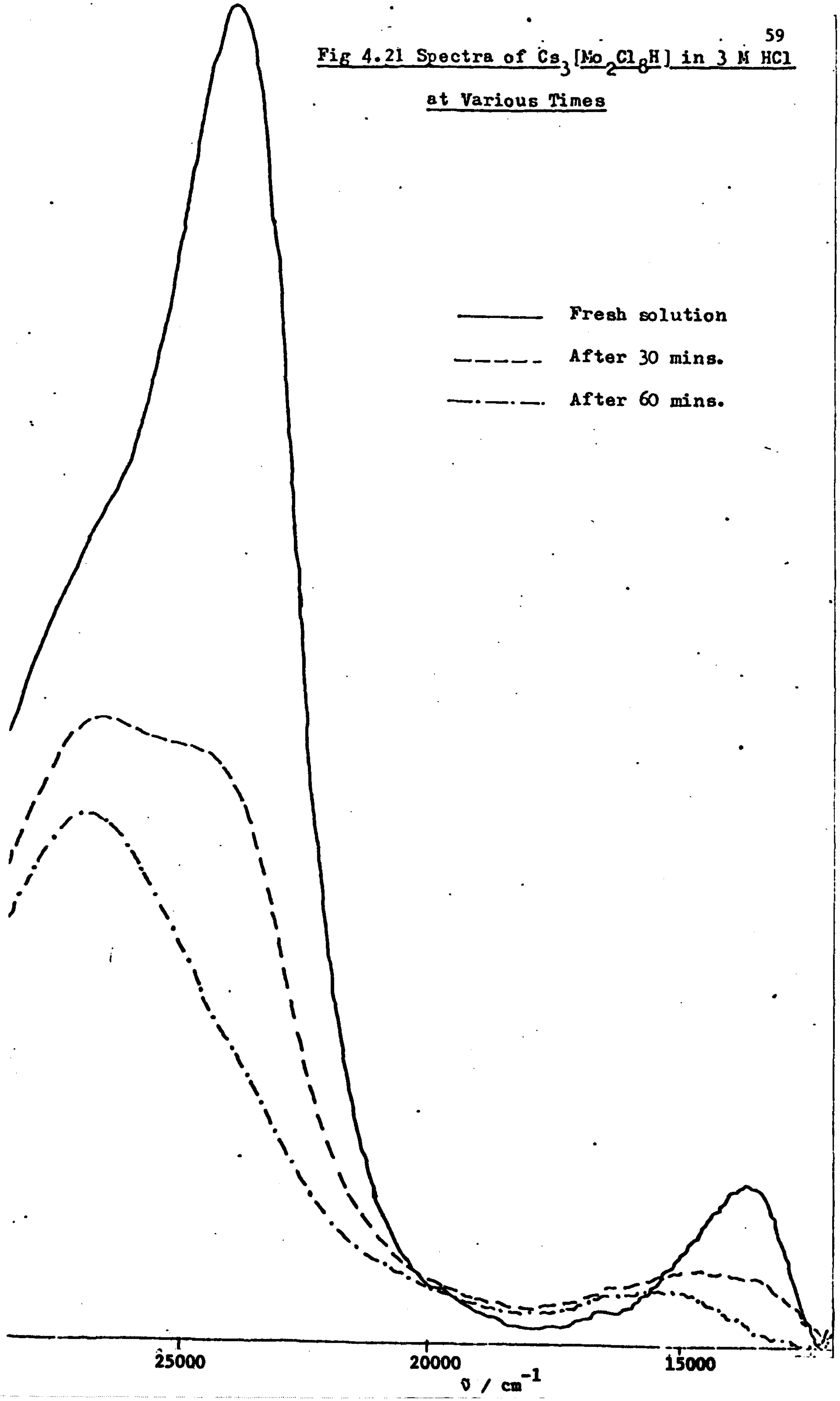


Fig 4.21 Spectra of $Cs_3[Mo_2Cl_8H]$ in 3 M HCl at Various Times

Fig 4.22 Basic Melt Spectra of Molybdenum Dimers and $K_3[MoCl_6]$

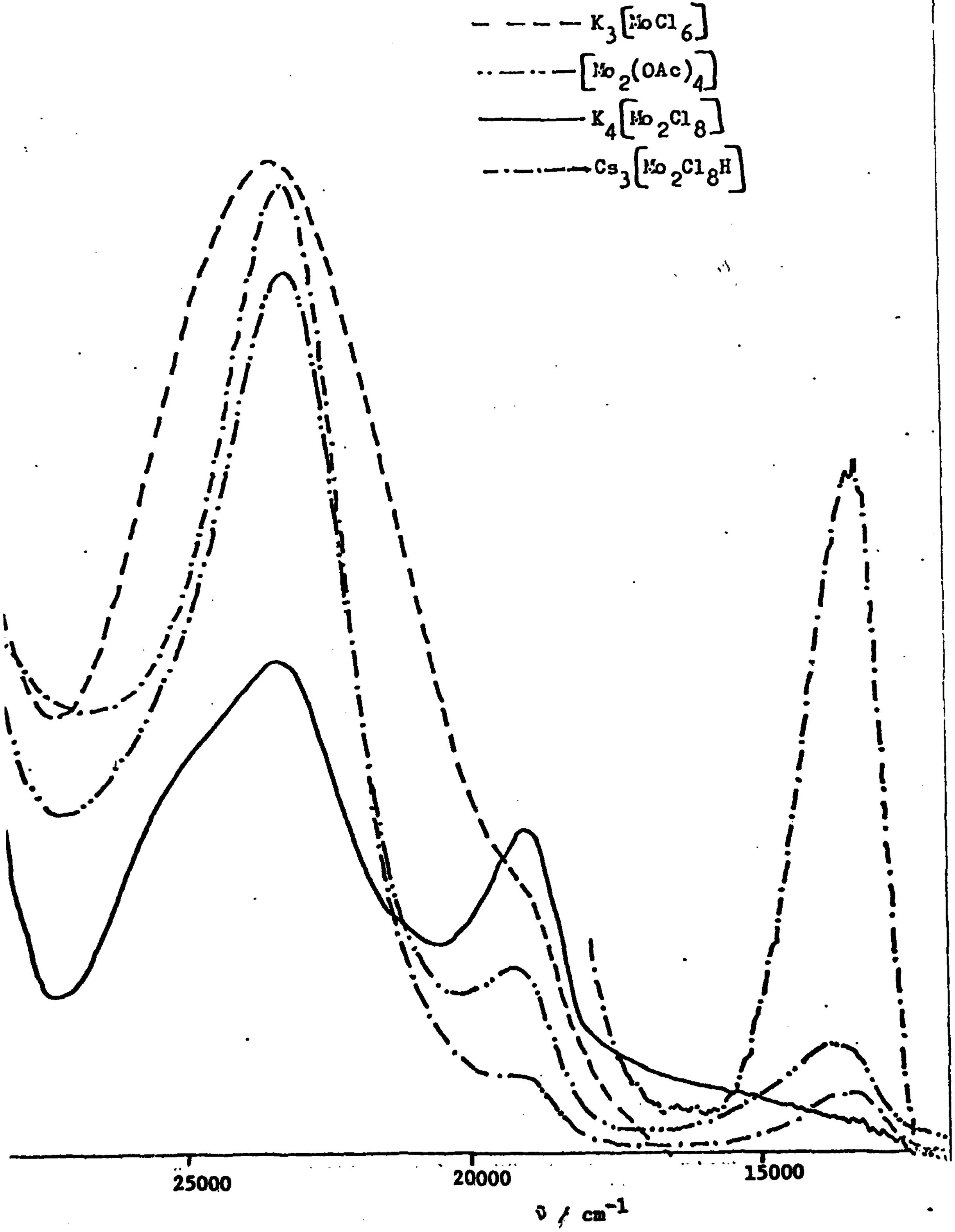


Fig 4.23 Comparison of $K_3[MoCl_6]$ and $K_4[Mo_2Cl_8]$ Electronic Spectra

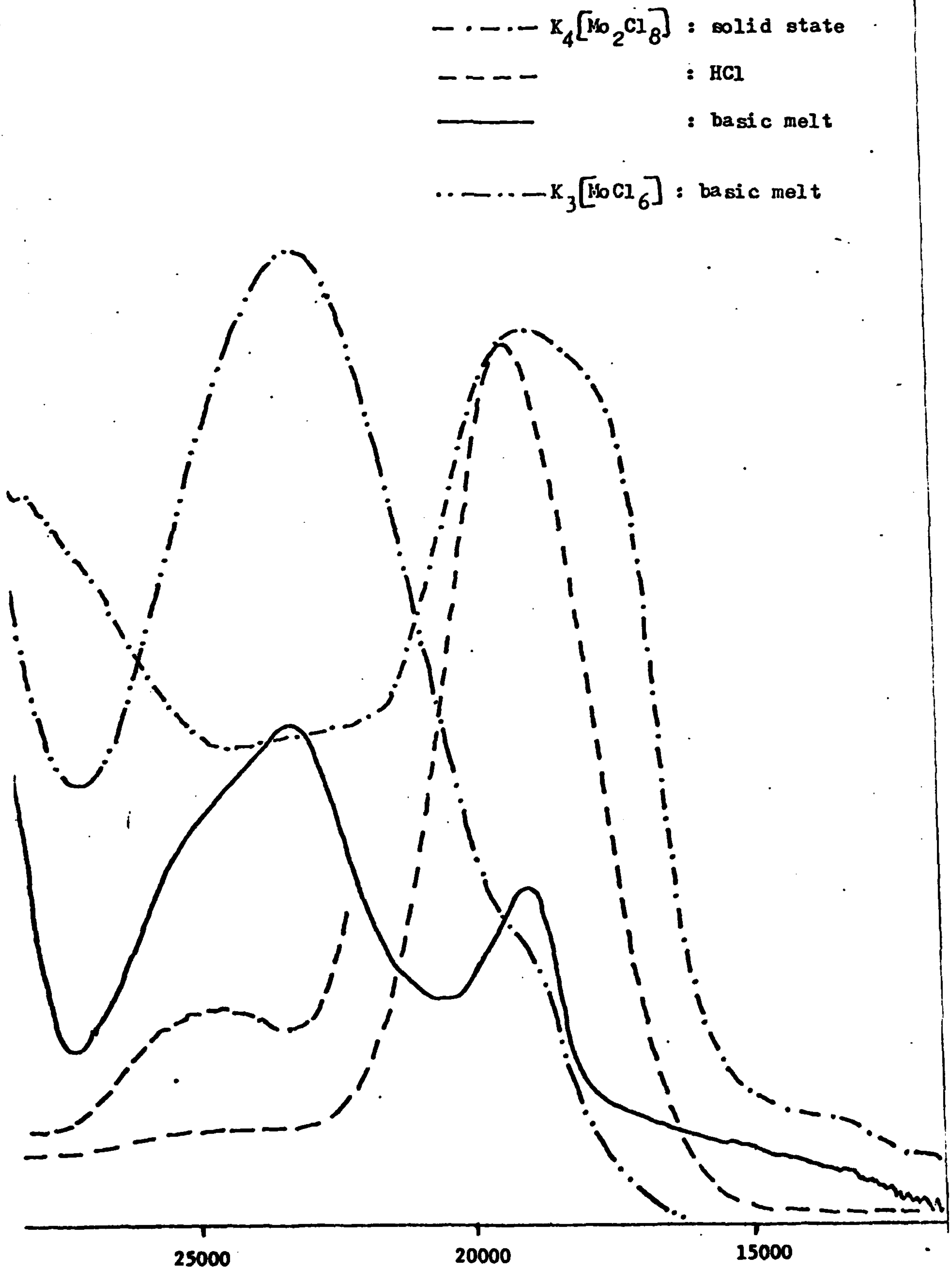
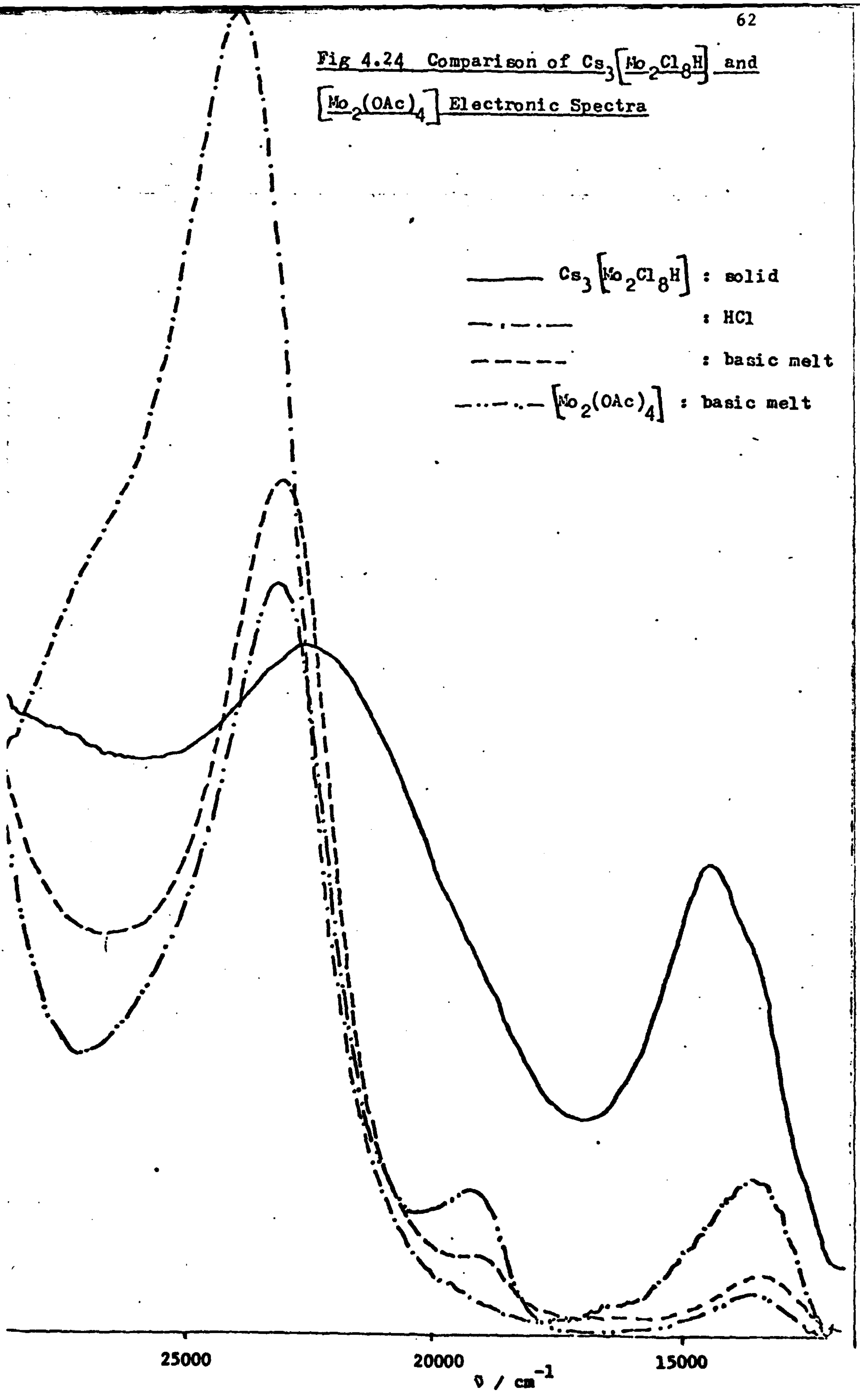


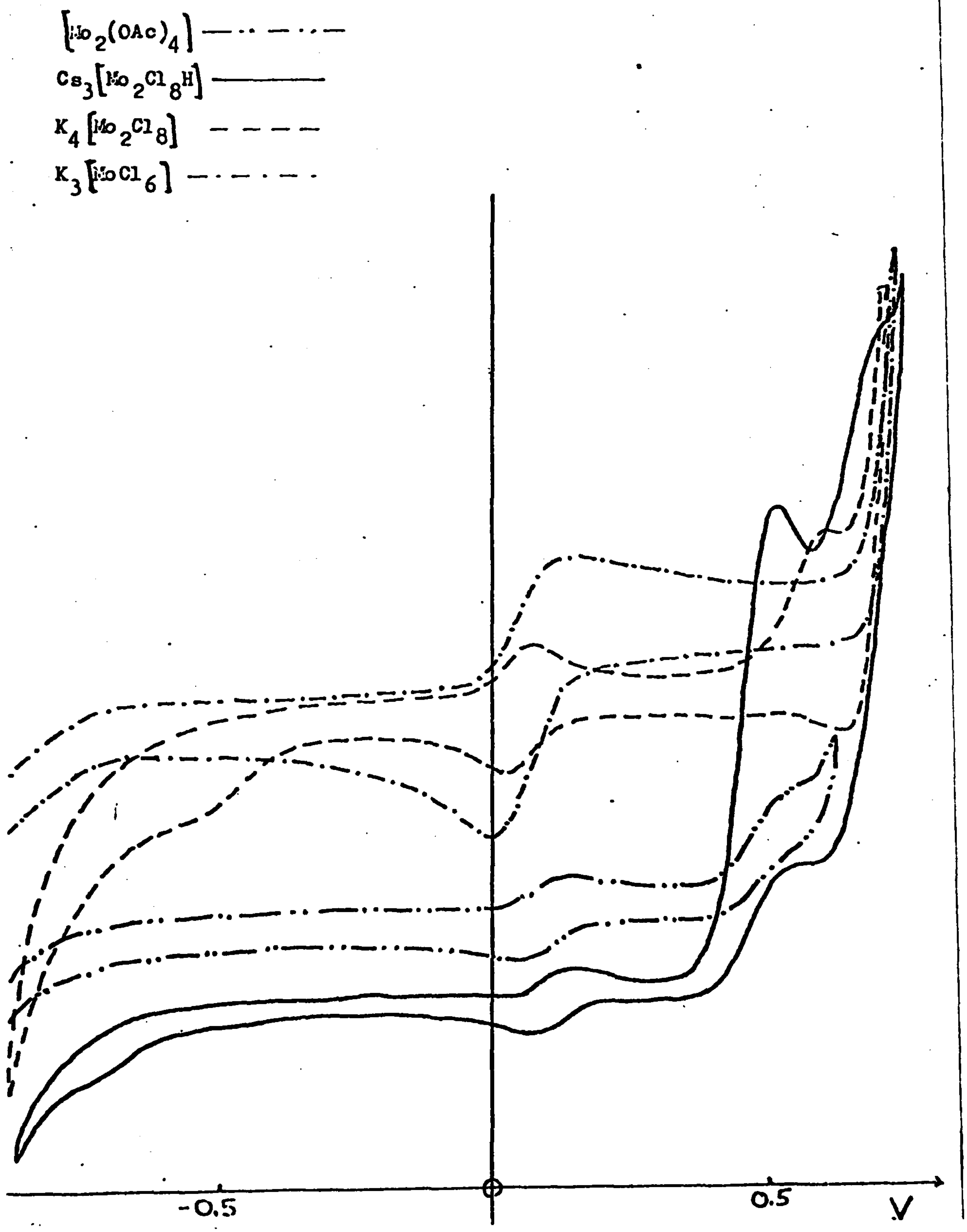
Fig 4.24 Comparison of $Cs_3[Mo_2Cl_8H]$ and $[Mo_2(OAc)_4]$ Electronic Spectra



