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Bidentate Sulfur-Donor Complexes of Quadrivalent Metal Halides

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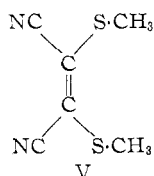
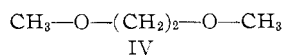
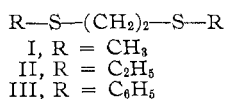
The metal halides $TiCl_4$, $TiBr_4$, VCl_4 , and $SnCl_4$ react with the bidentate sulfur-donor ligands (L) 1,2-dimethylthioethane, 1,2-diethylthioethane, 1,2-diphenylthioethane, and *cis*-dimethylthiomaleonitrile to yield 1:1 adducts ($MX_4 \cdot L$) which are shown to be six-coordinate monomers in solution. Analogous complexes with 1,2-dimethoxyethane were obtained in order to compare the donor properties of oxygen- and sulfur-donor ligands. Attempts to treat these adducts with an excess of the ligand failed to yield eight-coordinate 1:2 adducts of the type $MX_4 \cdot 2L$, such as have been observed recently with a bidentate arsine. The general physical properties of the 20 complexes are presented, and the infrared spectra ($4000\text{--}200\text{ cm}^{-1}$) are discussed in detail with particular reference to the configuration of the ligands and to the assignment of metal-halogen and metal-sulfur stretching vibrations. From an analysis of the electronic spectra of the vanadium derivatives it is inferred that the ligand field strength of the sulfur-donor ligands is similar to that of the chloride ion.

Introduction

Apart from a few reports concerned essentially with monodentate ligands,¹ there have been no systematic investigations of the reactions of sulfur-donor ligands with the group IV and V metal halides. The early transition elements occur in that part of the periodic table usually associated with class A behavior;² *i.e.*, the order of coordinating ability of donor atoms is $F \gg Cl > Br > I$ and $O \gg S \sim Se \sim Te$. Thus, the heats of formation of the titanium tetrahalides follow the above order. Nevertheless, the recent isolation of well-characterized arsine complexes³ of the titanium and vanadium subgroups suggests that the elements may be sufficiently close to the borderline of class A-class B character to permit also the formation of stable complexes with sulfur-donor ligands.

Moreover, bidentate sulfur-donor ligands are of particular interest in view of the possibility that they might stabilize the coordination number of 8 for the metal. This possibility was realized recently³ for a bidentate arsine, *o*-phenylenebisdimethylarsine, with the tetrachlorides and tetrabromides of titanium, zirconium, hafnium, and niobium and with the tetrachloride of vanadium.

The reactions of the bidentate ligands 1,2-dimethylthioethane (I), 1,2-diethylthioethane (II), 1,2-diphenylthioethane (III), 1,2-dimethoxyethane (IV), and *cis*-dimethylthiomaleonitrile (V) with titanium tetrachloride and tetrabromide, vanadium tetrachloride, and stannic tetrachloride have been investigated and are reported below.



Experimental Section

Preparation of Compounds.—*cis*-Dimethylthiomaleonitrile⁴ and 1,2-diphenylthioethane⁵ were prepared by published methods. The other ligands were obtained from commercial sources and were stored over sodium wire.

The complexes were prepared by mixing solutions containing equal molecular proportions of the tetrahalides and the ligands. This operation was carried out in a completely enclosed system under specially purified nitrogen; the solvent (benzene or carbon tetrachloride) was distilled from lithium aluminium hydride directly into the reaction vessel as required. The complexes, which precipitated immediately, were filtered and washed under nitrogen, before drying under vacuum. The complexes were finally sealed in glass manifolds under a vacuum. The vanadium complex with 1,2-dimethoxyethane was purified by vacuum sublimation at 100° .

Spectra.—Diffuse reflectance spectra were recorded using a Unicam SP 500 spectrophotometer, fitted with the reflectance attachment supplied by the makers, and using magnesium carbonate as the reference reflector.

Infrared spectra were recorded on Grubb-Parsons double-beam grating spectrometers, Type G.S. 2A for the region $4000\text{--}400\text{ cm}^{-1}$, and Type D.M.2 for the region $450\text{--}200\text{ cm}^{-1}$. The region $1300\text{--}400\text{ cm}^{-1}$ was also scanned with a Perkin-Elmer Model 337 spectrometer. The complexes were made into mulls with both Nujol and hexachlorobutadiene in a glove box under dry nitrogen.

Magnetic Susceptibilities.—The magnetic susceptibilities of the complexes at room temperature were determined by the Gouy method. The magnetic moments were also computed from the *g* values, obtained from the electron spin resonance spectra of the vanadium complexes, using a Varian (V.P. 4500) electron paramagnetic resonance spectrometer.

X-Ray Powder Photographs.—X-Ray powder photographs were taken with a Philips Debye-Scherrer camera of 114.8-mm diameter and copper $K\alpha$ radiation with a nickel filter. Finely ground samples were prepared in a drybox and sealed into Lindemann glass capillaries.

