For a trigonal-bipyramida' complex having full D_{3h} symmetry two d–d bands due to transitions $^2E'' \rightarrow {}^2E'$ and $^2E'' \rightarrow {}^2A_1'$ are expected, and the former should occur well into the near-infrared region. The five-coordinate species proposed here are of the form MX_4L and could have either C_{3v} or C_{2v} symmetry. In the latter case both E levels will be split and as many as four d–d bands could be observed; only three of these would appear at energies above *ca.* 5.0 kK. In each case we observe three such bands, but these cannot be interpreted unambiguously as transitions of only the five-coordinate species since bands arising from undissociated dimer may also be present.

Conclusions

Clearly three different types of adducts are formed between alkyl sulfides and niobium(IV) halides. Diadducts are formed by the cyclic thioether tetrahydrothiophene and by methyl sulfide. Vibrational spectra are consistent with a *cis* arrangement of the ligands. It is important to note however that small amounts of a *trans* isomer would be difficult to detect using the procedures described here. With the bulkier ethyl sulfide as well as with methyl sulfide, monoadducts could be obtained. These are very likely metal–metal-bonded and halogen-bridged dimers in the solid state, but in nondonor solvents extensive dissociation to monomeric five-coordinate species occurs. Such species should be paramagnetic. We attempted to measure the epr spectra of such solutions but observed no signals. It is perhaps significant that when we attempted to observe the nmr spectrum of methyl and methylene protons in $NbCl_4[S(C_2H_5)_2]$ only very broad ill-defined spectra were obtained as would be expected if the solutions contained paramagnetic species. Since the order of increasing space requirements of the ligands, $S(CH_2)_4 < S(CH_3)_2 < S(C_2H_5)_2$, corresponds with the order of decreasing stability of diadducts, the operation of a steric effect as earlier suggested by Brown and Newton[8] is definitely indicated. It is significant however that with respect to formation of the diadducts the qualitative order of stability of the proposed dimers, $Nb_2Cl_8[SR_2]_2 > Nb_2Br_8[SR_2]_2 \gg$ "$Nb_2I_8[SR_2]_2$," is inconsistent with the steric requirement of the halogen atoms. This suggests the importance of the metal–metal bond strength when it is further noted that *d*(Nb–Nb) for bonded niobium atoms in $NbCl_4$ and NbI_4 are 3.10[9] and 3.31 Å,[10] respectively.

Acknowledgment.—The authors wish to thank Miss Evelyn Conrad for the far-infrared spectra reported in this paper and Professors G. W. A. Fowles and R. A. Walton for making a preprint of the paper given in ref 6c available prior to its publication.

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Addition Compounds of Niobium(IV) Halides and Zirconium(IV) Chloride Formed with 1,2-Dimethylthioethane. Synthesis, Spectra, and Magnetism[1]

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The reactions of 1,2-dimethylthioethane with NbX_4 (X = Cl, Br, or I) and $ZrCl_4$ gave complexes of stoichiometry $MX_4[(CH_3SCH_2-)_2]_2$. Infrared and far-infrared spectra of the solids are consistent with coordination of two molecules of the bidentate sulfide ligand per molecule of MX_4, eight-coordination, and a triangular dodecahedral configuration about the niobium atom. Solid-state electronic spectra exhibit correspondences with reported spectra of dodecahedral $NbX_4(diars)_2$ (X = Cl, Br, or I; diars = *o*-phenylenebis(dimethylarsine)). The adducts are paramagnetic with magnetic moments of the chloride and bromide only slightly lower than the spin-only value for a d^1 ion.

Introduction

In a previous paper[2] a series of adducts formed by monodentate alkyl sulfides with niobium(IV) halides was described. In conjunction with that study an investigation of reactions of these halides with the bidentate donor 1,2-dimethylthioethane (more commonly referred to as 2,5-dithiahexane or dth) was undertaken. Clark and coworkers[3] had earlier established that the bidentate arsenic donor *o*-phenylenebis(dimethylarsine) formed eight-coordinate adducts with NbX_4 (X = Cl, Br, or I). A triangular dodecahedral configuration for $NbX_4(diars)_2$ (X = Cl or Br) was indicated by their isomorphism with $MX_4(diars)_2$ (M = Ti, Zr, Hf, or V and X = Cl; M = Ti, Zr, or Hf and X = Br). Clark and Errington[4] studied the reactions of several bidentate sulfur donors, including dth, with TiX_4 (X = Cl or Br), VCl_4, and $SnCl_4$. In each case only adducts in which the ratio of acceptor to donor was 1:1 were obtained.

