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COORDINATION CHEMISTRY OF THE GROUPS IV and V METAL

R. N. KELLER

UNIVERSITY OF COLORADO
BOULDER, COLORADO

CONTRACT NO. AF 33 (657)-8321
PROJECT NO. 7023

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AEROSPACE RESEARCH LABORATORIES
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FOREWORD

This report was prepared under Contract No. AF33(657)-8321, Project No. 7023, Task No. 7023-02, "Coordination Chemistry of the Groups IV and V Metals." It covers work done from 1 March 1962 to 1 March 1966. The work was performed at the University of Colorado, and was sponsored by Aerospace Research Laboratories, Chemistry Research Laboratory, with J. E. Schwarberg as Project Engineer.

For the University of Colorado, Dr. R. N. Keller served as the Principal Investigator.

ABSTRACT

It has been shown that vanadium(V) (as V_2O_5) can be reduced to vanadium(IV) at 80-100°C. (aqueous solutions or in some cases by the pure reductant if a liquid) with any of the following substances: glycolic, lactic, tartaric, formic, citric, oxalic, and malonic acids; amino acids such as ethylenediaminetetracetic acid, 2-hydroxyethyliminodiacetic acid, methyliminodiacetic acid, nitrilotriacetic acid, and glycine; and hydroxy compounds such as ethylene, propylene glycol, glycerine, and catechol. Most of the reducing agents subsequently react with the vanadium(IV) to form characteristic complexes. Many of these complexes can also be formed by allowing the above compounds to react with vanadium(III) in the presence of oxygen. The use of V_2O_5 has the advantage of allowing the reaction to proceed smoothly and facilitating the preparation of certain complexes containing free carboxyl groups which would be difficult to prepare in any other way. Some of these complexes when dissolved in water titrate as though they are mono- or diprotic acids. This appears to be due to the presence of uncoordinated carboxyl groups in the periphery of the coordination sphere or to coordinated hydroxyl groups showing acidic properties.

Exhaustive efforts in both aqueous and non-aqueous solutions to prepare derivatives of the octafluoroniobate(V) ion, NbF_8^{3-}, failed. Attempts were inconclusive to prepare complexes of niobium(V) and tantalum(V) containing the ion $MX_n^{-(n-5)}$ (where X is a halogen other than fluorine), and compounds containing a diamide chelating group such as $^-HNCH_2CH_2NH^-$.

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Introduction

The research carried out in connection with this contract centered around the chemistry of the three elements vanadium, niobium, and tantalum. The object of the research was to extend our knowledge of some of the fundamental chemistry of these elements in both simple and more complicated molecules and in solvents other than water.

Summary of the reactions and systems investigated

It is convenient to list the investigations pertaining to vanadium separately and those pertaining to niobium and tantalum together.

Chemistry of vanadium

The bulk of the reactions involving vanadium were carried out in aqueous media and in general utilized the plus three and plus five oxidation states, although most of the resulting complexes contained vanadium in the plus four oxidation state.

(1) Reduction of V^{V} to V^{IV} by interaction with various organic ligands and subsequent complex formation.

(2) Formation of V^{IV} complexes by interaction of organic ligands with V^{III} in presence of oxygen.

(3) Reaction of metal salts of carboxyl-containing ligands with vanadyl ion.

(4) Reaction of liquid reagents with solid $V_2 0_5$.

(5) Reduction of $V_2 0_5$ in a bomb with various reagents.

(6) Reaction of amines with V^{V}.

(7) Reaction of ω-(methylsulfinyl)-acetophenone with $V0^{2+}$ ion and solid $V_2 0_5$.

(8) Miscellaneous reactions.

Chemistry of niobium and tantalum

(1) Attempted preparation of octafluoride ion of niobium (V).

(2) Preparation of derivatives of $MX_n^{-(n-5)}$ ions where X is a halogen other than fluorine.

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(3) Attempts to prepare aryl amide derivatives and chelates containing diamide ligands, such as $^{-}HNCH_2CH_2NH^{-}$.

Experimental details

Vanadium chemistry

(1) Reduction of V^{V} to V^{IV} by interaction with various organic ligands and subsequent complex formation.

It was found that solid V_2O_5 could be made to interact in aqueous solution at temperatures between 80-100° C. with a variety of substances; the initial reaction is reduction of the V^{V} to V^{IV} and then excess of the reducing agent acts as a coordinating entity to form a complex with the reduced form of the vanadium. The general procedure for preparing these compounds was qualitatively the same. Excess solid V_2O_5 and the reducing agent-coordinating ligand compound were heated together in water at 80-100° for an hour or more depending upon the rate of the reaction; the resulting solution (usually blue in color) was separated from excess V_2O_5 and the complex obtained by concentrating the filtrate and adding ethanol as well as ether in certain cases. Purification could generally be carried out by re-precipitating from water several times. Most of these blue complexes were found to be soluble in water but insoluble or only slightly soluble in the common organic solvents.

(2) Formation of V^{IV} complexes by interaction of organic ligands with V^{III} in presence of oxygen.

It was found that most of the compounds obtainable by reducing V_2O_5 as outlined above could also be obtained by allowing the coordinating groups to interact with V^{III} in the air. The procedure was essentially as for the reactions with V_2O_5 except V_2O_3 was the starting oxide (or $VOCl_2$ can also be used).

(3) Reaction of metal salts of carboxyl-containing ligands with vanadyl ion.