Cyclic voltammograms of solutions of $K_4[Mo_2Cl_8]$, $Cs_3[Mo_2Cl_8H]$ and $[Mo_2(OAc)_4]$ in basic melt were obtained. These are reproduced in Figure 4.25. The reversible wave for the $K_4[Mo_2Cl_8]$ solution had a potential of 0.45V, which is the value of the $[MoCl_6]^{3-/2-}$ couple in basic melt. This is in accordance with the conclusion that basic melt solutions of $K_4[Mo_2Cl_8]$ contain $[MoCl_6]^{3-}$. The reversible wave for $Cs_3[Mo_2Cl_8H]$ in basic melt had a potential of 0.51V, confirming the conclusion that this solution does not contain $[MoCl_6]^{3-}$. Unfortunately, the reversible wave given by the basic melt solution of $[Mo_2(OAc)_4]$ had a potential of 0.49V and it was therefore not possible to assign this wave to either $[MoCl_6]^{3-}$ or $[Mo_2Cl_8H]^{3-}$. *However*, this observation neither confirms nor refutes the conclusion reached about the nature of the basic melt solution species from $[Mo_2(OAc)_4]$.

The results presented in this chapter have confirmed the previous conclusion that in basic melt molybdenum(V) is reduced to molybdenum(IV). It also seems likely that a far slower reduction of molybdenum(IV) to molybdenum(III) occurs in the melt. New work on molybdenum dimers in basic melt has shown that $Cs_3[Mo_2Cl_8H]$ dissolves in the melt without chemical reaction, but $K_4[Mo_2Cl_8]$ is partially oxidised to $[MoCl_6]^{3-}$. It is reasonably certain that $[Mo_2(OAc)_4]$ reacts with basic melt to form $[Mo_2Cl_8H]^{3-}$ and hence this work reports the first recorded inorganic transformation in aluminium(III) chloride/BPC molten salts.

Fig 4.25 Cyclic Voltammograms of Some Molybdenum Dimers and K_3MoCl_6 in Basic Melt



5.1 EXPERIMENTAL

5.1.1 Preparation of Cobalt(II) chloride

A slight excess of freshly distilled thionyl chloride (55 cm^3) was added to finely ground $CoCl_2.6H_2O$ (20 g). After the effervescence had ceased, the pink cobalt(II) salt had turned dark blue. The remaining slurry was heated under reflux for about 2 h. Excess thionyl chloride was then removed in vacuo and the remaining thionyl chloride clinging to the product was removed by continuous evacuation with heating to 120 °C for 5 h., followed by continuous evacuation for over 24 h.

5.1.2 Preparation of Nickel(II) chloride

The above method was repeated using thionyl chloride (55 cm^3) and $NiCl_2.6H_2O$ (20 g). After effervescence had ceased, the lime green nickel(II) salt had become yellowish in colour.

5.1.3 Preparation of Copper(II) chloride

The method above was repeated with thionyl chloride (25 cm^3) and $CuCl_2.2H_2O$ (10 g). After effervescence had ceased, the blue copper(II) salt had turned brown.

The products of these reactions are all hygroscopic and so were transferred to dry containers and kept in the dry box.

	Colour	% Cl (found)	% Cl (theoretical)
$CoCl_2$	Blue	52.58	54.61
$NiCl_2$	yellow-brown	52.90	54.70
$CuCl_2$	brown	50.70	52.74

5.1.4 Preparation of Iron(III) chloride

The method used to prepare the anhydrous metal(II) chlorides (Section 5.1.1) was also used to prepare iron(III) chloride. Freshly distilled thionyl chloride (25 cm^3) was added to yellow $FeCl_3.6H_2O$ (10 g). After effervescence had ceased, a black slurry remained. The excess thionyl chloride was removed as described in Section 5.1.1.

5.1.5 Preparation of Chromium(III) chloride

The above method was also used to prepare chromium(III) chloride. Freshly distilled thionyl chloride (25 cm^3) was added to green

$CrCl_3.6H_2O$ (10 g). After effervescence had ceased, a violet slurry remained. The excess thionyl chloride was removed as described in Section 5.1.1.

Both chlorides are extremely hygroscopic, and were transferred as quickly as possible into a dinitrogen-filled dry-box, where all transfers of these solids were performed. The chlorides were stored in sealed ground glass containers.

	Colour	% Cl (found)	% Cl (theoretical)
$CrCl_3$	violet	63.30	67.20
$FeCl_3$	black	60.04	65.62

5.1.6 Preparation of vanadium(III) chloride

Sulphur monochloride (15 cm^3) was added to vanadium(V) oxide (5 g) in a round-bottomed flask (50 cm^3) which had been flushed with dry dinitrogen and a condenser fitted. The mixture was heated under a constant flow of dry dinitrogen for 8 h. The flask was then sealed quickly with a suba-seal and standard Schlenk line filtration techniques were used to isolate the reaction product. The violet solid remaining was washed four times with dry carbon disulphide (4 x 10 cm^3) to remove the sulphur which was obviously present from the yellow deposits observed in the condenser. The flask was quickly attached to the vacuum line and evacuated for 24 h. to remove any remaining S_2Cl_2 or CS_2, and then transferred to the dry box where it was stored in a ground glass container. The resulting violet solid was extremely hygroscopic.

	% Cl (found	% Cl (theoretical)
VCl_3	66.29	67.66

5.1.7 Preparation of $[Et_4N]_2[CoCl_4]$

Tetraethylammonium chloride hydrate (1.8 g) and $CoCl_2.6H_2O$ (1.2 g) in the molar ratio 2:1 were dissolved in absolute ethanol (5 cm^3). The two solutions were filtered, mixed together, and boiled for a few minutes to remove some of the excess solvent. On cooling, blue crystals precipitated, which were collected by filtration and dried *in vacuo* for 24 h.

5.1.8 Preparation of $[Et_4N]_2[NiCl_4]$

The above method was repeated using $NiCl_2.6H_2O$ (1.2 g) in the place of $CoCl_2.6H_2O$. This product was also blue.

5.1.9 Preparation of $[Et_4N]_2[CuCl_4]$

The same method as above was employed using $CuCl_2.2H_2O$ (0.85 g) in the place of $CoCl_2.6H_2O$. The product was yellow.

5.1.10 Preparation of $[Et_4N]_2[FeCl_4]$

Tetraethylammonium chloride hydrate (1.8 g) and $FeCl_2.6H_2O$ (0.8 g) were dissolved in degassed absolute ethanol (5 cm^3). The solutions were prepared and subsequently handled using the Schlenk line. The two solutions were filtered and mixed on the line with a constant flushing of dry dinitrogen to prevent oxidation to iron(III). The creamy-white product was obtained using standard Schlenk filtration techniques.

The analysis figures for each of the above compounds is given in Table 5.0, with the theoretical figures in parentheses.

TABLE 5.0 Analysis Figures for $R_2[MCl_4]$ Salts (M = Mn, Fe, Co, Ni or Cu ; R = $[Et_4N]$, $[Ph_4As]$ or [pyH])

The figures in parentheses are the theoretical figures.

	% C	% H	%N	%Cl
$[Et_4N]_2[CoCl_4]$	41.57 (41.66)	9.81 (8.74)	6.05 (6.07)	30.06 (30.74)
$[Et_4N]_2[NiCl_4]$	40.48 (41.68)	9.06 (8.75)	5.77 (6.07)	30.03 (30.76)
$[Et_4N]_2[CuCl_4]$	41.50 (41.25)	9.48 (8.65)	6.02 (6.01)	30.10 (30.44)
$[Et_4N]_2[MnCl_4]$	41.75 (42.03)	9.21 (8.82)	6.03 (6.13)	30.87 (31.01)
$[Et_4N]_2[FeCl_4]$	40.80 (41.94)	9.71 (8.74)	5.87 (6.12)	31.12 (31.02)
$[Ph_4As]_2[CoCl_4]$	59.37 (59.58)	3.26 (4.14)	————	13.62 (14.69)
$[Ph_4As]_2[NiCl_4]$	58.62 (59.61)	4.20 (4.17)	0.45 (0.00)	13.87 (14.66)
$[Ph_4As]_2[CuCl_4]$	55.38 (59.31)	3.98 (4.15)	————	11.56 (14.59)
$[pyH]_2[CoCl_4]$	33.18 (33.23)	2.95 (3.27)	7.74 (7.80)	38.46 (39.39)

5.1.11 Preparation of $[Et_4N][FeCl_4]$

The method described in Section 5.1.7 was repeated using a 1:1 molar ratio of tetraethylammonium chloride to $FeCl_3.6H_2O$. The product was pale yellow in colour.

	% C	% H	%N	%Cl
found	29.45	6.39	4.12	42.16
theoretical	29.27	6.10	4.27	43.29

5.1.12 Preparation of $[Ph_4As]_2[CoCl_4]$

The method described in Section 5.1.7 was repeated using tetraphenylarsonium chloride, to obtain blue $[Ph_4As]_2[CoCl_4]$. The analytical data are contained in Table 5.0.

5.1.13 Attempted preparation of $[Ph_4As]_2[NiCl_4]$

The method described in Section 5.1.7 was repeated using tetraphenylarsonium chloride in the place of tetraethylammonium chloride. No precipitate was observed even on heating, although a blue solution was obtained, which returned to a green colour on cooling.

A second attempt was made, with prolonged heating, and using ethanentitrile (5 cm^3) as a solvent for the nickel(II) salt (1.2 g). This time the blue solution obtained on heating did not return to a green colour on cooling. Ethoxyethane (20 cm^3) was added and a blue precipitate slowly formed. Analytical data (Table 5.0) showed that the compound was slightly impure.

5.1.14 Attempted preparation of $[Ph_4As]_2[CuCl_4]$

The method described in Section 5.1.7 was repeated using tetraphenylarsonium chloride. No precipitate was observed on heating. Ethoxyethane (20 cm^3) was added and a yellow precipitate slowly formed. Analytical data (Table 5.0) showed that the compound was highly impure.

5.1.15 Preparation of $[pyH]_2[CoCl_4]$

The method described in Section 5.1.7 was repeated using pyridinium hydrochloride in place of tetraethylammonium chloride.

The analytical data are given in Table 5.0.

5.1.16 Attempted preparation of $K_2[CoCl_4]$

Potassium chloride (4.97 g) was intimately mixed with $CoCl_2.6H_2O$ (7.93 g) and the mixture heated in a pyrex beaker (150 cm^3) in air at 200-250 °C for 3 h. The pink cobalt(II) salt turned dark blue on heating and slowly became lighter in colour.

5.1.17 Attempted preparation of $K_2[NiCl_4]$

The above method was repeated using $NiCl_2.6H_2O$. The lime-green nickel(II) salt turned light brown on heating and became lighter in colour on further heating.

Diffuse reflectance spectra of the products showed that the $[MCl_4]^{2-}$ ions were not present, and the products were a mixture of potassium chloride with the corresponding anhydrous metal(II) halide.

5.1.18 Preparation of $[Co(NH_3)_6]Cl_3$

Ammonium chloride (3.2 g) and $CoCl_2.6H_2O$ (4.8 g) were added to water (4 cm^3). The mixture was shaken until both salts had dissolved. Activated decolourising charcoal (0.1 g) was added, followed by concentrated ammonia (10 cm^3). Air was bubbled vigorously (but not too strongly because this removes the ammonia), through the red solution until it became yellow-brown (ca 4 h). A large air inlet was used to prevent blocking.

The crystals and carbon were collected and then added to concentrated hyrdochloric acid in water (30 cm^3), enough acid being present to give an acid mixture. The mixture was heated to effect complete solution and filtered hot. Concentrated hydrochloric acid (8 cm^3) was then added to the filtrate turning the solution orange. The solution was slowly cooled to 0 °C. An orange solid slowly precipitated. This was filtered and then washed first with 60 % ethanol : 40 % distilled water and then 95 % ethanol : 5 % distilled water (2 x 30 cm^3). The precipitate was dried in vacuo for 24 h.

A diffuse reflectance spectrum confirmed the solid contained the $[Co(NH_3)_6]^{3+}$ ion. The analysis figures were

	% C	% H	% N	%Cl
found	—	6.80	30.65	39.40
theoretical	—	6.75	31.52	39.59

5.1.19 Attempted preparation of $[Co(NH_3)_6][CuCl_5].H_2O$

$CuCl_2.2H_2O$ (1 g) was added to the solution of $[Co(NH_3)_6]Cl_3$ (Section 4.4.1, 1 g) in distilled water (30 cm^3) and the solution was heated to 70 °C.

While maintaining this temperature, concentrated hydrochloric acid (10 cm^3) was added slowly with continuous stirring. The solution turned cloudy and an orange coloured solid precipitated. The solid was filtered, dried in vacuo and a diffuse reflectance spectrum obtained. This confirmed that the solid was $[Co(NH_3)_6]Cl_3$ and not the desired compound.

5.1.20 Discussion

The initial approach was to prepare the anhydrous chloride MCl_n (n = 2 or 3) and the $[Et_4N]_{4-n}[MCl]_4$ salt for each metal. However the results with cobalt (Section 5.2) and nickel (Section 5.3) seemed to imply that only one metal containing compound was generally required. The most convenient one was then generally made.

Commercially available chromium(III) chloride was found to be insoluble in the basic melt, making necessary the preparation of an active form.

The $[Et_4N]_{4-n}[MCl_4]$ (n = 2 or 3) salts are not particularly soluble in non-co-ordinating solvents, such as dichloromethane. For this reason an attempt to prepare the tetraphenylarsonium salts, which are generally soluble in dichloromethane, was made in a number of cases.

The difficulties encountered in the preparation of the $[Ph_4As]_2[MCl_4]$ (M = Cu or Ni)salts (Sections 5.1.13 and 5.1.14) is probably due to a lattice energy effect. The lattice energy is well known as a factor influencing the feasible isolation of a given salt.

The preparation of $K_2[MCl_4]$ (M = Co or Ni) was attempted, because a spectrum without the interference due to an organic cation was thought to be desirable. It seems likely the literature preparation quotes too low a temperature, because fusion of the two solids did not occur.

Investigation of the copper(II) system revealed the need to prepare complexes other than $[CuCl_4]^{2-}$ (see Section 5.4). The failure to prepare the $[CuCl_5]^{2-}$ salt may have been due to the scaling down of the reaction quantities.

5.2 COBALT(II)

5.2.1 Introduction

The cobalt(II) case is a convenient system to consider first because the solubility and spectroscopic characteristics of cobalt(II) make it an ideal probe solute to investigate the co-ordination of transition metals in the melt. Further, considerable investigation has been undertaken of cobalt(II) in related systems, enabling useful comparisons to be made.

The blue colour observed when cobalt(II) chloride is dissolved in concentrated hydrochloric acid has long been attributed as being due to the formation of $[CoCl_4]^{2-}$. Zeltmann <u>et al</u> [35] calculated the concentrations of the cobalt species present in concentrated hydrochloric acid from ^{17}O and ^{35}Cl nmr data (Fig. 5.1). They concluded that the dominant species in concentrated hydrochloric acid was $[CoCl_4]^{2-}$, attributing the small difference in the oscillator strength between $[Ph_4As]_2[CoCl_4]$ in dichloromethane and the cobalt(II) species in concentrated hydrochloric acid, as being due to relatively strong ion-solvent coupling in aqueous solution. However Cotton <u>et al</u> [36] correlated the spectral and magnetic data for many $[CoCl_4]^{2-}$containing salts, noting that there were often small but noticeable variations between the spectra of the solids and their solution in organic solvents. They concluded that, if the species present in the solutions of the compounds in solvents of relatively low dielectric constant and co-ordinating power were $[CoCl_4]^{2-}$ ions, then the spectra obtained for the solutions in concentrated hydrochloric acid are largely due to some other tetrahedral species. The supposition that these other species were probably $[CoCl_3(H_2O)]^-$ ions, was supported by the observation that the band energies in aqueous systems was always higher than the true band energies for the $[CoCl_4]^{2-}$ ion (Dq for water is greater than Dq for chloride ligands). The spectrum of the $[CoCl_4]^{2-}$ ion in solvents of relatively low dielectric constant consists of three well resolved components of an intense band spanning the region 13000-18000 cm^{-1} and a band in the near infra-red at about 5600 cm^{-1}. The visible spectrum is due to a transition from the $^4A_2$ ground state to the $^4T_1$ excited state with multiple components due to mixing with formally forbidden quartet-doublet transitions. However there is also throught to be some contribution from the splitting of orbitally degenerate electronic states by low symmerty components of the ligand field [37].