We report here the synthesis of paramagnetic adducts

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(1) Work was performed at the Ames Laboratory of the USAEC.

(2) J. B. Hamilton and R. E. McCarley, *Inorg. Chem.*, **9**, 1333 (1970).

(3) R. J. H. Clark, D. L. Kepert, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2865 (1965).

(4) R. J. H. Clark and W. Errington, *ibid.*, **5**, 650 (1966).

TABLE I

LIGAND INFRARED SPECTRA OF SOME $MX_4(dth)_2$ ADDUCTS (SOLIDS)[a]

Assignment[b]	dth	$NbCl_4$	$ZrCl_4$	$NbBr_4$
CH_2 wag (T, G)	1281 sh	. . .	. . .	. . .
CH_2 wag (G)	1268 s	1260 m	1267 m, 1263 sh	1257
CH_2 wag (T)	1208 s	. . .	. . .	. . .
CH_2 twist (G)	1200 sh	1182, 1170 m	1181 m	1182 m, 1164 m
CH_2 twist (G)	1130 s	1142 m		1139 m
CC str (T, G)	1030 w	1029, 1023 s	1032 m	1031 sh, 1021 s
CH_3 rock (T, G)	972 sh	975 w, sh	982 w	982 w
CH_2 rock and CH_3 rock (T, G)	960 s	956 s	962 m	960 s
CH_2 rock (G)	840 s	843 m, 834 m	843 m	840 m, 831 m
CS str (T)	739 s	. . .	. . .	. . .
CS str (T)	688 s	. . .	. . .	. . .
CS str (T, G)	655 vw	644 w, 640 w	650 w	640 w, 636 w

[a] Abbreviations: T, *trans;* G, *gauche;* s, strong; m, moderate; w, weak; vw, very weak; sh, shoulder. [b] The assignments given are from M. Hayashi, Y. Shiro, T. Oshima, and M. Murata, *Bull. Chem. Soc. Japan*, **39**, 118 (1966).

$NbX_4(dth)_2$ (X = Cl, Br, I) and $ZrCl_4(dth)_2$. The infrared, far-infrared, and electronic spectra as well as the magnetic behavior of the addition compounds are discussed relative to models for eight-coordinate complexes.

Experimental Section

Synthesis.—Niobium(IV) halides were prepared using the procedures described previously.[2] Zirconium(IV) chloride was prepared *via* the direct reaction of zirconium metal turnings with chlorine in sealed evacuated tubes at 400°. Pure white $ZrCl_4$ was obtained *via* sublimation at 300°.

1,2-Dimethylthioethane was purchased from Columbia Chemicals and dried *in vacuo* over $LiAlH_4$. This mixture was filtered in an inert-atmosphere box and the dry sulfide obtained as filtrate was stored in the box until needed.

Spectrograde benzene was purchased from commercial sources and dried as described earlier.[2]

Since the products and the anhydrous halides were sensitive to oxygen and/or moisture, they were handled only *in vacuo* or in an inert-atmosphere drybox. The procedure was virtually the same in all cases. A 2–3-g sample of the halide was introduced into a 100-ml round-bottom flask containing an excess of dry dithiahexane and a magnetic stirring bar. This flask was evacuated to *ca.* 10^{-5} Torr and 50 ml of dry benezene was distilled into it. After extensive outgassing *in vacuo* the contents of the flask were frozen, pumped to 10^{-5} Torr, and isolated from the vacuum system. The mixture was warmed to room temperature and stirred for 4–5 days. The progress of the reaction was easily followed by observing the disappearance of the microcrystalline halide and the formation of a distinctly differently colored fine precipitate. Dark brown $NbCl_4$ formed a light brown powder, dark blue $NbBr_4$ gave a green powder, and gray NbI_4 produced a brown powder. With $ZrCl_4$ both the starting material and the product were white. The supernatant liquid in all of the preparations was colorless or light red indicating the low solubility of the halide and its adduct. It was necessary to extend the time of reaction of NbI_4 to 10 days. After 5 days the composition was intermediate between a 1:1 and a 1:2 (acceptor:donor) adduct (but closer to the latter). At the end of the reaction excess ligand and solvent were removed into cold traps under a dynamic vacuum and the products obtained were dried *in vacuo* over 24 hr.