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(3) R. J. H. Clark, J. Lewis, R. S. Nyholm, P. Pauling, and G. B. Robertson, *Nature*, **192**, 222 (1961); R. J. H. Clark, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2460 (1962); R. J. H. Clark, D. L. Kepert, J. Lewis, and R. S. Nyholm, *Nature*, **199**, 559 (1963); *J. Chem. Soc.*, 2865 (1965); R. J. H. Clark and W. Errington, unpublished results.

(4) G. Bähr and G. Schleitzer, *Ber.*, **88**, 1771 (1955); **90**, 438 (1957).

(5) R. F. Brooks, J. E. Cranham, W. A. W. Cummings, D. Greenwood, B. S. Jackson, and H. A. Stevenson, *J. Sci. Food Agr.*, **8**, 31 (1957).

TABLE I
ANALYTICAL DATA

Complex	% C		% H		% halogen		% S		% M		% N	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
TiCl ₄ (CH ₃ SCH ₂) ₂	15.4	15.5	3.2	3.7	45.5	46.0	20.5	20.6	15.4	15.4
TiBr ₄ (CH ₃ SCH ₂) ₂	9.8	10.1	2.0	2.4	65.3	65.1	13.1	12.8	9.8	10.0
VCl ₄ (CH ₃ SCH ₂) ₂	15.3	15.5	3.2	3.5	45.1	45.0	20.3	20.8	16.2	16.1
SnCl ₄ (CH ₃ SCH ₂) ₂	12.6	13.0	2.6	2.6	37.1	37.0	16.7	16.7	31.0
TiCl ₄ (C ₂ H ₅ SCH ₂) ₂	21.2	21.5	4.1	4.6	41.7	42.1	18.8	18.9	14.1	14.1
TiBr ₄ (C ₂ H ₅ SCH ₂) ₂	13.9	13.9	2.7	3.2	61.8	61.6	12.4	12.3	9.3	9.2
VCl ₄ (C ₂ H ₅ SCH ₂) ₂	21.0	21.9	4.1	4.2	41.4	40.8	18.7	17.6	14.9	14.7
SnCl ₄ (C ₂ H ₅ SCH ₂) ₂	17.5	17.3	3.4	3.6	34.5	34.6	15.6	15.5	28.9
TiCl ₄ (C ₆ H ₅ SCH ₂) ₂	38.6	38.9	3.2	3.7	32.5	32.2	14.7	14.6	11.0	10.8
TiBr ₄ (C ₆ H ₅ SCH ₂) ₂	27.4	27.7	2.3	2.7	52.1	51.8	10.4	10.5	7.8	7.8
VCl ₄ (C ₆ H ₅ SCH ₂) ₂	38.3	36.5	3.2	3.1	32.3	...	14.6	...	11.6	11.4
SnCl ₄ (C ₆ H ₅ SCH ₂) ₂	33.2	33.3	2.8	3.1	28.0	27.9	12.6	12.6	23.4
TiCl ₄ (CH ₃ OCH ₂) ₂	17.2	17.2	3.6	3.9	50.7	50.5	17.1	17.2
TiBr ₄ (CH ₃ OCH ₂) ₂	10.5	10.5	2.2	2.4	69.9	69.5	10.5	10.4
VCl ₄ (CH ₃ OCH ₂) ₂	17.0	17.1	3.5	3.9	50.1	49.8	18.0	17.8
SnCl ₄ (CH ₃ OCH ₂) ₂	13.7	13.7	2.9	3.0	40.5	40.5	33.9
TiCl ₄ (CH ₃ S·CNC≡) ₂	20.0	19.9	1.7	2.0	39.4	39.4	17.8	17.4	13.3	13.2	7.8	7.8
TiBr ₄ (CH ₃ S·CNC≡) ₂	13.4	13.3	1.1	1.6	59.5	59.5	11.9	11.7	8.9	8.9	5.2	5.1
VCl ₄ (CH ₃ S·CNC≡) ₂	19.9	20.0	1.7	2.2	39.1	39.0	17.6	...	14.0	14.2	7.7	7.7
SnCl ₄ (CH ₃ S·CNC≡) ₂	16.7	16.8	1.4	1.9	32.9	33.5	14.9	14.1	27.6	...	6.5	6.5

Nuclear Magnetic Resonance.—Proton magnetic resonances were observed with a Perkin-Elmer R.10 spectrometer. The complexes were examined in saturated benzene solutions, using tetramethylsilane as the internal reference.

Analyses.—Metals were determined by ignition to the oxides. Halogens were determined gravimetrically as the silver halides. Carbon and hydrogen analyses were carried out by the micro-analytical service of this department, and nitrogen and sulfur were determined at the Max-Planck Institut für Kohlenforschung, Mulheim, Germany.

Molecular Weight Determinations.—Molecular weights were determined in benzene solutions using a Gallenkamp ebulliometer.

Results

The complexes formed from the metal tetrahalides TiCl₄, TiBr₄, VCl₄, and SnCl₄ with the four bidentate sulfur-donor ligands and 1,2-dimethoxyethane are in each case 1:1 adducts, and the analytical data characterizing these compounds are given in Table I. The compounds are analytically fairly pure, with the exception of the vanadium adduct with 1,2-diphenylthioethane, which, despite several attempts, could not be obtained in a pure form.