Fig 5.2 compares the spectrum of cobalt(II) chloride in concentrated hydrochloric acid with the spectrum of $[Ph_4As]_2[CoCl_4]$ in dichloromethane and the solid state diffuse reflectance spectrum of

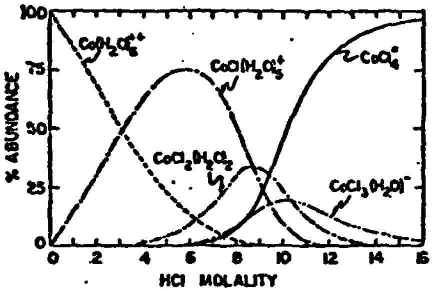


Fig 5.1 Calculated concentrations of cobalt(II) species in hydrochloric acid [35]

$[Ph_4As]_2[CoCl_4]$ in dichloromethane and the solid state diffuse reflectance spectrum of $[Et_4N]_2[CoCl_4]$. Table 5.1 lists the position of the band maxima with their corresponding extinction coefficients. Also listed are the calculated values of the ligand field splitting parameter, Dq, the first Racah parameter, B, and the predicted position of the third transition.

The spectra clearly confirm the conclusions of Cotton et al [36]. There is a small but significant difference between the spectrum of $[Ph_4As]_2[CoCl_4]$ in dichloromethane and the solid state reflectance spectrum of $[Et_4N]_2[CoCl_4]$. There is also a difference noticeable when the spectrum due to the cobalt(II) species present in hydrochloric acid is compared with the spectrum of $[Ph_4As]_2[CoCl_4]$ in dichloromethane. The bands in the spectrum due to the cobalt(II) species in hydrochloric acid occur at higher energy than the corresponding bands in the spectrum of $[Ph_4As]_2[CoCl_4]$ in dichloromethane. This is expected if water molecules are present in the co-ordination sphere of the cobalt(II) ion.

This supposition can be tested by using Jørgensen's rule of average environment. If the species present in hydrochloric acid is represented on average by the formula $[CoCl_{4-\underline{x}}(H_2O)_{\underline{x}}]^{(4-\underline{x})-}$, where $0 < \underline{x} < 4$, then Dq for this species will be given by

$$Dq = (4-\underline{x}).Dq(Cl) + \underline{x}.Dq(H_2O)$$

where Dq(Cl) and $Dq(H_2O)$ are the theoretical contributions to Dq for a single particular ligand (e.g. Dq for $[Co(H_2O)_6]^{2+}$ is 920 cm^{-1} so $Dq(H_2O)$ will be 920/6, since six water ligands contribute to Dq).

Fig 5.2 Electronic spectra of $[CoCl_4]^{2-}$ species

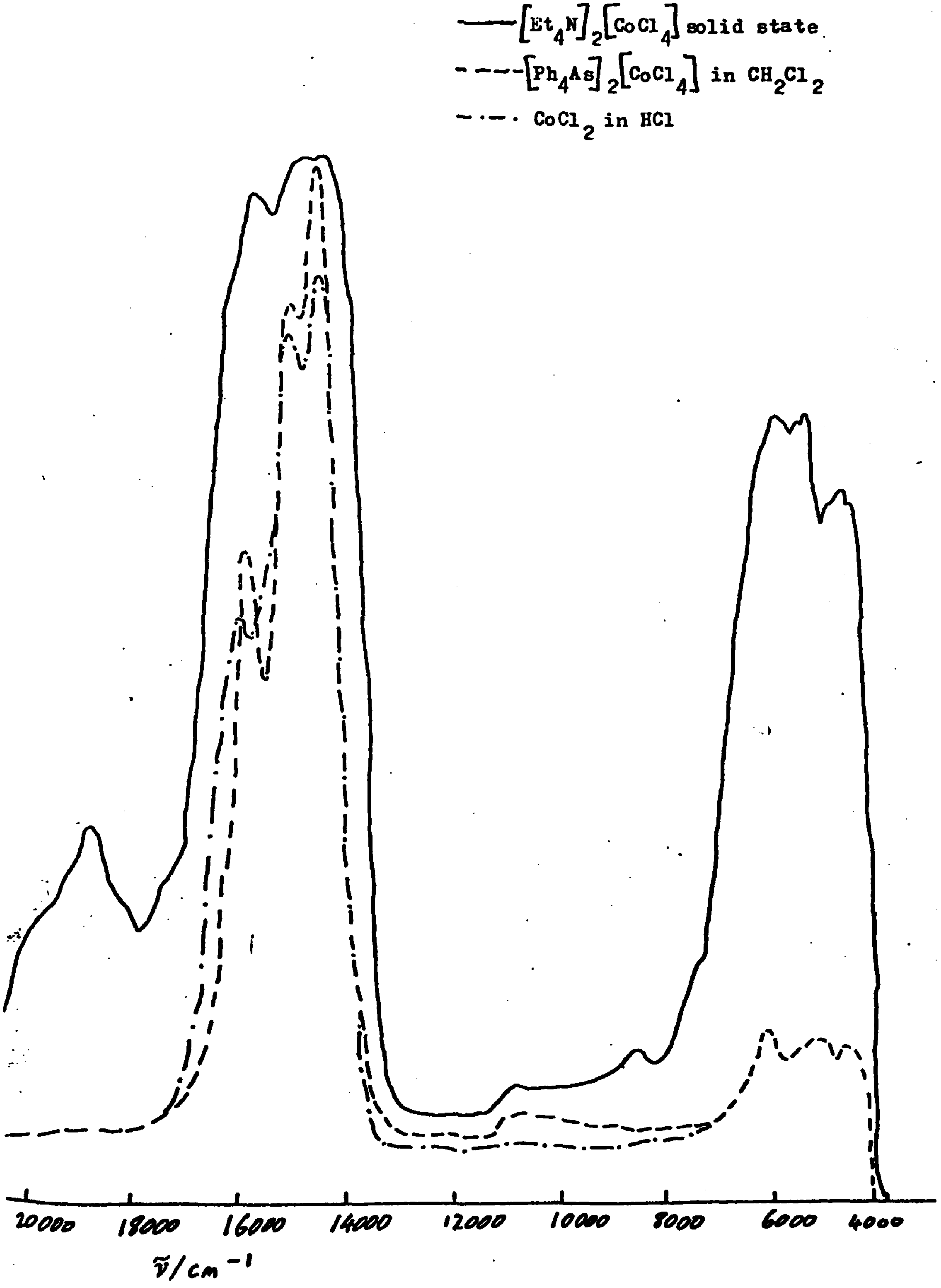


TABLE 5.1 Spectral data for cobalt(II) species in various chloride environments

Species	Transition	Position of maxima $\tilde{\nu}/cm^{-1}$	Extinction Coefficients $\varepsilon/lmol^{-1}cm^{-1}$	Dq/cm^{-1}	B/cm^{-1}	Third band (cm^{-1})
		14480	582			
$CoCl_2$ in	$^4A_2 \rightarrow {}^4T_1(P)$	15100	543	—	—	—
HCl/H_2O		16010	357			
		5630	—			
	$^4A_2 \rightarrow {}^4T_1(P)$					
		6170	—			
$Co(ClO_4)_2$		14490	463	343	691	—
in HCl/H_2O	$^4A_2 \rightarrow {}^4T_1(F)$	15040	422			
		16080	272			
(ref. 36)		16400 (sh)	—			
		5170				
	$^4A_2 \rightarrow {}^4T_1(P)$	5450	76			
		6030				
$[Ph_4As]_2[CoCl_4]$		14400	664	311	699	3134
in CH_2Cl_2		14940	569			
	$^4A_2 \rightarrow {}^4T_1(F)$	15770	398			
		16260(sh)	—			
		4870	71			
	$^4A_2 \rightarrow {}^4T_1(P)$	5180	75			
		5440	78			
		14310	750			
$[Bu_4N]_2[CoCl_4]$		15000	630	301	729	—
	$^4A_2 \rightarrow {}^4T_1(F)$	15600	—			
in CH_2Cl_2		15770	450			
(ref.36)		16260	—			

TABLE 5.1 (Continued)

Species	Transition	Position of maxima $/cm^{-1}$	Extinction Coefficients $/lmol^{-1}cm^{-1}$	Dq/cm^{-1}	B/cm^{-1}	Third band (cm^{-1})
$[Bu_4N]_2[CoCl_4]$ in CH_2Cl_2 with 0.1 M $[Bu_4N]Cl$ (ref. 36)	$^4A_2 \rightarrow {}^4T_1(P)$	4812	74	300	729	—
		5152	80			
		5420	82			
	$^4A_2 \rightarrow {}^4T_1(F)$	14310	766			
		14950	646			
		15600(sh)	—			
		15750	469			
		16200	—			
$[Et_4N]_2[CoCl_4]$ solid state	$^4A_2 \rightarrow {}^4T_1(P)$	4900	—	311	699	3134
		6200	—			
	$^4A_2 \rightarrow {}^4T_1(F)$	14400	—			
		14900	—			
		15750	—			
$[Et_4N]_2[CoCl_4]$ in basic melt	$^4A_2 \rightarrow {}^4T_1(P)$	4890	44	306	696	3096
		5210				
		5470				
		6080				
	$^4A_2 \rightarrow {}^4T_1(F)$	14340	417			
		14910	357			
		15740	253			
		16180(sh)	—			

Using values from reference 36, then

$$3426 = (4-\underline{x}).(3003/4) + \underline{x}.(9200/6)$$
$$\underline{x} = 0.54$$

Thus 54 % of the cobalt is present as $[CoCl_3(H_2O)]^-$ and 46 % as $[CoCl_4]^{2-}$. This calculation, although crude, does support the conclusion of Cotton *et al* [36]; that is that $[CoCl_4]^{2-}$ is not the dominant species, but is in equilibrium with $[CoCl_3(H_2O)]^-$

5.2.2 Cobalt(II) in the basic melt

The solid state diffuse reflectance spectrum of $[Et_4N]_2[CoCl_4]$ lacks the detail observable in the solution spectra. (A single-crystal study at low temperature however reveals much more detail, as illustrated by Ferguson's study [37] on crystals of $R_2[CoCl_4]$ salts (R = Cs, Me_4N or quinolinium).

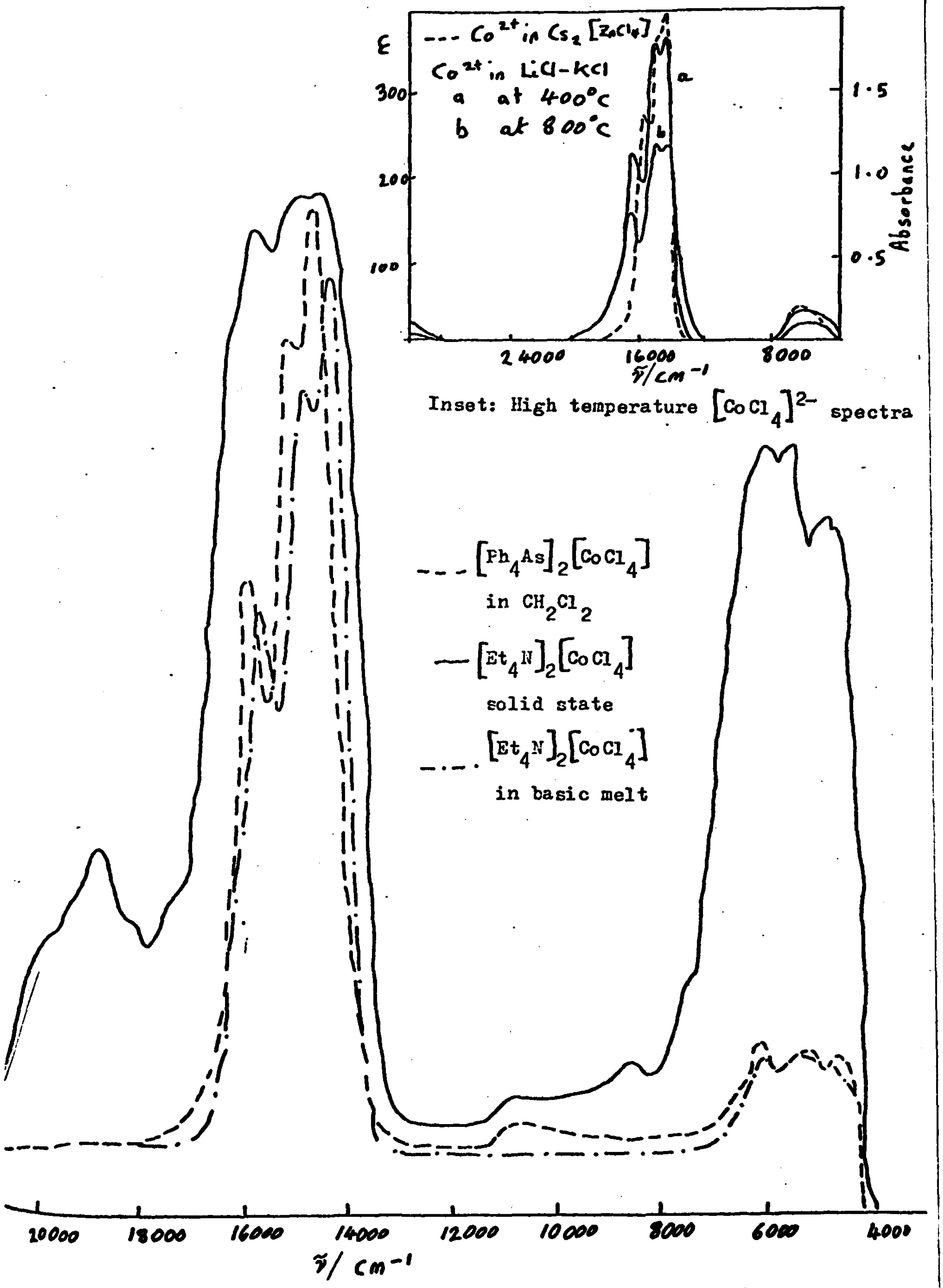
A solvent which has an inherent excess of chloride ions, to ensure the only cobalt(II) specie capable of existing at significant concentrations is $[CoCl_4]^{2-}$ should enable the definitive $[CoCl_4]^{2-}$ solution spectrum to be recorded. Basic chloride melts fulfill the above criterion, having an extremely chloride-rich environment.

Fig 5.3 shows the spectrum of $[Et_4N]_2[CoCl_4]$ in basic melt (N.B. The spectrum of $CoCl_2$ in the basic melt is identical). The spectrum of $[Ph_4As]_2[CoCl_4]$ in dichloromethane and the solid state diffuse reflectance spectrum of $[Et_4N]_2[CoCl_4]$ are given for comparison. The spectral data for $[Et_4N]_2[CoCl_4]$ in the basic melt are contained in Table 4.1.

The species present in the basic melt is clearly $[CoCl_4]^{2-}$. The value of Dq for the melt specie is 5 cm^{-1} lower than in the solid. However, in view of the results obtained by Cotton *et al* [36] (see Table 5.1), this difference is probably of no great significance.

The advantages of the system used in the present study over higher temperature liquids can be seen by considering the spectrum of $CoCl_2$ in the LiCl-KCl eutectic (see Fig. 5.3 inset) as investigated by the Gruen and McBeth [38]. This system has also been investigated by other workers [39,40], but Gruen and McBeth's work [38] is the most detailed. The loss of resolution, due to temperature broadening is clear when comparison is made with the room temperature spectrum. Tetrahedral $[CoCl_4]^{2-}$ also has been found to exist in other chloride systems. This

Fig 5.3 Electronic spectra of $[CoCl_4]^{2-}$ species



Inset: High temperature $[CoCl_4]^{2-}$ spectra species is present in a pyridinium hydrochloride melt [41], in chloride-rich KCl-$AlCl_3$ at 300 °C [41], in $ZnCl_2$-rich $ZnCl_2$-$AlCl_3$ mixtures [42] and in $AlCl_3$-2-methylpyridinium chloride at 140 °C [43]. Hussey and Laher [44] obtained a partial spectrum of the $[CoCl_4]^{2-}$ ion in $AlCl_3$-BPC. They also found that potentiometric measurements on the cell

$$\mathrm{Co}\ \Big|\ \mathrm{Co(II)_{dil}}\ \text{BPC-rich}\ AlCl_3\text{-BPC}\ \Big\vdots\ \text{fritted disc}\ \Big\vdots\ 2{:}1\ AlCl_3{:}\mathrm{BPC}\ \Big|\ \mathrm{Al}$$

revealed a fourth power dependence of the cell potential on the logarithm of the chloride ion mole fraction which is consistent with the formation of $[CoCl_4]^{2-}$. It was also noted that the extinction coefficients of cobalt(II) in molten chlorides follow the general trend of increasing with decreasing temperature. The room temperature melt conforms with this trend.