The complexes obtained above with coordinating substances containing carboxyl groups by the reduction of V^{V} or the oxidation of V^{III} can also in general be obtained by preparing the barium salt of these carboxyl-containing substances and interacting the barium salt with $VOSO_4$. Here $BaSO_4$ precipitates and the vanadyl complex in solution can be isolated by concentrating the solution and precipitating the blue complexes with ethanol. This method is not as convenient as the one starting with V_2O_5 and was used only to synthesize certain compounds to verify that we were in fact obtaining derivatives of V^{IV} by the other methods.

(4) Reaction of liquid reagents with solid V_2O_5.

In some cases where the reagent being used was liquid, such as ethyleneglycol, the pure liquid and solid V_2O_5 were heated at 80-90° for several hours or until the reaction was completed. The solid material obtained was washed several times with alcohol in order to eliminate excess of the organic compound.

(5) Reduction of V_2O_5 in a bomb with various reagents.

The compound V_2O_5 appears to be reducible in a bomb at elevated temperatures by a number of reagents. In general the reagents were heated in a bomb at 500-600° for several hours or longer.

(6) Reaction of amines with V^{V}.

Direct reaction of a number of liquid amines with solid V_2O_5 has resulted in compound formation.

(7) Reaction of ω-(methylsulfinyl)-acetophenone with VO^{2+} ion and solid V_2O_5.

A reaction product of this β-ketosulfoxide with V^{IV} has been obtained in four ways: (a) excess ketosulfoxide is refluxed with a vanadyl salt in aqueous solution, and the black oil which accompanies the formation of a light green precipitate is separated with acetone or ethanol;

(b) vanadyl chloride and the ketosulfoxide are allowed to interact in benzene solution under reflux for five hours; (c) finely powdered V_2O_5 is allowed to interact with the ketosulfoxide in benzene solution; V^V is first reduced to V^{IV} and the latter interacts with the ketosulfoxide; (d) interaction of V_2O_5 with a melt of the ketosulfoxide.

(8) Miscellaneous reactions.

The silver salt of (2-hydroxyethylimino) diacetic acid reacts with VCl_3 to give a yellowish-green crystalline compound which apparently contains Ag^+.

Acetonitrile and propionitrile react with V_2O_5 or with vanadic acid in water to give pale green solid substances.

Chemistry of niobium and tantalum

(1) Attempted preparation of octafluoride ion of niobium(V).

Attempts were made in aqueous solution as well as in certain non-aqueous media to place eight F^- ions about the Nb^{5+} ion. These attempts are summarized below.

A. Aqueous solutions

(a) Nb_2O_5 was fused with NH_4F (NH_4^+/Nb mole ratio of 20) and the product dissolved in a minimum amount of water; crystals were then grown from this solution by evaporation at room temperature. These conditions give, in the case of tantalum, the octafluoride.

(b) An $NH_4F \cdot Nb_2O_5$ fusion was made with an NH_4^+/Nb mole ratio of 20. An alkali metal fluoride was then added to the melt so that the MF/Nb mole ratio was 20 (M = Na and K). This mixture was then melted over the oxygen gas torch, cooled, dissolved in water, and crystals grown by slow evaporation at room temperature.

(c) Nb_2O_5 was dissolved in 24 M HF, an amount of alkali metal fluoride added so that the MF/Nb mole ratio was 20 (M = Na, K, Rb, and Cs), the mixture evaporated to dryness, and finally melted. The white product was dissolved in water and crystals grown slowly at room temperature

(d) Nb_2O_5 was fused with NH_4F and the product dissolved in water; alkali metal fluoride solutions were added to aliquots of this solution so that the MF/Nb ratio was four. Crystals were then grown slowly at room temperature.

(e) Saturated solutions of MF in 3 M HF were prepared (M = Na, K, Rb, Cs) and an aliquot of a saturated solution of Nb_2O_5 in 24 M HF was added to each MF solution so that the MF/Nb mole ratio was eight. Where precipitates were not obtained immediately, the solutions were evaporated slowly at room temperature.

(f) Since in (e) some oxy-species were obtained, this suggested the use of a higher concentration of HF. A series of experiments were performed similarly to those in (e) except that saturated solutions of MF in 6 M HF were used.

(g) One gram of potassium heptafluoroniobate was dissolved in a minimum amount of 6 M HF and this was mixed with a solution containing 2 g. of KF dissolved in a minimum amount of 6 M HF. The resulting solution was then evaporated at room temperature.

B. Non-aqueous solutions.

(a) A 0.1 millimole sample of K_2NbF_7 was placed in one arm of a Y-reaction tube along with 0.1 millimole of KCl; about 20 ml. of SO_2 was condensed onto the mixture. The Y-tube was sealed and allowed to come to room temperature with occasional agitation. The supernatant liquid was decanted into the other arm of the Y-tube and the SO_2 distilled from this arm back to the other. No residue remained--i.e., the reactants (and possible products) evidently were practically insoluble in SO_2.

(b) NbF_5 and a metal fluoride, such as KF (giving a fluoride ion ratio of 3 moles to 1 of NbF_5) was each dissolved separately in IF_5. This required a temperature of 80° or slightly higher. The resulting solutions were filtered if necessary and then mixed together and the IF_5 vacuum distilled until the solution had become cloudy with crystals.

The crystals were removed by means of a sintered glass filter, dried as far as possible in the vacuum line, and then placed in a vacuum desiccator.

