

$$J = A_1 \cos^2 \varphi, \quad 0^\circ \leq \varphi \leq 90^\circ \quad (2)$$

$$J = A_2 \cos^2 \varphi, \quad 90^\circ \leq \varphi \leq 180^\circ \quad (3)$$

where A_1 and A_2 are constants. Using the projected H-C-H geminal angle, θ , and the smaller vicinal angle, ω , the Karplus relations can be rewritten for the EDTA backbone pattern as

$$J_{CC}^{\text{EDTA}} = A_2 \cos^2 (\theta_T + \omega_T) \quad (4)$$

$$J_{CD}^{\text{EDTA}} = A_1 \cos^2 \omega_T \quad (5)$$

$$J_{DD}^{\text{EDTA}} = A_1 \cos^2 (\theta_T - \omega_T) \quad (6)$$

Similarly, for the EDDA analog (α -cis isomer)

$$J_{CC}^{\text{EDDA}} = A_2 \cos^2 (\theta_D + \omega_D) \quad (7)$$

$$J_{CD}^{\text{EDDA}} = A_1 \cos^2 \omega_D \quad (8)$$

$$J_{DD}^{\text{EDDA}} = A_1 \cos^2 (\theta_D - \omega_D) \quad (9)$$

These relations have been used to calculate the values of ω_T , θ_T , ω_D , and θ_D , where the subscripts T and D refer to the backbone structures of the EDTA and EDDA complexes, respectively. The resulting values are ω_T , 52; θ_T , 95; ω_D , 50; and θ_D , 113°.

The method of calculation is a simple iterative process. A reasonable value of ω_T is assumed; from eq 5, a value of A_1 is calculated and used in eq 6 to find $(\theta_T - \omega_T)$. From ω_T and $(\theta_T - \omega_T)$, the value of $(\theta_T + \omega_T)$ is found and used in eq 4 to calculate A_2 . The process is repeated for several values of ω_T between 40 and 70°. Any ω_T which results in $(\theta_T + \omega_T) > 180^\circ$ is discarded. Also rejected are ω_T values which yield $A_2 < J_{CC}^{\text{EDDA}}$ (if $A_2 < J_{CC}^{\text{EDDA}}$, then eq 7 yields \cos^2

$(\theta_D + \omega_D) > 1$, which is meaningless). As a result of these two restrictions, $\omega_T < 55^\circ$.

The A_2 values are used in eq 7 to calculate $(\theta_D + \omega_D)$, and the A_1 values are used in eq 8 to calculate ω_D . Knowing $(\theta_D + \omega_D)$ and ω_D , then θ_D and $(\theta_D - \omega_D)$ are obtained by subtraction. As a final check, $(\theta_D - \omega_D)$ is calculated by putting the A_1 value into eq 9. The discrepancy between the $(\theta_D - \omega_D)$ values obtained by subtraction and those from eq 9 is an indication of the correctness of the initial ω_T value.

Comparison of the two structures indicates that the protons on the $[\text{VO}_2\text{EDTA}]^{3-}$ backbone are more compressed than those in the EDDA complex. The compression is attributed to crowding of the ethylenic backbone by the unbonded acetate groups of EDTA. Replacement of these acetates with hydrogen atoms yields the EDDA complex; the crowding is minimized and the backbone protons are able to spread further apart. However, the $[\text{VO}_2\text{EDDA}]^-$ backbone does not attain the "perfect" nonstrained configuration with $\theta = 120^\circ$ and $\omega = 60^\circ$. The proton-proton angles are still slightly compressed, probably due to some strain in the five-membered V-N-C-C-N ring.

