

asymmetric on the low-frequency side, as expected, and has a width at half-peak-height of 7.5 cm^{-1} .

Conclusion

The vibrational spectra and force constants of the hexahalo anions of the early transition elements are internally consistent and comparable with those of the later transition and post-transition element hexahalo anions.

The bond stretching force constants on both the MUBFF and the GVFF bases exhibit the expected trends with respect to changing the oxidation state of the metal atom and changing the halogen from chloride to bromide. The difference between the bond stretching force constants $K(\text{MUBFF})$ and $f_r(\text{GVFF})$ for a given hexahalo species arises because of the different restoring forces assumed in the two treatments. The GVFF method takes into account both *cis* (f_{rr}) and *trans* (f_{rr}') bond stretching interactions, whereas the MUBFF method retains the latter (as k) but replaces the former by an XX repulsive interaction (F). The force constant matrix elements (F_{nn}) formed in each treatment are different and lead to the conclusions^{16,18}

$$F_{11} - 4F = K + k; F = (\lambda_1 - \lambda_2)/3.3\mu_X \quad (\text{MUBFF})$$

$$F_{11} - 4f_{rr} = f_r + f_{rr}'; f_{rr} = (\lambda_1 - \lambda_2)/6\mu_X \quad (\text{GVFF})$$

where $\lambda = 5.889 \times 10^{-2}\nu^2$ and $\mu_X =$ reciprocal mass of X.

As the magnitudes of F and f_{rr} are clearly different, the other constants K , k and f_r , f_{rr}' must likewise be different, despite their having the same physical significance.

The occurrence of a negative force constant (H) in the MUBFF treatment arises because of the distinction made between the adjacent XX repulsions (F) and the bond angle bending forces (H), a distinction which is not justified. The only requirement is that the sum $H + 0.55F$ be positive,¹⁸ which is true in every case. The matter is aggravated by the arbitrary assumption¹⁸ that the nonadjacent XX repulsive force constants equal $-0.1F$.

Acknowledgment.—L. M. thanks the University of Padova for a leave of absence, and W. v. B thanks the I.C.I. Co. Ltd. for the award of a fellowship. Part of this research was supported by NATO Grant No. 341, which is gratefully acknowledged. We are also grateful to the University of London for the use of the Cary 81 laser Raman spectrometers.

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Studies of Some Niobium and Tantalum Hexaisothiocyanate Complexes^{1,2}

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The reaction of potassium thiocyanate with NbCl_5 , NbCl_4 , and TaCl_5 in acetonitrile gives the complex anions $\text{Nb}(\text{NCS})_6^-$, $\text{Nb}(\text{NCS})_6^{2-}$, and $\text{Ta}(\text{NCS})_6^-$, respectively. Metatheses between $\text{KM}(\text{NCS})_6$ ($M = \text{Nb}, \text{Ta}$) and tetrabutylammonium chloride and tetraphenylarsonium chloride give rise to compounds containing these cations. Infrared data indicate that the thiocyanate groups are nitrogen bonded in all cases. A detailed study of the conductance of these compounds in acetonitrile showed that dissociation takes place at low concentrations which must be taken into account when interpreting the visible-ultraviolet spectra.

Introduction

The preparation and partial characterization of the hexaisothiocyanate complexes of niobium(V)³ and tantalum(V)^{3,4} have been reported. The relatively low frequency of the CN stretch in these d^0 complexes was of interest and led us to an investigation of the similar niobium(IV) complex, a d^1 case. Further studies have been made on all of the +5 complexes since the original reports. While this work was being completed, Boland and coworkers^{5,6} reported the

preparation of several complexes of niobium(V) and tantalum(V) containing thiocyanate ion. A more complete examination of the acetonitrile solutions of these complexes indicated that dissociation occurs at concentrations used to obtain the visible-ultraviolet spectra and must be taken into account when interpreting the results. The results of these investigations are now presented along with a description of the niobium(IV) complex.

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 As were carried out by Alfred Bernhardt Laboratories, Mülheim, Germany. Nio-

(1) Abstracted in part from the Ph.D. dissertation submitted by G. F. Knox to the Graduate School of Arizona State University, Tempe, Ariz., 1968.

(2) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(3) T. M. Brown and G. F. Knox, *J. Am. Chem. Soc.*, **89**, 5296 (1967).

(4) H. Boland and E. Tiede, *J. Less-Common Metals*, **13**, 224 (1967).

(5) H. Boland and E. Zenker, *ibid.*, **14**, 397 (1968).

(6) H. Boland, E. Tiede, and E. Zenker, *ibid.*, **15**, 89 (1968).

biom and tantalum were analyzed by conversion to the oxide in the usual manner.

Preparation of Niobium(V) and Tantalum(V) Hexaisothiocyanates.—The potassium salts of niobium(V) and tantalum(V) hexaisothiocyanates were prepared in the manner previously described.³ Compounds of the +5 metal complexes were also prepared having tetrabutylammonium or tetraphenylarsonium as the cation in place of potassium. These compounds had a relatively high solubility in chlorinated hydrocarbon solvents, thus allowing studies of the $M(NCS)_6^-$ unit in a solvent other than acetonitrile.

