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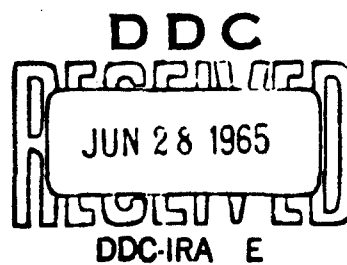
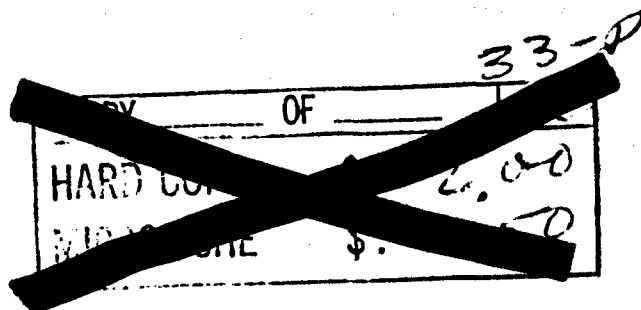
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Aerospace Research Laboratories

PHYSICAL AND PREPARATIVE STUDIES OF TRANSITION METAL CHELATES

R. D. ARCHER
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NEW ORLEANS, LOUISIANA



OFFICE OF AEROSPACE RESEARCH
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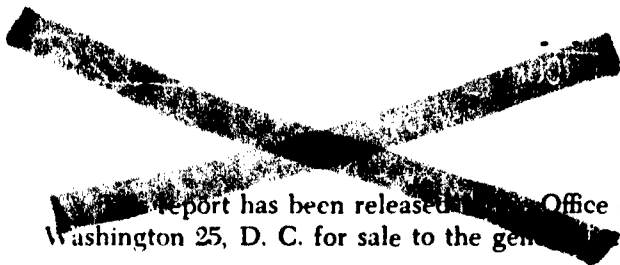
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TRANSITION METAL CHELATES**

R. D. ARCHER

**TULANE UNIVERSITY
NEW ORLEANS, LOUISIANA**

APRIL 1965

Contract AF 33(615)-1043

Project 7023

Task 7023-02

**AEROSPACE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

FOREWORD

This technical report was prepared by Tulane University, New Orleans, Louisiana, on Contract AF 33(615)-1043 for the Aerospace Research Laboratories, Office of Aerospace Research, United States Air Force. The research reported herein was accomplished on Task 7023, "Chemical Research on Matter" of Project 7023-02, "Research in Analytical and Inorganic Chemistry" under the technical cognizance of Dr. Robert E. Sievers of the Chemistry Research Laboratory of ARL.

The report includes research on some unsaturated β -ketoamine inner chelates (Part I), some molybdenum complexes (Part II), some tungsten complexes (Part III), and calculations concerning the spectra of several inner trifluoromethyltetrazolyl complexes (Part IV). Addenda to the report include an abstract of a paper on β -ketoamine complexes presented at the Southwest Regional American Chemical Society Meeting, Houston, Texas, December, 1963 (Addendum I) and another paper on β -ketoamine complexes of nickel submitted to Inorganic Chemistry, August, 1964 (Addendum II).

The diligent research effort of Mr. William Andruchow, M.S., College of the Holy Cross, and presently studying for the Ph.D. at Tulane University is gratefully acknowledged as is the reliability and versatility of a Newcomb College undergraduate Miss Marilyn G. Moffitt, who worked as both secretary and laboratory helper during the summer of 1964.

The intermittent help of several undergraduate research students, namely, Miss Jill Covell, Mr. Wesley Bonds, and Mr. Raymond Bertin is also acknowledged as is the monetary and scientific support of the chemists at the Chemistry Research Laboratory, Aerospace Research Laboratories, Wright-Patterson Air Force Base.

August 1964

R. D. Archer

ABSTRACT

The "partial paramagnetism" of several nickel(II) unsaturated β -ketoamine complexes has been found to be due to decomposition and water effects. Several other ketoamine complexes have been prepared, but none has been found suitable for vapor phase chromatography. A new 8-hydroxyquinolato complex of molybdenum has been isolated and the isomers of trichlorotripyridinemolybdenum(III) have been studied. Investigations of tungsten(III) and -(IV) complexes are in progress. Calculations of absorption band spectra for several trifluoromethyltetrazolyl complexes have been made and structures determined.

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PART I. UNSATURATED β -KETOAMINE COMPLEXES

INTRODUCTION

Considerable recent interest in the complexes of unsaturated β -ketoamines¹⁻⁷ has yielded some apparently contradictory results. For example, this laboratory group has reported that the nickel(II) chelate of 4-amino-3-pentene-2-one is square-planar,¹ but another laboratory has reported resolution of the complex.² Even more recently R. H. Holm and his coworkers have suggested tetrahedral complexes on the basis of NMR contact shifts;³ however, another investigator has observed no such shifts.⁴ In another case one group has implied the impossibility of forming the complexes in water,⁵ whereas this laboratory has had success in certain cases.¹ Because of the discrepancies, some of which relate to results of this laboratory, painstaking effort has been made to resolve these questions.

NICKEL(II) CHELATES

Measurements of the magnetic susceptibilities of the solid unsaturated β -ketoamine complexes of nickel(II) from room temperature to 150° (see Addendum I)⁸ have given no indication of tetrahedral species. On the other hand, detailed temperature variation studies of the magnetic susceptibilities and absorption spectra of solutions of the nickel(II) β -ketoamine complexes have shown an increase in solution paramagnetism with increasing temperature and near-infrared absorption peaks (see Addendum II).⁹ Such observations are often considered indicative of tetrahedral-square-planar equilibria; however, water and irreversible decomposition have been shown to be responsible for the paramagnetism and near-infrared peaks of these complexes. Details are given in the addenda.

Although no color change has been observed upon the addition of pyridine, the complexes change from diamagnetic to paramagnetic [$\mu = 3.16$ B.M. for bis(1,1,1-trifluoro-4-amino-3-pentene-2-ono)-nickel(II)] and the first visible absorption band drops in intensity as a new band appears in the near infrared, consistent with the tetragonal field approaching an octahedral configuration, a common phenomena for "square-planar" nickel complexes. The chelate bis-(4-amino-3-pentene-2-ono)nickel(II) sublimes at 85° in vacuo. Attempts to use the complex and others of this type for vapor phase chromatography studies have been plagued with decomposition of the complexes.

CHELATES OF OTHER METALS

Initial investigations on unsaturated β -ketoamine complexes

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of iron(III), manganese(II), chromium(III), copper(II), and molybdenum(VI) previously have been reported by the principal investigator.⁶ In general it has been found that these chelates are thermally less stable than the corresponding β -diketone complexes and appear less useful for vapor phase chromatographic investigations. The stabilities vary considerably, however. The molybdenum(VI) chelates decompose upon vacuum filtration at room temperature, but some of the nickel(II) chelates are stable in boiling water for short periods of time.

The rapid hydrolysis of 4-amino-3-pentene-2-one in the presence of iron(III) could be used for a test of iron(III) in the presence of iron(II) since the latter gives a light green complex rather than the red complex formed by the iron(III). Although the sensitivity is much lower than that of the thiocyanate ion, for some applications this actually may be an advantage.

PART II. MOLYBDENUM COMPLEXES

INTRODUCTION

The lack of many completely-chelated molybdenum complexes recently has been noted. The recent preparation of molybdenum(III) acetylacetonate^{8,10} independently by several research groups does not mean that molybdenum(III) chelates are to become as plentiful as those of chromium(III). The biggest problem is the ease of oxidation of molybdenum(III) compounds, the dry hexachloro ion being an apparent exception. The studies of 8-hydroxyquinoline outlined below are indicative of the problems commonly encountered.