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Niobium(IV) and Tantalum(V) Pseudohalide Complexes with Nitrogen Donor Ligands

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Complexes of the type NbX_4L_2 and $\text{TaX}_5(2,2'\text{-bipyridine})$ ($\text{X} = \text{NCS}^-$ or NCSe^- , $\text{L} = 2,2'\text{-bipyridine}$ or $4,4'\text{-dimethyl-2-2'-bipyridine}$) have been prepared by the reaction of the hexaisothiocyanate or hexaiselenocyanate complexes with the organic ligand under anhydrous conditions. $\text{Nb}(\text{NCS})_4(\text{C}_{10}\text{H}_8\text{N}_2)_2$ and $\text{Nb}(\text{NCSe})_4(\text{C}_{10}\text{H}_8\text{N}_2)_2$ were also prepared by the reduction of the hexaisothiocyanate and hexaiselenocyanate complexes of Nb(V). The niobium complexes appear to be eight-coordinate. The pyridine complexes, $\text{Nb}(\text{NCS})_4(\text{py})_2$ and $\text{Ta}(\text{NCS})_5(\text{py})$, were prepared in an analogous manner. The mode of bonding in the thiocyanate and selenocyanate moiety has been investigated using infrared spectra. In all cases these ambidentate ligands are N-bonded and corresponding shifts in the C-N, C-S or C-Se, M-N stretching and N-C-S or N-C-Se bending regions are observed. The ultraviolet-visible spectra and magnetic susceptibility data are also discussed.

Introduction

The product obtained from the reaction of niobium(IV) or tantalum(V) halides with various nitrogen donor ligands is critically dependent upon the reaction conditions, e.g., whether the reaction is carried out under an inert atmosphere or under high vacuum, the temperature, and the solvent employed.¹ Depending

on the conditions, both the 5+ and 4+ metal halides give rise to complexes with pyridine which are of the type $\text{MX}_4(\text{C}_5\text{H}_5\text{N})_2$ ($\text{M} = \text{Nb}, \text{Ta}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$).¹⁻⁵ 2,2'-Bipyridine reacts with the tetrahalides to yield the

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TABLE I
 ANALYTICAL DATA FOR NIOBIUM AND TANTALUM ADDUCTS

Compound	Found, %					Calcd, %					Decomp point, °C	Color
	C	H	N	S	Se	C	H	N	S	Se		
Nb(NCS) ₄ (C ₁₀ H ₈ N ₂) ₂	45.14	2.50	17.72	19.94		45.21	2.51	17.48	20.10		280	Brown
Nb(NCS) ₄ (C ₁₀ H ₈ N ₂) ₂ ^a	44.93	2.36	17.39	19.96								
Nb(NCSe) ₄ (C ₁₀ H ₈ N ₂) ₂	35.06	2.05	13.49		38.23	34.91	1.94	13.57		38.30	227	Brown
Nb(NCSe) ₄ (C ₁₀ H ₈ N ₂) ₂ ^a	34.46	1.75	13.20		37.89							
Nb(NCS) ₄ (C ₁₂ H ₁₂ N ₂) ₂	48.34	3.52	16.28	18.33		48.48	3.46	16.16	18.47		234	Brown
Nb(NCSe) ₄ (C ₁₂ H ₁₂ N ₂) ₂	37.93	2.76	12.66		35.98	38.14	2.72	12.71		35.87	116	Brown
Nb(NCS) ₄ (C ₈ H ₈ N ₂) ₂	34.92	2.15	17.18	26.24		34.78	2.07	17.39	26.50		57	Purple
Ta(NCS) ₅ (C ₁₀ H ₈ N ₂)	28.85	1.43	15.46	25.46		28.71	1.28	15.63	25.52		188	Dark red
Ta(NCSe) ₅ (C ₁₀ H ₈ N ₂)	20.57	1.14	11.15		46.11	20.88	0.93	11.37		45.82	110	Blue-black
Ta(NCS) ₅ (C ₈ H ₈ N ₂)	22.04	1.05	15.10	28.82		21.82	0.91	15.27	29.10		130	Light brown

^a Obtained from the reduction of Nb(NCS)₆⁻ and Nb(NCSe)₆⁻.

monoadduct⁶ while the pentahalides give rise to MX₅-(C₁₀H₈N₂). In the presence of acetonitrile at low temperatures, solvent-insoluble complexes of the general formula MCl₅(C₁₀H₈N₂)(CH₃CN) were obtained.⁷ Under the same conditions NbBr₅ and TaI₅ yield complexes of the type MX₅(C₁₀H₈N₂)₂. The MCl₅(C₁₀H₈N₂)(CH₃CN) complex appears to be seven-coordinate with a molecule of lattice acetonitrile. The MX₅(C₁₀H₈N₂)₂ complexes may be eight-coordinate species of the type MX₄(C₁₀H₈N₂)₂+X⁻. In view of the above results, it was of interest to investigate the reactivity of the pseudohalide complexes with some nitrogen donor ligands in order to determine the course of reaction and type of complexes formed. We present here the results of these investigations.