The tetrabutylammonium and tetraphenylarsonium compounds were obtained by placing 1:1 stoichiometric quantities of the potassium complex salt and the chloride of the cation desired in opposite ends of the vessel shown in Figure 1. By proceeding in a manner similar to that described below for the preparation of $K_2Nb(NCS)_6$, one can extract the chloride into the $KM(NCS)_6$ solution using acetonitrile as a solvent. Insoluble KCl and the soluble complex result. By removing the acetonitrile solvent from this mixture by vacuum distillation and distilling a suitable halohydrocarbon (e.g., 1,2-dichloroethane or chloroform) into the vessel, the soluble complex species can be extracted from the KCl. The tetraphenylarsonium salts crystallize readily upon removal of the solvent. The tetrabutylammonium complex salts failed to crystallize upon similar treatment, forming an oil-like material instead. Solid product was obtained by introducing *ca.* 20 ml of CCl_4 into a 50-ml $CHCl_3$ solution of the complex salt. Stirring this mixture resulted in the formation of a solid precipitate of the tetrabutylammonium complex salt.

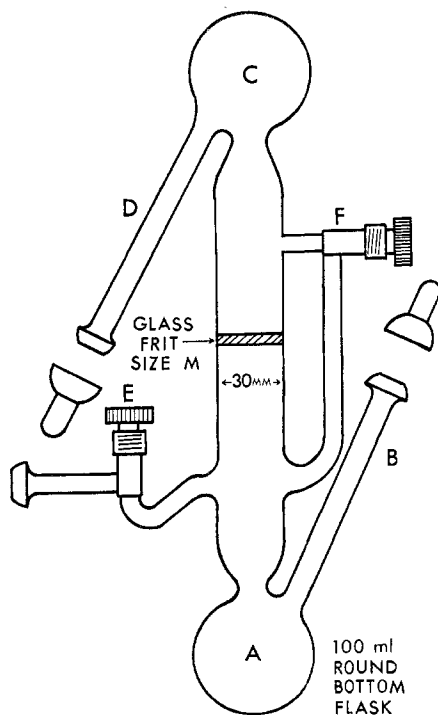


Figure 1.—Apparatus for the preparation of thiocyanate complexes.

Anal. Calcd for $(C_6H_5)_4AsNb(NCS)_6$: Nb, 11.27; As, 9.08; C, 43.69; N, 10.19; S, 23.33; H, 3.08. Found: Nb, 11.31; As, 9.01; C, 43.62; N, 9.90; S, 23.63; H, 2.51. Color, lustrous blue; mp $222 \pm 2^\circ$. Calcd for $(C_6H_5)_4AsTa(NCS)_6$: Ta, 19.82; As, 8.21; C, 39.48; N, 9.21; S, 21.08; H, 2.21. Found: Ta, 19.86; As, 8.06; C, 39.44; N, 9.50; S, 20.92; H, 2.40. Color, orange; mp $226 \pm 2^\circ$. Calcd for $(C_4H_9)_4NNb(NCS)_6$:

Nb, 13.59; C, 38.64; N, 14.34; S, 28.13; H, 5.31. Found: Nb, 13.30; C, 38.72; N, 14.18; S, 28.33; H, 5.47. Color, lustrous blue; mp $122 \pm 2^\circ$. Calcd for $(C_4H_9)_4NTa(NCS)_6$: Ta, 23.44; C, 34.23; N, 12.70; S, 24.93; H, 4.70. Found: Ta, 23.38; C, 34.16; N, 12.55; S, 25.21; H, 4.70. Color, orange; mp $130 \pm 2^\circ$.

All of the niobium compounds appeared blue after removal of solvent. This appears to be a surface effect due to the method of preparation as the compounds were observed to undergo a color change to red-brown when ground to a fine powder.

Preparation of Niobium(IV) Hexaisothiocyanate Complex.—The hexaisothiocyanate complex of niobium(IV) was prepared by placing 3.53 g (0.015 mol) of finely ground $NbCl_4$ into chamber A (Figure 1) through side arm B, along with a Teflon-coated magnetic stirring bar. The vessel was then inverted, and 8.75 g (0.90 mol) of KCNS and a stirring bar were placed in chamber C *via* side arm D. The side arms were capped, and the vessel was removed from the drybox to a vacuum line where side arms B and D were sealed off under vacuum. Approximately 60 ml of rigorously dried acetonitrile was then distilled into chamber A, the vessel was removed from the vacuum system, and stirring was initiated in chamber A. In this manner, the insoluble $NbCl_4$ was transformed into the soluble $NbCl_4(CH_3CN)_2$ species in about 24 hr. By closing Teflon needle valve F and immersing chamber A in a 60° water bath, the solvent was distilled into chamber C, forming a solution of the KCNS. When all of the solvent was removed from chamber A, the vessel was inverted. Chamber C was placed in the warm water bath and stirring was initiated. Teflon valve F was then opened, and the solvent was allowed to distil into the upper chamber, thus dissolving the $NbCl_4(CH_3CN)_2$ complex and carrying it through the glass frit into the KCNS solution, where ligand replacement occurred readily as evidenced by the precipitation of KCl. This technique ensures that an excess of KCNS will be present in solution for reaction with the metal halide until the termination of extraction.