Attempts to coordinate a second molecule of ligand to the various 1:1 adducts by heating the latter in an excess of the ligand were unsuccessful. This is surprising in view of the success of the ligand *o*-phenylene-bisdimethylarsine in stabilizing eight-coordination of titanium and vanadium, and no explanation for this difference in behavior of bidentate sulfur- and arsenic-donor ligands is yet apparent.

The complexes are all extremely unstable to moisture. Qualitative observations for samples exposed to the atmosphere suggest that the ether and thioether complexes are of comparable stability, while the *cis*-dimethylthiomaleonitrile complexes are even less stable. Hydrolysis of the vanadium complexes does not appear to stop after the formation of the vanadyl species, as has been observed⁶ for 2,2'-bipyridyl and *o*-phenanthroline complexes.

TABLE II

PHYSICAL PROPERTIES OF METAL-SULFUR COMPLEXES

Complex	Color	Mp, °C	μ_{eff} , BM
TiCl ₄ (CH ₃ SCH ₂) ₂	Yellow	187 dec	Diamag
TiBr ₄ (CH ₃ SCH ₂) ₂	Orange	140	Diamag
VCl ₄ (CH ₃ SCH ₂) ₂	Violet	121 dec	{ 1.69 (Gouy) 1.71 (esr)
SnCl ₄ (CH ₃ SCH ₂) ₂	White	208 dec	Diamag
TiCl ₄ (C ₂ H ₅ SCH ₂) ₂ ^a	Orange	126	Diamag
TiBr ₄ (C ₂ H ₅ SCH ₂) ₂ ^b	Red	135 dec	Diamag
VCl ₄ (C ₂ H ₅ SCH ₂) ₂	Black	130 dec	{ 1.69 (Gouy) 1.68 (esr)
SnCl ₄ (C ₂ H ₅ SCH ₂) ₂	White	180	Diamag
TiCl ₄ (C ₆ H ₅ SCH ₂) ₂	Red	140	Diamag
TiBr ₄ (C ₆ H ₅ SCH ₂) ₂	Red	146 dec	Diamag
VCl ₄ (C ₆ H ₅ SCH ₂) ₂	Black	60 dec	1.69 (esr)
SnCl ₄ (C ₆ H ₅ SCH ₂) ₂	Yellow	141	Diamag
TiCl ₄ (CH ₃ OCH ₂) ₂	Yellow	161 dec	Diamag
TiBr ₄ (CH ₃ OCH ₂) ₂ ^c	Red	126	Diamag
VCl ₄ (CH ₃ OCH ₂) ₂	Black	134 sub	{ 1.74 (Gouy) 1.71 (esr)
SnCl ₄ (CH ₃ OCH ₂) ₂	White	141 sub	Diamag
TiCl ₄ (CH ₃ S·CNC≡) ₂	Red	150 dec	Diamag
TiBr ₄ (CH ₃ S·CNC≡) ₂	Red	136 dec	Diamag
VCl ₄ (CH ₃ S·CNC≡) ₂	Black	130	{ 1.73 (Gouy) 1.70 (esr)
SnCl ₄ (CH ₃ S·CNC≡) ₂	Yellow	124	Diamag

^{a,b,c} Molecular weight values determined in $\sim 10^{-2}$ M benzene solutions (found/calcd): *a*, 352/340; *b*, 530/518; *c*, 445/458.

A few of the titanium complexes are sufficiently soluble in benzene to enable molecular weights to be determined ebullioscopically. Where this is possible (see Table II), the complexes are shown to be monomers. Infrared data, to be discussed later, suggest that the metal atoms in all of the complexes are six-coordinated.

The X-ray powder photographs for all of the complexes were recorded; those for a given ligand are very similar, but they do not indicate isomorphism.

Proton magnetic resonance spectra for the titanium

tetrabromide adducts with 1,2-diethylthioethane and 1,2-dimethoxyethane were recorded, and the chemical shifts are given in Table III. These data indicate the equivalence of the two alkyl groups attached to the donor atoms and therefore indicate that both donor atoms are coordinating with the metal.

TABLE III
PROTON MAGNETIC RESONANCE DATA^a

Compound	CH ₃	CH ₂	CH ₂ in C ₂ H ₅
(C ₂ H ₅ SCH ₂) ₂	8.90	7.41	7.69
TiBr ₄ ·(C ₂ H ₅ SCH ₂) ₂	9.00	8.36	7.52
(CH ₃ OCH ₂) ₂	6.76	6.55	
TiBr ₄ ·(CH ₃ OCH ₂) ₂	6.78	6.46	

^a τ is expressed in ppm relative to (CH₃)₄Si in benzene solutions.

The titanium and tin derivatives are diamagnetic as expected for d⁰ and d¹⁰ complexes, respectively, whereas the vanadium complexes have magnetic moments of about 1.7 BM consistent with the presence of one unpaired d electron per vanadium atom.