Experimental Section

Since some of the starting materials, as well as the products of the following syntheses, were unstable in the presence of oxygen or water vapor, all work was carried out in an inert atmosphere drybox or under vacuum. All solvents and vessels used in the reactions were thoroughly dried by accepted methods. The elemental analyses of C, H, N, S, and Se were carried out by Alfred Bernhardt Laboratories, Mulheim, Germany.

Synthesis.—The potassium salts of the metal hexaisothiocyanates and hexaiselenocyanates were prepared using procedures described previously.^{8,9} The complexes Nb(NCS)₄L₂ and Nb(NCSe)₄L₂ (L = 2,2'-bipyridine and 4,4'-dimethyl-2,2'-bipyridine) were prepared by reacting a slight excess of the appropriate organic ligand with K₂Nb(NCS)₆ or K₂Nb(NCSe)₆ in acetonitrile for 4 hr. The insoluble product was separated from the soluble potassium pseudohalide and excess ligand by filtration. The product was dried for 24 hr *in vacuo*. The 2,2'-bipyridine complexes were also prepared by reduction of the hexaisothiocyanate and hexaiselenocyanate complexes of Nb(V). The appropriate pseudohaloniobium(V) salt was reacted with a twofold excess of 2,2'-bipyridine in *ca.* 50 ml of acetonitrile for 4 hr. The insoluble product was removed by filtration.

The 2,2'-bipyridine adducts of tantalum(V) were prepared from 2,2'-bipyridine and a stoichiometric amount of KTa(NCS)₅ or KTa(NCSe)₅ in 1,2-dichloroethane. The insoluble potassium pseudohalide which formed during the reaction was removed by filtration. The solvent was removed by vacuum distillation and the product dried for 72 hr *in vacuo*. The pyridine complexes were prepared by stirring the appropriate pseudohalide complex with a large excess of pyridine for 8 hr. After removal of the excess pyridine *in vacuo*, the product was extracted away from the insoluble potassium pseudohalide with 1,2-dichloroethane. After removal of the solvent, the product was dried for 72 hr *in vacuo*. Analytical data for all the adducts are summarized in Table I.

Physical Measurements.—Infrared (4000–200 cm⁻¹), visible,

and ultraviolet spectra, conductivity measurements, and magnetic susceptibility measurements were obtained using methods described previously.^{8,10} Diffuse reflectance measurements were obtained on a Cary Model 14 spectrophotometer equipped with a diffuse reflectance attachment (Type I illumination).

Results and Discussion

Preparation of Complexes.—Reaction of the hexaisothiocyanate and hexaiselenocyanate complexes of niobium(IV) with bipy (bipy = 2,2'-bipyridine) and dmbipy (dmbipy = 4,4'-dimethyl-2,2'-bipyridine) proceeded readily in acetonitrile, producing the insoluble complexes Nb(NCS)₄(bipy)₂, Nb(NCSe)₄(bipy)₂, Nb(NCS)₄(dmbipy)₂, and Nb(NCSe)₄(dmbipy)₂. The rapid precipitate formation indicates that the thiocyanate ion is easily displaced by bipy or dmbipy in these reactions. The isothiocyanate complexes are unusually stable in the atmosphere. There are no reports in the literature of air-stable complexes of niobium(IV) or tantalum(V) unless the metal is coordinated to one or more oxygen donors. All evidence indicates that these complexes are completely air-stable. While the isoselenocyanate complexes showed increased stability toward the atmosphere *vs.* K₂Nb(NCSe)₆, after 48 hr of exposure the complexes took on a red coloration, probably due to the formation of free selenium, which indicated that hydrolysis and/or oxidation had occurred.

Several unsuccessful attempts were made to prepare the analogous 1,10-phenanthroline complex, Nb(NCS)₄(phen)₂, in a similar manner. After the addition of 1,10-phenanthroline to the K₂Nb(NCS)₆ solution, an insoluble species was formed and isolated. The analytical data obtained on these products varied quite erratically and did not fit any suitable stoichiometry.