When the $NbCl_4(CH_3CN)_2$ had been extracted from chamber A, the solution in chamber C was stirred for several hours to ensure completion of the reaction and then inverted. The highly soluble $K_2Nb(NCS)_6$ salt then passed through the frit, separating it from the relatively insoluble KCl. The solvent was removed by vacuum distillation, and after drying at 60° and 10^{-5} Torr for 72 hr, the product was taken into the drybox where it was transferred to a vessel similar to that in Figure 1, but with side arm D deleted. This allowed further purification of the product. The vessel was removed from the drybox, side arm B was sealed while under vacuum, and 50 ml of a mixed-solvent system consisting of *ca.* 95% 1,2-dichloroethane and 5% acetonitrile by volume was added to chamber A. This solvent mixture extracted the slightly soluble $K_2Nb(NCS)_6$ from the impurities (primarily KCl). After purification, the excess solvent was removed under vacuum, and the product was dried for 72 hr at *ca.* 60° and 10^{-5} Torr. *Anal.* Calcd for $K_2Nb(NCS)_6$: K, 15.05; Nb, 18.05; N, 16.17; C, 13.87; S, 37.03. Found: K, 14.68; Nb, 18.00; N, 16.38; C, 14.03; S, 36.91.

Physical Measurements.—Infrared spectra in the range 4000 – 200 cm^{-1} were recorded on a Beckman IR-12 spectrophotometer. Sodium chloride was used as window material between 4000 and 600 cm^{-1} , while high-density polyethylene was employed in the 600 – 200 cm^{-1} range for sample studies. Nujol mulls were prepared in the normal manner but within a drybox. Solution samples were prepared within the confines of a solvent box, which was maintained in an anhydrous and oxygen-free condition.

Visible and ultraviolet spectra were obtained with a Cary Model 14 spectrophotometer. Both acetonitrile and 1,2-dichloroethane were used as solvents for all compounds except $K_2Nb(NCS)_6$, which was soluble only in acetonitrile. The solutions for these studies were also prepared in the solvent box.

Conductivity measurements were made in the solvent box using a platinum black electrode cell which was connected to an Industrial Instruments Type RC conductivity bridge outside this box.

TABLE I
 INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF HEXAISOTHIOCYANATE COMPLEXES

Compound	Medium ^a	$\nu(\text{CN})^b$	$\nu(\text{CS})^b$	$\delta(\text{MNCS})^b$		$\nu(\text{MN})^b$
				Mode 1	Mode 2	
$\text{KNb}(\text{NCS})_6$	M	2080 m, 2025 s, sh, 2005 s	888 w	499 m	399	340 m
		1980 s, 1949 s, 1910 m	930 sh, 927 m ?	490 sh		
$(\text{C}_4\text{H}_9)_4\text{NNb}(\text{NCS})_6$	M	2027 m, 1981 vs, 1935 sh	<i>c</i>	511 m	402 m	353 m
		1978 vs, 1950 s, 1915 m, sh	932 m, 913 m ?	502 m	<i>d</i>	330 vs
$(\text{C}_6\text{H}_5)_4\text{AsNb}(\text{NCS})_6$	M	2022 m, 1980 s, 1935 m	<i>c</i>	510 m	395 s	355 m
		1978 s	<i>c</i>	505 m	412 m	341 m
$(\text{C}_6\text{H}_5)_4\text{AsTa}(\text{NCS})_6$	M	1990 m, sh, 1954 vs, 1911 m	922 w ?	510 m	<i>d</i>	335 s
		1984 vs, 1929 m	<i>c</i>	506 m	402 m	341 vs
$\text{K}_2\text{Nb}(\text{NCS})_6$	M	2077 m, 2020 s, sh, 2005 s	888 w	504 m	<i>d</i>	342 s
		1980 s, 1948 s, 1908 m	935 sh, 928 m ?			
$\text{KTa}(\text{NCS})_6$	M	2080 m, sh, 2035 s	<i>c</i>	512 w	392 s	330 s
		2095 m, 2035 s, sh, 2015 s	897 m	501 m	400 m	313 s
$(\text{C}_4\text{H}_9)_4\text{NTa}(\text{NCS})_6$	M	1992 s, 1965 s, sh, 1922 m, sh	940 sh, 932 m ?			
		2055 m, 2005 vs, 1950 m, sh	<i>c</i>	508 m	398 m	343 m
$(\text{C}_6\text{H}_5)_4\text{AsTa}(\text{NCS})_6$	M	2050 m sh, 1978 vs, 1962 s	938 sh, 921 m ?	504 s	<i>d</i>	298 s
		1933 m, sh				
$(\text{C}_6\text{H}_5)_4\text{AsTa}(\text{NCS})_6$	M	2045 m, sh, 2008 vs	<i>c</i>	509 m	400 s	344 s
		2065 sh, 1937 vs, 1920 m	928 m ? 848 w	505 m	401 m	314 m
	B	1987 vs, 1945 m, sh	<i>c</i>	506 m	406 m	322 s