Discussion

Infrared Spectra.—Disubstituted ethanes may exist in the *cis*, *trans*, or *gauche* forms, depending upon the angle of internal rotation.

exists, and this is usually the *trans* form. By comparing the spectra of the free and coordinated disubstituted ethanes, one might expect to obtain information concerning the conformation of the coordinated ligand. For monomers, this information also indicates the coordination number of the metal in the complex.

(a) **1,2-Dimethylthioethane Complexes.**—1,2-Dimethylthioethane has been studied in the liquid and solid states by several workers,^{9,10} and fairly complete assignments have been given. The absorption maxima in the spectra of the 1,2-dimethylthioethane complexes are given in Table IV, along with those of the ligand.

The strong bands characteristic of the *trans* form of the ligand (e.g., at 1205 cm⁻¹) are absent from the spectra of the complexes. On the other hand, those modes associated with the *gauche* form reappear, frequently with increased intensities (e.g., at about 1260 and 959 cm⁻¹). This evidence suggests that the ligand is coordinated in the *gauche* configuration; certainly the *trans* form appears to be ruled out. The frequently assumed *cis* configuration is excluded if one accepts the assignments given¹⁰ for the free ligand. Thus, the presence of two CH₂ rocking modes in the infrared spectra of the complexes indicates C₂ rather than C_{2v} symmetry for the ligands; for C_{2v} symmetry only one CH₂ rocking mode would be infrared active.

TABLE IV
INFRARED SPECTRA^a OF 1,2-DIMETHYLTHIOETHANE COMPLEXES IN THE REGION 2000–400 CM⁻¹

Assignment ^b	1,2-Dimethylthioethane		Complexes				
	Solid ^b	Liquid	TiCl ₄ ·L	TiBr ₄ ·L	VCl ₄ ·L	SnCl ₄ ·L	NiI ₂ ·L ₂ ^c
CH ₂ bend	1430 vs	1429 vs	1418 s, sh 1410 s	1420 s 1404 s	1416 s	1428 s 1409 s	
CH ₃ sym bend	1320 m	1322 m	1319 sh 1314 m	1318 m	1323 m 1314 m	1324 m 1307 m	1325 w
CH ₂ wag (<i>gauche</i>)		1269 s	1258 m	1256 m	1259 m	1262 w	1256 m
CH ₂ wag (<i>trans</i>)	1210 vs	1205 vs	1176 m 1146 m	1146 m	1172 w 1147 w	1180 w 1158 w	1140 w
CH ₂ twist (<i>trans</i>) (<i>gauche</i> ?)	1137 s	1134 m 1023 w	1028 vs	1026 vs	1028 s	1028 vs	1023 s
C–C str (<i>gauche</i>)		1010 vw					
CH ₃ rock	964 s	977 w, sh 958 s	971 s 969 s 959 vs	971 m 959 vs	979 vs 961 s 954 s	974 s, sh 962 s	976 m 968 m 959 s 952 s
CH ₂ rock (<i>gauche</i>)		885 vw	890 vw	887 m	885 m	888 s	879 m
CH ₂ rock (<i>gauche</i>)		844 w	838 s 759 w, br	837 s 760 s, br	833 s 735 m, br	837 s 735 w, br	842 m 733 m, br
C–S str	735 s	735 m	721 w	725 s, br	720	723 m	719 m, br
C–S str (<i>trans</i>)	678 vs	683 m					
C–S str (<i>gauche</i>)		649 vw, sh	648 m	646 m	645 w	646 m 634 m	646 w 450 m, sh
			445 s	447 m		450 s	

^a vw = very weak, m = medium, s = strong, vs = very strong, sh = shoulder, br = broad, w = weak. ^b From ref 9 and 10. ^c Monomer prepared according to R. Backhouse, M. E. Foss, and R. S. Nyholm, *J. Chem. Soc.*, 1714 (1957).

Spectral⁷ and other physical measurements⁸ on the disubstituted ethanes in the liquid and solid states have shown that in the liquid state the *trans* and *gauche* forms are present. In the solid state, only one form

This conclusion in favor of a *gauche* configuration for the ligand gains some support from a rough calculation of interatomic distances. On the basis of covalent bond radii,¹¹ the titanium–sulfur distance would

(7) S. Mizushima, Y. Morino, I. Watanabe, T. Simanouti, and S. Yanaguchi, *J. Chem. Phys.*, **17**, 591 (1949); I. Nakagawa and S. Mizushima, *ibid.*, **21**, 2195 (1953); J. T. Neu and W. D. Gwinn, *ibid.*, **18**, 1642 (1950).

(8) H. J. Bernstein, *ibid.*, **18**, 897 (1950); J. Y. Beach and K. J. Palmer, *ibid.*, **6**, 639 (1938).

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

(10) D. Welti and D. Whittaker, *J. Chem. Soc.*, 4372 (1962).

(11) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948.