The synthesis of Ta(NCS)₄(bipy)₂ from TaCl₅ was also investigated. Fowles, *et al.*,⁸ and McCarley¹¹ have found that the formation of the diadduct, TaCl₄·2CH₃CN, in acetonitrile is complicated by an unknown side reaction. After the addition of bipyridine, no precipitate formation was observed. Thus, it appears that the Ta(IV) complex cannot be made by this method.

For the synthesis of Ta(NCS)₅(bipy), Ta(NCSe)₅(bipy), Ta(NCS)₅(py), and Nb(NCS)₄(py)₂ the use of acetonitrile was precluded because all reactants and products were soluble in this solvent. It was found that 1,2-dichloroethane was suitable in this case, due

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TABLE II
 SUMMARY OF INFRARED ABSORPTION FREQUENCIES FOR NITROGEN DONOR COMPLEXES (cm⁻¹)

Compound	$\nu(\text{CN})$	$\nu(\text{CS})$ $\nu(\text{CSe})$	$\delta(\text{NCS})$ $\delta(\text{NCSe})$	$\nu(\text{MN})$	Coordinated donor
Nb(NCS) ₄ (C ₁₀ H ₈ N ₂) ₂	2075 sh, 2035 vs, 2010 sh	906 w	492 m 481 w	328 vs 305 s	1606 s, 1600 s, 766 vs, 732 s, 424 m
Nb(NCSe) ₄ (C ₁₀ H ₈ N ₂) ₂	2050 sh, 2025 vs	698 m	464 m	312 sh, 305 vs	1606 sh, 1600 m, 769 s, 732 s, 422 m
Nb(NCS) ₄ (C ₁₂ H ₁₂ N ₂) ₂	2095 sh, 2048 vs	900 w	509 m 495 m	344 s, 322 s, 305 sh	1621 s, 437 m
Nb(NCSe) ₄ (C ₁₂ H ₁₂ N ₂) ₂	2085 sh, 2055 sh, 2040 vs	695 w	450 m	325 sh, 314 s, 304 sh	1621 s, 436 m
Nb(NCS) ₄ (C ₅ H ₅ N) ₂	1970 vs	892 w	508 m 493 m	313 s	1604 m, 635 m, 438 w
Ta(NCS) ₅ (C ₅ H ₅ N)	1975 vs, 1920 m, 1875 m	922 m	499 m 487 sh	308 s, 290 s	1607 w, 637 w, 433 w
Ta(NCS) ₅ (C ₁₀ H ₈ N ₂)	1975 s, 1915 m	918 m	494 m	305 sh, 280 s	1605 m, 764 m, 727 m, 425 w
Ta(NCSe) ₅ (C ₁₀ H ₈ N ₂)	1930 s	697 m	465 m	238 m, 228 sh	1605 m, 766 m, 729 m, 425 w

to the insolubility of KCNS and KCNSE in this solvent. Although most of the tantalum(V) halides are reduced in the presence of bipyridine and pyridine under certain conditions, no undesirable by-products due to reduction appeared to be present under these conditions. The pyridine complexes of niobium(IV) and tantalum(V) are very susceptible to air oxidation and hydrolysis. However, the bipyridine complexes of tantalum(V) display the same trend as the niobium(IV) complexes, *i.e.*, Ta(NCS)₅(bipy) seems to be air-stable, while Ta(NCSe)₅(bipy) shows signs of slow decomposition on exposure to the atmosphere. Conductivity measurements on Ta(NCS)₅(bipy) and Ta(NCSe)₅(bipy) indicate that these complexes behave as 1:1 electrolytes in acetonitrile and 1,2-dichloroethane. Hence they are probably best formulated as [Ta(NCS)₄(bipy)][CNS] and [Ta(NCSe)₄(bipy)][CNS].