All of these reactions had to be carried out in a closed system or in a dry box. Experiments were performed with alkali metal, aluminum, antimony(III), thallium(I), and ammonium fluorides.

(c) A sample of K_2NbF_7 was recrystallized from IF_5. The solid phase in equilibrium with the solution was $K_3Nb_2F_{13}$.

(d) A number of experiments were carried out in dimethylformamide solutions. These experiments generally consisted of first preparing a fairly concentrated aqueous solution containing Nb^V and HF (by dissolving Nb_2O_5 in HF) and diluting this solution with about four times its volume of DMF. To these solutions were added DMF solutions of NaI (NaI is quite soluble in DMF and this allowed a build-up of a high concentration of Na^+ ions). The resulting solutions were then evaporated at about 50° on a hot plate until the solutions had become cloudy with crystals. The crystals were collected, washed with DMF and dried under vacuum. In these experiments the ratio of Na/Nb/F was changed over a wide range.

(2) Preparation of derivatives of $MX_n^{-(n-5)}$ ions where X is a halogen other than fluorine.

Several experiments were carried out in which $TaBr_5$ was heated with varying ratios of dry KBr in an evacuated sealed tube at temperatures above the boiling point of $TaBr_5$. After several hours of heating there was no deposit of $TaBr_5$ crystals on the wall of the tube on cooling. The massive product was dark yellow-gray but when finely divided it became bright yellow and no longer resembled $TaBr_5$.

A large number of experiments involving the following general procedure were carried out. A non-aqueous solution of NbX_5 or TaX_5 (alone or in the presence of HX) was prepared and treated with an HX-solution of a large amine in the same solvent, or the niobium or tantalum halides and amine were dissolved and then gaseous HX added to the mixture; or the large cations were added as ammonium-type salts. In addition, phosphonium and arsonium compounds were also used. The basic idea was to find conditions favoring the formation of ions of the type $MX_n^{-(n-5)}$ and removing these with large cations which are compatible with the non-aqueous systems involved. Some of the solvents used were acetone, chloroform, carbon disulfide, dimethylformamide, and 1,2-dichloroethane.

Antimony(III) chloride and antimony(III) bromide (solids) were also used as reaction media for obtaining halide complexes of niobium(V) and tantalum(V). In this case the alkali halide (MX) and the Nb^V or Ta^V halide were mixed with solid SbX_3 and the whole mass fused and maintained at about 140° for some time. In some cases solid phases separated in the molten mixture. After these mixtures were allowed to cool, the solid plugs were extracted in a Soxhlet extractor with CS_2 to remove excess Sb^{III} halide.

(3) Attempts to prepare aryl amide derivatives and chelates containing diamide ligands, such as $^{-}HNCH_2CH_2NH^{-}$.

A. Reactions with amines

Ortho-, meta-, and para-phenylenediamine were allowed to react with $TaCl_5$ and $NbCl_5$ in several different solvents, including dimethylsulfoxide (DMS0), 1,2-dichloroethane, and dimethylformamide (DMF). In some cases white precipitates formed immediately when the solutions were mixed while in others solids formed after the solutions had stood for some time. In several cases it appeared that the amine decomposed. Where precipitates had formed, these were removed and the filtrate concentrated for the formation of additional crystals. Essentially the same experiments were carried out with p-nitroaniline, aniline, and ethylenediamine.

B. Reactions of alkali metals in amine solutions

A reaction mixture containing o-phenylenediamine, $NbCl_5$ and sodium metal in 1,2-dichloroethane gave no visible reaction after two days of stirring. A similar reaction was tried in DMF with potassium metal; the potassuim reacted giving a red solution and a brown precipitate. Para-nitroaniline was treated with potassium metal in ether; a red solid was isolated which upon being dried caught fire. Another sample of this red solid was prepared, but not dried, and allowed to interact with $NbCl_5$ in dry chloroform. After 72 hours of stirring, the yellow solution became dark red and a precipitate was present.

Metallic lithium was placed in carefully dried ethylenediamine; the solution became blue. Upon heating this solution the blue color faded. The excess ethylenediamine was distilled off and a cream colored solid remained.

C. Reactions with n-butyl lithium

A solution of n-BuLi in hexane was added to ethylenediamine in hexane. At first a chocolate colored precipitate formed along with a small volume of gas. After the mixture had refluxed for two hours, 3.5 liters of gas were obtained along with a white solid, which is very air and moisture sensitive. This same reaction was tried in toluene but it was later shown that toluene itself reacts with n-BuLi to give butane gas. The addition of n-BuLi in hexane to a suspension of $NbCl_5$ in pentane produced a dark brown solution but apparently no solid reaction products.

D. Spectra of solutions containing m-phenylenediamine and $NbCl_5$

Visible absorption spectra were obtained of solutions in DMF containing 1, 2, and 3 moles m-phenylenediamine per mole of $NbCl_5$. The visible spectra were about the same for the samples containing one and two moles diamine per mole $NbCl_5$. A distinct decrease in transmittance was found in the region of 540 mμ for the third solution. Solid phases separated from the first two solutions and these were shown to be m-phenylenediamine dihydrochloride.

Physical measurements and analyses

Most of the visible and ultraviolet spectra were obtained with a Beckman DB Spectrophotometer, and the infrared spectra with a Beckman Model 5 and a Carey Model 14. Infrared spectra were obtained by means of the KBr pellet technique; however, some of the results by this technique were checked and confirmed by spectra obtained from Nujol mull suspensions between rock salt plates.