The occurrence of $\text{Mo}(\text{pyridine})_3\text{Cl}_3$ in two crystal forms has been rediscovered¹¹ while preparing the complex by the method of Jonassen and Bailin.¹² Investigation of these isomers is discussed below.

MOLYBDENUM 8-HYDROXYQUINOLATES

A new air-stable maroon complex of molybdenum and 8-hydroxyquinoline has been prepared by the following procedure:

Ten grams (10.0 g., 23 mmoles) K_3MoCl_6 and 10.0 g. (69 mmoles) 8-hydroxyquinoline were added to 150 ml. H_2O . The resulting suspension was maintained in air at 50-55°C with constant stirring for a period of one hour. During this period the solution turned from orange-red to brown. The solution was allowed to cool to room temperature and then to 0°C by placement in an ice bath for two hours. The precipitate which formed was filtered and washed with cold water to remove any traces of K_3MoCl_6 . The maroon product was recrystallized from 95% ethanol and dried in vacuo at 70° for two hours over P_4O_{10} .

Anal. Calcd. for $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_8\text{NO})_4$: C, 52.94%; H, 2.94%; N, 6.86%; Mo, 23.52%. Found: C, 52.87%; H, 3.06%; N, 6.81%; Mo, 21.87%.

The low molybdenum analysis is probably due to the inadequacies of the precipitation method and/or incomplete decomposition of the complex prior to precipitation.

The complex is stable in air, decomposes at 320°, is diamagnetic, slightly soluble in acetone and ethanol, more soluble in benzene, and very soluble in chloroform. The molybdenum-oxygen infrared peak is found at about 920 cm.⁻¹ for this complex. The diamagnetism is not uncommon for complexes of molybdenum(V).¹³ The formula suggested is analogous to that of the diamagnetic xanthate complex $[(C_2H_5OCS_2)_2MoO]_2O$, the molecular structure of which has been determined.¹⁴ The assumed structure for the 8-hydroxyquinolate would be similar to that shown in Fig. 1. Several isomers could exist. The isomer as shown is a *meso*-form with regard to the molybdenum atoms so that *D,D*- and *L,L*-isomers with the same geometric configuration of oxygens and nitrogens about the molybdenum are possible. The isomer shown has *cis*-quinolate oxygens to both the bridging and terminal oxo groups. Three other independent geometric configurations for each molybdenum atom are possible giving a total of 16 potential geometrical isomers each of which could have three optical isomers. Needless to say, to date all of these 48 isomers have not been separated.

TRICHLOROTRIPYRIDINEMOLYBDENUM(III)

Two crystal forms of this compound were first observed by Rosenheim and Abel,¹¹ who prepared $Mopy_3Cl_3$ (in which py=pyridine) by a high pressure reaction between anhydrous pyridine and K_3MoCl_6 . Some crystals were obtained upon cooling. Yellow needles resulted by adding aqueous HCl. Recrystallization of the needles in chloroform yielded octahedra of the same composition. Another preparation involving precipitation from aqueous solution without the necessity of high pressures has been reported.¹² No statement regarding crystal form was noted in the latter reference, although we have found that needles are found in the aqueous precipitation and that octahedra occur in recrystallization from pyridine as well as from chloroform.

Molecular Weight for $Mopy_3Cl_3$. Calcd: 439.6 g./mole. Found: Unrecrystallized, 436.8 g./mole; needles, 423.7 g./mole; octahedra, 408.3 g./mole.

Molecular weight determinations have been made with a Mechrolab Vapor Pressure Osmometer. The results are slightly low, but within experimental error for single determinations. A slight amount of solution dissociation would also account for these values.

Inasmuch as these complexes are monomeric and uncharged, vapor phase chromatography might appear useful for separating the potential isomers. However, decomposition occurs before appreciable vapor pressure is attained. Column chromatography on "Florosil" has yielded double peaks suggesting two isomers, but equilibration between the two forms has allowed only a qualitative evaluation

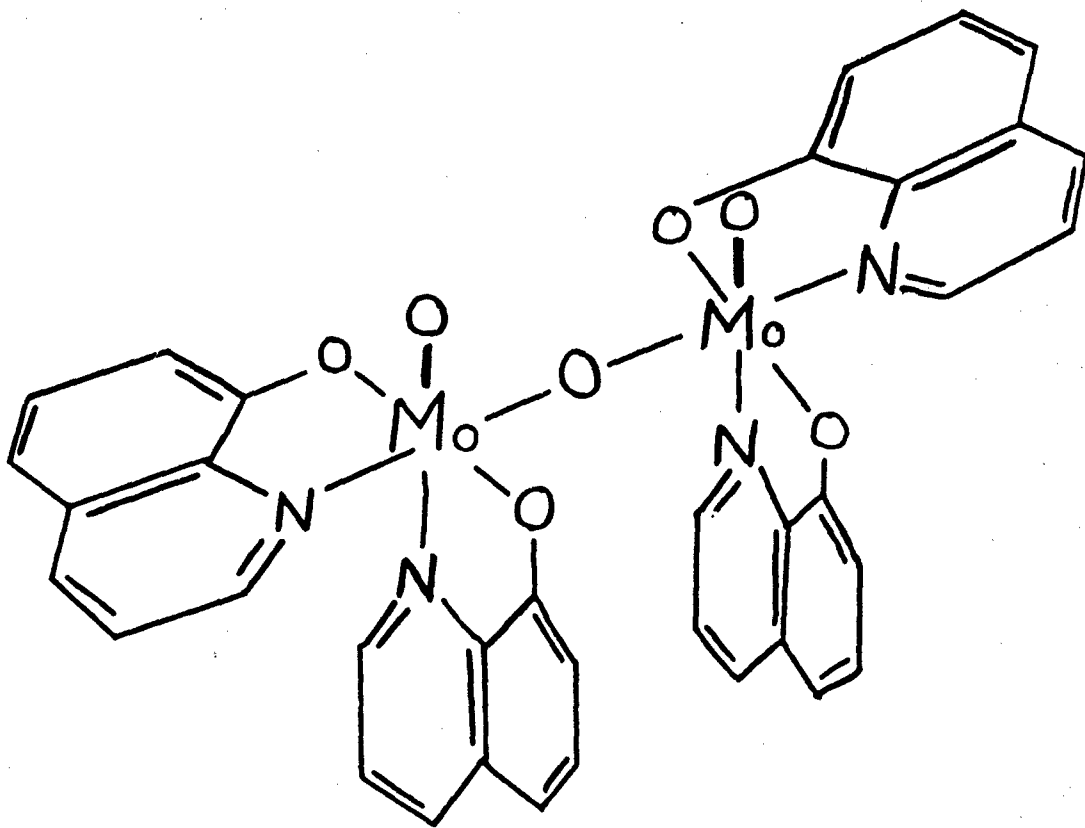


Fig. 1. -- Suggested structure for $\text{Mo}_2\text{O}_3(\text{C}_9\text{H}_6\text{NO})_4$.

of the situation. The ultraviolet absorption spectra of the two forms are different, indicative of separate isomers. Work is still in progress.