The reaction of potassium hexaisothiocyanatoniobate(V) with bipyridine in 1,2-dichloroethane was investigated to determine whether the analogous complex, Nb(NCS)₅(bipy), could be prepared. The formation of a brown insoluble material during the reaction and the chemical analysis of this material indicated that reduction had occurred and that the major product was Nb(NCS)₄(bipy)₂. Potassium hexaisothiocyanatoniobate(V) and potassium hexaiselenocyanatoniobate(V) underwent reduction readily in the presence of bipyridine in acetonitrile to give Nb(NCS)₄(bipy)₂ and Nb(NCSe)₄(bipy)₂, respectively. The spectra (uv, visible, ir) and magnetic data of these compounds are in agreement with the data obtained for the products obtained directly from Nb(IV).

Infrared Studies.—The main infrared absorption bands of interest are given in Table II. The most definitive spectral changes in coordinated pyridine are in-plane ring vibrations at 1580 and 605 cm⁻¹ which are shifted *ca.* 25 cm⁻¹ toward higher energies, and the out-of-plane mode at 405 cm⁻¹ which occurs at *ca.* 435 cm⁻¹. In the case of 2,2'-bipyridine, the in-plane vibration at 1588 cm⁻¹ is shifted to *ca.* 1605 cm⁻¹ and the out-of-plane vibration at 404 cm⁻¹ is shifted to *ca.* 425 cm⁻¹. The disappearance of the 621-cm⁻¹ absorption and the appearance of several absorptions around 650 cm⁻¹ are also characteristic of coordinated 2,2'-bipyridine. However, the most informative spectral change is the splitting of the strong C-H out-of-plane bending mode at 760 cm⁻¹. This absorption splits into two major bands with one at *ca.* 765 cm⁻¹ and the other near 725 cm⁻¹. The strong in-plane ring vibration of 4,4'-dimethyl-2,2'-bipyridine undergoes the

most noticeable change upon coordination. This absorption shifts from 1596 to 1621 cm⁻¹ in the coordinated ligand. The changes observed in the infrared spectra for the bidentate nitrogen ligands indicate that they are completely coordinated.

All of the complexes investigated here have very intense absorptions in the 2000-cm⁻¹ region which are due to the C-N stretch. The width of the bands and presence of multiple peaks and shoulders implies that several different C-N bond strengths exist in the solid state of the complexes. This variation in C-N bond strengths is not uncommon in isothiocyanate and isoselenocyanate complexes, and is most likely due to distortions present in the crystal structures.

As can be seen in Table II, the most intense C-N absorption band for all of the isothiocyanate complexes occurs below 2053 cm⁻¹, the energy of the C-N stretch in KCNS. Likewise, in the isoselenocyanate complexes, these absorptions are below the 2072-cm⁻¹ value for KCNSE. This decrease in energy of the C-N stretch with respect to the free ion is characteristic of nitrogen bonding in both cases. It should also be noted that in the analogous pairs of isothiocyanate and isoselenocyanate complexes, the C-N stretching energy is slightly lower in the isoselenocyanate complexes than in the isothiocyanate complexes. While this correlation does not exist in all analogous pairs of isothiocyanate-isoselenocyanate complexes, it is present in the hexaisothiocyanate and hexaiselenocyanate complexes of niobium(IV) and tantalum(V).^{8,9}

In isothiocyanate complexes the carbon-sulfur bond order increases over that in the free ion and this should increase the energy of this absorption. Generally this absorption occurs in the 760-930-cm⁻¹ region. In thiocyanate complexes this absorption is lowered in energy and falls between 690 and 750 cm⁻¹. For the complexes under consideration the region from 690 to 930 cm⁻¹ is fairly complicated in that a number of absorption bands are present due to the organic ligands. Goldstein, *et al.*,¹² have found that these ligand vibrations are relatively insensitive to the oxidation state of the metal ion and to the bonding characteristics of the other ligands. The absorption bands in this region due to the organic ligand were determined and eliminated as possible choices for the C-S absorption. In most cases only one absorption band remained and this band was assigned to the C-S stretching frequency. Assign-

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ments of the C-Se stretching frequencies and NCS and NCSe bending frequencies were made in a similar manner. The band assignments are summarized in Table II. The observed shifts all indicate that the pseudohalides are bonded to the metal through the nitrogen atom.