Magnetic moments were obtained at room temperature on solid samples by the Gouy method on our local magnetic susceptibility measuring set-up. Analyses were done in our laboratories or by the Galbraith Laboratories, Inc., Knoxville, Tennessee.

Titration curves were obtained at 27° by following the change in pH caused by the addition of 0.10 N carbonate-free NaOH to 10^{-2} M solutions of the complexes under an atmosphere of nitrogen.

Results and discussion

Vanadium chemistry

It was shown by our work that V^{V} (as V_2O_5 or HVO_3) is reduced to V^{IV} at 80-100° (aqueous solutions or in some cases by the pure reductant if a liquid) with any of the following substances: glycolic, lactic, tartaric, formic, citric, oxalic, and malonic acids; amino acids such as ethylenediaminetetracetic acid, 2-hydroxyethyliminodiacetic acid, methyliminodiacetic acid, nitrilotriacetic acid, and glycine; and hydroxy compounds such as ethylene glycol, propylene glycol, glycerine, and catechol. Most of these reducing agents subsequently react with the V^{IV} which is produced to form characteristic complexes. Many of these complexes can also be formed by allowing the above compounds to react with V^{III} in the presence of oxygen. It is therefore possible to control conditions so that the same compound is obtained by starting with V^{III}, V^{IV}, and V^{V}. The use of V_2O_5 as the starting point for some of these complexes of V^{IV} has the advantage of proceeding more smoothly in some cases than if a V^{IV} or a V^{III} compound had been used and also V_2O_5 yields only water as a by-product with acidic ligands. We were consequently able to make certain complexes containing free carboxylic acid radicals which would be difficult to make in any other way.

Table I summarizes some of the physical properties of a group of compounds obtained in this work. As Table II indicates, some of these compounds when dissolved in water titrate as though they are mono- or diprotic in character. This is presumably due either to the fact that uncoordinated carboxyl groups are present in the periphery of the coordination sphere, or coordinated hydroxyl groups are showing acidic properties.

Vanadyl complex with EDTA $H_2[VO(C_{10}H_{12}N_2O_8)(H_2O)]\cdot H_2O$

This complex is prepared by heating V_2O_5 with ethlenediaminetetracetic acid in water at 80-100° for two hours. The blue solution obtained is filtered from excess V_2O_5 and concentrated; addition of ethanol precipitates the complex. Purification is accomplished by re-solution in water and re-precipitation with alcohol. It can also be crystallized by slow evaporation from water solution. The blue complex is very soluble in water but insoluble in most organic solvents. The same complex was also obtained from V_2O_3 and VO_2.

Anal. Calculated for above: C, 30.54; H, 4.57. Found: C, 30.20; H, 4.66.

Vanadyl complex with 2-hydroxyethyliminodiacetic acid

$VO(C_6H_9NO_5) \cdot 2H_2O$

This complex has been prepared in two ways. In one case V_2O_5 and 2-hydroxyethyliminodiacetic acid were heated together in aqueous medium; in the other equivalent amounts of barium 2-hydroxyethyliminodiacetate were allowed to react in warm water. After removal of either excess V_2O_5 or $BaSO_4$ the blue solution is concentrated and the complex precipitated with alcohol. The blue complex is soluble in water but insoluble in common organic solvents. The complex appears to lose its water when heated at about 30°.

Anal. Calculated for $VO(C_6H_9NO_5) \cdot 2H_2O$: C, 25.89; H, 4.66; N, 5.04. Found: C, 25.80; H, 4.70; N, 4.95.

Calculated for $VO(C_6H_9NO_5)$: C, 29.75; H, 3.71; N, 5.78. Found: C, 29.48; H, 3.68; N, 5.60.

Vanadyl complex with nitrilotriacetic acid $VO(C_6H_7NO_6) \cdot 2H_2O$

This complex was prepared and purified by a method analogous to that used for the EDTA complex. The complex is blue, very soluble in water but insoluble in the common organic solvents.

Anal. Calculated for above: C, 24.65; H, 3.76. Found: C, 24.21; H, 3.60.

Vanadyl complex with glycolic acid $VO(CH_2OHCOOH)_2.H_2O$

This complex is prepared by heating an excess of 70% glycolic acid and a few grams of V_2O_5 at 80-100° for several hours. The blue solution was concentrated on a steam bath to about 15 ml and then 200 ml of ethanol added; addition of ether to this mixture precipitates the solid complex. Purification was carried out by redissolving in water and re-precipitation as above. The blue compound is quite soluble in water and insoluble in common organic solvents. Although the complex was re-precipitated several times and appears pure, some difficulty was experienced in getting a good carbon analysis.

Anal. Calculated for above: C, 20.42; H, 3.40. Found: C, 19.18; H, 3.30.

Vanadyl complex with lactic acid $VO(CH_3CHOHCOOH)_2.H_2O$

For the preparation of this complex 85% lactic acid was used in the same manner as described above for glycolic acid. The blue compound is very soluble in water but insoluble in most organic solvents.

Anal. Calculated for above: C, 27.37; H, 4.56. Found: C, 26.82; H, 4.54.

Vanadyl complex with tartaric acid $VO(C_4H_4O_6).2.5H_2O$

This complex is prepared by interacting V_2O_5 and tartaric acid in aqueous solution. The blue complex is quite water soluble but insoluble in common organic solvents.