Anal. Calcd for $NbCl_4[(CH_3SCH_2-)_2]_2$: Nb, 19.39; Cl, 29.59; C, 20.05; H, 4.21. Found: Nb, 19.92; Cl, 29.61; C, 19.04; H, 3.96. Calcd for $NbBr_4[(CH_3SCH_2-)_2]_2$: Nb, 14.14; Br, 48.65; C, 14.62; H, 3.07. Found: Nb, 14.34; Br, 48.63; C, 14.02; H, 2.98. Calcd for $NbI_4[(CH_3SCH_2-)_2]_2$: Nb, 10.99; I, 60.07; C, 11.37; H, 2.39. Found: Nb, 11.01; I, 62.05; C, 10.61; H, 2.44. Calcd for $ZrCl_4[(CH_3SCH_2-)_2]_2$: Zr, 19.10; C, 20.14; H, 4.22. Found: Zr, 19.05; C, 20.09; H, 4.03.

TABLE II

FAR-INFRARED SPECTRA OF SOLID $MX_4(dth)_2$ ADDUCTS (CM^{-1})[a]

Assignment	$NbCl_4$	$ZrCl_4$	$NbBr_4$	NbI_4
ν(M–X)	310 s, sh		245 s, sh	165 m
	303 s	305 s	235 s	142 m
ν(M–S)	281 s		278 m	276 m
	260 w	275 s	261 m	254 m
CCS def	245 w		(245)[b]	
CSC def	235 w	230 wm	(235)[b]	230 w
CSC def	204 w	202 wm		213 m
Unassigned	193 w	175 m	194 w, sh	123 w, sh
	180 w	137 m	185 w	108 m
	119 w		164 m	63 w
	97 m		135 w	59 w
	81 m		118 m	
			113 m, sh	
			97 m	
			72 m	

[a] Abbreviations: s, strong; m, moderate; w, weak; sh, shoulder. [b] Also assigned as ν(Nb–Br) because of relative intensity (see text).

Physical Measurements.—Solid-state and solution-phase electronic and vibrational spectra were recorded using the instruments and procedures given earlier.[2]

Electron paramagnetic resonance spectra at room temperature and −196° were obtained on powders using a Strand Model 601 spectrometer operating at X-band frequencies in conjunction with a cylindrical Strand cavity or a Varian general purpose rectangular cavity. The microwave frequencies were measured to wavemeter accuracy and the magnetic field measurements were made using a proton magnetometer with a frequency counter.

Results

Adducts with compositions approaching $MX_4(dth)_2$ were isolated from all of the reactions. Virtual insolubility in nondonor solvents such as benzene or cyclohexane was characteristic of the adducts, while with solvents such as acetonitrile solubility with reaction was observed. This was not surprising since acetonitrile is known to form adducts, $NbX_4(ac)_2$, with the tetrahalides.[5] We undertook an investigation of infrared, far-infrared, and electronic spectra as well as the magnetic properties of the solids. In Tables I and II data from the infrared and far-infrared spectra are summarized and Figure 1 is a reproduction of the latter.

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(5) B. A. Torp, and R. E. McCarley, to be submitted for publication.

TABLE III

MAGNETIC SUSCEPTIBILITIES AND MOMENTS FOR $NbX_4(dth)_2$

Temp, °K	$10^6(\chi_M - \chi_D)$, emu/mol	μ_{eff}, BM	μ,[a] BM	$10^6\chi_{TIP}$,[b] emu/mol
		X = Cl		
297	1124	1.63	1.60	+58
161	2040	1.62		
150	2171	1.61		
140	2328	1.61		
131	2504	1.62		
118	2755	1.61		
113	2929	1.63		
77	4126	1.59		
		X = Br		
297	1193	1.68	1.61	+98
202	1712	1.66		
192	1795	1.66		
183	1875	1.66		
176	1939	1.65		
150	2255	1.64		
140	2384	1.63		
77	4272	1.62		
		X = I		
298	839	1.41	1.28	+162
200	1176	1.37		
178	1316	1.37		
151	1511	1.35		
132	1692	1.34		
77	2813	1.32		

[a] Calculated from the slope of the Curie plot. [b] Intercept of the Curie plot at $T^{-1} = 0$.