TABLE V
 INFRARED SPECTRA OF 1,2-DIETHYLTHIOETHANE COMPLEXES IN THE REGION 2000-400 CM⁻¹

Assignment ^a	1,2-Diethylthioethane		Complexes			
	Solid	Liquid	TiCl ₄ ·L	TiBr ₄ ·L	VCl ₄ ·L	SnCl ₄ ·L
	1455 s	1452 s	1449 s	1449 s	1450 s	1449 s
	1448 s					
	1440 s					
	1418 s	1424 s	1416 s	1412 s	1410 s	1413 s
			1408 s			
CH ₃ sym bend	1374 m	1375 m	1376 s	1374 s	1375 s	1375 s
CH ₂ wag	1264 s	1262 vs	1271 m, sh	1269 m	1268 s, sh	1269 m, sh
CH ₂ wag (<i>gauche</i> ?)		1256 s, sh	1264 m		1261 s	1261 vs
	1239 m		1253 s	1253 s	1250 s	
CH ₂ wag (<i>trans</i>)	1209 s	1199 vs				
			1172 m		1169 w	1152 m
	1145 s		1142 m	1143 m	1142 m	1142 m, sh
CH ₂ twist (<i>trans</i>)		1128 m				
	1053 m	1050 m	1051 m	1050 w	1050 w	1054 m
	1025 w		1033 w	1035 w	1031 w	1039 w
			995 vw	982 w	980 m	978 m
CH ₃ rock		970 s	977 s			
			909 m, sh	910 vs		907 s, sh
	892 m		905 vs	903 m, sh	906 vs	901 vs
CH ₂ rock (<i>gauche</i>)		853 w	844 vs	846 vs	841 s	843 s
	784 m	782 m	771 vs	773 vs	785 s	773 vs
		763 w		760 s	768 s, sh	
		758 m, sh				
	739 m					
	721 m	718 vs	721 m	726 s	723 w, sh	720 m
	671 m					
C-S stretch	654 w	650 s	652 m	634 w	645 w	634 w
			454 s	448 m	455 m, sh	451 m

^a Largely based upon ref 10.

be 2.40 Å, and in an undistorted octahedron the distance between the two sulfur atoms would then be 3.39 Å. In the *cis* form of the ligand the distance between the sulfur atoms would be 2.75 Å, while in the *gauche* form it is 3.29 Å. The latter figure is clearly more compatible with a relatively undistorted structure.

(b) **1,2-Diethylthioethane Complexes.**—The infrared spectra of these complexes are given in Table V. These spectra are understandably more complicated than those obtained for 1,2-dimethylthioethane complexes, and the ligand bands have not been so completely assigned. Arguments similar to those employed above, once again suggest that the ligand is coordinated in the *gauche* (or possibly *cis*) form rather than the *trans* form. The weak band at 853 cm⁻¹ associated with a CH₂ rocking mode in the free ligand, reappears in the complexes at a slightly lower frequency, but with a greatly increased intensity. The second CH₂ rocking mode expected for the *gauche* configuration, however, cannot be identified with certainty. Either of the bands at 763 or 758 cm⁻¹ in the spectrum of the free ligand may be the second CH₂ rocking mode, and certainly a strong band appears in this region for two of the complexes. Thus, a *gauche* configuration seems probable.

(c) **1,2-Diphenylthioethane Complexes.**—The spectra of these complexes are extremely complicated owing to the overlapping of many bands. The strong band at 1206 cm⁻¹ of the free ligand, probably due to a CH₂ wagging mode in the *trans* form, does not occur in any of the complexes. On the other hand, a weak band at

1269 cm⁻¹, which is in the region anticipated for the corresponding *gauche* mode, reappears in the spectra of the complexes in the range 1255-1260 cm⁻¹ and with increased intensity.

The region in which CH₂ rocking modes should occur is too heavily overlapped by CH out-of-plane deformations associated with the benzene ring to be of any interpretative value. However, the ligand is probably, once again, coordinated in the *gauche* form.

(d) **1,2-Dimethoxyethane Complexes.**—The most prominent features of these spectra are the very intense C=O stretching bands.¹² In the free ligand these occur as a very intense quartet from 1079 to 1142 cm⁻¹, but on coordination as a very strong band around 1070 cm⁻¹ with an equally intense doublet at about 1000 and 1010 cm⁻¹.

It is impossible to assign the bands in the spectrum of 1,2-dimethoxyethane simply by comparing with the corresponding sulfur compound since the electronegativities of the donor atoms are so different. Miyake,¹³ however, has assigned the CH₂ rocking modes, assigning the band at 853 cm⁻¹ as an a_u mode, while the bands at 938 and 925 cm⁻¹ were attributed to the *gauche* form.

Miyake's assignments are considered to be incorrect since they would appear to indicate that the ligand coordinates in the *trans* form (*i.e.*, the 853-cm⁻¹ *trans* band is present in the complexes, while the 938-

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Methuen and Co. Ltd., London, 1958.

(13) A. Miyake, *J. Am. Chem. Soc.*, **82**, 3040 (1960).

and 925-cm⁻¹ *gauche* bands are missing). This conclusion is unacceptable since the titanium tetrabromide complex was shown to be monomeric and to contain equivalent methyl groups.