The metal-nitrogen stretching vibrations are found in the far-infrared region from 400 to 200 cm^{-1} . Except in the case of $\text{Nb}(\text{NCS})_4(\text{py})_2$, these absorptions are broadened by the presence of shoulders or are composed of several peaks. The assignments for the M-N (NCS or NCSe) stretch are shown in Table II. The lack of solubility of these adducts in organic solvents precluded solution studies of the far-infrared spectra of these compounds. Considering the differing number of bands for compounds with seemingly similar structure, it is difficult to utilize this information at the present time to deduce structure.

In the case of $\text{Nb}(\text{NCS})_4(\text{py})_2$, the infrared spectrum is useful in determining whether the complex exists in the cis- or trans-octahedral structure.¹³ In the trans form only one Nb-N (NCS) stretching vibration is allowed. Unlike the other complexes under consideration, the metal-nitrogen stretch in $\text{Nb}(\text{NCS})_4(\text{py})_2$ is a sharp peak at 313 cm^{-1} with no shoulders. This complex is thus assumed to be in a trans configuration.

The M-N stretch (bipy, dmbipy, or py) are known to occur in the region between 250 and 200 cm^{-1} . Bands were present in this region for all complexes. Since these absorptions were usually weak, indistinct, and near the cut-off point of the instrument, assignments can only be tentative at this time.

Visible-Ultraviolet Spectra.—The visible-ultraviolet spectra observed are given in Table III.

TABLE III
ULTRAVIOLET-VISIBLE SPECTRA OF NITROGEN
DONOR COMPLEXES

Compound	Medium	Absorption bands, kK
$\text{Nb}(\text{NCS})_4(\text{bipy})_2$	CH_3CN	41.3, 33.2, 26.2
	$\text{C}_2\text{H}_4\text{Cl}_2$	40.8, 33.3, 24.8
$\text{Nb}(\text{NCSe})_4(\text{bipy})_2$	CH_3CN	41.5, 33.1, 25.0
	CH_3CN	40.0, 33.2, 26.2
$\text{Nb}(\text{NCS})_4(\text{dmbipy})_2$	CH_3CN	40.3, 33.4, 25.1
	$\text{C}_2\text{H}_4\text{Cl}_2$	38.8, 33.3, 25.5
$\text{Ta}(\text{NCS})_5(\text{py})$	$\text{C}_2\text{H}_4\text{Cl}_2$	39.0, 29.2
	CH_3CN	40.8, 30.0
$\text{Ta}(\text{NCS})_5(\text{bipy})$	$\text{C}_2\text{H}_4\text{Cl}_2$	40.8, 29.2
	$\text{C}_2\text{H}_4\text{Cl}_2$	40.8, 31.2, 24.7

The eight-coordinate complexes of Nb(IV) were not sufficiently soluble in nonaqueous solvents to observe the d-d transitions. However, solid-state reflectance spectra revealed the presence of additional bands at 20.8, 17.8, and 13.9 kK. These transitions agree well with those reported for other eight-coordinate compounds.^{14,15} The lowest energy band, usually observed at ca. 11 kK, was outside the range of our instrument.

Mulliken¹⁶ and Walsh¹⁷ have classified and discussed the energy levels of the NCS^- ions. Day¹⁸ has

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ascribed the absorptions in the 20.0–40.6 kK region to charge-transfer transitions in thiocyanate and selenocyanate complexes.

The lowest energy transition for the nitrogen donor complexes of niobium(IV) in solution occurs near 26.3 kK. This agrees quite well with the lowest energy transition observed for the hexaisothiocyanate complex of niobium(IV), which occurs at 26.6 kK and was assigned to a ligand-to-metal ($t_{1u} \rightarrow t_{2g}$)³ charge-transfer band. Likewise, in the nitrogen donor complexes of niobium(IV) containing selenocyanate, the band occurring near 25.0 kK agrees with that found in the hexaisoselenocyanate complex at 24.8 kK.⁹ Thus, it appears that the ligand-to-metal charge-transfer band in these complexes is not significantly different from that found in the hexacoordinated complexes. The energy of the charge-transfer bands is related to the relative reducing power of the ligand (*i.e.*, as the reducing power of the ligand increases the energy of the ligand-to-metal electron transfer should decrease). The decrease in transition energy in the selenocyanate *vs.* the thiocyanate complexes agrees with the relative reducing power of the ligand.