^a M = Nujol mull, A = acetonitrile, B = 1,2-dichloroethane. ^b Relative intensities: s, strong; m, medium; w, weak; v, very; sh, shoulder. ^c Region masked by solvent system and/or cation. ^d Absorption band not observed.

Results and Discussion

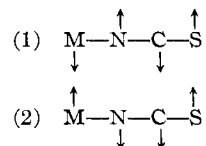
X-Ray powder diffraction data show the niobium(V) and tantalum(V) as well as the tungsten(V) complexes to have similar structures. In the case of tungsten it is necessary to use a different solvent, *e.g.*, diethyl ether, to prevent reduction of the starting halide to the +4 oxidation state. In the presence of an excess of thiocyanate ion, niobium and tantalum do not show any tendency to expand their coordination number to greater than 6 in acetonitrile although the formation of $\text{K}_2\text{Nb}(\text{NCS})_7(\text{DMF})_8$ in dimethylformamide has been reported by Golub and Sych.⁷

Infrared Spectra.—The positions and assignments of the observed infrared bands of the hexaisothiocyanate complexes are given in Table I. As can be seen, these complexes all have several bands in the CN as well as in the CS stretching region when studied in the solid state (mull spectra). This is indicative of several different CN and CS bond strengths in the crystal, similar to the differences in CN and CS bond distances found by Knox and Eriks⁸ in their crystallographic study of $\text{K}_2\text{Mo}(\text{NCS})_6 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{COOH}$.

The CS stretching vibrations which are assigned to bands between *ca.* 880 and 940 cm^{-1} in the $\text{M}(\text{NCS})_6^-$ complexes are significantly higher in frequency than normally observed. Bands due to $2\delta(\text{NCS})$ are often observed in the region greater than 900 cm^{-1} which might make our assignments somewhat tentative. However, in view of the low CN stretching frequencies of these +5 metal complexes and the reciprocal relation found for CN and CS stretching frequencies for organic isothiocyanates by Ham and Willis⁹ and $\text{Si}(\text{NCS})_4$ by Carlson,¹⁰ this high-energy vibration assignment appears reasonable. On the basis of the positions of these

CN and CS stretching frequencies, and the recent reports concerning the relationship between these frequencies and the mode of coordination, the complexes discussed in this paper are classified as nitrogen bonded.

Carlson¹⁰ has shown that two different bending modes are infrared active for coordinated thiocyanate. These can best be described as mode 1 and mode 2



In the solution spectra, three distinct bands are observed in the region between 200 and 600 cm^{-1} . Lattice effects cause some splitting of these bands in mull spectra. In addition to the two bending modes discussed above, the metal-nitrogen stretching frequency is also expected to occur in this region. Based upon position and observed shifts with different metal ions, the bands observed in the 350–300- cm^{-1} region are assigned to the metal-nitrogen stretch. It should be noted that these bands occur in the vicinity of the metal-chlorine stretches.^{11,12} It has been suggested¹³ that isothiocyanates appear to have strong bands at values slightly above the metal-chlorine stretches in chloro complexes of the same symmetry whereas thiocyanate complexes give bands which fall approximately halfway between the corresponding chloro and bromo complexes. The positions of the bands reported here for the niobium and tantalum complexes further indicate the presence of N-bonded thiocyanate. Work presently in progress on thiocyanates and selenocyan-

(7) A. M. Golub and A. M. Sych, *Russ. J. Inorg. Chem.*, **9**, 593 (1964).

(8) J. R. Knox and K. Eriks, *Inorg. Chem.*, **7**, 84 (1968).

(9) M. S. Ham and J. B. Willis, *Spectrochim. Acta*, **16**, 279 (1960).

(10) G. L. Carlson, *ibid.*, **18**, 1529 (1962).

(11) For $(\text{C}_2\text{H}_5)_4\text{NNbCl}_6$ and $(\text{C}_2\text{H}_5)_4\text{NTaCl}_6$, $\nu(\text{M}-\text{Cl})$ is located at 348 and 328 cm^{-1} , respectively, in acetonitrile.¹²

(12) I. R. Beattie, T. R. Wilson, and G. A. Ozin, *J. Chem. Soc.*, 2765 (1968).

(13) D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 715 (1965).

ates of other second- and third-row transition metals will help to substantiate these band assignments.