OTHER MOLYBDENUM COMPLEXES

The inner complex $[\text{Mo}(\text{C}_4\text{F}_6\text{S}_2)_3]$ has been synthesized in methylcyclohexane from molybdenum hexacarbonyl and 3,4-bis(trifluoromethyl)-1,2-dithietene,¹⁵ which previously had been synthesized from the reaction of hexafluoro-2-butyne in sulfur heated under reflux conditions.¹⁶ The properties of the inner complex agree with those reported by King.¹⁵ It has been found that the crude complex etches glass, but that double sublimation gives a more chemically stable product; however, the physical properties do not vary appreciably as a result of the extra purification. The complex is formally a molybdenum(VI) chelate, potentially separable into two mirror image isomers. Resolution of this complex appears plausible because of the high formal charge on the metal but has not been accomplished to date. The greater stability of this chelate in air relative to the molybdenum(III) acetylacetonate is also encouraging. Attempts to resolve the complex have been initiated using optically active quartz and lactose. The latter compound has the disadvantage of potentially being an optically active ligand (cf. discussion of Addendum II) or of giving induced asymmetry if partially dissolved. Good resolution of β -diketone complexes has been obtained using this ligand however.¹⁷

The contention by this group⁶ that the brown oxidation product of molybdenum(III) acetylacetonate is not another isomer of the yellow dioxomolybdenum(VI) acetylacetonate has been verified by Larson and Moore,¹⁸ a reversal of their earlier conclusions.¹⁸ Its constitution is still indefinite, but unlike the stable 8-hydroxyquinolate discussed above, the β -diketone complex apparently decomposes in solution.

PART III. TUNGSTEN COMPLEXES

Although no new chelates of tungsten in lower oxidation states have been completely characterized, some progress has been made. For example, 2,2'-bipyridyl reacts with $\text{K}_3\text{W}_2\text{Cl}_9$ in wet methanol or in bipyridyl itself. The tungsten chloro starting material is not soluble enough in scrupulously dry methanol for reaction to occur.

A method has been developed for preparing the mixed complex $\text{K}_4[\text{W}(\text{OH})_4(\text{CN})_4]$ by the use of ultraviolet light on aqueous KOH solutions of $\text{K}_4[\text{W}(\text{CN})_6]$, as follows:

Three grams (3.0 g., 5 mmoles) $K_4[W(CN)_8] \cdot 2H_2O$ were dissolved in a solution of 5.6 g. (100 mmoles) KOH in 150 ml. H_2O in a 250 ml. Pyrex erlenmeyer flask. The solution was irradiated with a mercury lamp (Cenco 87272) for a period of 24 hours. During that time the color of the initially yellow solution changed successively to brown, orange-red, red-violet, and deep-violet. The violet solution was allowed to evaporate under reduced pressure at 60° until the volume was reduced to 25 ml. Solid KOH was added to the orange-brown solution until precipitation of orange-brown crystals began (approximately 10 g. (180 mmoles) solid KOH were added). The solution then was cooled in an ice bath. The deep orange crystals which formed were filtered and washed with ethanol and ether. Yield: 1.9 g., 60%. The crystals dissolved and hydrolyzed in water giving a violet solution as previously observed.^{2b}

This reliable procedure is preferred to the previously reported preparation from $WO(OH)_3$ by Mikhalevich and Litvinchuk.²⁰ The tungsten(V) hydroxide had been obtained from a complex formulated as $(NH_4)_2O_2W_2O_3(C_2O_4H)_2 \cdot 4H_2O$, which had been synthesized by electrolytic reduction of paratungstate in the presence of oxalate. The tungsten(V) hydroxide has been found to vary in its reactivity and is difficult to handle.

An improvement in the synthesis of $K_4[W(CN)_8]$ from $K_3W_2Cl_9$ also has been found. The best published procedure²¹ uses fractional crystallization from the KCl contaminant to obtain the octacyano complex. Increasing the quantity of KCN allows precipitation of the complex before the potassium chloride.

PART IV. TETRAZOLYL COMPLEXES

The structures of several inner complexes of the trifluoromethyltetrazolyl anion have been determined²² from previously published data^{23,24} and reflectance spectra obtained by Harris.²⁵ Ligand field parameters for octahedral symmetry have been calculated using modifications of the Tanabe and Sugano secular₇ determinants reproduced by McClure²⁶ or as given by Jorgensen.²⁷ The complexes appear to be σ -bonded octahedral or distorted octahedral complexes rather than π -bonded as had once been proposed.^{24,25}

Using the atomic ground state as zero, the energies of the spin-allowed absorption bands for octahedral d^7 complexes are given by the following set of secular equations:

$$|12 D_q - E(^4A_{2g})| = 0 \quad (1)$$

$$| 2 D_q - E(^4T_{2g}) | = 0 \quad (2)$$

$$\begin{vmatrix} 15 B - E(^4T_{1g}) & 4 D_q \\ 4 D_q & -6 D_q - E(^4T_{1g}) \end{vmatrix} = 0 \quad (3)$$

An alternative set²⁴ has been used for a check on the calculations. The best fit for the spectra of $\text{Co}(\text{C}_2\text{F}_3\text{N}_4) \cdot 6\text{H}_2\text{O}$ has been obtained with $D_q = 1160 \text{ cm.}^{-1}$ and the Racah parameter $B = 820 \text{ cm.}^{-1}$. For these values, equations (1), (2), and (3) yield energies of 13.9, 2.3, and -8.0 and 13.3 kK, (1 kK = 1000 cm.^{-1}), respectively. (Equation (3) yields two values corresponding to the $^4T_{1g}$ component of the F and P states.) These energies put the spin-allowed transitions at 10.3, 21.3, and 21.9 kK in good agreement with the observed absorption bands (Table 1 and Fig. 2).

The energies of the spin-allowed absorption bands for octahedral d^6 complexes have been calculated from the appropriate secular equations, which differ from those for d^7 only in multiplicity and a sign change on each D_q inclusion, i.e.,

$$| E(^3A_{2g}) + 12 D_q | = 0 \quad (4)$$

$$| E(^3T_{2g}) + 2 D_q | = 0 \quad (5)$$

$$\begin{vmatrix} 15 B - E(^3T_{1g}) & -4 D_q \\ -4 D_q & 6D_q - E(^3T_{1g}) \end{vmatrix} = 0 \quad (6)$$

The best fit for $\text{Ni}(\text{C}_2\text{F}_3\text{N}_4)_2 \cdot 4\text{H}_2\text{O}$ has been obtained with $D_q = 1140 \text{ cm.}^{-1}$ and $B = 800 \text{ cm.}^{-1}$. These parameter values give energies of -13.68, -2.28, and 4.18 and 14.66 for equations (4), (5), and (6) respectively, and transitions at 11.4, 17.9, and 28.3 in good agreement with the observed spectral bands (Table 1 and Fig. 3).