In their study of cobalt(II) in molten KCl-$AlCl_3$, Øye and Gruen [41] pointed out that although the species present was probably $[CoCl_4]^{2-}$, species such as $[CoCl_3(AlCl_4)]^{2-}$ could not be completely ruled out. However the latter ion would have possessed undistorted tetrahedral co-ordination about the cobalt ion, in order to account for the observed spectrum.

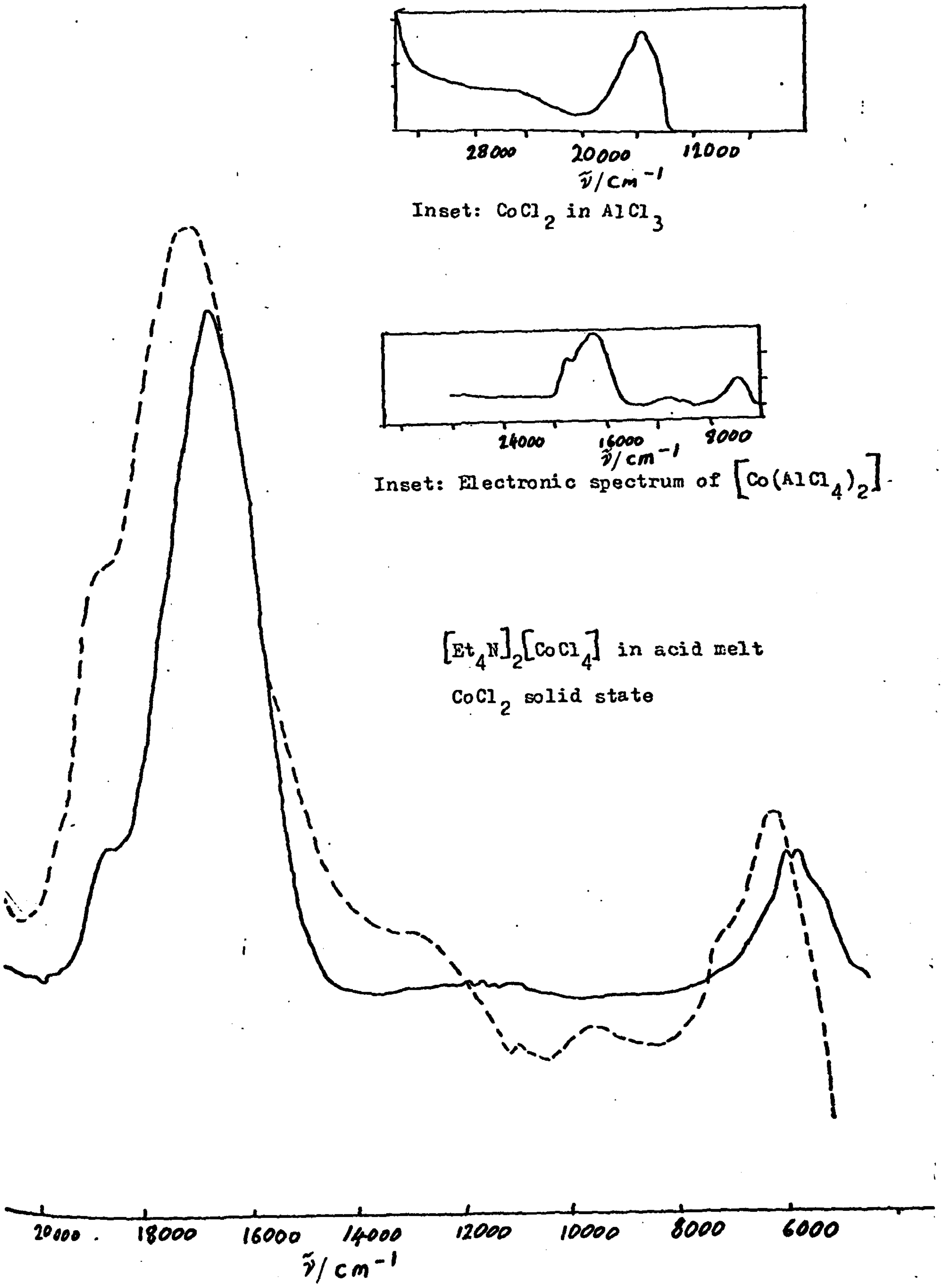
In the basic melt, there is a significant concentration of $[AlCl_4]^-$ ions and it might be thought that this ion rather than Cl^- may be co-ordinated to the cobalt ion, resulting in species such as $[CoCl_3(AlCl_4)]^{2-}$. However, the results of Hussey and Laher [44] showing the fourth power dependence on the chloride ion concentration enable this possibility to be ruled out. Thus it can be concluded that the cobalt(II) species present in the basic melt is indeed the $[CoCl_4]^{2-}$ ion.

5.2.3 Cobalt(II) in the acid melt

The spectrum of $[Et_4N]_2[CoCl_4]$ in the acid melt is recorded in Fig. 5.4, with other spectra for comparison. The relevant spectral data are given in Table 5.2, along with calculated values of Dq, B and the predicted position of the third transition.

Before discussing the structure of the cobalt(II) in molten aluminium chloride at 227 °C and 5.6 atmospheres was interpreted in terms of octahedrally co-ordinated $[Co(Al_2Cl_7)_2]$ [45].. The main band at 16000 cm^{-1} was assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition with the

Fig 5.4 Electronic spectra of cobalt(II) in octahedral environments



Inset: $CoCl_2$ in $AlCl_3$

Inset: Electronic spectrum of $[Co(AlCl_4)_2]$

$[Et_4N]_2[CoCl_4]$ in acid melt

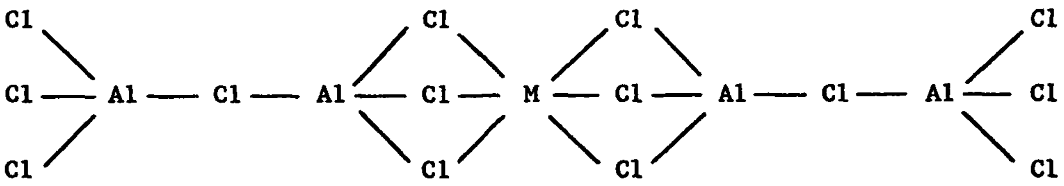
$CoCl_2$ solid state

shoulders at high energy suggested to be due to quartet doublet transitions. The other two spin allowed transitions $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ were not reported.

Øye and Gruen [41] suggested that on addition of transition metal to an $AlCl_3$-rich KCl-$AlCl_3$ melt the following reaction occurs.

$$MCl_2 + 2[Al_2Cl_6] \rightleftharpoons [M(Al_2Cl_7)_2]$$

The structure of the product was reported as :



Emf measurements [46] on a cell containing two different concentrations of cobalt(II) chloride dissolved in a molten mixture of various alkali chlorides and aluminium chloride, supported the assumption of the formation of $[Co(Al_2Cl_7)_2]$ in $AlCl_3$-rich mixtures.

It was reported [41] that on addition of KCl to an $AlCl_3$ melt containing cobalt(II), in the range 0-35.5 mol % KCl a completely new spectrum was produced, while at compositions above 50 mol % KCl, the spectrum was characteristic of tetrahedral $[CoCl_4]^{2-}$, although species such as $[CoCl_3(AlCl_4)]^{2-}$ could not be completely ruled out (but see Section 5.2.2).

In the 35.5-49.9 mol % KCl, spectra analysis in terms of equilibria (5.1) and (5.2) led to $n_2 = 1$ but could not distinguish between $n_1 = 1$ and $n_1 = 2$. The authors assumed the simplest case, $n_1 = 1$.

$$Cl^- + [Al_2Cl_7]^- \rightleftharpoons 2[AlCl_4]^- \qquad (5.1)$$

$$[Co(Al_2Cl_7)_2] + n_1[AlCl_4]^- \rightleftharpoons [Co(Al_2Cl_7)_{2-n_2}(AlCl_4)_{n_1}]^{(n_1-n_2)-} + n_2[Al_2Cl_7]^- \qquad (5.2)$$

Johnson and Dickinson [47] have interpreted the results differently, suggesting that in pure $AlCl_3$, the species $[Co(Al_2Cl_7)_2]$ exists with two chlorides of each $AlCl_3$ unit giving 8-fold co-ordination. However this view is not compatible with most results, and, as will be demonstrated below, octahedral co-ordination seems more likely.

TABLE 5.2 Spectral Data for Cobalt(II) in Various Chloride Environments

Species	Transition	Position of maxima $\tilde{\gamma}$/cm^{-1}	Extinction coefficient ε/lmol^{-1}cm^{-1}	Dq/cm^{-1}	B/cm^{-1}	Third band (cm^{-1})
CoCl$_2$ solid state	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$	6180	—	712	778	13287
	$^4T_{1g}(F) \rightarrow {}^4A_{2g}$	13000	—			
	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	16890	—			
	—	18610	—			
[Et$_4$N]$_2$[CoCl$_4$] in the acid melt	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$	5750	—	664	791	12351
	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	16690	22			
	—	18870	—			

In a recent study [44] of cobalt(II) in 2:1 molar ratio $AlCl_3$-BPC, octahedral co-ordination was suggested on the basis of an incomplete spectrum. The species was postulated as being $[Co(Al_2Cl_7)_{\underline{m}}]^{(\underline{m}-2)-}$ with $\underline{m} = 2$. However potentiometric measurements on the cell

Co | $Co(II)_{dil}$ $AlCl_3$-rich $AlCl_3$-BPC ¦ fritted disc ¦ 2:1 $AlCl_3$-BPC | Al
suggested $\underline{m} > 2$.

The spectrum of $[Et_4N]_2[CoCl_4]$ in the acid melt (this work) bears a striking resemblance to the diffuse reflectance spectrum of $CoCl_2$ and to that of $[Co(AlCl_4)_2]$ (Fig. 5.4). [41]. Both of these structures contain octahedrally co-ordinated cobalt in a chloride environment. The crystal structure of $[Co(AlCl_4)_2]$, prepared by melting $AlCl_3$ and $CoCl_2$ together at about 225 °C in a sealed tube and condensing crystals at the cool end of the tube, is given in Fig 4.6 [48]. In $[Co(Al_2Cl_7)_2]$ each cobalt atom is surrounded by four $[AlCl_4]^-$ units. Two of these act as bidentate ligands and the remaining two bond through one chloride to the cobalt. The cobalt-chlorine distances are approximately equal but the octahedron is trigonally distorted.

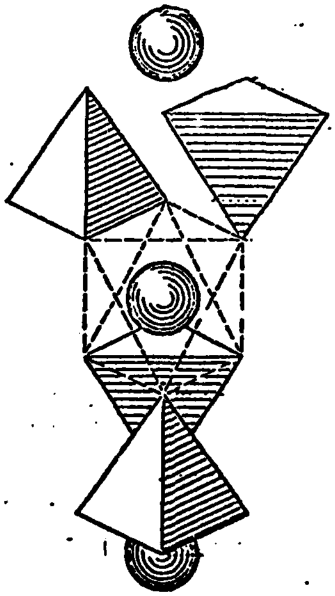


Fig 5.5 Crystal structure of $[Co(AlCl_4)_2]$. The tetrahedra represent $[AlCl_4]^-$ groups, chlorine atoms at the vertices and an aluminium atom in the centre.

In view of the similarity of the spectrum of $[Et_4N]_2[CoCl_4]$ in the acid melt, the solid state spectrum of $CoCl_2$ and the solid state spectrum of $[Co(AlCl_4)_2]$ (Fig. 5.4), it seems likely that cobalt(II) is octahedrally co-ordinated in the acid melt. The values of Dq for this specie and the much lower extinction coefficients compared to $[CoCl_4]^{2-}$ support this view. For $[CoCl_4]^{2-}$ Dq is 306 cm^{-1}, while for cobalt(II) species in the acid melt it is 664 cm^{-1}, approximately 2.17 times that for $[CoCl_4]^{2-}$. (The theoretical figure is $9/4 = 2.25$).

Having established octahedral co-ordination, the nature of the ligands and their arrangement about the cobalt(II) ion has to be considered, Three possibilities for ligands are Cl^-, $[AlCl_4]^-$ and $[Al_2Cl_7]^-$.

The possibility of $[AlCl_4]^-$, on the basis of the similarity between the spectrum of cobalt(II) in the acid melt and the spectrum of $[Co(AlCl_4)_2]$, can be dismissed because there is not a significant concentration of the species present in the acid melt. However, further consideration of the similarities with $[Co(AlCl_4)_2]$ is worthwhile. The species $[Al_2Cl_7]^-$ is present at significant concentrations in the acid melt, and it can function as a bidentate ligand in two ways, as represented schematically in Fig. 5.6.

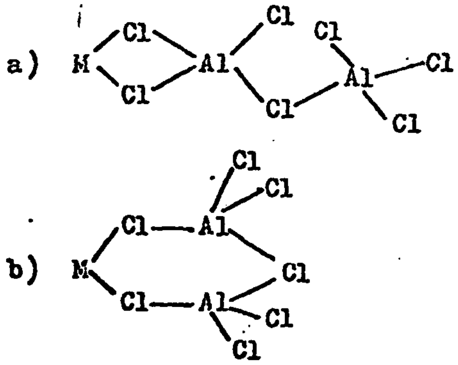


Fig 5.6 Bonding modes for $[Al_2Cl_7]^-$

If the two chlorides are attached to the same aluminium atom (Fig. 5.6 a) then co-ordination similar to that found in $[Co(AlCl_4)_2]$ is possible, with $[Al_2Cl_7]^-$ ions replacing the $[AlCl_4]$ ions.

The $[AlCl_4]^-$ species can only function as a bidentate ligand in one way, whereas the $[Al_2Cl_7]^-$ ion has an alternative mode (Fig. 5.6 b). The functioning of $[Al_2Cl_7]^-$ as a bidentate chelating ligand has been postulated in gas phase complexes [49,50] and the structure of $[Al_2Cl_7]^-$ as determined in solid $[Te_4(Al_2Cl_7)_2]$ [51] supports this possibility. The gas-phase complex $[Co(Al_2Cl_7)_2]$ formed between $CoCl_2$(s) and $AlCl_3$(g) has been postulated to contain $[Al_2Cl_7]^-$ ligands [52] with tetrahedral co-ordination about the cobalt atom. To date $[Co(Al_2Cl_7)_3]^-$ has not been reported.

Electrochemical studies by Hussey [53] suggest that two chlorides may remain attached to the cobalt upon solution, and that only two $[Al_2Cl_7]^-$ ligands are co-ordinated to the central cobalt atom. If the unprecedented co-ordination of three chlorides connected to the same aluminium atom is discarded, only two feasible structures remain. These are shown in Fig. 5.7 (M = Co).

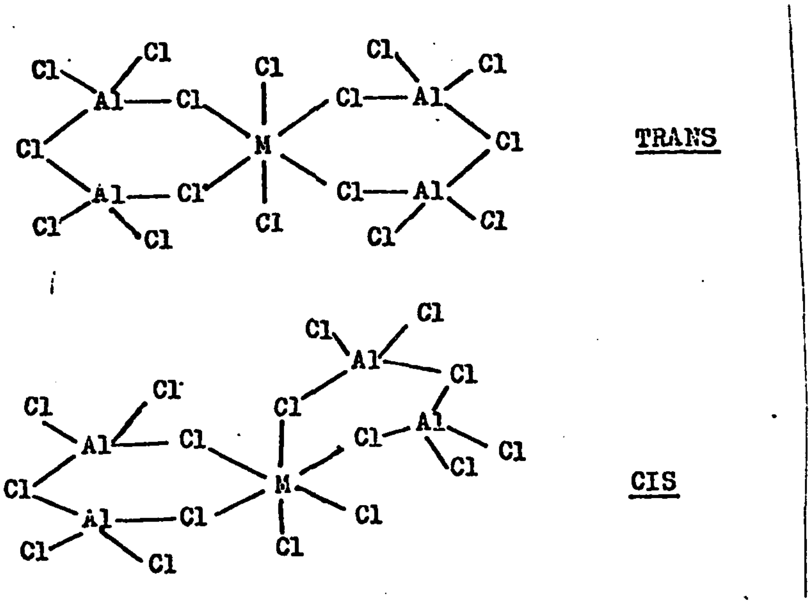


Fig. 5.7 Possible structures for Co(II) in acid melts

Although the involvement of two different species co-ordinating to the cobalt atom might be thought to distort the symmetry noticeably from octahedral, there is evidence that in the gaseous complex $[VAl_3Cl_{11}]$ [49] and $[TiAl_3Cl_{11}]$ [52], the co-ordination is nearly perfectly octahedral, despite two different ligands being present.

Considering the proposed structures for the cobalt(II) species in the acid melt further, the <u>trans</u> isomer will be able to relieve strain between an unco-ordinated chlorine attached to an aluminium atom and the adjacent chloride attached to the cobalt more easily than the cis isomer (see Fig. 5.8), and this has been supported by building the appropriate models.

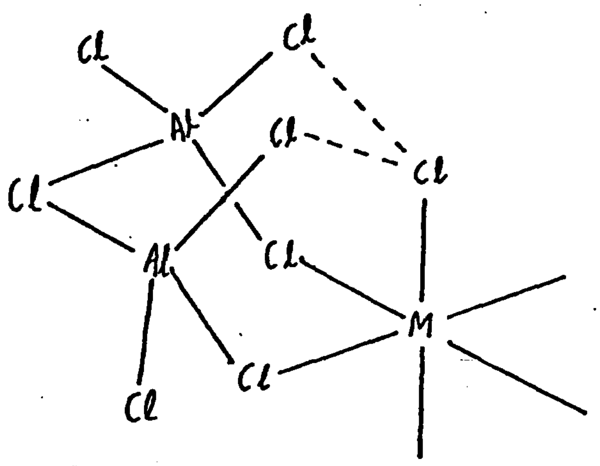


Fig 5.8 Schematic illustration of steric interactions in the proposed melt species.