The infrared spectrum of $K_2Nb(NCS)_6$ is quite similar in appearance in the solid state to that of $KNb(NCS)_6$. As indicated by the band positions listed for these two compounds in Table I, the band maxima occur at essentially the same frequency in the mull spectra. In solution, however, the most intense band in the CN region of the +5 niobium complex appears at 1981 cm^{-1} , while the +4 complex has its intense CN absorption at 2035 cm^{-1} . This band position in the +4 complex is very near the positions of the previously reported transition metal isothiocyanates.^{10,14,15} The significant change in the position of this band (54 cm^{-1}), when the oxidation number of the transition metal changes by one unit, appears to be due to a combination of relatively high oxidation state of the +5 niobium and the lack of valence shell d orbitals on this central metal ion. In the previously studied transition metal isothiocyanate complexes, d electrons have been available in the valence shell for interaction with the ligand, as is the case in the +4 niobium complex.

Quantitative studies of the CN stretching frequency in 1,2-dichloroethane solutions of $(C_6H_5)_4NTa(NCS)_6$ showed that this absorption followed Beer's law in the concentration range studied ($(0.6\text{--}5.0) \times 10^{-3}\text{ M}$). The extinction coefficient of this CN absorption was found to be *ca.* $1500\text{ M}^{-1}\text{ cm}^{-1}$ per thiocyanate unit. The value of this coefficient in the free ion has been determined to be $537\text{ M}^{-1}\text{ cm}^{-1}$ by Fronaeus and Larsson.¹⁶ These workers also found that typical N-bonded complexes had ϵ values ranging from *ca.* 900 to $1500\text{ M}^{-1}\text{ cm}^{-1}$, depending on the solvent used. Sulfur-bonded complexes had values in the $200\text{--}490\text{ M}^{-1}\text{ cm}^{-1}$ region.

From the work of Pecile¹⁷ the product of $\nu_{1/2}\epsilon$ gives two sets of values. S-Bonded thiocyanate complexes range from 0.24×10^4 to *ca.* $0.59 \times 10^4\text{ M}^{-1}\text{ cm}^{-2}$ while the N-bonded complexes range from *ca.* 2.5 to $4.0 \times 10^4\text{ M}^{-1}\text{ cm}^{-2}$. Our calculations of $\nu_{1/2}\epsilon$ for the tantalum compound yield a value of $4.05 \times 10^4\text{ M}^{-1}\text{ cm}^{-2}$ lending further support to the proposed N-bonded structure. Similar treatment of the niobium(V) complex leads to a value which is indicative of N bonding in this complex also.

Conductance Measurements.—The equivalent conductances of the compounds studied are found in Table II. It has recently been shown¹⁸ that conductance measurements should be carried out at various concentrations to differentiate between 1:1 electrolytes of the type MX and 2:1 electrolytes of the type $[M]_2[X_2]$. From the Onsager limiting law, $\Lambda_0 - \Lambda_c = A\sqrt{C}$, one can easily determine A and Λ_0 by plotting the Λ_c value of several different concentrations (C in equivalents per liter) *vs.* \sqrt{C} . The slope A is indicative of the electrolyte type in that solvent. The values of A in

TABLE II
LIMITING EQUIVALENT CONDUCTANCE VALUES OF COMPLEXES STUDIED IN THIS WORK AND THOSE USED AS STANDARD ELECTROLYTES

Compound	Solvent	Λ_0	Λ_{exptl}
KCNS	CH ₃ CN	194	580
KNb(NCS) ₆	CH ₃ CN	150 ^a	500
KTa(NCS) ₆	CH ₃ CN	158 ^a	520
K ₂ Nb(NCS) ₆	CH ₃ CN	185 ^a	800
(C ₆ H ₅) ₄ AsCl	C ₂ H ₄ Cl ₂	44.0	222
(C ₆ H ₅) ₄ AsNb(NCS) ₆	C ₂ H ₄ Cl ₂	28.0	178
(C ₆ H ₅) ₄ AsTa(NCS) ₆	C ₂ H ₄ Cl ₂	27.0	168
(C ₄ H ₉) ₄ NNb(NCS) ₆	C ₂ H ₄ Cl ₂	31.2	196
(C ₄ H ₉) ₄ NTa(NCS) ₆	C ₂ H ₄ Cl ₂	30.9	203

^a "Ideal" limiting conductance, as defined in Results and Discussion.

Table II are those which were determined experimentally. A known electrolyte which was very similar in nature to the complexes reported here was also studied in each solvent system for purposes of comparison. The experimental values of A and Λ_0 for these known electrolytes are also found in Table II.