On the basis of a simple calculation of interatomic distances, the *gauche* configuration seems probable. The distance between the two oxygen atoms in an undistorted octahedron is calculated to be 2.86 Å, assuming a titanium-oxygen distance of 2.02 Å, while the distance between the oxygen atoms in the *gauche* form is 2.82 Å, and in the *cis* form is 2.49 Å.

(e) **Metal-Halogen and Metal-Sulfur Stretching Frequencies.**—The metal-halogen stretching vibrations in all of these complexes are very strong and do not vary very much in position within a series. Of the four vibrations expected (2a₁ + b₁ + b₂), three are identified with fair certainty (Table VI). The metal-halogen stretching frequencies are very similar to those reported previously for 2,2'-bipyridyl and *o*-phenanthroline complexes of titanium, vanadium,⁶ and tin,¹⁴ and for bidentate arsine complexes of titanium,¹⁵ and they are, in each case, characteristic of six-coordinate complexes of the respective metals.

Metal-sulfur stretching vibrations could not be identified with certainty. However, a medium to strong band appeared in the spectra of all of the disubstituted thioethane complexes in the range 455–445 cm⁻¹, and this may be a metal-sulfur stretching vibration. No bands appeared in this region in the spectra of the 1,2-dimethoxyethane and *cis*-dimethylthiomaleonitrile complexes; since in the latter complexes bonding could occur *via* the cyanide groups, this observation is not inconsistent with the above assignment.

Few assignments for metal-sulfur stretching vibrations have yet been made. However, tin(IV)-sulfur asymmetric stretching modes have been assigned¹⁶ in the region 440–488 cm⁻¹ consistent with the present results. Moreover, a normal coordinate analysis¹⁷ of the chelate ring of the dithiooxalatoplatinum(II) ion indicates that the platinum-sulfur stretching vibrations occur at 440–420 and at 320 cm⁻¹.

Visible Spectra.—The vanadium complexes are brownish black, and the diffuse reflectance spectra of the solids have been obtained. Broad asymmetric bands are located in the region from 17000–20000 cm⁻¹, and these can be assigned to d-d transitions since the corresponding titanium (d⁰) complexes do not absorb in this region. The general appearance of these bands is illustrated in Figure 1, and the spectrum of one of the titanium complexes is added for comparison. The actual band positions are recorded in Table VII.

The asymmetry of the bands can be interpreted by assuming that the ligand field acting on the ion is not perfectly cubic. Indeed, the inequivalence of the six donor atoms reduces the symmetry of the ligand field

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TABLE VI

Ligand	METAL-HALOGEN STRETCHING VIBRATIONS (IN CM ⁻¹)		
	b ₁ and b ₂		a ₁
	TiCl ₄ adducts		
(CH ₃ SCH ₂ —) ₂	385 vs	370 vs	309 m
(C ₂ H ₅ SCH ₂ —) ₂	389 vs	376 vs	318 w
(C ₆ H ₅ SCH ₂ —) ₂	406 s	383 vs	313 w
(CH ₃ OCH ₂ —) ₂	382 vs	375 vs	309 w
(CH ₃ SCNC≡) ₂	408 vs	391 vs	319 w
2,2'-Bipyridyl ^a	384 vs	366 vs	307 w
<i>o</i> -Phenanthroline ^a	379 vs	356 vs	303 w
	TiBr ₄ adducts		
(CH ₃ SCH ₂ —) ₂	309 vs	299 vs	256 w
(C ₂ H ₅ SCH ₂ —) ₂	310 vs	304 vs	256 w
(C ₆ H ₅ SCH ₂ —) ₂	319 vs	300 vs	260 w
(CH ₃ OCH ₂ —) ₂	315 vs	308 vs	261 w
(CH ₃ SCNC≡) ₂	327 vs	313 vs	290 w
2,2'-Bipyridyl	303 vs	284 vs	253 w
<i>o</i> -Phenanthroline	311 vs	289 vs, br	242 w
	VCl ₄ adducts		
(CH ₃ SCH ₂ —) ₂	345 vs, br		
(C ₂ H ₅ SCH ₂ —) ₂	350 vs	325 vs	276 w
(C ₆ H ₅ SCH ₂ —) ₂	350 vs	333 vs	275 w
(CH ₃ OCH ₂ —) ₂	374 vs	362 vs	...
(CH ₃ SCNC≡) ₂	373 vs	358 vs	299 w
2,2'-Bipyridyl ^a	366 vs	356 vs	301 w
<i>o</i> -Phenanthroline ^a	380 vs	361 vs	298 w
	SnCl ₄ adducts		
(CH ₃ SCH ₂ —) ₂	327 vs	316 vs	288 w
(C ₂ H ₅ SCH ₂ —) ₂	330 vs	325 vs	292 w
(C ₆ H ₅ SCH ₂ —) ₂	334 vs	324 vs	292 w
(CH ₃ OCH ₂ —) ₂	357 vs	336 vs	298 w
(CH ₃ SCNC≡) ₂	350 vs	336 vs	300 w
2,2'-Bipyridyl ^b	327 vs, br		280 s, br
<i>o</i> -Phenanthroline ^b	328 vs, br		275 s, br

^a From ref 6. ^b From ref 14.

to C_{2v}. The effect of the lower C_{2v} (C₂, σ_v) symmetry is that the ground ²T_{2g} term in O_h symmetry is split into three (²B₂, ²B₁, and ²A₂) and the upper ²E_g term is split into two (both ²A₁). It is not possible to specify which of the former is now the ground term, but, in any case, two transitions should be expected in the visible region, from the ground term to the two ²A₁ terms.