Table I

SPECTRAL ASSIGNMENTS FOR SEVERAL 5-TRIFLUOROMETHYLTETRAZOLYL COMPLEXES

Complex	$\bar{\nu}$, cm. ⁻¹	Assignment
Ni(C ₂ F ₃ N ₄) ₂ ·4H ₂ O(solid)	11,400	³ A _{2g} → ³ T _{2g}
	(13,200) ^a	Footnote b
	18,500	³ A _{2g} → ³ T _{1g} (F)
Ni(C ₂ F ₃ N ₄) ₂ (aqueous soln.)	28,500	³ A _{2g} → ³ T _{1g} (P)
	17,500 ^c	³ A _{2g} → ³ T _{1g} (F)
	27,800 ^c	³ A _{2g} → ³ T _{1g} (P)
Cu(C ₂ F ₃ N ₄) ₂ ·H ₂ O(solid)	9,000	² B _{1g} → ² A _{1g}
	14,700	² B _{1g} → ² B _{2g}
	17,900	² B _{1g} → ² E _g
Fe(C ₂ F ₃ N ₄) ₂ ·2H ₂ O(solid)	19,300	¹ A _{1g} → ¹ T _{1g}
Co(C ₂ F ₃ N ₄) ₂ ·6H ₂ O(solid)	10,400	⁴ T _{1g} (F) → ⁴ T _{2g}
	21,300	⁴ T _{1g} (F) → ⁴ T _{1g} (P)

^aA breakdown of the spectrum into individual bands shifts this shoulder to approximately 14,000 cm.⁻¹. ^bAlthough this shoulder has been assigned as ¹E_g, C. K. Jorgensen, Acta Chem. Scand., 9, 1362 (1955), this designation has been challenged because of the intensity of the peak, see ref.28. ^cCalculated from the data in ref.23

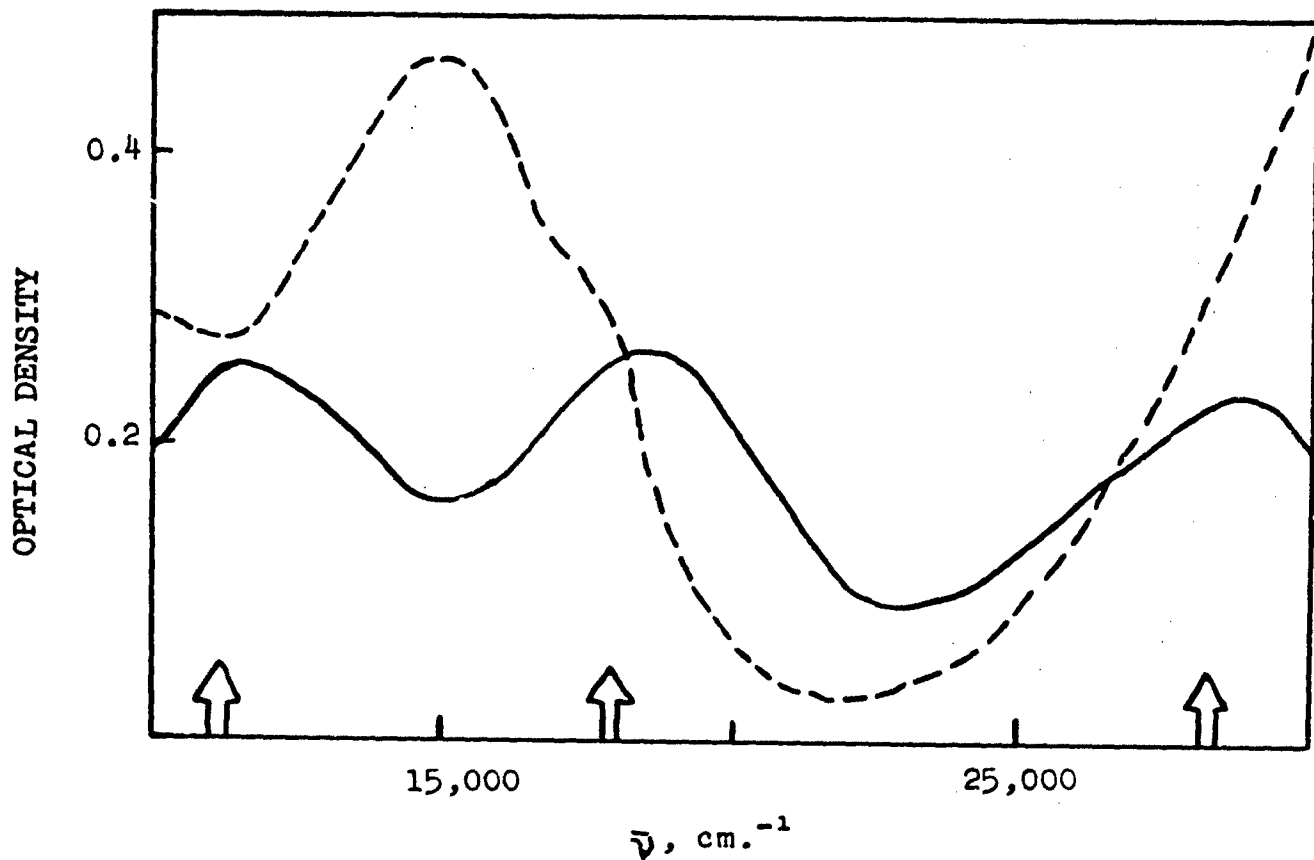


Fig. 2. -- Reflectance spectra of $\text{Ni}(\text{C}_2\text{F}_3\text{N}_4)_2 \cdot 4\text{H}_2\text{O}$ (solid line) and $\text{Cu}(\text{C}_2\text{F}_3\text{N}_4)_2 \cdot \text{H}_2\text{O}$ (dashed line). Calculated absorption peaks for nickel(II) complex are indicated by arrows.