Figure 2 represents a plot of Λ_c *vs.* \sqrt{C} for acetonitrile

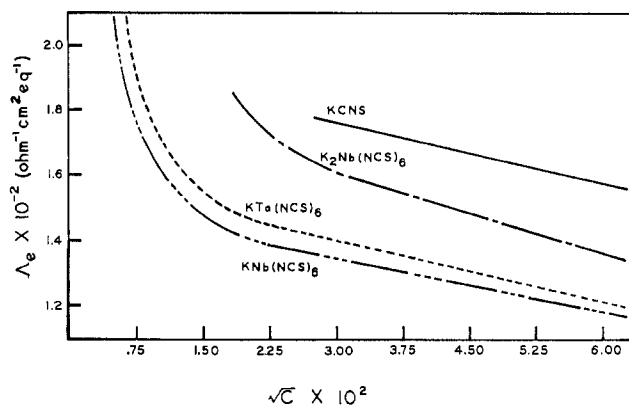


Figure 2.—The equivalent conductances of isothiocyanate complexes in acetonitrile.

solutions of the potassium salts of the isothiocyanate complexes, as well as potassium thiocyanate. As can be seen from the figure, a straight line is not obtained for the conductance of these complexes in this solvent over the entire concentration range studied. Similar observations have been reported by Cotton, *et al.*, for $Re_2Cl_8^{2-}$ and $Re_2(NCS)_6^{2-}$ complexes in acetonitrile.¹⁹

In a general equation depicting substitution for the coordinated thiocyanate by the solvent represented by eq 1, the conductances of solutions where $n = 0$ and

$$KM(NCS)_6 + n(CH_3CN) \rightleftharpoons M(NCS)_{6-n}(CH_3CN)_n^{n-1} + K^+ + nCNS^- \quad (1)$$

$n = 1$ would of course be essentially identical. One cannot, therefore, determine the concentration where $n = 1$ is predominant over $n = 0$ from these data. If the curvature of the lines in Figure 2 can be attributed to replacement of the thiocyanate by acetonitrile, then this curvature would increase in the concentrations where $n = 2$ becomes important. In the case of these

(19) F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, *Inorg. Chem.*, **6**, 929 (1967).

(14) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

(15) A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965).

(16) S. Fronaeus and R. Larsson, *Acta Chem. Scand.*, **16**, 1448 (1962).

(17) C. Pecile, *Inorg. Chem.*, **5**, 210 (1966).

(18) R. D. Feltham and R. G. Hayten, *J. Chem. Soc.*, 4587 (1964).

complexes, this appears at about 10^{-3} equiv l. $^{-1}$. From these data, it appears that the $M(NCS)_6^-$ species are not present as such in acetonitrile solutions less than *ca.* 10^{-3} *M*. In view of this, the Λ_0 listed in Table II for the potassium salts is an "ideal" value obtained by extrapolating the linear portion of the line concentrations of 5×10^{-3} to 5×10^{-4} *M* to infinite dilution. The A value listed for these complexes is similarly obtained from this straight-line section.

The conductance values of the $(C_4H_9)_4N^+$ and $(C_6H_5)_4As^+$ salts of the niobium(V) and tantalum(V) hexaisothiocyanates in 1,2-dichloroethane are given in Figure 3. The straight lines obtained in these cases are as predicted. This indicates no further dissociation beyond that expected of a 1:1 electrolyte in this solvent, even at concentrations less than *ca.* 7×10^{-5} *M*. Thus, it appears that the $M(NCS)_6^-$ unit remains undissociated at low concentrations in this solvent.

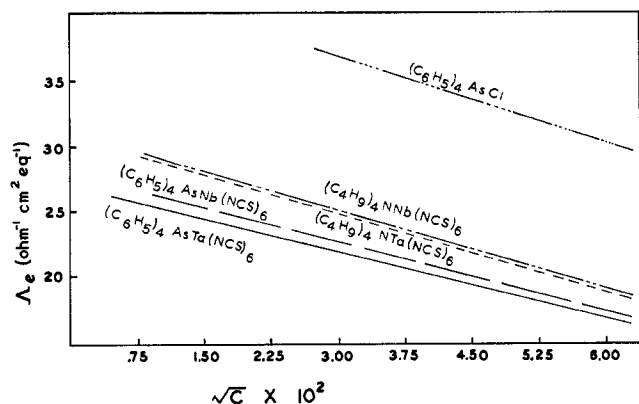


Figure 3.—The equivalent conductances of isothiocyanate complexes in 1,2-dichloroethane.

Visible-Ultraviolet Spectra.—Examination of Figure 4 reveals that two absorptions are present in the visible-ultraviolet spectra of these hexaisothiocyanate complexes in acetonitrile solution. The positions of these band maxima are listed in Table III. Interpretation of these absorptions is based upon further spectral studies, as well as the conductance data.

When the hexaisothiocyanate complexes are dissolved in 1,2-dichloroethane, only one absorption band is noted between 800 and 230 $m\mu$ (see Table III). It can be seen that this band occurs at approximately the same energy as the low-energy absorption band of the complex in acetonitrile. Solid-state spectra of the complexes are also void of any absorptions in the region of the high-energy absorption of acetonitrile solutions. Thus, the band at *ca.* 240–260 $m\mu$ in these solutions appears to be related in some way to the solvent system.