TABLE IV

SOLID-STATE ELECTRONIC SPECTRA OF $NbX_4(dth)_2$

Compound	Freq, kK[a]
$NbCl_4(dth)_2$	12.3, 14.0, 18.8, 24.4, 31.0
	(15.3 sh,[b] 10.7, 13.8, 17.3, 22.7)[c]
$NbBr_4(dth)_2$	11.6, 13.7, 16.9, 22.7, 28.6
	(10.6, 13.8, 16.7, 21.2)
$NbI_4(dth)_2$	10.1, 12.7, 15.2, 18.4, 26.3
	(10.2, 13.1, 15.2, 19.7)

[a] 1 kK = 1000 cm^{-1}. [b] Shoulder. [c] Values in parentheses are for analogous diarsine adducts and are taken from ref 3.

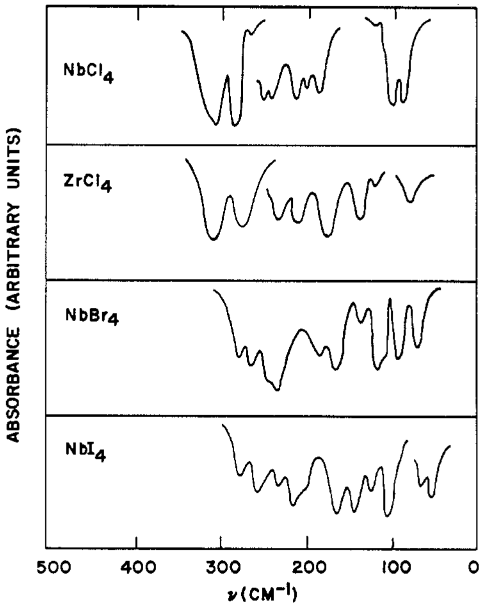

Figure 1.—Far-infrared spectra of $MX_4(dth)_2(s)$.

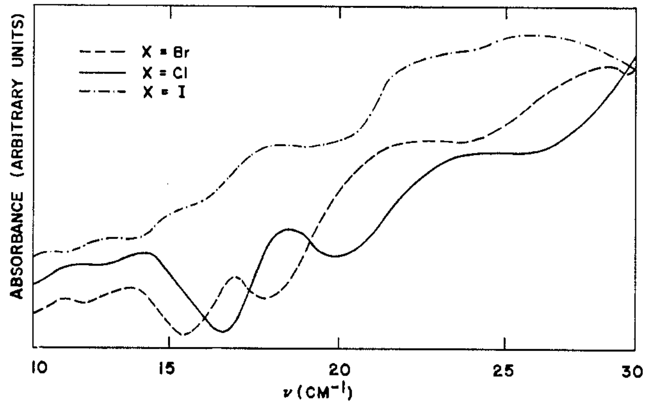

Figure 2.—Solid-state electronic spectra of $NbX_4(dth)_2$.

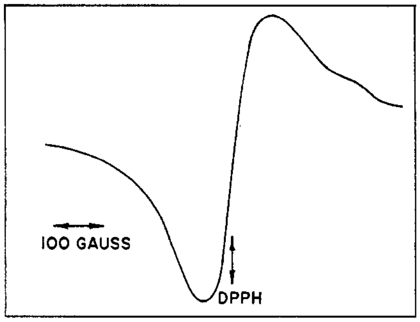

Figure 3.—Epr spectrum of powdered $NbCl_4(dth)_2$ at *ca.* −196°.

Data from the magnetic susceptibility measurements are summarized in Table III. Figure 2 gives the electronic spectra of the solids, and the wave number maxima of bands appearing in these are listed in Table IV. Figure 3 is a reproduction of the epr spectrum of $NbCl_4(dth)_2$.