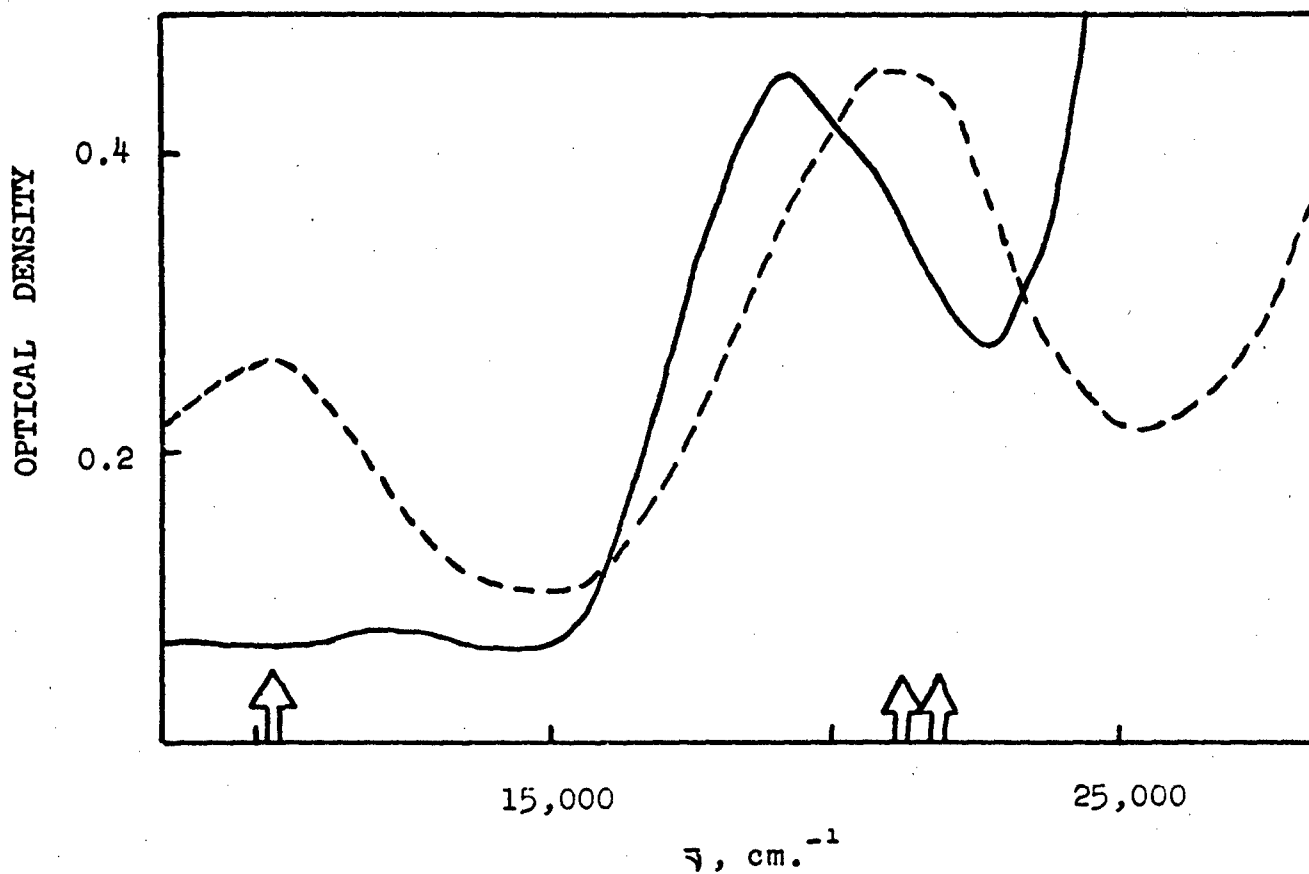


Fig. 3. -- Reflectance spectra of $\text{Fe}(\text{C}_2\text{F}_3\text{N}_4)_2 \cdot 2\text{H}_2\text{O}$ (solid line) and $\text{Co}(\text{C}_2\text{F}_3\text{N}_4)_2 \cdot 6\text{H}_2\text{O}$ (dashed line). Calculated absorption peaks for cobalt(II) complex are indicated by arrows.

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ADDENDUM I

α , β -UNSATURATED- β -KETOAMINE COMPLEXES OF THE TRANSITION ELEMENTS

RONALD D. ARCHER AND RICHARD L. LUTZ

Complexes of nickel(II), copper(II), manganese(II), iron(III), chromium(III), and molybdenum(VI) are among those studied to date. A complicating factor in the study of these complexes is the hydrolysis reaction which the β -ketoamines undergo and which is catalyzed by certain metal ions. Iron(III) is particularly effective in this regard.

A detailed magnetic study including diamagnetic corrections with bis(4-amino-3-pentene-2-ono)nickel(II), bis(1,1,1-trifluoro-4-amino-3-pentene-2-ono)nickel(II), and bis(3-phenylamino-1,3-diphenyl-2-propene-1-ono)nickel(II) indicates a small temperature independent paramagnetism often found in "diamagnetic complexes" as a result of the higher paramagnetic states mixing with the diamagnetic ground state. Although the third complex exhibits a greater paramagnetism than the others, little, if any, temperature dependence has been found in susceptibility measurements on the solid from room temperature to 145°C. These results exclude any appreciable amount of tetrahedral nickel(II) β -ketoamine species, one of which has been shown to be predominately trans-N₂O₂ square-planar nickel(II) based on absorption spectra, molecular weight, and magnetic susceptibility.² Possible explanations for the reported optically active solutions containing this class of complex³ can be rationalized without the use of tetrahedral or polymeric β -ketoamine complexes.

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- (1) A contribution of the Departments of Chemistry, Tulane University, New Orleans, and University of California, Riverside; supported by Aerospace Research Laboratories, U.S.A.F., presented at the Southwest Regional Meeting, Am. Chem. Soc., Houston, December, 1963, and published in *Southwest Retort*, 16, Nr. 4, 56 (1963).
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ADDENDUM II

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
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ANOMOLOUS MAGNETIC AND SPECTRAL BEHAVIOR OF NICKEL(II) COMPLEXES OF UNSATURATED β -KETOAMINES

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ABSTRACT

Detailed temperature variation studies of the magnetic susceptibilities and absorption spectra of several unsaturated β -ketoamine complexes of nickel(II) have shown an increase in solution paramagnetism and near-infrared absorption peaks often considered indicative of tetrahedral square-planar equilibria; however, water and irreversible decomposition have been shown to be responsible for the paramagnetism of these complexes.

INTRODUCTION

Two apparently contradictory articles^{1,2} appeared recently concerning nickel complexes of simple α,β -unsaturated- β -ketoamines. One¹ concluded on the basis of magnetic, molecular-weight, and spectral data that bis(4-amino-3-pentene-2-ono)nickel(II) is planar, whereas the other article² reported a slight resolution of this complex. The planar nature of the complex in the solid state has been substantiated by preliminary X-ray data.³ The X-ray data does not preclude the possibility that a planar-tetrahedral equilibrium could exist in solution—although the resolution study² suggested a fairly inert system, so that the equilibrium changes should be slow.

In order to ascertain the nature of the unsaturated β -ketoamine complexes in solution, detailed temperature variation studies have been made of the magnetic susceptibility and absorption spectra of several model complexes. The results indicate that bis(4-amino-3-pentene-2-ono)nickel(II) and other simple unsaturated β -ketoamines do not have appreciable quantities of tetrahedral species in solution. Even when the ligand has bulky groups substituted on the nitrogen atom, the planar form appears to be favored. An increase in the solution paramagnetism of these complexes with increasing temperature is sometimes noted. Secondly, an absorption peak in the

near infrared sometimes appears for the N-phenyl substituted complexes. Since a well-documented, related tetrahedral species has been found by X-ray investigation,⁴ the infrared peak plus the solution paramagnetism naively might be attributed to the formation of tetrahedral nickel(II) species.⁵ However, caution is necessary in drawing such conclusions because even though the phenomena exist in "nominally-dry" systems, they sometimes disappear in "scrupulously-dry" environments.

EXPERIMENTAL

GENERAL

Analytical reagent or spectral grade chemicals were used throughout this research. All organic solvents were distilled from an appropriate drying agent (normally sodium); all glassware was flamed-out; materials for the "scrupulously-dry" conditions were handled in plastic dry bags flushed with P₄O₁₀-dried, pre-purified-grade nitrogen.

LIGANDS

The preparation of 4-amino-3-pentene-2-one used in this laboratory has been reported previously.¹ The other ligands were also prepared by condensation of the appropriate β -diketone and amine or ammonia.⁶ The melting points ($^{\circ}$ C) and literature values for the latter ligands are respectively: 1,1,1-trifluoro-4-amino-3-pentene-2-one, 80-82 $^{\circ}$, unreported; 4-phenylamino-3-pentene-2-one, 47-48 $^{\circ}$, 48 $^{\circ}$ ⁸; 3-phenylamino-1,3-diphenyl-2-propene-1-one, 99-100 $^{\circ}$, 98.5-100 $^{\circ}$.⁷ All of the ligands were handled and stored in a dry atmosphere.

BIS(4-AMINO-3-PENTENE-2-ONO)NICKEL(II)

This complex was prepared as previously described.¹ Recrystallization from chloroform or absolute ethanol was used in some instances, but this treatment did not seem to improve the purity of the compound.

The complex was also formed in the reaction of 4-phenylamino-3-pentene-2-one with aqueous nickel(II) by amine exchange when ammonia was added.

BIS(1,1,1-TRIFLUORO-4-AMINO-3-PENTENE-2-ONO)NICKEL(II)

This complex was prepared by the reaction of 0.35 g. (2.3 mmoles) of 1,1,1-trifluoro-4-amino-3-pentene-2-one with 0.48 g.