Further, the trans isomer has higher symmetry (D_{4h}) that the cis isomer (C_{2v}) and so less splitting of the energy levels is expected.

The non-observation of $[Co(Al_2Cl_7)_3]^-$ can be rationalised on steric grounds ; the steric interactions similar to those mentioned above cannot be relieved by any small distortion of the molecule, making the molecule inherently unstable with respect to dissociation.

From the observations it seems likely the cobalt(II) specie present in the 2:1 $AlCl_3$:BPC melt is $[CoCl_2(Al_2Cl_7)_2]^{2-}$. This can exist in two configurations, and at present it is not possible to determine which is the predominant species directly. However consideration of steric interactions leads to the conclusion that the trans isomer is probably favoured. This is further supported by the work of Ludi and Feitknecht [54], who showed that moderate distortions of octahedral symmetry do not show up in the absorption spectrum. The expected C_{2v} splitting which should have been observed for the cis isomer is not seen in the spectrum.

5.3 NICKEL(II)

The nickel(II) ion in chloride melts has been intensively studied and many attempts to rationalise the observations have been made [38].

Before considering the results obtained for the $AlCl_3$-BPC system it is worthwhile to briefly review the previous investigations of nickel(II) in chloride-rich melts.

5.3.1 Nickel(II) in chloride-rich melts

The electronic spectrum of nickel(II) in the LiCl–KCl eutectic in the temperature range 360-540 °C, was first reported by Boston and Smith [55]. It was tentatively suggested that the spectral changes were due to equilibria between two or more nickel(II) species.

Jørgensen [56] interpreted the high temperature spectrum as being due to tetrahedral $[NiCl_4]^{2-}$, which at that time had not been previously observed. The octahedral $[NiCl_6]^{4-}$ was suggested to be in equilibrium with $[NiCl_4]^{2-}$, with increasing temperature favouring the tetrahedral species.

However, Harrington and Sundheim [39,57] and Gruen and McBeth [58] argued that the results could be explained by means of a gradual distortion model. At higher temperatures the outer co-ordination shell contains a nearly random arrangement of Li^+ and K^+ ions. On lowering the temperature, Li^+ ions predominate, inducing a tetragonal distortion of the $[NiCl_4]^{2-}$ tetrahedron by these more strongly polarising ions.

By doping a $Cs_2[ZnCl_4]$ crystal with nickel(II), Gruen and McBeth [58] proved that in the pyridinium chloride, CsCl and $Cs_2[ZnCl_4]$ salts, nickel(II) exists as tetrahedral $[NiCl_4]^{2-}$ species. They also claimed that the spectrum in LiCl-KCl at 360 °C showed no similarities with that of nickel(II) doped in a $CsCdCl_3$ crystal. Boston and Smith [59] confirmed that the spectrum in the CsCl melt was due to tetrahedral $[NiCl_4]^{2-}$ by obtaining the complete spin-allowed spectrum of this ion. The spectra of nickel(II) in CsCl, RbCl and KCl melts were also assigned to tetrahedral species with that in the CsCl melt being the least distorted [60].

Smith <u>et al</u> [61] studied the CsCl-$NiCl_2$ system, and up to 20 mole % $NiCl_2$ the spectra were due to tetrahedral $[NiCl_4]^{2-}$ chromophores. At higher $NiCl_2$ compositions a specie, with an undefined geometry, was suggested as being in equilibrium with $[NiCl_4]^{2-}$.

In an attempt to identify the non-tetrahedral specie, a detailed study of nickel(II) in the LiCl-KCl eutectic was undertaken [62]. A model was proposed which had nickel(II) partitioned between two types of centre, labelled T and O in equilibrium. The T:O ratio increased with increasing temperature and KCl content. The co-ordination geometries are best described as being distributions about particular averages. At low temperatures, T centres have a co-ordination distribution closely averaging to tetrahedral. The outer shell cations are mostly K^+. At high temperatures, the distribution broadens and in LiCl-rich melts, Li^+ invades the outer shells. O-centres can only be accurately studied at rather low temperatures, since they have relatively broad distributions of co-ordination geometries, with the average not tetrahedral. The outer shell cations are largely Li^+. Qualitatively similar behaviour was observed for nickel(II) in the $MgCl_2$-KCl system [63].

Angell and Gruen [64] examined nickel(II) in the KCl-$ZnCl_2$ system as a function of temperature and composition. The spectral changes were interpreted to indicate the existence of a two species equilibrium involving nickel(II) in octahedral and distorted tetrahedral sites. The transformation of the octahedral specie to the highly distorted tetrahedral one was proposed to occur by a continuous distortion process rather than by an equilibrium.

5.3.2 Nickel(II) in the basic melt

Gale et al [65] obtained the electronic absorbtion spectrum for $NiCl_2$ dissolved in 0.8:1 $AlCl_3$:BPC, which showed that nickel(II) was present as $[NiCl_4]^{2-}$. The fourth power dependence of the potential on the Cl^- ion concentration in the basic region is consistent with $[NiCl_4]^{2-}$ formation [64].

Fig. 5.9 shows the electronic spectrum of $[Et_4N]_2[NiCl_4]$ dissolved in the basic melt, together with that of solid $[Et_4N]_2[NiCl_4]$.

The relevant spectral data are contained in Table 5.3. The spectrum of $NiCl_2$ in the basic melt is identical to that of $[Et_4N]_2[NiCl_4]$ in the melt.

The spectrum is clearly in agreement with the observations of Gale et al [65].. The specie present in the basic melt is unambiguously $[NiCl_4]^{2-}$. The advantages of the room temperature liquid are clearly seen by comparison of nickel(II) in a high temperature melt (Fig 5.9 inset), and by consideration of some of the previous studies, summarised above, where the exact nature of the nickel(II) species is often unclear.

There is a very small difference between the spectrum of

Fig. 5.9 Electronic spectra of $[NiCl_4]^{2-}$ species

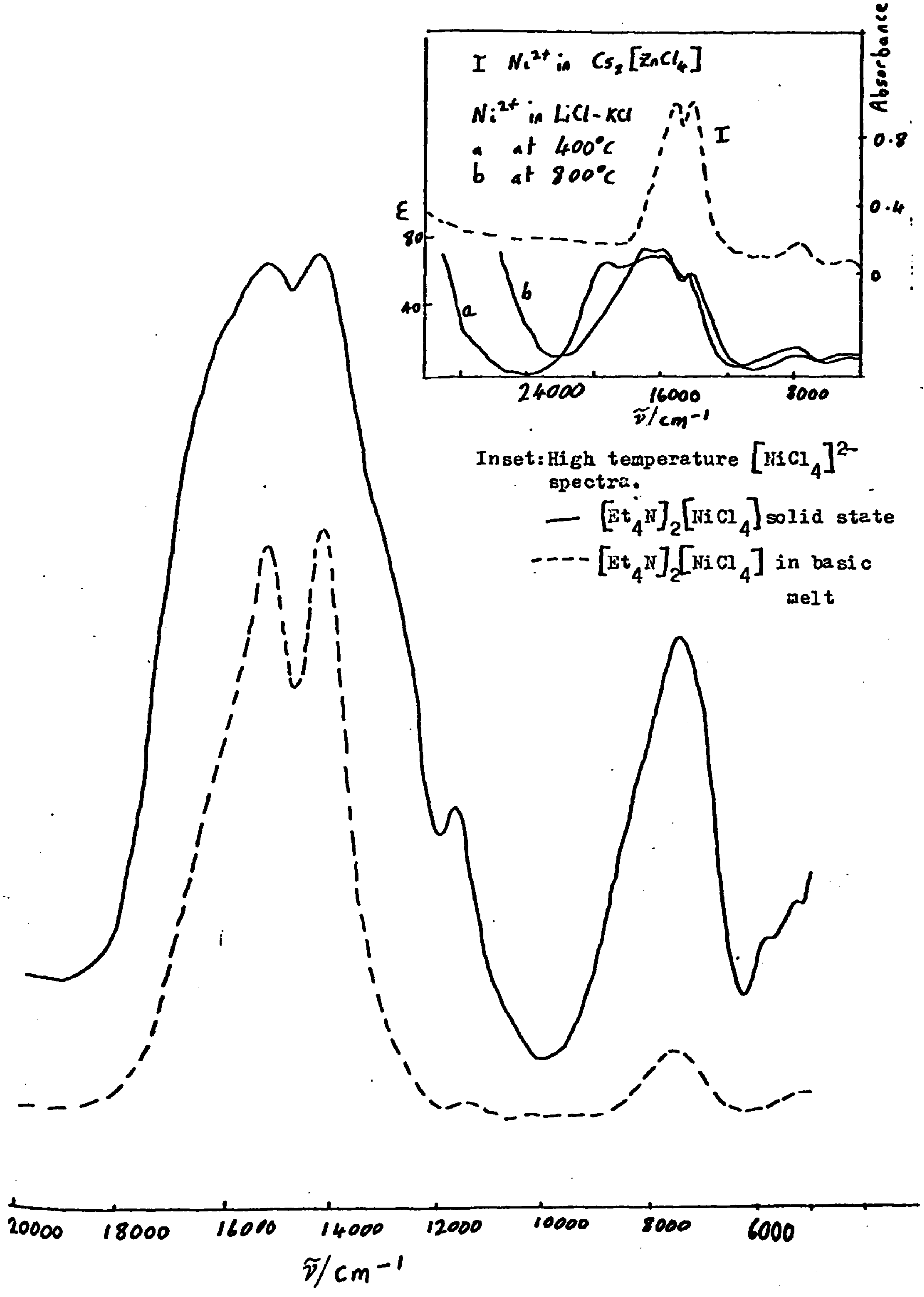


TABLE 5.3 Spectral Data for Nickel(II) in Chloride-Rich Media

Species	Transition	Position of maxima $\tilde{\nu}$/cm^{-1}	Extinction coefficient ε/mol^{-1}cm^{-1}	Dq/cm^{-1}	B/cm^{-1}	Third band (cm^{-1})
	$^3T_1(F) \rightarrow {}^3A_2$	7540	—			
[Et$_4$N]$_2$[NiCl$_4$] solid state	—	11600	—			
		14180	—	405	794	3414
	$^3T_1(F) \rightarrow {}^3T_1(P)$	15150	—			
	—	23800	—			
[Et$_4$N]$_2$[NiCl$_4$] in basic melt	$^3T_1(F) \rightarrow {}^3A_2$	7490	20			
	$^3T_1(F) \rightarrow {}^3T_1(P)$	14140	120	405	794	3414
		15190	116			
	$^3T_1(F) \rightarrow {}^3A_2$	7549	21			
		8700(sh)	—			
	—	11630	6			
Cs$_2$[NiCl$_4$] in MeCN (Ref.66)		14250	160	409*	—	—
	$^3T_1(F) \rightarrow {}^3T_1(P)$	15240	160			
		15950(sh	—			

* The value given in the original paper is different from this figure, but subsequent papers quote the value given in the table.

$[Et_4N]_2[NiCl_4]$ in the melt and the solid state spectrum of $[Et_4N]_2[NiCl_4]$ as noted for cobalt, but the same value for Dq is obtained for the two nickel systems.

The electronic spectrum of the $[NiCl_4]^{2-}$ ion consists of a band around 7800 cm^{-1} and a more intense one in the range 13000-20000 cm^{-1}, which contains two resolved peaks. The band at 7800 cm^{-1} has been assigned to the $^3T_1(F) \rightarrow {}^3A_2(F)$ transition, whilst the more intense band has been assigned to the $^3T_1(F) \rightarrow {}^3T_1(P)$ transition. Spin-orbit coupling is largely responsible for the splitting of the energy levels, resulting in the observed splitting of the band.

It can be concluded that the nickel(II) specie in the basic melt is $[NiCl_4]^{2-}$. The degree of distortion from tetrahedral symmetry is probably about the same as in the solid $[Et_4N]_2[NiCl_4]$ in view of the close similarity between the solid state spectrum and the melt spectrum.

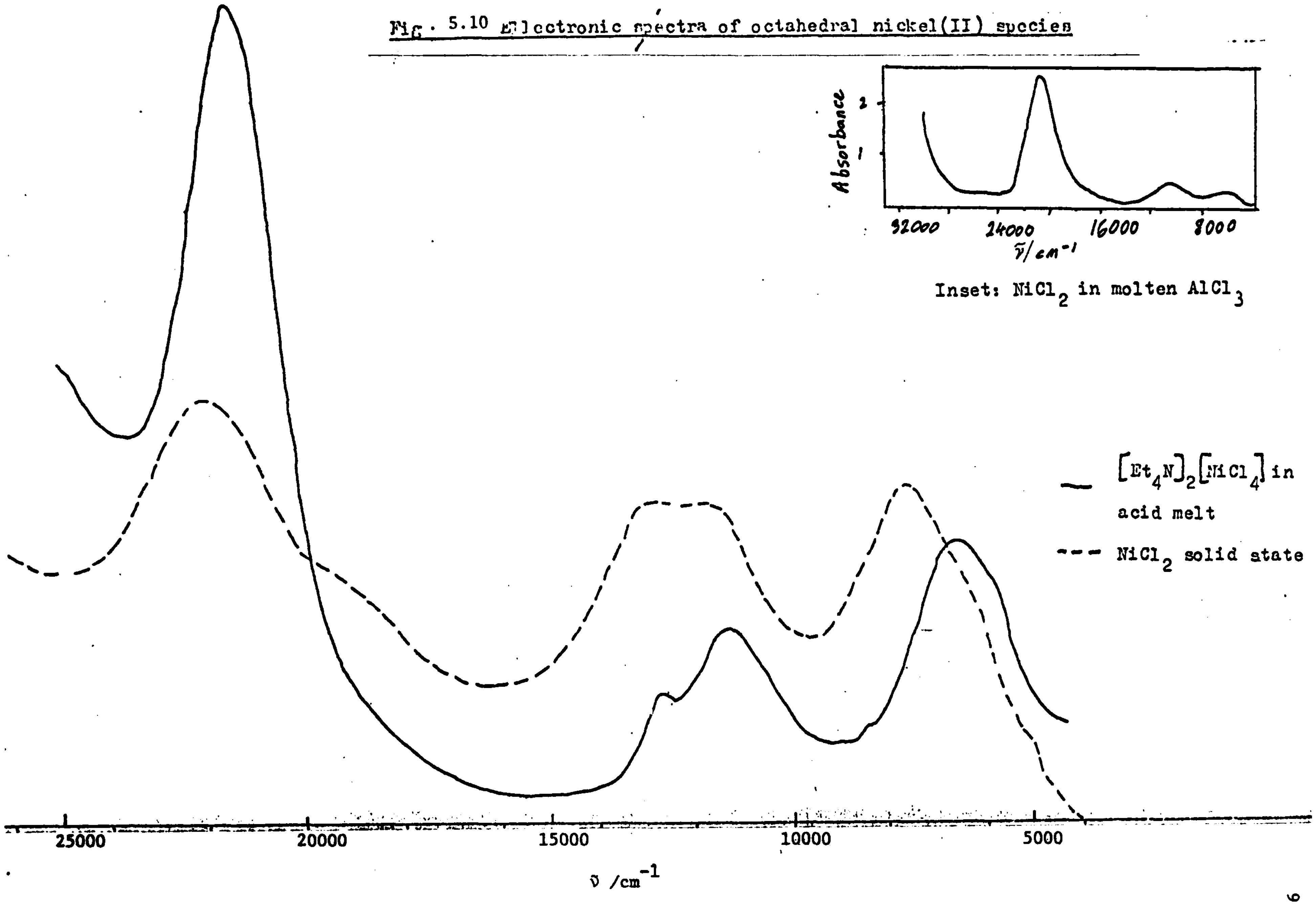
5.3.3 Nickel(II) in the acid melt

The spectrum of nickel(II) in liquid aluminium chloride at 227 °C (see Fig. 5.10 inset) has been interpreted as being due to octahedral nickel(II), probably $[Ni(Al_2Cl_7)_2]$ [45].

The absoprtion spectrum obtained by Gale et al [65] for nickel(II) in a 1.5:1 $AlCl_3$:BPC melt consisted solely of a peak at approximately 547 nm. It was suggested that this result could be consistent with the supposition that nickel(II) is in an uncomplexed state or that it is only weakly solvated. However, the results obtained in this work for nickel(II) in a 2:1 $AlCl_3$:BPC melt are significantly different. The spectrum of $[Et_4N]_2[NiCl_4]$ dissolved in the acid melt is given in Fig. 5.10. (The spectrum of $NiCl_2$ dissolved in the acid melt is identical). For comparison, the solid state spectrum of $NiCl_2$ is given. The position of the maxima with the relevant spectral parameters are contained in Table 5.4.