Anal. Calculated for above: C, 18.46; H, 3.46. Found: C, 18.39; H, 3.65.

The spectrophotometric measurements show that all these compounds have maximum absorptions between 760-780 mμ and 580-610 mμ; this appears to be characteristic of vanadium(IV) derivatives. As is evident from Table I, the magnetic moments for all these compounds is very close to the spin only value of 1.73 B.M. for a singly unpaired electron; this is consistent with a d^1 configuration for vanadium(IV).

The coordination number for vanadium in vanadyl complexes appears to be generally six and infrequently five. In all cases, in solution as well as in the solid state, the VO grouping maintains its identity and so one of the coordination positions is always occupied by oxygen from the vanadyl radical. In this work we have assumed that the normal coordination number is six in aqueous solution and have in some cases suggested coordinated water is present; our results cannot, however, distinguish between coordinated water and water of crystallization.

Our infrared results have been useful in deriving reasonable structures for the above complexes. These results can be used to distinguish coordinated from un-coordinated carboxyl groups. Since the -COOH group absorbs in a region different from that of a carboxyl group coordinated to a metal ion, it should often be possible to detect the existence of such groups in the presence of each other. The actual peak maxima for the carbonyl group in -COOH is apparently related to the degree of covalency in the metal-carboxylate bond. A free -COOH group absorbs near 1700 cm^{-1} while a coordinated carboxyl group has a carbonyl stretching frequency in the region 1590-1650 cm^{-1} depending upon the degree of covalency of the metal-carboxylate bond.

The IR spectrum of the vanadyl complex with EDTA suggests two kinds of carboxyl groups are present. The very strong peak at 1625 cm^{-1} is attributed to coordinated carboxyl groups while the weaker peak at 1730 cm^{-1} is an indication of free carboxyl groups. In view of the fact that this complex titrates like a diprotic acid, with pK_1 and and pK_2 differing by a factor of only about 10, suggests that two carboxyl groups are free. One isomer of this complex could be pictured as in Fig. 1 (only skeleton portions of parts of the EDTA ligand are shown for simplicity).

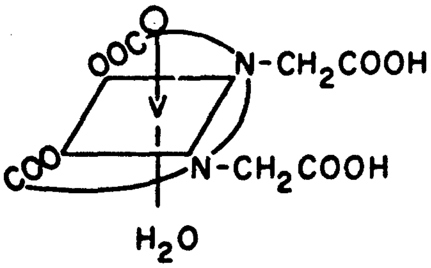


Fig. 1

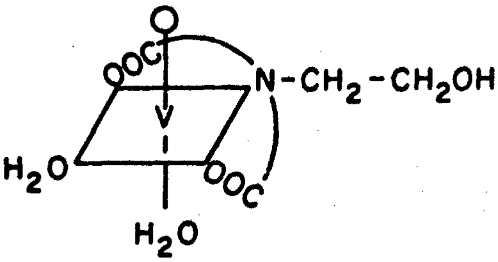


Fig. 2

The IR spectrum for the vanadyl complex with 2-hydroxyethyliminodiacetic acid shows a single very strong carbonyl absorption peak at 1600 cm^{-1}. This indicates only coordinated carboxyl groups are present in the complex. Moreover, this compound is not acidic. Fig. 2 indicates a possible structure for this complex.

As indicated above, the two water molecules appear to be lost when the 2-hydroxyethyliminodiacetic acid complex is heated. Further work is being carried out on this compound inasmuch as the structure of the anhydrous material would be of interest. With two coordination positions vacated, it would seem likely that the -OH group would coordinate and the 2-hydroxyethyliminodiacetic acid molecule would act as a tetradentate ligand; furthermore, if the resulting molecule has the shape of a tetragonal pyramid, the vanadyl oxygen would of necessity have to be one of the atoms in the base of the pyramid.

For the vanadyl complex of nitrilotriacetic acid two IR absorption peaks are present. The very strong peak at 1620 cm^{-1} is attributed to coordinated carboxyl groups while the weaker peak a. 1730 cm^{-1} is indicative of a free carboxyl group. Consistent with this is the fact that the complex titrates as a monoprotic acid. Fig. 3 shows a reasonable structure for this complex.

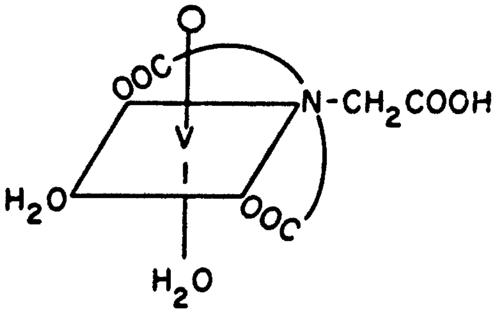


Fig. 3

Only coordinated carboxyl groups seem to be present in the vanadyl complexes of glycolic and lactic acids. The structures shown in Figures 4 and 5 appear to be consistent with the IR and analytical data.