(1.6 mmoles) of $\text{Ni}(\text{NO})_3 \cdot 6\text{H}_2\text{O}$ in 10 ml. of cold, 50% v/v methanol, and 6 ml. of 6 M aqueous NH_3 . A red-orange precipitate was obtained from the solution after standing in the cold for several hours. The product was filtered, washed with distilled water, recrystallized from chloroform and dried in vacuo over P_4O_{10} for twelve hours at 55°C ; Yield, 75%, m.p. 198°C .

Anal: Calcd. for $\text{NiC}_{10}\text{H}_{10}\text{F}_8\text{N}_2\text{O}_2$: C, 33.09%; H, 2.77%; N, 7.71%. Found: C, 33.06%; H, 2.71%; N, 8.03%.

BIS(4-PHENYLAMINO-3-PENTENE-2-ONO)NICKEL(II)

The dropwise addition of 20 ml. of 0.5 M methanolic KOH (10 mmoles) to a solution of 0.5 g. (3 mmoles) anhydrous NiCl_2 and 2.0 g. (11 mmoles) 4-phenylamino-3-pentene-2-one in 40 ml. absolute methanol (dried with Mg) gave a dark green solution, which was allowed to evaporate to one fourth its volume in vacuo. The resulting green precipitate was filtered and washed with sodium-dried petroleum ether (45° fraction). Further evaporation of the filtrate gave additional product. The desired green chelate was recrystallized from dry petroleum ether and dried in vacuo over P_4O_{10} for six hours at 50°C . Yield, 38%; m.p. 163°C .

Anal: Calcd. for $\text{NiC}_{22}\text{H}_{24}\text{N}_2\text{O}_2$: C, 64.86%; H, 5.89%; N, 6.87%. Found: C, 64.44%; H, 5.86%; N, 6.80%.

BIS(3-PHENYLAMINO-1,3-DIPHENYL-2-PROPENE-1-ONO)NICKEL(II)

The complex was prepared according to a previously published procedure² with comparable yields and properties.

PHYSICAL MEASUREMENTS

The magnetic susceptibilities were determined by the Gouy method. The samples were suspended in glass tubes in a field gradient of 8000 gauss (Alpha Al-foil electromagnet with tapered pole faces and an appropriate power supply). The change in weight was measured on a Mettler automatic balance. The sample tubes were calibrated with water ($\chi_g = -0.720 \times 10^{-6}$ c.g.s. at 20°C with a temperature coefficient of 0.12 per cent per degree).⁹ The sample tube was surrounded by a strip-silvered tube which in turn was wound with Nichrome wire and insulated. Current passed through the wire was closely controlled with two Powerstats wired in cascade, and the temperature was monitored with an iron-constantan thermocouple and a potentiometer.

The absorption spectra were measured in one cm. cells using a Cary model 14 or Beckman DK-1 spectrophotometer. Temperature control was maintained with a Haake model Fe temperature control bath and thermostated cell holders.

RESULTS

The four model nickel(II) unsaturated β -ketoamine complexes which have been studied are indicated in Table I. In order to evaluate the effect of a bulky group on the nitrogen of the unsaturated β -ketoamine, bis(4-phenylamino-3-pentene-2-ono)nickel(II) was prepared. The conditions suggested by Archer¹ for bis(4-amino-3-pentene-2-ono)nickel(II) are too mild for the N-phenyl complex, and those of Hseu, Martin, and Moeller² give (4-amino-3-pentene-2-ono)nickel(II) rather than the desired N-phenyl chelate. Similar amine exchange reactions have been noted previously.¹⁰ The successful preparation of the desired N-phenyl chelate requires a solvent with very little water and no ammonia. The N-phenyl complex reacts with traces of moisture as indicated in Fig. 1. The near infrared peak was found under the following circumstances: (1) When nominally-dry solutions of the complex were prepared several hours before making the spectral measurements; (2) when a few milligrams of water were added to solutions prepared under scrupulously-dry conditions which did not possess the infrared peak prior to the addition of water; and (3) when the chelate had been washed with water during its preparation. No such peak was observed when the complex was prepared and handled under very stringent conditions. Water added to dry solutions of the chelate does not immediately produce the infrared peak. The corresponding 1,3-diphenyl chelate is too insoluble to make quantitative measurements.

Magnetic measurements from room temperature to 150°C have not shown any detectable temperature dependence.¹¹ The slight paramagnetism of bis(4-amino-3-pentene-2-ono)nickel(II) in nominally-dry benzene and chloroform increases with temperature (Table II). On the other hand, no such change has been found for the complex under scrupulously-dry conditions. The trifluoro complex appears similar to the non-fluorinated compound. The N-phenyl complex decomposes upon heating in dry benzene solution and the complex with three phenyls per ligand is not soluble enough for quantitative measurements.

The spectral data for bis(4-amino-3-pentene-2-ono)nickel(II) at 25° and 55° are shown in Fig. 2. The slight shift appears to be reversible as indicated by quenching experiments. Although changes of considerably greater magnitude have been obtained with the corresponding 4-phenylamino complex, slow but irreversible decomposition takes place in this case as noted above even in very dry benzene. 4-Amino-3-pentene-2-one has a very slightly greater ligand field strength than the trifluoro ligand which in turn is somewhat greater than the N-phenyl ligands (cf. Table I). Two separate, visible absorption bands of approximately equal

Table I

VISIBLE ABSORPTION MAXIMA FOR BIS(α , β -UNSATURATED- β -KETOAMINE)NICKEL(II)
CHELATES IN NON-COORDINATING SOLVENTS

Ligand	$\bar{\nu}$, cm. ⁻¹	ϵ
4-Amino-3-pentene-2-one	18,100 (21,500) ^a	43 (45)
1,1,1-Trifluoro-4-amino-3-pentene-2-one	18,000 (21,300)	30 (30)
4-Phenylamino-3-pentene-2-one	16,400 (20,000)	39 (45)
3-Phenylamino-1,3-diphenyl-2-propene-1-one	(16,100) ^b	(30)

^aManual analyses of the absorption curves have been made to determine position and intensity of shoulders, which are indicated in parentheses. ^bEven the first $d \leftrightarrow d$ band is a shoulder for this complex and the position of the second band is unobservable.