That the nickel(II) specie in the melt has octahedral co-ordination is indicated by consideration of the values of Dq. The value of Dq for $[NiCl_4]^{2-}$ in the basic melt is 405 cm^{-1}, whilst for the nickel(II) specie in the acid melt it is 668 cm^{-1}. The theoretical ratio for octahedral to tetrahedral is 9/4 = 2.25, compared with the value of 1.65 obtained for the two nickel species under consideration. The reason for the lack of agreement appears to be due to the high value of Dq for $[NiCl_4]^{2-}$. The

Fig. 5.10 Electronic spectra of octahedral nickel(II) species



Inset: $NiCl_2$ in molten $AlCl_3$

TABLE 5.4 Spectral Data for Nickel(II) in Chloride Environments

Specie	Transition	Position of maxima $\tilde{\gamma}$/cm^{-1}	Dq/cm^{-1}	B/cm^{-1}	Third band (cm^{-1})
	$^3A_{2g} \rightarrow {}^3T_{2g}$	7770			
$NiCl_2$	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	11580 12730	779	771	12409
solid state	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	22080			
	$^3A_{2g} \rightarrow {}^3T_{2g}$	6400			
$NiCl_2$ in aluminium	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	10800	640	—	—
chloride (ref. 45)	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	21000			
	$^3A_{2g} \rightarrow {}^3T_{2g}$	6670			
$[Et_4N]_2[CoCl_4]$	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	11220 12780(sh)	668	862	11259
in acid melt	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	21640			

value of Dq in the acid melt for cobalt(II) is 664 cm^{-1}, extremely close to that obtained for nickel(II), 668 cm^{-1}. However Dq for $[CoCl_4]^{2-}$ in the basic melt is 306 cm^{-1} compared to 404 cm^{-1} found for $[NiCl_4]^{2-}$ in the basic melt. The likely explanation for this anomalous behaviour is that the $[NiCl_4]^{2-}$ specie is distorted from true tetrahedral geometry, allowing π-bonding to affect the situation to a greater extent. The theoretical 9/4 value comes from a purely crystal field model, and the occurrence of π-bonding will result in a large deviation from this value.

The similarity between the solid state spectrum of $NiCl_2$ and the spectrum of $[Et_4N]_2[NiCl_4]$ in the acid melt indicates that the co-ordination of nickel(II) in the acid melt is similar to that found in $NiCl_2$, although the values of Dq are significantly different (779cm^{-1} for $NiCl_2$; 668 cm^{-1} for nickel(II) in the acid melt). Presumably this difference is due to there being less negative charge density on a chlorine atom co-ordinated as part of an $[Al_2Cl_7]^-$ ligand, than there is on a chlorine atom of a co-ordinated chloride ion.

The slight difference in shape of the second band (about 12000 cm^{-1}) is probably due to this transition being close to the spin-forbidden band ($^3A_{2g} \rightarrow {}^1E_g$). The two transitions are closer in energy in the case of $NiCl_2$, than for the nickel(II) specie in the melt, resulting in a greater enhancement of the forbidden transition, by spin orbit coupling, being observed for $NiCl_2$.

The spectrum of nickel(II) in the acid melt also bears a remarkable similarity to that of nickel(II) chloride in aluminium chloride (Fig. 5.4 inset) [45], where octahedral nickel(II), possibly $[Ni(Al_2Cl_7)_2]$ was postulated.

The reaction of $AlCl_3(g)$ with $NiCl_2$ produces species similar to those found for $CoCl_2$ [67] and again no $[Ni(Al_2Cl_7)_3]^-$ species have been reported to date. In addition, electrochemical studies have indicated the co-ordination of two chloride ions attached directly to the nickel ion in the acid melt [53].

These observations, together with considerations similar to those made in the cobalt(II) case (Section 5.2.3) concerning the nature of the ligands, lead to the proposal of species analogous to those proposed for cobalt(II) (Fig. 5.7 (M = Ni)).

For the same reasons as those advanced for the cobalt(II) case

(Section 5.2.3), the <u>trans</u> isomer is likely to be favoured on steric grounds.

It can be concluded that nickel(II) is present in the acid melt as $[NiCl_2(Al_2Cl_7)_2]^{2-}$ with octahedral co-ordination about the nickel(II) ion. The <u>trans</u> isomer is likely to be favoured on steric grounds.

5.4 COPPER(II)

5.4.1 Introduction

The spectrum of copper(II) in the LiCl-KCl eutectic contains a single band at 9500 cm^{-1}, which Gruen and McBeth [68] have assigned to the $^2T \rightarrow {}^2E$ transition of the $[CuCl_4]^{2-}$ complex (see Fig.5.11). In $Cs_2[CuCl_4]$ [69] and in $Cs_2[Zn_{1-\underline{x}}(Cu)_{\underline{x}}Cl_4]$ [38] the band maximum occurs at 7000 cm^{-1}, compared to 12400 cm^{-1} for octahedral co-ordination in $CsCd_{1-\underline{x}}(Cu)_{\underline{x}}Cl_3$. Therefore in the LiCl-KCl eutectic the maximum occurs about halfway between the maxima for an octahedral and a tetrahedral site.

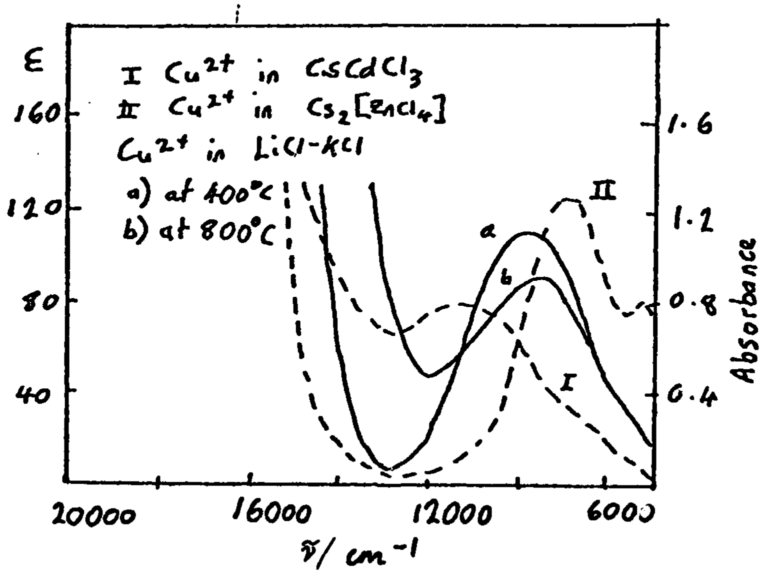


Fig 5.11 Cu^{2+} in high temperature melts

The $[CuCl_4]^{2-}$ ion in $Cs_2[CuCl_4]$ has a distorted (D_{2d}) geomerty [69,70]. The Cl-Cu-Cl bond angles were found to be 124.9°, 123.3°, 102.9° and 102.5° (all ± 0.7°) [70]. On the basis of the electronic absorption spectrum, Harrington and Sundheim [39] postulated that an even more severely distorted $[CuCl_4]^{2-}$ specie was present in the melt, with increasing temperature resulting in less distortion. Gruen and McBeth [38] supported this supposition. Battaglia <u>et al</u> [71] have reported that

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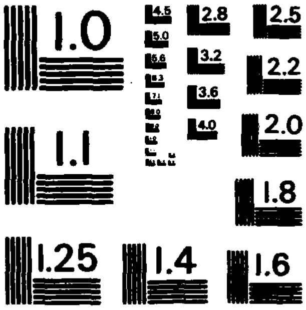

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an inverse linear correlation exists between the maximum of the d-d transition (in cm^{-1}) and the dihedral angle (in degrees) for various $[CuCl_4]$ containing salts (see Table 5.5).

TABLE 5.5 Correlation of Band Maxima with Dihedral Angle for some $[CuCl_4]^{2-}$ containing Species

Specie	Maximum of d-d transition Calculated $\tilde{\nu}/cm^{-1}$	 Found $\tilde{\nu}/cm^{-1}$	Dihedral angle θ /degrees
tetrahedral	6680	——	90
$Cs_2[CuCl_4]$	9060	9050	67.9
$[PhCH_2NMe_3]_2[CuCl_4]$	9200	9250	66.6
$[Et_3NH]_2[CuCl_4]$	9510	9390	63.7
$[NPhpipzH_2][CuCl_4]$	10790	10750	51.6
$[Pt(en)_2Cl_2][CuCl_4]$	12425	12990	35.7
$[PhCH_2CH_2NH_2Me]_2[CuCl_4]$	16260	16100	0

5.4.2 Copper(II) in the basic melt

The spectrum of copper(II) in the basic melt is given in Fig. 5.12, with the spectrum of solid $[Et_4N]_2[CuCl_4]$ given for comparison. The spectral data are summarised in Table 5.6.

The spectrum can be partially rationalised in terms of distortion of the $[CuCl_4]^{2-}$ specie, however the absorption band in the basic melt is extremely broad, and Hussey [53] could not rationalise potentiometric data in terms of the $[CuCl_4]^{2-}$ ion.

The presence of a second copper specie may account for the broad absorption band reported in this work, and may also explain why Hussey[53] could not rationalise the potentiometric data in terms of $[CuCl_4]^{2-}$. It would not be unreasonable to postulate that in addition to the $[CuCl_4]^{2-}$ ion, the five co-ordinate $[CuCl_5]^{3-}$ may be present in this solution with such a high excess of chloride present. Copper dimers or higher oligomeric species, can be discounted because the concentration of copper(II) is not great enough to favour their production. The chloride-rich environment will favour the production of the higher co-ordination

Fig. 5.12 Spectrum of $[Et_4N]_2[CuCl_4]$ in basic melt

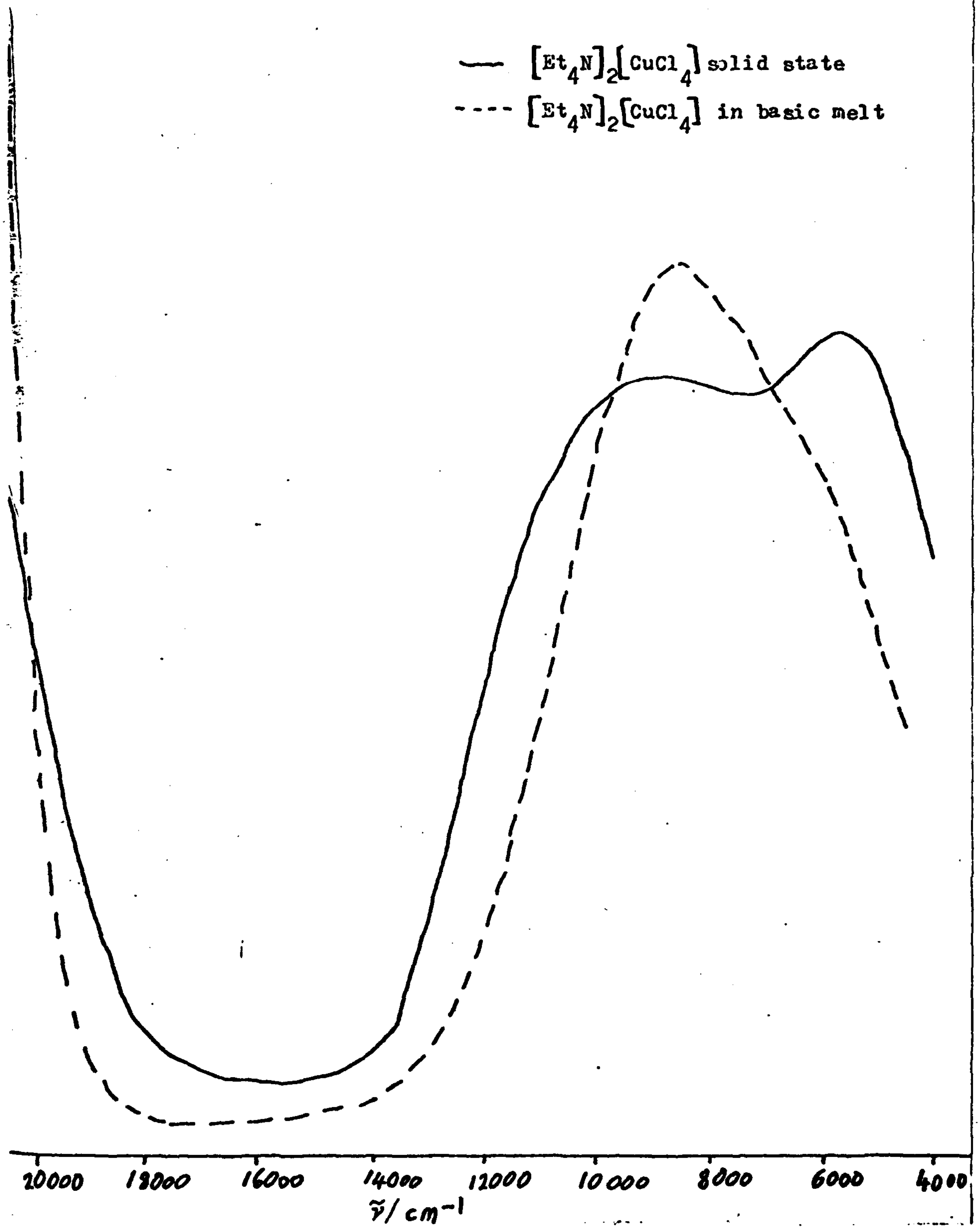


TABLE 5.6 Spectral Data for Copper(II) in Various Chloride Environments

Species	Transitions	Position of maxima $\tilde{\nu}/cm^{-1}$	Extinction coefficient $\varepsilon/l mol^{-1} cm^{-1}$	Dq/cm^{-1}
$[Et_4N]_2[CuCl_4]$ solid state	$^2E \rightarrow {}^2T_2$	7810	—	7810
$Cs_2[CuCl_4]$ solid state	$^2E \rightarrow {}^2T_2$	8720	—	8720
$[Bu_4N]_2[CuCl_4]$ solid state (Ref. 72)	$^2E \rightarrow {}^2T_2$	9430	—	9430
$[Bu_4N]_2[CuCl_4]$ in CH_2Cl_2 with added $[Bu_4N]Cl$	$^2E \rightarrow {}^2T_2$	8650	145	8650
$[Et_4N]_2[CuCl_4]$ in basic melt	$^2E \rightarrow {}^2T_2$	8590	81	8590

species, such as $[CuCl_5]^{3-}$.

Although at this stage no definite conclusions can be made concerning the nature of the copper(II) species present in the basic melt, a tentative suggestion of an equilibrium (5.3) between two copper species can be made.

$$[CuCl_4]^{2-} + Cl^- \rightleftharpoons [CuCl_5]^{3-} \quad (5.3)$$

5.4.3 Copper(II) in the acid melt

The spectrum of $CuCl_2$ in molten aluminium chloride has been obtained by Øye and Gruen [45] (see Fig. 5.13 inset), and interpreted as being due to octahedral co-ordination, the species probably being $[Cu(Al_2Cl_7)_2]$.

The spectrum of $[Et_4N]_2[CuCl_4]$ in the acid melt is given in Fig.5.13 (N.B. the spectrum of $CuCl_2$ in the acid melt is identical). However both copper(II) compounds were soluble only to a limited extent and some solid remained undissolved in both cases. The spectrum of $CuCl_2$ is given for comparison. The spectral data are summarised in Table 5.7.

The spectrum of copper(II) in the acid melt bears no similarity to that of $CuCl_2$, and there is a significant difference between the spectrum due to copper(II) in aluminium chloride and that due to copper(II) in the acid melt. The spectrum of the copper(II) species in the acid melt bears a slight resemblance to the spectrum of $[Bu_4N][CuCl_3]$ which contains planar $[Cu_2Cl_6]^{2-}$ ions) (Fig. 5.13 inset) [72]. It is thus possible that copper present in the acid melt may have square planar co-ordination, or a grossly tetragonally distorted octahedral structure.