Discussion

Infrared Spectra.—Several workers[6–8] have investigated the spectrum of 2,5-dithiahexane and assigned the observed bands. In the most detailed study,[8] and the most recent, bands were assigned in relation to ten expected rotational isomers or conformers. These arise when hindered rotation about the C–S bonds in addition to the C–C bonds leads to the *gauche* (G) or *trans* (T) configuration of groups adjacent to these bonds. On the basis of this later study it was concluded that the GTG′ and GGG[9] molecular forms exist in the gaseous and liquid states, while in the solid state the GTG′ form alone persists. The present data are clearly consistent with the *gauche* conformer prevailing in the adducts. This is indicated by the absence in the spectra of adducts of the strong band at 1208 cm^{-1} as well as the absence of the less intense C–S

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(6) D. M. Sweeny, S. Mizushima, and J. V. Quagliano, *J. Am. Chem. Soc.*, **77**, 6521 (1955).

(7) D. Welti and D. Whittaker, *J. Chem. Soc.*, 4732 (1962).

(8) M. Hayashi, Y. Shiro, T. Oshima, and H. Murata, *Bull. Chem. Soc. Japan*, **39**, 118 (1966).

(9) The notation is from Hayashi, *et al.*,[8] with the symbols G and T (*gauche* and *trans*) referring to molecular forms around each internal rotation axis. GGG refers from left to right to molecular forms around a C–S, a C–C, and a C–S axis.

stretching bands at 739 and 688 cm^{-1} (due entirely to the *trans* conformer) and the concomitant appearance with increased relative intensity of bands at ~840, 1140, 1180, and 1260 cm^{-1} due solely to the *gauche* conformer. The doublet structure of some of these bands as well as the appearance of some bands in the far-infrared region suggested that in the coordinated state a molecular form other than GGG might be present. According to Hayashi, *et al.*,[8] bands due to the GGG conformer should appear at only slightly different frequencies than TGT if the region above 600 cm^{-1} is considered and on this basis they concluded that this region was relatively insensitive to rotational isomerism about C–S bonds. In the present spectra doublets are observed at 1180–1160, 1030–1020, 1268–1260, 840-830, and in the region of 640 ± 10 cm^{-1}. The energy difference between bands in the doublet is small and could possibly arise from differences in the local symmetry of the ligands; however, the calculations of Hayashi, *et al.*,[9] suggest that this doublet structure could also arise from the presence of both the TGT and GGG conformers in the coordination sphere of the central metal.

The far-infrared region (below 600 cm^{-1}) was found to be more sensitive to conformation about C–S bonds, and for the TGT form bands are predicted at 446, 245, 231, 204, 176, 168, 84, 56, and 49 cm^{-1} while for the GGG form bands should occur at 428, 340, 272, 177, 170, 110, 51, and 41 cm^{-1}. The principal differences for these two forms are the bands predicted to occur in the region 200–240 cm^{-1} for one (TGT) and not at all for the other (GGG). We observe two or more bands in this region for all the adducts and on this basis propose that the TGT form is present in these compounds. The possible presence of the GGG form cannot be excluded since other bands in the spectra remain unassigned.