The transitions exhibited by these complexes near 33 and 40 kK may be ascribed to intraligand $\pi \rightarrow \pi^*$ transitions within the aromatic ligand present. Transitions of this type have been observed and reported for the free ligands and for numerous complexes.^{6,19,20} Although a detailed study of the effect of coordination upon these intraligand transitions has not been made, these workers have found that the bands are shifted to lower energies with respect to the free ligand upon complexation.

The lowest energy transition for $\text{Ta}(\text{NCSe})_5(\text{bipy})$ occurs at 24.7 kK which agrees with the 24.6-kK band in $\text{KTa}(\text{NCSe})_6$.⁹ The high-energy intraligand transition near 41 kK does not appear to be affected in going from niobium(IV) to tantalum(V); however, the lower intraligand transition appears to shift to lower energy. This band occurs near 33 kK in the niobium(IV) complexes and near 31 kK in $\text{Ta}(\text{NCSe})_5(\text{bipy})$. The shift in this band in the $\text{Ta}(\text{NCSe})_5(\text{bipy})$ compound is significant in the interpretation of the spectra of $\text{Ta}(\text{NCS})_5(\text{py})$ and $\text{Ta}(\text{NCS})_5(\text{bipy})$. The absorption spectra of the isothiocyanate adducts of tantalum(V) exhibit only two bands, one near 40 kK and the other near 30 kK. The band near 40 kK is assigned to the high-energy intraligand transition which is found in all the complexes, while the band near 30 kK is a combination of the low-energy intraligand transition plus the ligand-to-metal charge-transfer transition. The latter assignment is supported by the relative intensity of the bands and by the position of the charge-transfer band in $\text{KTa}(\text{NCS})_6$. The ligand-to-metal charge-transfer transition in $\text{KTa}(\text{NCS})_6$ was observed at 30.1 kK. From the close agreement found in the position of charge-transfer bands between the hexacoordinate complexes and those under discussion, it is reasonable to expect this band to occur near 30 kK in $\text{Ta}(\text{NCS})_5(\text{py})$ and $\text{Ta}(\text{NCS})_5(\text{bipy})$. In all of the other nitrogen donor complexes it was observed that the two intraligand transitions were of similar intensity;

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(20) T. M. Brown, D. K. Pings, L. R. Lieto, and S. J. DeLong, *Inorg. Chem.*, **5**, 1695 (1966).

however, the relative intensity of the band near 30 kK in Ta(NCS)₅(py) and Ta(NCS)₅(bipy) is much greater than the band near 40 kK. The combination of the intraligand and charge-transfer transitions would be expected to increase the intensity of this band with respect to the other intraligand band. It was not possible to resolve this band into its component parts.

Magnetic Susceptibilities.—The magnetic data for the

nitrogen donor complexes of niobium(IV) are shown in Table IV. It can be seen that the magnetic moments of the 2,2'-bipyridine and 4,4'-dimethyl-2,2'-bipyridine complexes range from *ca.* 1.6 to 1.7 BM, which is very close to the spin-only value of 1.73 BM. This agrees quite well with other recently reported magnetic moments for eight-coordinate complexes of niobium(IV). McCarley and Hamilton¹⁴ have reported magnetic moments of *ca.* 1.6–1.7 BM for complexes of the general formula NbX₄(dth)₂ (where X is Cl or Br and dth is 1,2-dimethylthioethane). Similar moments have also been reported by Kepert and Deutscher¹⁵ for eight-coordinate complexes of the type NbX₄(diars)₂ (where X is Cl, Br, or I and diars is *o*-phenylenebis(dimethylarsine)).

The moment of 0.97 BM observed for Nb(NCS)₄(py)₂ is lower than the spin-only value, but moments as low as 0.90 have previously been reported. McCarley, *et al.*,⁵ found that the moments of NbX₄(py)₂ (where X is Cl, Br, or I) obey a Curie law with values of 1.37 (Cl), 1.26 (Br), and 1.05 (I) BM. The low moments for these complexes were accounted for on the basis of distortion from octahedral symmetry and electron delocalization. It is quite reasonable that similar effects are present in Nb(NCS)₄(py)₂ and are responsible for the observed moment.