A further illustration of the unusual behaviour of copper(II), compared to nickel(II) and cobalt(II) is given by the gaseous complex $[CuAl_2Cl_8]$. The cobalt and nickel analogues have been postulated to have octahedral [73] and tetrahedral [50] co-ordination, with the $[AlCl_4]^-$ ion behaving as a tridentate or bidentate ligand respectively. However the

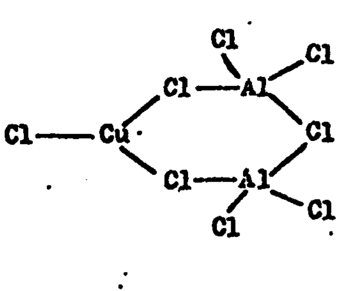
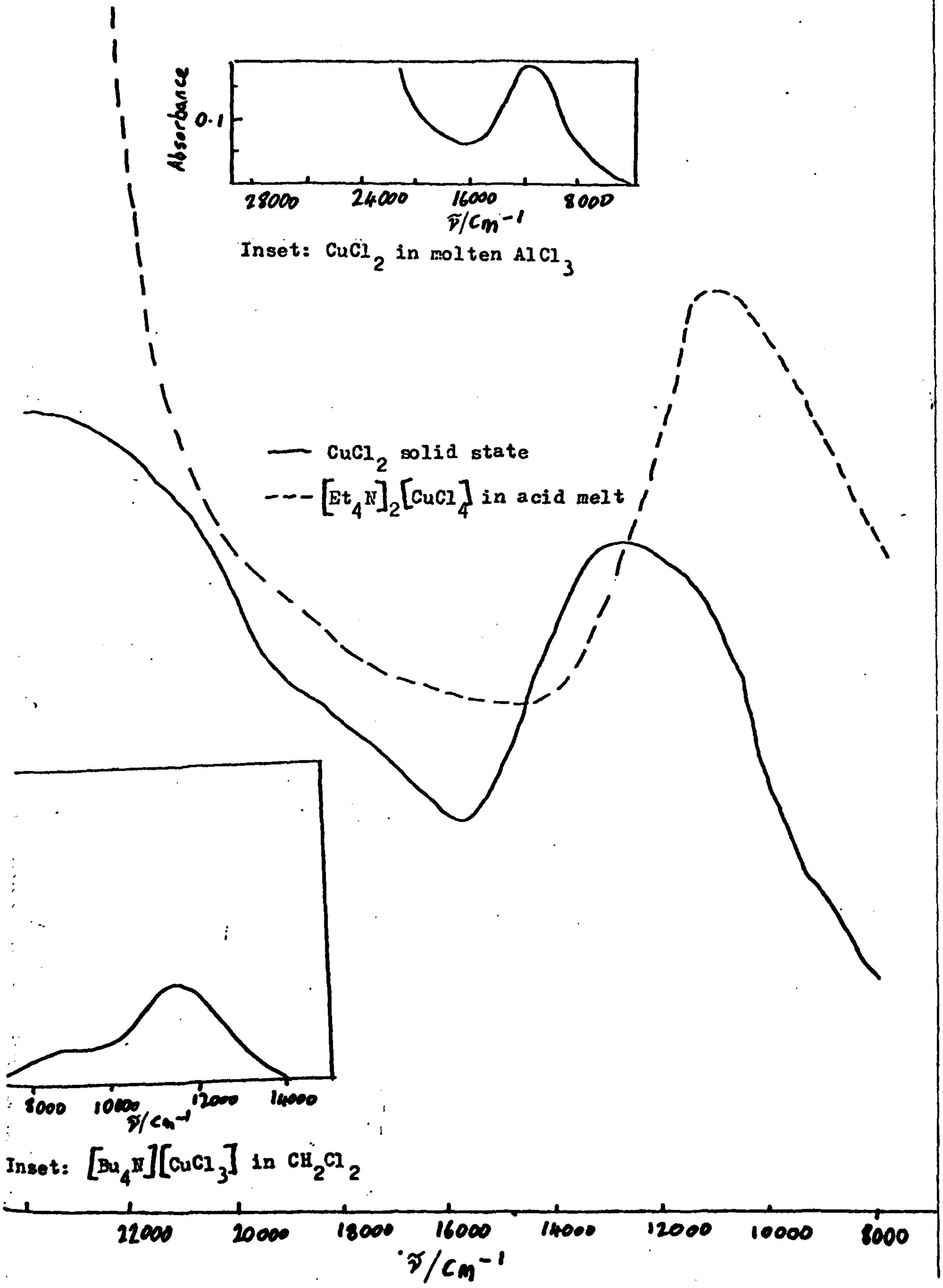


Fig 5.14 Structure of the gaseous complex $[CuAl_2Cl_8]$

Fig 5.13 Electronic spectrum of $[Et_4N]_2[CuCl_4]$ in the acid melt



Inset: $CuCl_2$ in molten $AlCl_3$

Inset: $[Bu_4N][CuCl_3]$ in CH_2Cl_2

copper complex is believed to contain trigonally co-ordinated copper [74] with the probable structure illustrated in Fig. 5.14.

TABLE 5.7 Spectral Data for Copper(II) in various Chloride Environments

Species	Transition	Position of maxima $\tilde{\nu}$/cm^{-1}	Dq/cm^{-1}
$CuCl_2$ solid state	$^2T_2 \rightarrow {}^2E$	12790	12790
$[Et_4N]_2[CuCl_4]$ in acid melt	$^2T_2 \rightarrow {}^2E$	11050	11050
$CuCl_2$ in $AlCl_3$ (Ref. 45)	$^2T_2 \rightarrow {}^2E$	11600	11600
$[Bu_4N][CuCl_3]$ in CH_2Cl_2 (Ref. 72)	—	9100 11500	—
$[Et_4N][CuCl_3]$ solid state (Ref. 72)	—	7800 11000	—

5.4.4 Summary

The copper(II) system in acid and basic melt requires a great deal more work to be performed, before definite conclusions can be made.

Copper(II) behaves anomalously when compared to cobalt(II) and nickel(II), its neighbours in the transition series. Jahn-Teller distortion may be partially responsible, causing non-octahedral geometries to be favoured.

In the basic melt, it is possible that $[CuCl_4]^{2-}$ (the expected species, by comparison with cobalt(II) and nickel(II)) is in equilibrium with another species, probably $[CuCl_5]^{3-}$.

In the acid melt, square planar co-ordination is a possibility, and the specie present is not the same as that present when copper(II) is dissolved in molten aluminium chloride.

5.5 VANADIUM(III)

5.5.1 Introduction

Harrington and Sundheim [39] interpreted the spectrum of vanadium(III) chloride in the LiCl-KCl eutectic at about 400 °C as being due to octahedral $[VCl_6]^{3-}$. At higher temperatures, Gruen and McBeth [75] interpreted the shifts of the absorption bands to longer wavelengths as being due to an octahedral-tetrahedral equilibrium of the form :

$$[VCl_6]^{3-} \rightleftharpoons [VCl_4]^- + 2\ Cl^- \qquad (5.4)$$

The observed spectra indicated that the equilibrium (5.4) lies well to the left even at 1000°C, and to obtain a spectrum of $[VCl_4]^-$, V^{3+} ions were doped into a $Cs[AlCl_4]$ lattice [76]. The similarity between this latter spectrum and the high temperature spectrum in $K[AlCl_4]$ [81] was taken to confirm $[VCl_4]^-$ as the high temperature species. Gruen and McBeth [75] pointed out that vanadium(III) was a useful system with which to study the octahedral-tetrahedral equilibrium since at low temperatures the octahedral site stabilisation energy is just large enough to stabilise $[VCl_6]^{3-}$ but not enough to compete with chloride ion repulsions which favour tetrahedral $[VCl_4]^-$ complexes at high temperature. Some of the spectra discussed above are illustrated in Fig. 5.15.

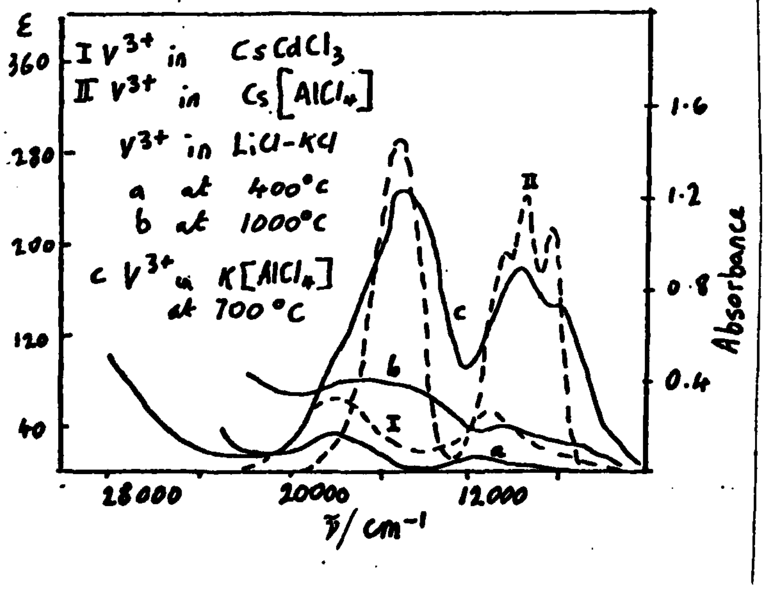


Fig 5.15 V^{3+} in high temperature melts

5.5.2 Vanadium(III) in the basic melt

The spectrum of VCl_3 in basic melt is shown in Fig. 5.16. The spectral data are summarised in Table 5.8. By comparison with Fig. 5.15, the spectrum of VCl_3 in basic melt is remarkably similar to V^{3+} doped in $Cs_3[ScCl_6]$ i.e. $[VCl_6]^{3-}$, and to the diffuse reflectance spectrum of $[pyH]_3[VCl_6]$ [78].

Thus it can be concluded that vanadium(III) is present in the basic melt as $[VCl_6]^{3-}$, in agreement with Gruen and McBeth's observations [75] in the LiCl-KCl eutectic at 400 °C.

The advantage of these room temperature liquids is illustrated by the sharpness of the bands compared to the high temperature melts (compare Figs. 5.15 and 5.16). In addition, attempts to obtain the spectrum of $[VCl_6]^{3-}$ in ethanenitrile [78] resulted in the fomation of $[VCl_4(MeCN)_2]^-$.

These observations once again indicate the usefulness of the room temperature liquids in obtaining definitive solution spectra of complex transition metal chlorides; for vanadium the first obtained at room temperature.

5.5.3 Vanadium(III) in the acid melt

The diffuse reflectance spectrum of vanadium(III) chloride was obtained (Fig. 5.17; data summarised in Table 5.9) for comparison with the vanadium(III) species present in the acid melt. However vanadium(III) chloride does not appear to be particularly soluble in the acid melt. The colour of the "solution" is similar to that of VCl_3 itself, but this could be due to the suspension of VCl_3 in the melt rather than the solution. Stirring the melt solution for several days did not seem to resolve this problem.

5.6 CHROMIUM(III)

5.6.1 Introduction

The spectrum of chromium(III) in LiCl-KCl eutectic was first observed by Harrington and Sundheim [39] and interpreted as being due to octahedral $[CrCl_6]^{3-}$. Gruen and McBeth [38] extended the temperature range studied to 1000 °C and found no indication of an octahedral-tetrahedral equilibrium in the LiCl-KCl eutectic. The absorption spectrum

Fig 5.16 Electronic spectrum of vanadium(III) in the basic melt

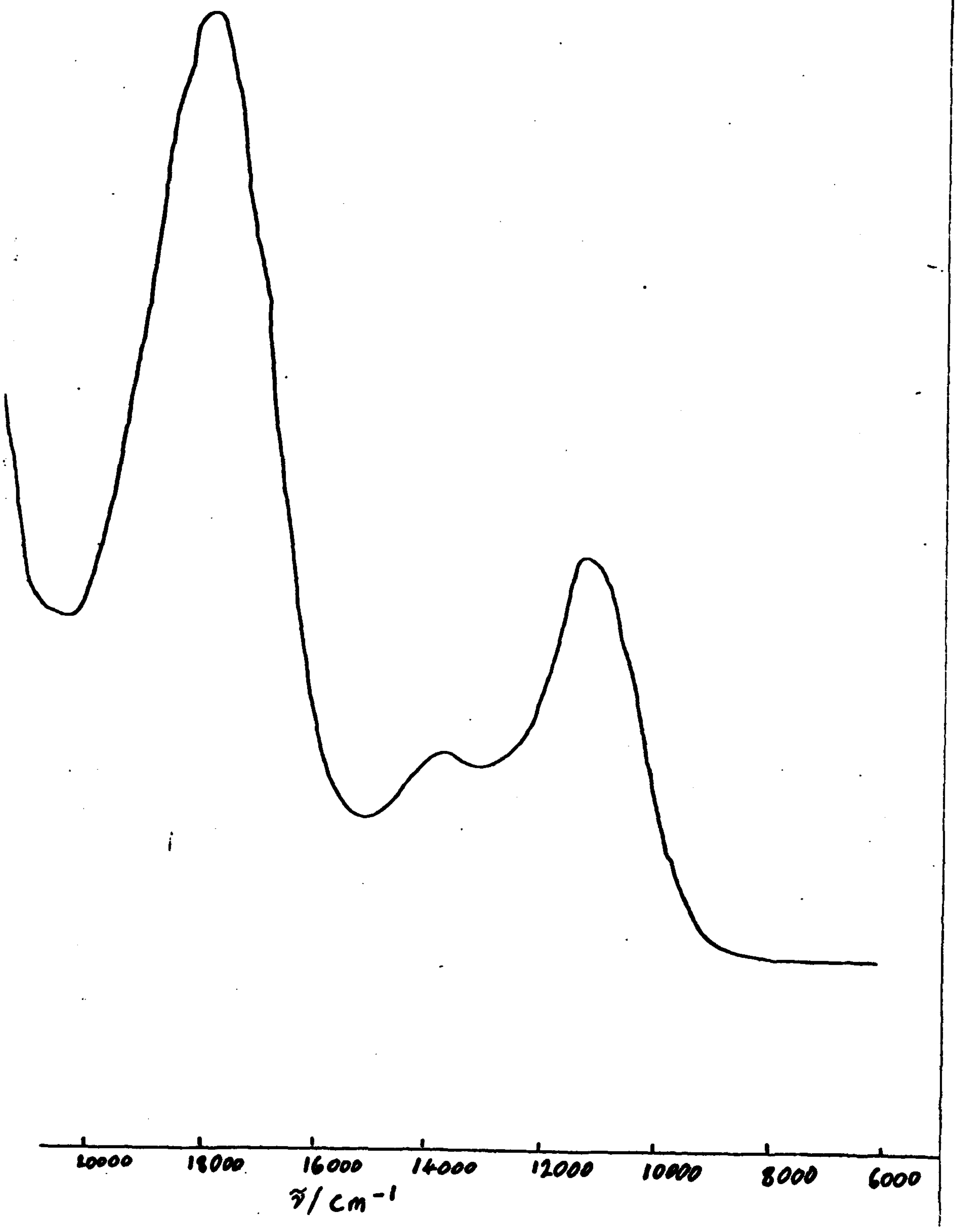
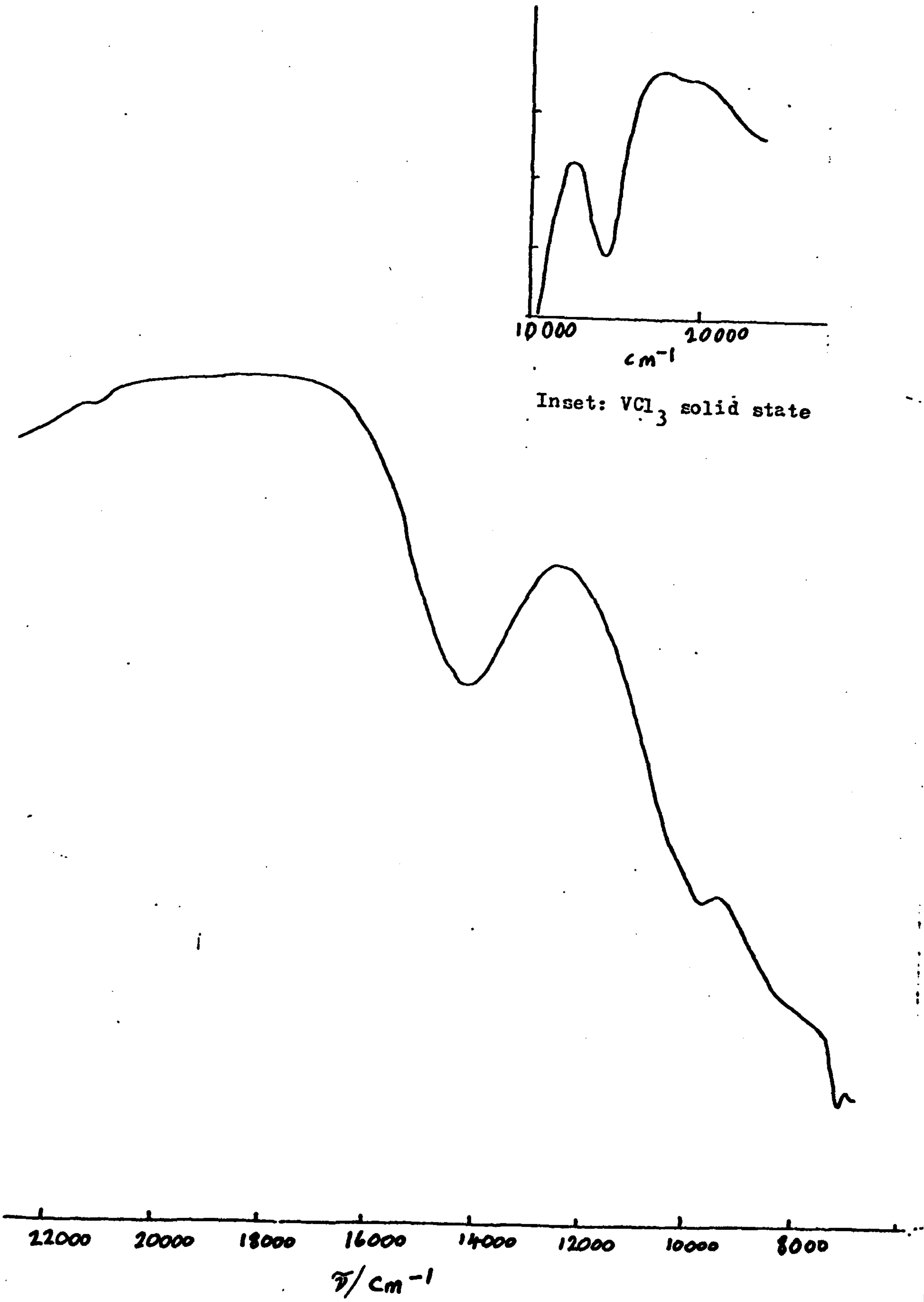


TABLE 5.8 Spectral Parameters for $[VCl_6]^{3-}$ Species

Species	Transition	Position of maxima $\tilde{\nu}/cm^{-1}$	Dq/cm^{-1}	B/cm^{-1}	Third band (cm^{-1})
VCl_3 in basic melt	$^3T_{1g} \rightarrow {}^3T_{2g}$(F)	11100	1223	525	23210
	—	13760			
	$^3T_{1g} \rightarrow {}^3T_{2g}$(P)	17950			
VCl_3 in LiCl-KCl eutectic (Ref. 76)	$^3T_{1g} \rightarrow {}^3T_{2g}$(F)	11000	1202*	538*	23155*
	$^3T_{1g} \rightarrow {}^3T_{2g}$(P)	18020			
$[pyH]_3[VCl_6]$ solid state (Ref. 77)	$^3T_{1g} \rightarrow {}^3T_{2g}$(F)	11400	1239*	506*	23790*
	$^3T_{1g} \rightarrow {}^3T_{2g}$(P)	18000			
$[pyH]_3[VCl_6]$ in MeCN (Ref. 77)	$^3T_{1g} \rightarrow {}^3T_{2g}$(F)	14000	1502*	481*	29022*
	$^3T_{1g} \rightarrow {}^3T_{2g}$(P)	20200			

* These figures were not given in the original papers, and have been calculated from the positions of the maxima in the same way as for the experimental data.