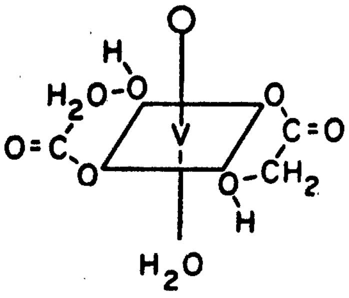


Fig. 4

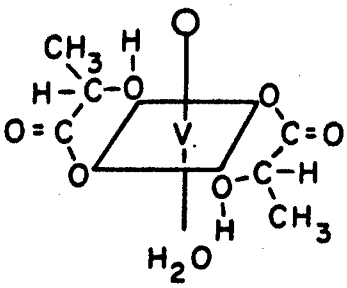


Fig. 5

The fact that these complexes titrate as diprotic acids imply that the hydroxyl hydrogens are probably involved as follows:

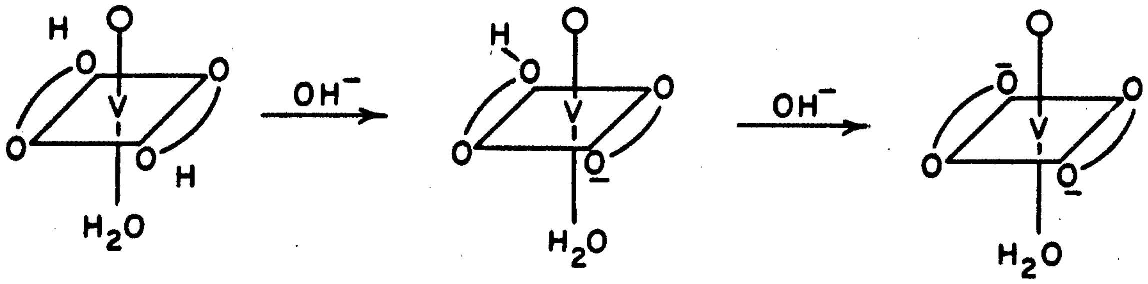


Fig. 6

It is interesting to note that during this titration the blue color changes to violet, and then to brownish-violet, but the original blue is easily restored with acid. It would certainly be expected that the hydroxyl hydrogens are more acidic than the hydrogens on the coordinated water molecule.

Similarly only coordinated carboxyl groups are indicated for the vanadyl complex with tartaric acid. A possible structure for this complex is indicated in Fig. 7.

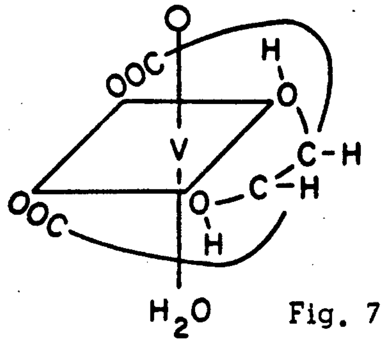
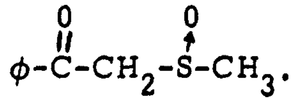


Fig. 7

Again, since this complex titrates as a diprotic acid, the hydroxyl hydrogens must be involved as shown above for glycolic and lactic acids. There is one interesting difference between the tartaric acid complex and the above two, however; the difference between pK_1 and pK_2 is greater for the tartaric acid complex than for the glycolic and lactic acid complexes. This conceivably could be due to the fact that the negative oxygens which are produced when both hydroxyl hydrogens are neutralized are cis to each other (i.e., closer together) in the tartaric acid complex and are trans to each other in the glycolic and lactic acid complexes.

Blue vanadium (IV) compounds can be isolated from the reaction of V_2O_5 with hydroxy compounds such as ethyleneglycol, propyleneglycol, catechol, and glycerine. These apparently correspond to the empirical relation of one vanadyl group (VO) to one hydroxy molecule (minus 2 H's). The nature of these compounds is perplexing and not yet fully elucidated.

A number of compounds of V^{IV} containing amines have been prepared; most of these are presumably salt-like substances although some may have nitrogen bound directly to vanadium. Amines include diethylamine, dimethylamine, diphenylamine, ethylenediamine, and ethanolamine. They probably correspond to substances with formulas such as $R_2NH_2^+VO_3^-$.

A green vanadyl compound can be obtained in a variety of ways from ω-(methylsulfinyl)-acetophenone,  $\phi\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}\overset{O}{\overset{\uparrow}{S}}\text{-}CH_3$. By analogy with β-diketones this compound might be expected to show a certain degree of enolization and to form chelates with appropriate metal ions. The spectra of these compounds show an absorption in the region normally attributed to metal-oxygen bonding, presumably a sulfoxide shift to 1000 cm^{-1}, a very marked double bond character (1600 to 1500 cm^{-1}), and weak carbonyl absorption at 1600 cm^{-1}. All of the preceding seem to indicate that a true chelate had formed with the vanadyl ion; however, a complete analysis of the compound obtained indicates virtually no sulfur is present. Evidently a more complicated reaction than chelation, as evidenced by the formation of the black oil, has taken place. The true nature of this compound has not yet been determined.

Pale green compounds are also obtained from the interaction of V_2O_5 in water (or vanadic acid) with acetonitrile and propionitrile. The nature of these compounds is likewise not understood at this time.

Vanadium(III) oxide was usually the product in the bomb experiments in which V_2O_5 was heated with various substances such as formaldehyde, acetaldehyde, formic acid, ammonia, and formamide. This reduction appears to be 96-97% complete with formaldehyde and formic acid, and 100% complete with NH_3 gas. Apparently formamide brings about the reduction even easier, with 100% conversion. There was also some indication that the oxidation product of the organic substances formed a compound with the V^{III} obtained in the reduction. Whereas NH_3 gas produced V_2O_3 from V_2O_5 at 500-600°, it produced pure NbN when heated with Nb_2O_5 for several hours at 1000-1100°.