For the far-infrared spectra the bands of highest energy for the chloride appear at 310 and 303 cm^{-1}, *ca.* 50 cm^{-1} lower than is observed for the six-coordinate adducts $NbCl_4L_2$ (L = acetonitrile and tetrahydrothiophene). Since these are the most intense bands in the spectrum, they very likely are due to niobium–chlorine stretching modes and are so assigned. It is of interest that for the triangular dodecahedral $NbCl_4(diars)_2$ a doublet is observed at 299 and 303 cm^{-1}.[10] Corresponding bands for the bromide and iodide adducts are expected in the regions 235 and 170 cm^{-1}, respectively, if the ratios $\nu(Nb\text{–}Br)/\nu(Nb\text{–}Cl) = 0.76$ and $\nu(Nb\text{–}I)/\nu(Nb\text{–}Cl) = 0.56$ obtained from spectra of $NbX_4[S(CH_2)_4]_2$ (X = Cl, Br, I)[2] are used in their estimation. A doublet is found at 235 and 245 cm^{-1} for $NbBr_4(dth)_2$ and 165 and 142 cm^{-1} for the iodide; these are assigned as ν(Nb–Br) and ν(Nb–I). Relative to six-coordinate adducts[2] these bands are shifted to lower wave number by *ca.* 30–40 cm^{-1}. Such large shifts are expected to correspond with an increase in the coordination number of the metal and are here indicative of a change from six- to eight-coordination of niobium(IV). Assuming negligible interaction between modes of the same symmetry, two metal–halide stretching and two metal–sulfur stretching modes, each pair transforming as B_2 + E representations of the D_{2d} point group, are expected for a model based on the triangular dodecahedron. A cursory glance at the spectrum of $NbI_4(dth)_2$ reveals a doublet at 276 and 254 cm^{-1}, well above the region where ν(Nb–I) should occur, and doublets occur at not very different wave numbers in the spectra of the chloride (281 and 260 cm^{-1}) and the bromide (278 and 261 cm^{-1}). These bands are tentatively assigned as ν(Nb–S) modes. The band at 275 cm^{-1} in the spectrum of the zirconium adduct lacks the doublet structure but is also assigned as ν(Zr–S). These assignments are tentative since it has been proposed that several bands in this region and below are due to skeletal vibrations of *gauche*-1,2-dithiahexane. In the spectrum of the free ligand only a broad asymmetric band with a maximum at *ca.* 220 cm^{-1} was observed.

In one case an adduct of composition $NbCl_4(dth)$ was obtained *via* the direct reaction of $NbCl_4$ and $NbCl_4(dth)_2$ in benzene. This product was obtained in very low yields and only a metal analysis was obtained, but it was indicative of a mono- rather than the diadduct. The far-infrared data were consistent with six-coordination for niobium(IV) as indicated by the appearance of bands in the region 310–370 cm^{-1}.

Magnetic Susceptibilities.—The molar magnetic susceptibilities exhibited a Curie law dependence upon reciprocal temperature. Table III lists the values of χ_{TIP} and μ which were determined from the Curie plots. As expected χ_{TIP} for these highly distorted adducts is much less than has been observed for *cis*-NbX_4L_2 (L = $S(CH_2)_4$). The magnitude of χ_{TIP} decreased in the expected order (I > Br > Cl). The magnetic moments of the chloride and bromide were only slightly (7%) less than the spin-only values for one unpaired electron. These were somewhat lower than the effective magnetic moments 1.7, 1.9, and 1.6 BM reported for $NbX_4(diars)_2$ (X = Cl, Br, I).[3]

Electronic Spectra.—Each spectrum consists of a group of five bands with wave numbers of their maxima exhibiting a systematic decrease in the order Cl > Br > I. The gross features suggest the presence of a similar ligand field environment for each of the niobium adducts, and a comparison with the data reported for analogous diarsine adducts[3] suggests that this is a triangular dodecahedral environment. Although solution spectra could not be obtained, a comparison with the reported spectra of NbX_4L_2 (X = Cl, Br, I; L = $S(CH_2)_4$)[2] suggests that the three bands at lower energy are due to transitions within the d manifold. McGarvey[11] as well as Ibers and Swalen[12] have shown that the d manifold is split into the levels B_1, A_1, E, and B_2 under the influence of a dodecahedral ligand field. From the relative energies of the levels the three d–d bands should result from the transitions $^2B_1 \rightarrow {}^2A_1$, $^2B_1 \rightarrow {}^2E$, and $^2B_1 \rightarrow {}^2B_2$. Lower symmetry ligand fields or distortions could result in a splitting of the E

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[10] R. J. H. Clark, *Spectrochim. Acta*, **21**, 955 (1965).

[11] B. R. McGarvey, *Inorg. Chem.*, **5**, 476 (1966).

[12] J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, **37**, 17 (1962).

level with four d-d bands being observed. This could explain the band observed as a shoulder at 15.3 kK in the spectrum of dodecahedral $NbCl_4(diars)_2$.