The average ligand field strength of the sulfur-donor complexes is ~18,000 cm⁻¹, which is significantly less than that of the oxygen-donor complex (~19,400 cm⁻¹) and certain nitrogen-donor complexes⁶ of the same stoichiometry (~19,600 cm⁻¹). Moreover, the energy difference between the two observed bands (δ¹) is customarily taken as a measure of the deviation of the ligand field from octahedral. As δ¹ is much less for the sulfur-donor complexes (~1000 cm⁻¹) than for oxygen-donor ones (~2000 cm⁻¹) or nitrogen-donor ones (~4000 cm⁻¹), it is evident that the ligand field strength of sulfur approaches that of chloride. This conclusion is supported by the following observation for vanadium tetrachloride; the ligand field strength is¹⁸ 7900 cm⁻¹, and on a 9/4 relationship between 10Dq for six octahedrally disposed and four tetrahedrally disposed ligands, the ligand field strength

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TABLE VII

DIFFUSE REFLECTANCE SPECTRA OF VANADIUM(IV) COMPLEXES

Complex	Peak positions, cm^{-1}		δ^1
$\text{VCl}_4 \cdot (\text{CH}_3\text{SCH}_2^-)_2$	17,400	18,300	900
$\text{VCl}_4 \cdot (\text{C}_2\text{H}_5\text{SCH}_2^-)_2$	17,500	18,500	1000
$\text{VCl}_4 \cdot (\text{C}_6\text{H}_5\text{SCH}_2^-)_2^a$		$\sim 18,200$	
$\text{VCl}_4 \cdot (\text{CH}_3\text{OCH}_2^-)_2$	18,500	20,400	1900
$\text{VCl}_4 \cdot (\text{CH}_3\text{S} \cdot \text{CNC}^-)_2$	17,500	18,500	1000

^a This compound only gave an ill-defined band, and the position of the shoulder could not be estimated.

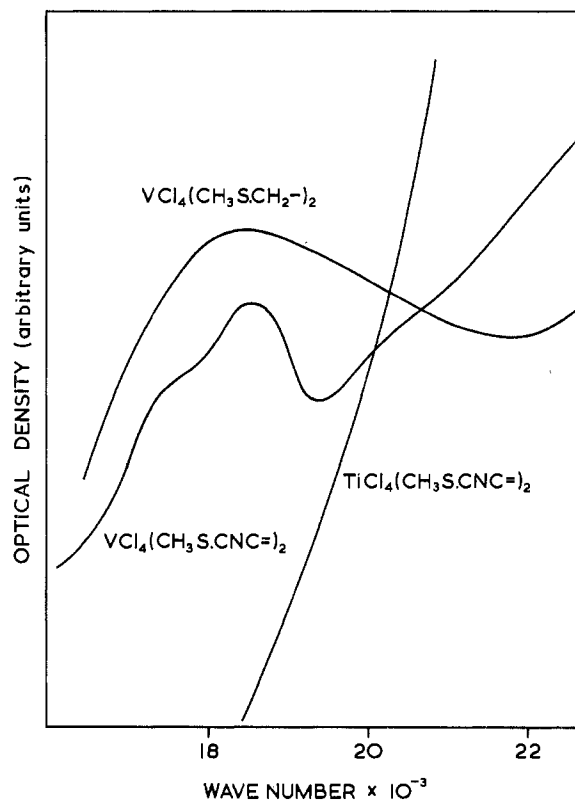


Figure 1.—Diffuse reflectance spectra of the complexes $\text{VCl}_4(\text{CH}_3\text{S} \cdot \text{CH}_2^-)_2$, $\text{VCl}_4(\text{CH}_3\text{S} \cdot \text{CNC}^-)_2$, and $\text{TiCl}_4(\text{CH}_3\text{S} \cdot \text{CNC}^-)_2$.

expected for the VCl_6^{2-} ion would be $\sim 17,800 \text{ cm}^{-1}$, *i.e.*, very close to that actually observed for the bidentate sulfur-donor complexes. Hence, the following spectrochemical series pertains to complexes of vanadium(IV): 2,2'-bipyridyl \sim 1,10-phenanthroline $>$ $(\text{CH}_3\text{O} \cdot \text{CH}_2^-)_2 >$ $(\text{RSCH}_2^-)_2 \geq \text{Cl}^-$.