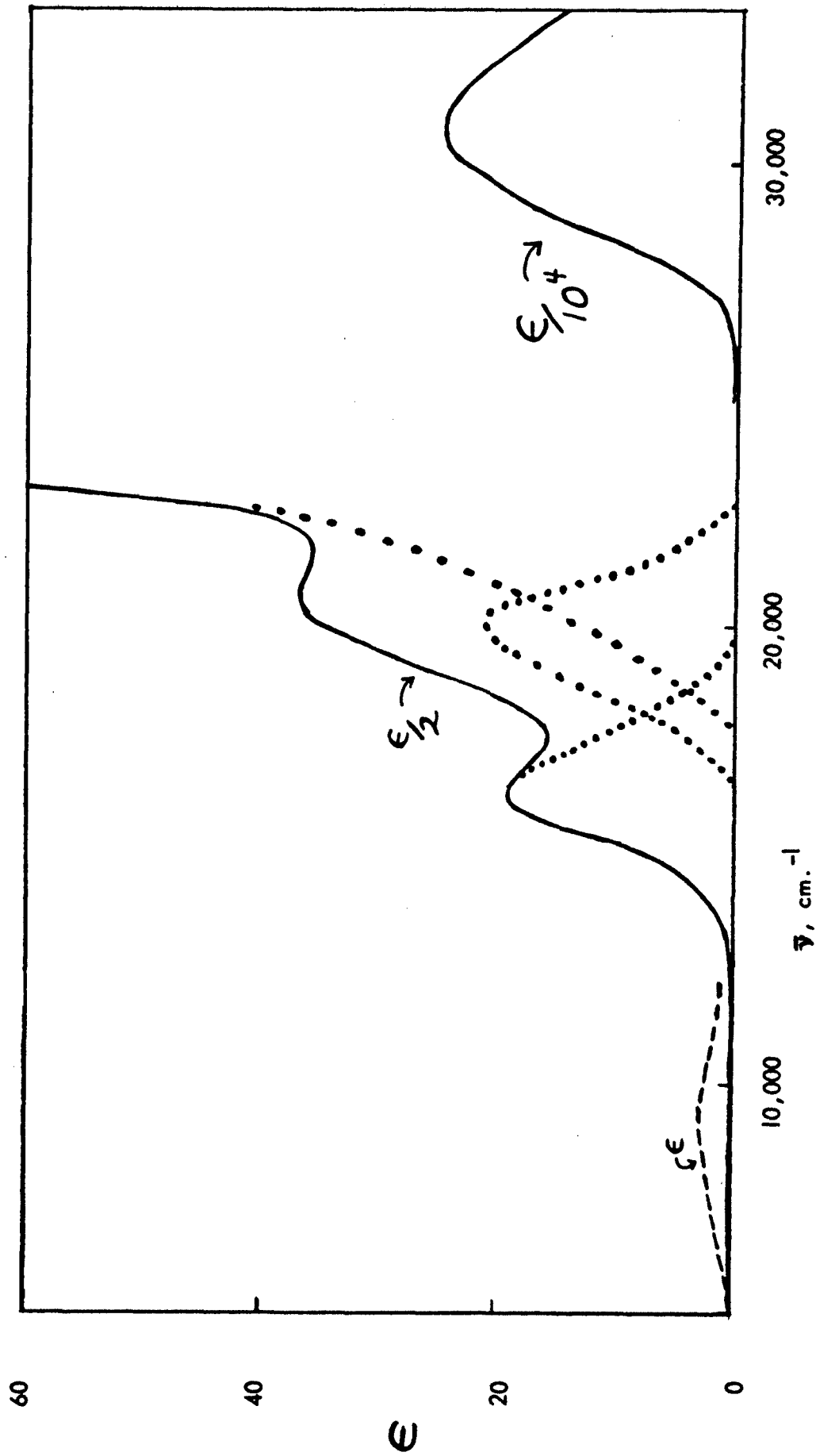


Fig. A1.—Absorption spectra of bis(4-phenylamino-3-pentene-2-ono)nickel(II) in benzene: — scrupulously-dry conditions; visible spectral band analysis for dry conditions; ----- normal conditions.

Table II

TYPICAL MAGNETIC BEHAVIOR OF BIS(4-AMINO-3-PENTENE-2-ONO)NICKEL(II)
IN REAGENT GRADE CHLOROFORM

Temp.	$\chi_M \times 10^6$ (cgs) ^a	$\chi_{\text{corr}} \times 10^6$ (cgs) ^b	μ (B.M.)	ΔE (kcal.) ^c	Triplet State ^d
25°C	- 90 ± 100	+ 10 ± 120	±	—	±
40°C	+ 50 ± 100	+150 ± 120	0.6	3	3%
47°C	+420 ± 100	+520 ± 120	1.2	2.1	14%
55°C	+850 ± 100	+950 ± 120	1.6	1.8	20%

^a0.74M solution. ^bThe diamagnetic corrections are based on some delocalization. ^cThe separation of levels has been calculated using the formula developed by A. D. Liehr and C. J. Ballhausen, J. Am. Chem. Soc., 81,538 (1959). ^dThe triplet state populations are based on 3.3 B.M., common for paramagnetic nickel(II) in both tetrahedral and octahedral geometries, cf. ref. 5b. ^eZero within experimental error.

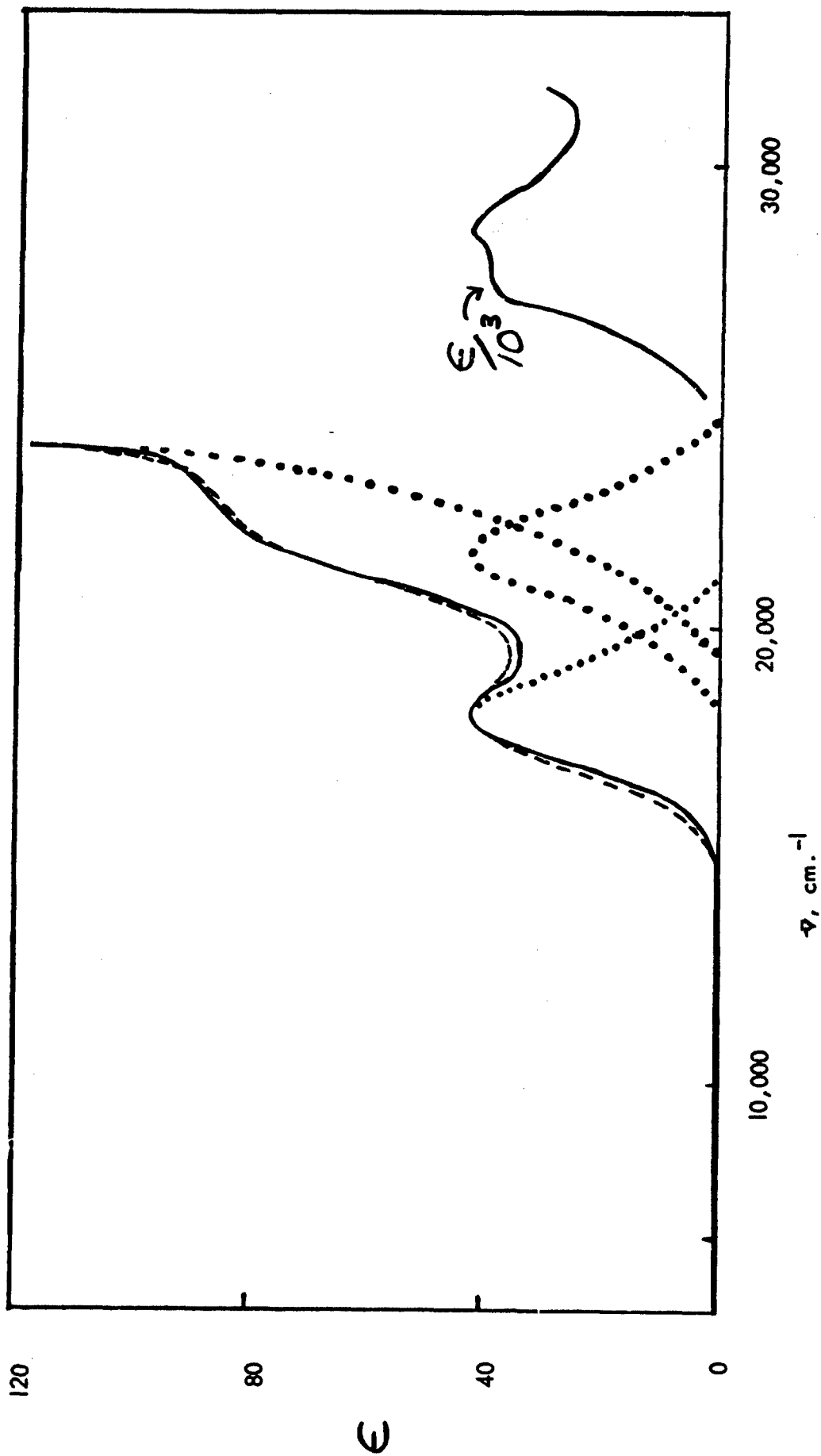


Fig. A2. —Absorption spectra of bis(4-amino-3-pentene-2-ono)nickel(II) in CHCl₃: — 25°C, - - - 55°C, ···· visible spectral band analysis of 25° spectrum.

intensity, a characteristic of the square-planar nickel(II) trans-N₂O₂ configuration,^{1,12} have been observed. The second peak is a shoulder of the more intense electron transfer bands, but its position has been readily determined by an analysis of the curves as shown in Fig. 1 through 3. The ambiguity in absorption band assignments for trans-N₂O₂ square planar nickel(II) complexes¹³ makes the assignment of Δ_K values¹⁴ fortuitous.