Electron Paramagnetic Resonance Spectrum.—From the epr spectrum of the chloride it was possible to obtain $g_{\perp} = 1.98$ and $g_{||} = 1.80$ from which the average g value of 1.92 gave a moment of 1.67 BM, only slightly higher than the value 1.60 BM obtained experimentally. With an Archimedean antiprism as a model it has generally been found that $g_{||} > g_{\perp}$,[11,13] while for a triangular dodecahedron usually $g_{||} < g_{\perp}$.[11,12]

Conclusions

Contrary to the report of Clark and Errington,[4] 2,5-dithiahexane is capable of forming eight-coordinate adducts. Since $TiCl_4$, VCl_4, and $SnCl_4$ are liquids it is possible that in the homogeneous reaction medium the low solubility of the 1:1 (acceptor:donor) adduct favors its formation; the effective radius of the metal atom or more limited participation of d orbitals may also be important factors. The paramagnetic behavior of $NbX_4(dth)_2$ seems to rule out a "topochemical" reaction in which the tetrahalides react without breakdown of their diamagnetic structures.

In addition to the stoichiometry of the complexes, the eightfold coordination and bidentate character of the ligands are clearly indicated by the spectra. Evidence from the infrared spectra shows that the coordinated dithiahexane adopts the *gauche* conformation, which is in contrast to the predominant *trans* conformation of the free ligand. The bidentate coordination of the ligand thus is indicated since the *gauche* conformation is required for coordination of both sulfur atoms to the same metal atom. The far-infrared results further suggest that the TGT form of the ligand is coordinated. This observation contrasts with the conclusion that the GGG form exists in the gaseous and liquid states.[8] However, the spectra in the region 600–1300 cm^{-1} suggest that molecular forms around the two C–S bonds can affect the bands occurring in this region, and the doublets which we have observed may be indicative of the presence of both the TGT and GGG forms.

Finally, the decrease of ν(Nb–X) by 30 to 50 cm^{-1} relative to six-coordinate niobium(IV) adducts corroborates the higher coordination number of the metal atom in the compounds reported here. Both the electronic spectra and magnetic properties are in accord with an eight-coordinate, triangular dodecahedral configuration about niobium. On the basis of these results and those reported for the ligand *o*-phenylenebis(dimethylarsine)[3] we expect that other bidentate ligands with heavy donor atoms should promote higher coordination numbers when coordinated to the earlier, heavy transition metal ions.

(13) B. R. McGarvey, *J. Chem. Phys.*, **37**, 2001 (1962).

CONTRIBUTION NO. 2602 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
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Chemistry of Polynuclear Metal Halides. III. Synthesis of Some Niobium and Tantalum $M_6X_{12}^{n+}$ Cluster Derivatives[1]

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Synthetic methods are given for the preparation of hydrated halides and halo complexes of the $Nb_6X_{12}^{n+}$ and $Ta_6X_{12}^{n+}$ (X = Cl, Br) clusters in each of the stable oxidation states n = 2, 3, or 4. Most of the compounds were crystallized from aqueous or alcohol solutions containing hydrogen halide for the cases where n = 3 or 4. Difficulties associated with oxidation and solvation of n = 2 derivatives made it desirable to prepare salts of the anions $(M_6Cl_{12})Cl_6^{4-}$ (M = Nb or Ta) by reduction of the anhydrous chlorides MCl_5 in the presence of alkali metal chloride at high temperature.

Introduction

This paper deals entirely with syntheses of many different derivatives containing the basic cluster units $M_6X_{12}^{n+}$, where M = Nb or Ta and X = halogen. Work on the structure, infrared spectra, magnetic properties, and electronic spectra will be published subsequently. These studies are part of a concerted program to understand the important features of the structure and bonding of the hexanuclear metal cluster compounds.

The early literature on the niobium and tantalum cluster containing compounds has been summarized in recent papers on new or improved preparative methods for formation of the basic $Ta_6X_{12}^{2+}$ and $Nb_6X_{12}^{2+}$ cluster units.[2,3] Subsequently it has been shown that both the tantalum[4,5] and niobium[6] clusters may assume

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(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) P. J. Kuhn and R. E. McCarley, *Inorg. Chem.*, **4**, 1482 (1965).

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(4) R. E. McCarley, B. G. Hughes, F. A. Cotton, and R. Zimmerman, *ibid.*, **4**, 1491 (1965).

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