TABLE IV

MAGNETIC PROPERTIES OF NITROGEN DONOR COMPLEXES ^a					
Nb(NCS) ₄ (C ₁₀ H ₈ N ₂) ₂	<i>T</i>	298	190	161	84
	χ_m'	1245	1934	2252	4589
	μ_{eff}	1.72	1.71	1.70	1.75
Nb(NCSe) ₄ (C ₁₀ H ₈ N ₂) ₂	<i>T</i>	298	205	148	86
	χ_m'	1223	1753	2563	4508
	μ_{eff}	1.72	1.70	1.74	1.76
Nb(NCS) ₄ (C ₁₂ H ₁₂ N ₂) ₂	<i>T</i>	301	221	152	86
	χ_m'	1224	1649	2451	4361
	μ_{eff}	1.72	1.71	1.73	1.73
Nb(NCSe) ₄ (C ₁₂ H ₁₂ N ₂) ₂	<i>T</i>	296	220	164	84
	χ_m'	1460	1839	2368	4349
	μ_{eff}	1.86	1.80	1.76	1.71
Nb(NCS) ₄ (C ₆ H ₅ N) ₂	<i>T</i>	301	218	156	84
	χ_m'	387	498	721	1308
	μ_{eff}	0.97	0.94	0.97	0.94

^a *T* in degrees Kelvin; $\chi_m' = \chi_m^{cor} \times 10^6$ emu/mol; μ_{eff} in Bohr magnetons.

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Water-Exchange Studies on Manganese(II) Nitrilotriacetate and Ethylenediaminetetraacetate Complexes by Oxygen-17 Nuclear Magnetic Resonance

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Oxygen-17 nmr studies have been made on manganese(II) complexes with the ligands NTA, EGTA, and EDTA. From consideration of paramagnetic shifts in the ¹⁷OH₂ nmr line and infrared studies, it is concluded that the following species are present in aqueous solution: Mn(NTA)(H₂O)₂²⁻, Mn(EGTA)³⁻ (hexadentate), and Mn(EDTA)(H₂O)₂²⁻ (seven-coordinate Mn(II)). The kinetic parameters for water exchange are the following (*k*₁ is per H₂O): Mn(NTA)(H₂O)₂²⁻, *k*₁(25°) = (1.50 ± 0.8) × 10⁸ sec⁻¹, Δ*H** = 6.6 kcal mol⁻¹, Δ*S** = 6 cal mol⁻¹ deg⁻¹; Mn(EDTA)(H₂O)₂²⁻, *k*₁(25°) = 4.4 × 10⁸ sec⁻¹, Δ*H** = 7.7 kcal mol⁻¹, Δ*S** = 7 cal mol⁻¹ deg⁻¹. Comparison of substitution on Mn(NTA)(H₂O)₂²⁻ with water exchange is made. The relations of the ¹⁷O nmr data to epr and proton nmr data are discussed.

Introduction

Most of the relatively few water exchange studies reported on manganese(II) species in aqueous solution have involved Mn(II)-enzyme complexes. In these complexes increased¹ and decreased² labilities of the coordinated water, relative to Mn(H₂O)₆²⁺, have been observed. To help understand these results it is advantageous to know more about how particular chemical groups affect the lability of coordinated water.

For manganese complexes containing ligands less complicated than enzymes, for example those of 1,10-phenanthroline³ and adenosine-5'-triphosphoric acid,⁴ only slightly increased water lability has been found.

Similarly, the presence of nitrogen donor ligands in the inner sphere of cobalt(II) and nickel(II) produces only increased lability of the remaining waters, the magnitude of the effect being dependent on the net electron donating capability of the nitrogen.⁵

Water-exchange studies on transition metal complexes with ligands containing carboxylate groups have received scant attention, presumably because of the general lack of precise stability constant and thermodynamic data, and the relative instability of the complexes. However, results reported for nickel(II) complexes of ethylenediaminetetraacetic acid⁶ (EDTA) and cobalt(II) complexes of malonic acid⁷ show that

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