Measurement of the extinction coefficients of these absorptions in the two solvent systems results in a relatively constant value for the one intense absorption band found in the halohydrocarbon solutions, while the two bands are found to be variable and dependent on complex concentration in acetonitrile solutions. As the complex concentration decreases in this solvent, the relative intensity of the low-energy band decreases,

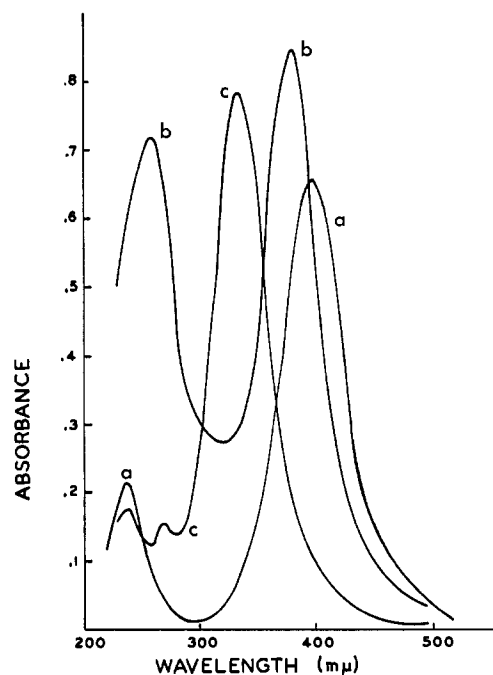


Figure 4.—Electronic absorption spectra in acetonitrile of (a) $Nb(NCS)_6^-$, (b) $Nb(NCS)_6^{2-}$, and (c) $Ta(NCS)_6^-$.

TABLE III
ELECTRONIC ABSORPTION SPECTRA

Compound	Solvent	Band max, kK		Assign-ment	ϵ_{max} , $M^{-1} cm^{-1}$
		Exptl	Calcd ^a		
$KNb(NCS)_6$	CH_3CN	25.3	23.4	c	b
		41.8		e	b
$KTa(NCS)_6$	$C_2H_4Cl_2$	24.6	23.4	c	b
		30.1	24.3	c	b
	CH_3CN	37.0		d?	b
		41.7		e	b
$(C_4H_9)_4NNb(NCS)_6$	$C_2H_4Cl_2$	29.3	24.3	c	
		36.4		d?	
$(C_4H_9)_4NTa(NCS)_6$	$C_2H_4Cl_2$	24.6	23.4	c	~54,000
$(C_4H_9)_4NTa(NCS)_6$	$C_2H_4Cl_2$	29.3	24.3	c	~53,000
$KTa(NCSe)_6$	$C_2H_4Cl_2$	36.0		d?	~8,000
$KTa(NCSe)_6$	$C_2H_4Cl_2$	24.9	24.3	c	
		24.6	23.4	c	~49,000
$(C_6H_5)_4AsNb(NCS)_6$	$C_2H_4Cl_2$	35.6		f	
		38.5		f	
		29.5	24.3	c	~50,000
$(C_6H_5)_4AsTa(NCS)_6$	$C_2H_4Cl_2$	35.6		f	
		38.5		f	
		26.6		c	b
$K_2Nb(NCS)_6$	CH_3CN	38.5		e	b
		25.9		c	~36,000
$[(C_6H_5)_4As]_2Nb(NCS)_6$	$C_2H_4Cl_2$	35.6		f	
		38.5		f	
		24.2	16.2	c	
$K_2Ti(NCS)_6$ ^g		24.2	16.2	c	
$K_2Zr(NCS)_6$	CH_3CN	~35.5	30	c	

^a Based on $\sigma_{cor} = (X_{opt}[X] - X_{opt}[M]) \times 30$ kK, using $X_{opt}[NCS] = 2.6$, $X[Nb(V)] = 1.82$, $X[Ta(V)] = 1.79$, $X[Ti(IV)] = 2.06$, and $X[Zr(IV)] = 1.60$. ^b Extinction coefficient varies with solute concentration. ^c $t_{1u} \rightarrow t_{2g}$ electron transition. ^d $t_{2u} \rightarrow t_{2g}$ electron transition. ^e Solvent to metal electron transition. ^f Cation charge-transfer absorption. ^g Data from O. Schmitz-DuMont and B. Ross, *Z. Anorg. Allgem. Chem.*, **342**, 82 (1966).

while the relative intensity of the high-energy band increases. In order to measure these absorptions, concentrations of less than *ca.* 10^{-4} *M* were necessary. Reference to Figure 2 and the preceding conductance discussion indicates that at these concentrations some acetonitrile as well as thiocyanate is coordinated to the transition metal. Thus, it appears that the high-energy

absorption arises from the coordinated acetonitrile. This is in agreement with the observation that the band intensity increases as concentration decreases, since lower concentrations give rise to greater displacement of thiocyanate by acetonitrile. This assignment is in disagreement with a recent paper⁶ which designated the high-energy band as an intraligand thiocyanate charge-transfer transition.