Fig 5.17 Diffuse reflectance spectrum of vanadium(III) chloride



Inset: VCl_3 solid state

of chromium(III) in the LiCl-KCl eutectic at 400 °C is illustrated in Fig. 5.18 (inset).

TABLE 5.9 Vanadium(III) Chloride Spectral Parameters

Species	Transition	Position of maxima $\tilde{\nu}/cm^{-1}$	Dq/cm^{-1}	B/cm^{-1}
VCl_3	$^3T_{1g}(F) \rightarrow {}^3T_{2g}$	12450		
solid state	C.T.	17500	1351	534
	$^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$	19400		
VCl_3	$^3T_{1g}(F) \rightarrow {}^3T_{2g}$	12500		
	C.T.	17300	1390	563
solid state (Ref. 79)	$^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$	19600		

5.6.2 Chromium(III) in the basic melt

The spectrum of chromium(III) in the basic melt is given in Fig. 5.18. The spectral data are summarised in table 5.10. The specie present is $[CrCl_6]^{3-}$, as can be seen by comparison with Fig. 5.19 (inset) and examination of Table 5.10. Fowles and Russ [78] found that $[pyH_3][CrCl_6]$ was insoluble in ethanenitrile, but even had it been soluble it is likely that $[CrCl_4(MeCN)_2]^-$ would have been produced, by analogy with the behaviour of $[VCl_6]^{3-}$ (see Section 5.5.2).

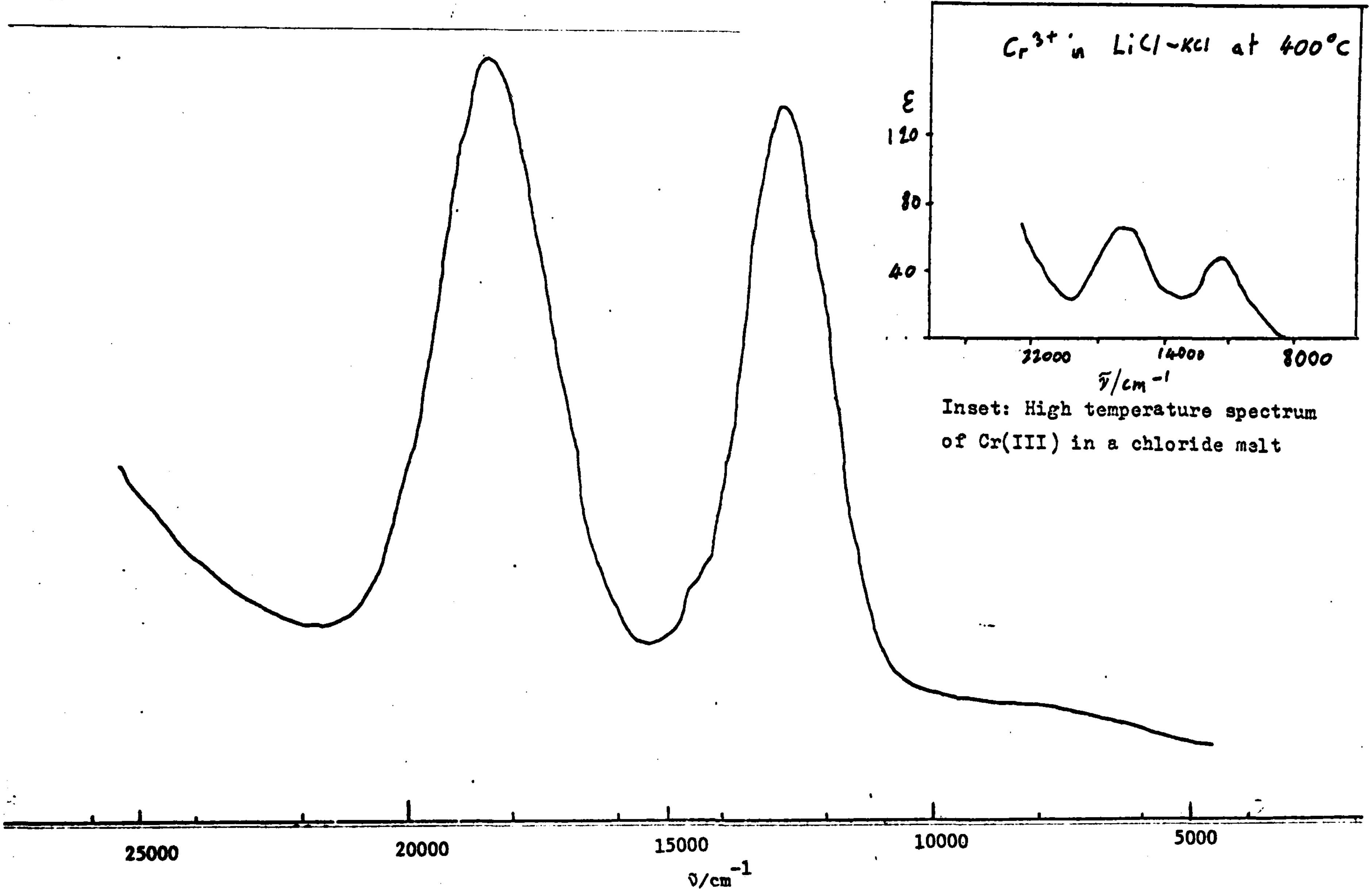
Thus chloride rich melts provide one of the few means of obtaining the solution spectrum of $[CrCl_6]^{3-}$. The advantages of the room temperature liquid over the high temperature melt are clear on comparison of the band widths in the two spectra (see Fig. 5.18).

Thus the specie present when $CrCl_3$ is dissolved in the basic $AlCl_3$-BPC melt is $[CrCl_6]^{3-}$.

5.6.3 Chromium(III) in the acid melt

The diffuse reflectance spectrum of chromium(III) chloride

Fig 5.18 Electronic spectrum of chromium(III) in basic melt



Inset: High temperature spectrum of Cr(III) in a chloride melt

TABLE 5.10 Chromium(III) in Chloride-Rich Environments

Species	Transition	Position maxima $\tilde{\nu}/\mathrm{cm}^{-1}$	Dq/cm^{-1}	B/cm^{-1}	Third band (cm^{-1})
Cr(III) in LiCl-KCl eutectic (Ref. 39)	$^4A_{2g} \rightarrow {}^4T_{2g}(F)$	12500	1294*	672*	29785*
	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$	18500			
$CrCl_3$ in basic melt	$^4A_{2g} \rightarrow {}^4T_{2g}(F)$	12750	1267	584	28489
	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$	18380			
$[pyH]_3[CrCl_6]$ solid state (Ref.78)	$^4A_{2g} \rightarrow {}^4T_{2g}(F)$	12700	1266	571	—
	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$	18200			

* These figures were not given in the original paper, and have been calculated from the positions of the maxima in the same way as for the experimental data.

(Fig. 5.19; details summarised in Table 5.11) was obtained for comparison with the chromium(III) species present in the acid melt. However the active form of chromium(III) chloride is only partially soluble in the acid melt, resulting in similar problems encountered for vanadium(III) chloride (see Section 5.5.3). As in the case of vanadium(III), the melt, "solution" was a similar colour to that of $CrCl_3$.

TABLE 5.11 Chromium(III) Chloride Spectral Parameters

Species	Transition	Position of maxima	Dq/cm^{-1}	B/cm^{-1}
$CrCl_3$	$^4A_{2g} \rightarrow {}^4T_{2g}(F)$	13500	13500	540
solid state	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$	18900		
$CrCl_3$	$^4A_{2g} \rightarrow {}^4T_{2g}(F)$	13500	13500	540
solid state (Ref. 79)	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$	18900		

5.7 IRON(II)

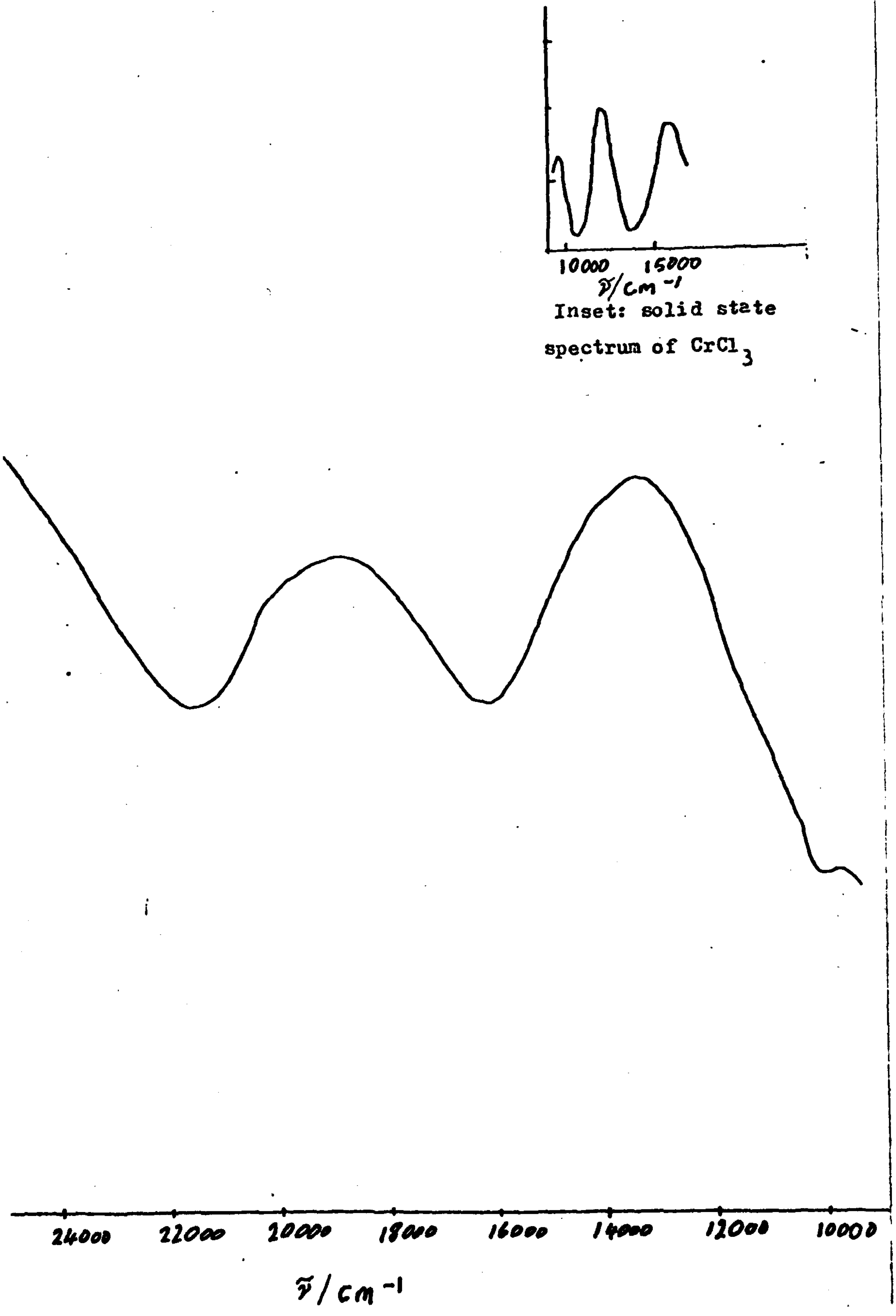
5.7.1 Introduction

Gruen and McBeth [38] found that the spectrum of iron(II) in the LiCl-KCl eutectic in the range 400-1000 °C was characterised by a single absorption band whose maximum moved to higher energy at higher temperature (see Fig. 5.20 inset). Gruen and McBeth [66] assigned this band to the $[FeCl_4]^{2-}$ complex and this was supported by consideration of studies on $Cs_2[Zn_{1-\underline{x}}(Fe)_{\underline{x}}Cl_4]$ and Cs $Cd_{1-\underline{x}}(Fe)_{\underline{x}}Cl_3]$ (see Fig. 5.20 inset). Gruen and McBeth [38] postulated increasing distortion of the tetrahedron to account for the shift of the maximum with temperature.

5.7.2 Iron(II) in the basic melt

The spectrum of $[Et_4N]_2[FeCl_4]$ in the basic melt and the solid state spectrum of $[Et_4N]_2[FeCl_4]$ are given in Fig. 5.20. Although no bands are visible, it is clear that there is a band just to the low energy end of the spectrum. Furlani et al [80] found that the absorption maximum for $R_2[FeCl_4]$ (R = $[Ph_4As]$,$[Me_4N]$) in $ClCH_2CN$ to be 4060 cm^{-1}. The solid state spectra of $[Ph_4As]_2[FeCl_4]$and$[Me_4N]_2[FeCl_4]$have maxima at 4550 cm^{-1} and 4480 cm^{-1} respectively. The band is due to the $^2E \rightarrow {}^2T_2$ transition.

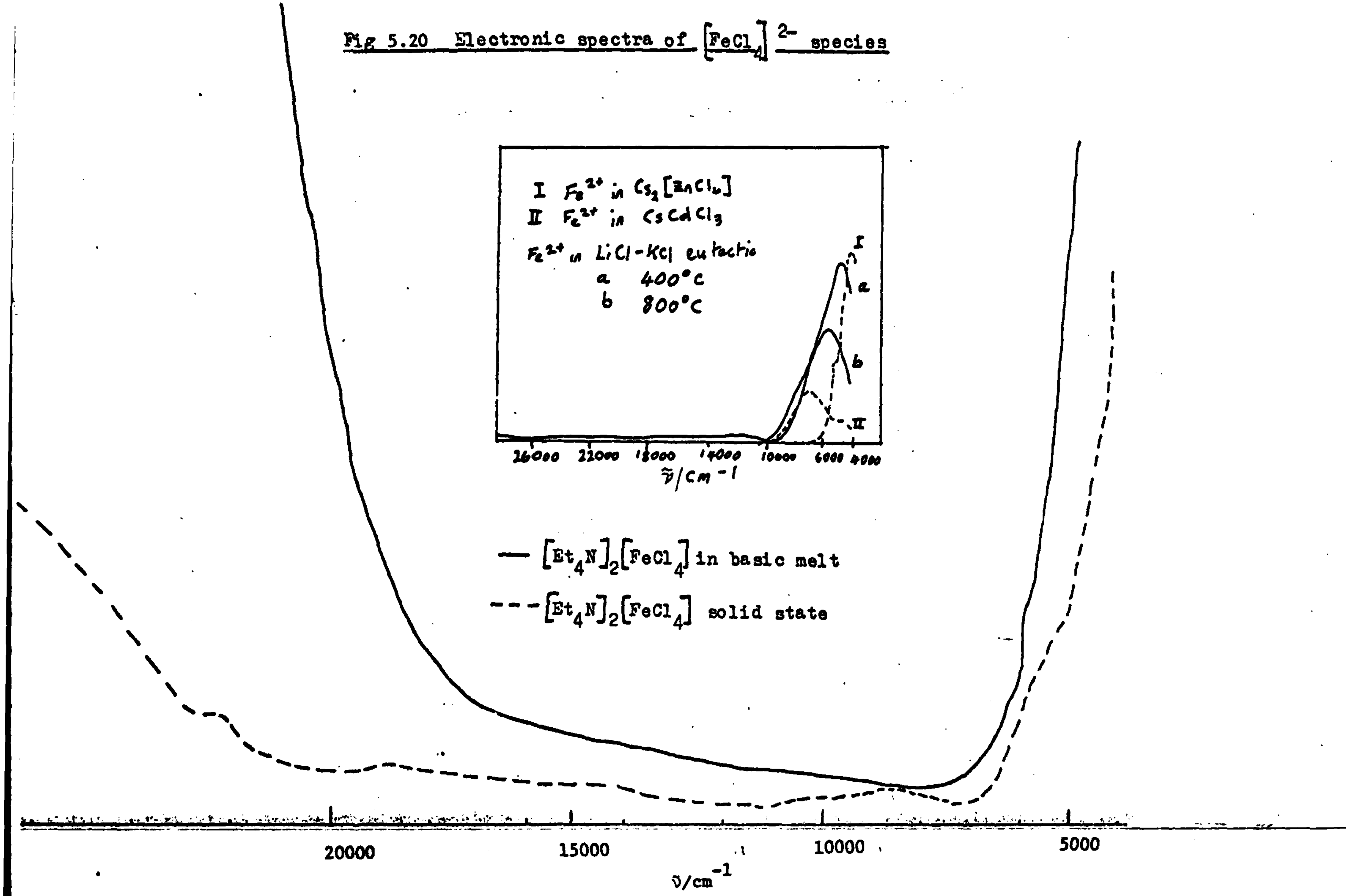
Fig 5.19 Diffuse reflectance spectrum of chromium(III) chloride



Inset: solid state spectrum of $CrCl_3$

It is unfortunate that this band is just outside the limit of the PE 330. However it is clear that there is a band present at the low energy end of the spectrum of $[Et_4N]_2[FeCl_4]$in the basic melt, in agreement with the supposition that the species present is $[FeCl_4]^{2-}$.

Fig 5.20 Electronic spectra of $[FeCl_4]^{2-}$ species



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