Chemistry of niobium and tantalum

Exhaustive attempts were made in aqueous solutions as well as in certain non-aqueous media to place eight F^- ions about the Nb^{5+} ion. On whatever basis one analyzes this problem--available orbitals, radius ratio relationships, ability of neighboring elements in the Periodic Table to form the octafluoride ion--it is difficult to see why the NbF_8^{3-} ion should not exist.

While we were not able to prepare this ion from aqueous solutions, our experiments pointed up the problems attending any such attempts. The aqueous solution must be acidic else oxyfluorides form, yet the more acidic the solution becomes (from the addition of HF) the more the F^- ions are reduced in concentration through the formation of HF_2^-, $H_2F_3^-$, $H_3F_4^-$, etc. species. If the solution is made acidic enough to prevent oxy-compounds from forming and then the F^- ion concentration is built up with NH_4F, KF, or the like, one can go through the hexafluoro stage, and finally get the heptafluoro ion, NbF_7^{2-}. Whether the octafluoro species is not there or whether all common cations make their most insoluble compounds with the hepta-ion is not known. This state of affairs is in marked contrast to that of the Ta^V system; here one can get successively potassium salts of the hexa-, hepta-, and finally the octafluoro species. The solubilities are such as to allow the progressive addition of F^- ions about the Ta^{5+} ion and the precipitation of these as insoluble compounds.

Undoubtedly several competing tendencies are involved and they are perhaps delicately balanced, which work against or in favor of forming a NbF_8^{3-} derivative. The NbF_8^{3-} compounds must of course crystallize in preference to derivatives of NbF_6^-, $NbOF_6^{3-}$, and NbF_7^{2-}. Also the MF, MF_2, or MF_3 starting compounds must not crystallize in preference to the desired octafluoride derivative. The size of the M^+, M^{2+}, or M^{3+} ions must be such as to pack in the crystal lattice satisfactorily. Thus, the ratio of the sizes of the cations used to the size of NbF_8^{3-} is critical. It might still be possible, with the right cation, to isolate the octafluoro ion from aqueous solution; however, in our work with a variety of cations we were unable to accomplish this.

Attempts were also made to prepare NbF_8^{3-} from non-aqueous systems. Iodine pentafluoride was first tried since it had been reported that molybdenum and tungsten octafluoro ions could be prepared from a solution of a soluble molybdenum or tungsten compound and KF in this solvent. The highest fluoro complex we were able to isolate from this solvent was the hepta-ion. With DMF as a solvent, experiments were carried out using a variety of conditions and concentrations of reactants. On several occasions solid phases were obtained which fit the empirical relationships shown by the formulas Na_3NbF_8 and Na_4NbF_9. It was not possible to show unambiguously that these are true compounds rather than fortuitous mixtures with this stoichiometric relationship of the components. Attempts to recrystallize these substances unchanged from a number of solvents and mixtures were unsuccessful. Unsuccessful attempts were also made in liquid $S0_2$ and dioxane.

Extended efforts were made to prepare complexes of Nb^V and Ta^V of the type $MX_n^{-(n-5)}$ where X is a halogen other than fluorine. Apparently none of these is known but it seems there is no fundamental reason why they should not exist, especially in the absence of water. What appears to be a rather promising method is the simple fusion of mixtures of solid MX (alkali halides) and solid NbX_5 or TaX_5 in correct stoichiometric ratios. In the experiments involving this method, a reaction appears to occur because the volatile tantalum halide is consumed and the product is entirely different from the original mixture. Work is still continuing on characterizing these products.

Another method which on paper appears attractive is the isolation of these ions, i.e., $NbCl_6^-$, $TaCl_6^-$, $NbBr_6^-$, etc., from non-aqueous systems with large cations of the ammonium, arsonium, or phosphonium type. In fact this method has proved satisfactory in at least one case--

the preparation of TiF_6^{2-} derivatives. A large number of experiments based upon this approach have been carried out in a variety of non-aqueous solvents including acetone, chloroform, CS_2, ethanol, DMF, 1,2-dichloroethane, and fused antimony(III) halides.

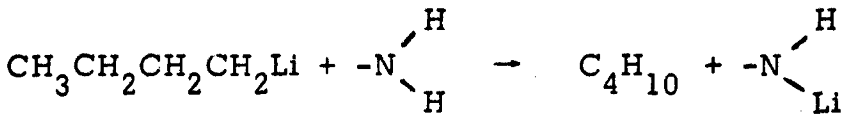
While some of the results appear promising, the experiments have been beset by many difficulties. Acetone and CS_2 seem to react with the halides of niobium and tantalum. Even with the most rigorous exclusion of water, oxy-compounds seem to form to the extent of contaminating what otherwise might be the desired products. Analytical problems have also been formidable. In spite of these disheartening results, we are convinced that the desired compounds can be made by this approach and are continuing these studies.

Amide derivatives of Nb^V and Ta^V are not unknown but appear to be limited to those obtained from ammonia and alkyl substituted ammonias. No derivatives apparently are known in which an aryl group is attached to nitrogen. This presumably is partly because of the less acidic character of the hydrogens on such nitrogens; substitution on the ring may have to be resorted to in order to increase the acidity sufficiently for amide formation to take place. In addition, no ring compounds are known in which two amide groups are present in the same ligand, e.g., $^-HNCH_2CH_2NH^-$.