The electronic absorptions we find for $\text{Ta}(\text{NCS})_6^-$ disagree somewhat with the findings of Boland and Zenker for the same complex.⁵ They observe a band at $395 \text{ m}\mu$ having an extinction coefficient of $\sim 1000 \text{ M}^{-1} \text{ cm}^{-1}$ which changes intensity and position within about 20 min. This band is not present in our spectra and those reported are not altered with time in the solvents used. The techniques employed do not allow measurement of spectra any sooner than about 15 min after dissolution and thus it might not be possible to observe the band previously reported with our techniques. Otherwise, this discrepancy is presently unaccounted for.

In view of the data presented here, the absorption bands occurring at *ca.* $250 \text{ m}\mu$ are assigned to a LaPorte-allowed electronic transition of the coordinated acetonitrile. This would be either a $\pi \rightarrow \pi^*$ intraligand or a π ligand to metal transition. The intense band which is present in the complex spectra obtained in both types of solvents is assigned to a thiocyanate to metal electron transfer of the type $t_{1u} \rightarrow t_{2g}$. This is based on the shift in position of the absorption when the central metal ion is changed and the manner in which these shifts occur. Of the central metal ions, niobium(V) is the most readily reduced, and the absorption occurs at a lower energy for the $\text{Nb}(\text{NCS})_6^-$ than for any other species studied here. The higher energy required for the transition in $\text{Ta}(\text{NCS})_6^-$ is in agreement with the general observation that the high oxidation states of the third-row transition metal ions are more stable than those of the second row. The niobium(IV) complex also exhibits this absorption at a higher energy than the niobium(V) complex, which is expected if the assignment is correct, owing to the lower electronegativity of the niobium(IV). The visible-ultraviolet absorption bands of the $\text{Nb}(\text{NCS})_6^-$ complex reported here agree well with the data reported by Boland for $\text{PyHNb}(\text{NCS})_6$.⁵

Using Jørgensen's values for optical electronegativity,²⁰ we have calculated the energies at which the absorption bands should occur for the niobium(V) and tantalum(V) complexes. The agreement is good for the niobium case but the observed value for $\text{Ta}(\text{NCS})_6^-$ occurs *ca.* 5 kK higher than predicted. This trend toward higher energies is also present in the titanium and zirconium thiocyanates. The corresponding isoselenocyanate complex of tantalum(V) has been pre-

pared using a procedure analogous to that used for $\text{Ta}(\text{NCS})_6^-$. Although Boland⁴ reported that the reaction between TaCl_5 and KCNSe results in the formation of free selenium, rigorous exclusion of water from the reaction does not give rise to selenium. The resulting isoselenocyanate is extremely sensitive to water, liberating free selenium or some form of polymeric selenocyanogen upon hydrolysis. For comparative purposes, the electron-transfer band in $\text{Ta}(\text{NCSe})_6^-$ has also been listed. This absorption is more in line with the predicted value and in agreement with the trend generally observed for metal isothiocyanates and isoselenocyanates.²¹ The difference between the observed and calculated electron-transfer bands in the $\text{Ta}(\text{NCS})_6^-$ spectrum is not readily explainable at the present time. The quoted values for electronegativities are correct to only *ca.* 0.1 unit. The observed absorption for the tantalum complex certainly falls within this limit. The possibility of the MNC angle having a value other than 180° could also be expected to cause serious changes in the position and intensity of the electron-transfer bands. Work in progress on the corresponding selenocyanates and the zirconium and hafnium thiocyanates should help to clarify this problem.

Thiocyanate, being an ambidentate ligand is capable of coordination to the central metal *via* nitrogen or sulfur. These different coordination modes would impress different ligand fields on the d orbitals, thus splitting the e_g and t_{2g} levels by different amounts after coordination. Sulfur coordination of thiocyanate has been found to split these d levels by about the same amount as chloride coordination, while nitrogen is known to cause greater energy separation than this. Torp has found the ligand field transition of NbCl_6^{2-} occurs at *ca.* $540 \text{ m}\mu$.²² No absorption is found in this region for the $\text{Nb}(\text{NCS})_6^{2-}$ complex. The absence of an observed ligand field transition in this niobium(IV) complex is an indication that the stronger field nitrogen, and not the relatively weak-field sulfur moiety, is coordinated to the central metal in this complex. This greater splitting effect would cause the energy for the LaPorte-forbidden d-d transition to fall in the same spectral region as the LaPorte-allowed charge-transfer absorption. If this is the case, the weak d-d transition would be obscured by the envelope of the ligand to metal charge-transfer absorption. This is a further indication that the niobium(IV) complex is N bonded rather than S bonded, and the similarity of its infrared absorption spectrum to the +5 metal complexes indicates that they are all coordinated in the same manner.

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