Dissolution of the trifluoro complex in pyridine gives a red solution, but a marked change in the magnetism ($\mu_{\text{EFF}} = 3.16$, based on an observed $\chi_M = 4040 \times 10^{-6}$ c.g.s. units at 23°C and a diamagnetic correction of -140×10^{-6} c.g.s. units) and the spectra (Fig. 3).

An interesting observation noted in our laboratory and independently by Collman¹⁵ is the rapidity with which iron(III) aids the hydrolysis of the unsaturated ketoamines. Aqueous iron(III) plus 4-amino-3-pentene-2-one immediately precipitates iron(III) acetylacetonate in good yields. This metal-catalyzed reaction and the reverse reaction are presently under investigation.

DISCUSSION

A comparison of the results noted above with some recently reported "extra peaks" at about 9000 cm.^{-1} for "planar-tetrahedral" equilibria of other nickel(II) complexes^{5b,d,16} suggests that the other investigators have been plagued by traces of water yielding small amounts of octahedral species. Traces of water would also explain the slight polymerization noted for some of salicylaldehyde derivatives^{5b} and the "resolution" of the planar bis(4-amino-3-pentene-2-ono)nickel(II) complex^{2,17} since the diketones are known to be primarily trimeric, octahedral species.¹⁸ The hydrolysis of the "resolved chelate" may have occurred while preparing the complex or during numerous hours on the chromatography column. The former is strongly implied by the method used to prepare the chelate (i.e., heating the unsaturated β -ketoamine and nickel(II) ion on a steam bath in a solution containing greater than 60% water) especially since the ligand and the complex are easily hydrolyzed. In fact, heating the ligand and nickel(II) ions in water even in the absence of base gives the diaquobis(2,4-pentanediono)nickel(II) complex.¹ Although this study is unable to rule out the possibility that traces of a tetrahedral species of this β -ketoamine complex might exist, such a species does not predominate in the solid state or in solution. The resolution of the other unsaturated β -ketoamine complexes² is understandable because the N-phenyl groups are not in the plane with the rest of the molecule and the bulkiness of

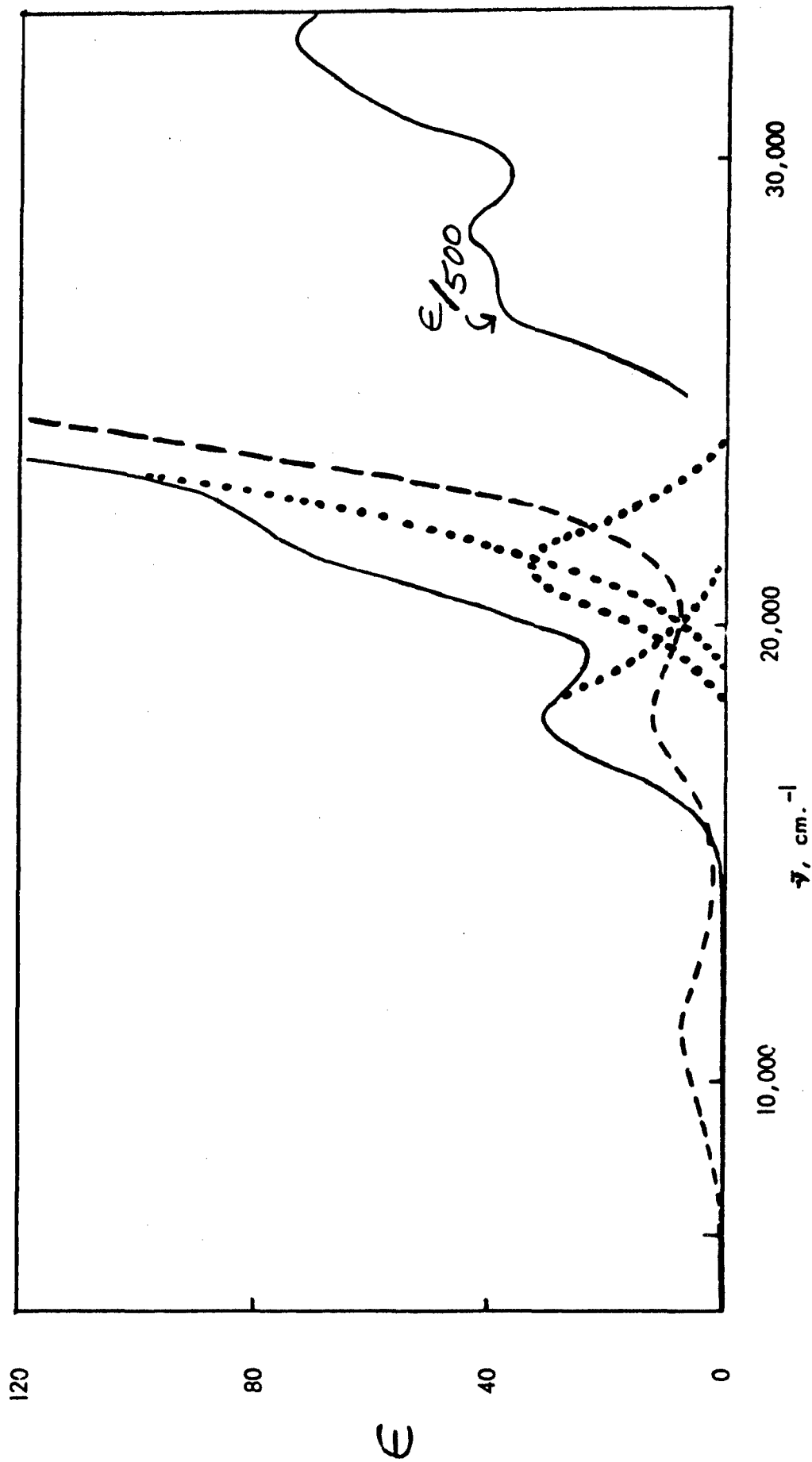


Fig. A3. — Absorption spectra of bis(1,1,1-trifluoro-4-amino-3-pentene-2-ono)nickel(II): — in benzene or chloroform; ---- in pyridine; visible spectral band analysis (for non-coordinating solvents).

the phenyl groups poses a large energy barrier (commonly called steric hindrance) to the normally rapid inversion of amine bonds. Molecular models of these complexes show large overlaps for the transformation geometry.

Water appears to play a dual role in properties of these complexes. With the N-phenyl (and more easily hydrolyzed N-alkyl) complexes water decomposes the chelate, while perturbation of the z-axis by water is observed with the N-H complexes.

Changes in the spectra with concentration gave the initial clue to a water effect in this investigation; but, if water has been used in the preparations, or if the complexes have been in contact with atmospheric moisture for any appreciable span of time, ideal behavior may be observed even though water has an effect on the chelates.

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