Attempts to prepare amide derivatives directly by interacting amines with NbX_5 and TaX_5 in non-aqueous solvents did not prove successful. In the case of the mixtures in dichloroethane, a puzzling reaction occurs; in a number of these, solids were formed which were shown to be phenylenediamine dihydrochlorides. The source of the HCl to make such hydrochlorides is not immediately apparent. Also in these mixtures, after filtering off the original solids, the solids obtained by evaporating the filtrate contained a molar ratio of only one Cl to one Nb (or Ta). This might indicate a compound of niobium or tantalum in which four of the chlorine atoms have been replaced by amide groups, but the nitrogen content of these was far too low for such compounds. The addition of metallic sodium or potassium to the above amine-metal halide solutions did not appear to aid in the production of the desired products.

Considerable time was spent in attempting to make a di-lithium salt of ethylenediamine. Surprisingly there seems to be no indication in the literature that this salt or analogous alkali metal salts have been prepared. The direct interaction of lithium metal with dry liquid ethylenediamine produced a cream colored solid, stable in air. However, analytical results and equivalent weight by titration points to a compound more of the nature $[CH_3CH_2NH]^-Li^+$.

A particularly attractive method for replacing a hydrogen atom on an amine group with a lithium atom involves the interaction of n-butyl lithium with the amine as follows:



$$CH_3CH_2CH_2CH_2Li + -N\begin{matrix}H\\H\end{matrix} \rightarrow C_4H_{10} + -N\begin{matrix}H\\Li\end{matrix}$$

Butane gas is produced and aids the reaction to go to completion. The lithium amide type compound thus formed can then be allowed to react with niobium and tantalum halides, with formation of LiX and hopefully simultaneous attachment of the amide group to the metal ion.

An effort was made to use the above method to produce the di-lithium salt of ethylenediamine. Ethylenediamine in hexane and n-BuLi in hexane were allowed to interact; a small volume of gas and a chocolate colored precipitate first formed. After 2 hours of refluxing, 3.5 liters of gas (butane) were obtained and the precipitate present at this point was white. This precipitate was filtered under nitrogen and was found to be air and moisture sensitive. The volume of gas evolved was just that which would be expected if two hydrogen atoms had been displaced from the ethylenediamine. At this point it is not definite that the compound so obtained is in fact the di-lithium salt of ethylenediamine. The equivalent weight obtained by titrating an aqueous solution of the compound does not seem to agree with the sought after compound $LiHNCH_2CH_2NHLi$. Elemental analyses of the compound are not yet complete. Whether or not a ring amidetype compound of Nb^V and Ta^V can be prepared must await definite preparation of a di-lithium or di-sodium salt of a diamine such as ethylenediamine, propylenediamine, o-phenylenediamine, or the like.

Table I

Spectral and Magnetic Data for Vanadyl Compounds

adyl complexes with:	Infrared assignments (cm^{-1}) C-H stretching frequency	 Carbonyl stretching frequency	λ_{max} ($m\mu$)	μ_{eff} (B.M.)
Ethylenediaminetetraacetic acid	2950^m	1625^{vs}	770	1.79
		1730^w	580	
2-Hydroxyethylimino-diacetic acid	2950^m	1600^{vs}	780	1.78
			610	
Nitrilotriacetic acid	2950^w	1620^{vs}	780	1.69
		1730^w	610	
Glycolic acid	2900^m	1600^{vs}	770	1.78
			580	
Lactic acid	2900^m	1600^{vs}	770	1.73
			600	
Tartaric Acid	2950^w	1625^{vs}	770	1.79
			580	

s, strong; v, very; m, medium; w, weak

Table II

pK_A Values for Vanadyl Compounds

Vanadyl complexes with:	pK_1	pK_2
(1) Ethylenediaminetetra-cetic acid	2.3	3.2
(2) Nitrilotriacetic acid	3.4	---
(3) Glycolic acid	3.2	5.3
(4) Lactic acid	3.3	5.3
(5) Tartaric acid	2.8	6.2

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BSTRACT

It has been shown that vanadium(V) (as V_2O_5) can be reduced to vanadium
/) at 80-100°C (aqueous solutions or in some cases by the pure reductant
a liquid) with any of the following substances: glycolic, lactic,
taric, formic, citric, oxalic, and malonic acids; amino acids such as
ylenediaminetetracetic acid, 2-hydroxyethyliminodiacetic acid, methyl-
nodiacetic acid, nitrilotriacetic acid, and glycine; and hydroxy compounds
h as ethylene, propylene glycol, glycerine, and catechol. Most of the
lucing agents subsequently react with the vanadium(IV) to form character-
ic complexes. Many of these complexes can also be formed by allowing the
ve compounds to react with vanadium(III) in the presence of oxygen. The
of V_2O_5 has the advantage of allowing the reaction to proceed smoothly
facilitating the preparation of certain complexes containing free
boxyl groups which would be difficult to prepare in any other way. Some
these complexes when dissolved in water titrate as though they are mono-
diprotic acids. This appears to be due to the presence of uncoordinated
boxyl groups in the periphery of the coordination sphere or to coordinated
roxyl groups showing acidic properties.

Exhaustive efforts in both aqueous and non-aqueous solutions to prepare
ivatives of the octafluoroniobate(V) ion, NbF_8^{3-}, failed. Attempts were
onclusive to prepare complexes of niobium(V) and tantalum(V) containing
ion $MX_n^{-(n-5)}$ (where X is a halogen other than fluorine), and compounds
taining a diamide chelating group such as $^{-}HNCH_2CH_2NH^{-}$.

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