Structure of the *cis*-Dimethylthiomaleonitrile Complexes.—These complexes are of particular interest since the ligand contains four potential donor atoms. The evidence provided by their diffuse reflectance spectra is that the ligand field strength of this ligand is closely similar to that of the simple bidentate sulfur donors. This information therefore suggests that the *cis*-dimethylthiomaleonitrile ligand coordinates to the metal *via* the sulfur atoms because nitriles are known to have much higher ligand field strengths than sulfur donor ligands.

The infrared evidence, however, apparently contradicts the above view. The infrared absorption bands for the series of complexes are given in Table VIII to-

TABLE VIII

INFRARED SPECTRA OF *cis*-DIMETHYLTHIOMALEONITRILE COMPLEXES

L	$\text{Na}_2(\text{CN}^- \cdot \text{SC})_2^a$	$\text{TiCl}_4 \cdot \text{L}$	$\text{TiBr}_4 \cdot \text{L}$	$\text{VCl}_4 \cdot \text{L}$	$\text{SnCl}_4 \cdot \text{L}$
2198 s	2198 s	2252 s	2247 s	2257 s	2232 s
1493 m	1450 m	1488 m	1488 m	1488 s	1500 s
1433 w, sh	1430 m	1427 m	1451 w	1431 m	1422 m
1421 m			1418 m	1418 m	
1326 w		1325 w	1319 m	1319 w	1321 w
1177 vs	1157 m	1185 s	1185 s	1192 vs	1181 vs
	1118 s				
1094 w		1099 w	1103 w	1097 w	1096 w
1064 w	1056 w	1071 w	1068 w	1074 w	1053 m
1046 w	1018 m	1029 w	1027 w	1021 w	1019 w
	1010 w				
970 m		977 w	976 w	967 w	972 m
		958 w	959 w	955 w	964 w
847 s	857 s	864 s	864 s	866 s	856 vs
		786 s	784 vs	788 s	788 m
			761 vs	766 m	760 vw
703 m				694 w	679 m
610 vw					
	542 w				
508 vs	520 s	518 s	518 s	518 s	515 vs
493 s		493 s	495 s	492 s	495 s

^a $\text{Na}_2(\text{CN}^- \cdot \text{NSC})_2$ is the sodium salt of the ligand maleonitriledithiol.

gether with those of the free ligand. The cyanide stretching frequency (at 2198 cm^{-1} in the free ligand) increases by about 50 cm^{-1} on coordination of the ligand to the metal. This frequency shift is typical of that found for coordinated nitriles. For example, in titanium(IV), tin(IV), and zirconium(IV) complexes¹⁹ with bidentate alkyl cyanides of the type $\text{NC}(\text{CH}_2)_n\text{CN}$, where coordination must take place *via* the cyanide groups, similar shifts of the cyanide stretching frequencies to those observed above have been reported. Moreover, in complexes²⁰ of the type $\text{R}_2(\text{ML}_2)$, where L is the dianion of maleonitriledithiol, X-ray structural investigations²¹ have shown that coordination takes place through the sulfur atoms. For this complex, the cyanide stretching frequencies are scarcely altered from their values in the free ligand (Table VIII). Similarly, in the maleonitriledithiol complex²² $((\text{C}_6\text{H}_5)_4\text{As})_2(\text{VS}_6\text{C}_6(\text{CN})_6)$, the cyanide stretching frequency is the same as that in the free ligand. All the infrared evidence, therefore, is in favor of coordination of the ligand *cis*-dimethylthiomaleonitrile to the metals by way of the nitrogen atoms.

It does not seem to be possible to decide between these contradictory lines of evidence on the mode of bonding of the ligand, and it may be that the molecules are polymeric with both nitrogen and sulfur coordination. The insolubility of the complexes of this ligand would be consistent with their formulation as chain polymers, but unfortunately it did not prove possible to grow any satisfactory crystals for X-ray analysis in order to make a final decision on the structure of the complexes.

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Conclusion

A series of complexes of titanium(IV), vanadium(IV), and tin(IV) with bidentate sulfur-donor ligands has been isolated and characterized. It is shown that, with the possible exception of the complexes of the ligand *cis*-dimethylthiomaleonitrile, the complexes are monomers with metal-sulfur bonding and the *gauche* conformation for the complexed ligand. While no quantitative information is available, the complexes

are apparently of comparable stability to those formed with oxygen-, nitrogen-, and arsenic-donor ligands. This suggests that titanium(IV) is close to the borderline of class A-class B behavior.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF SWARTHMORE COLLEGE, SWARTHMORE, PENNSYLVANIA

Solubility Studies of Tetramethylammonium Salts of Complex Halides. V. Tris(tetramethylammonium) Enneabromodibismuthate(III)

BY JAMES R. PREER¹ AND G. P. HAIGHT, JR.²

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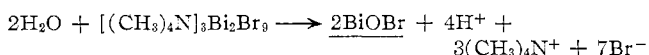
The solubility of $[(\text{CH}_3)_4\text{N}]_3\text{Bi}_2\text{Br}_9$ has been studied over the range $0.000 M < [\text{Br}^-] < 4.0 M$ in $4 M (\text{H}_2\text{SO}_4 + \text{HBr})$ at 25° . The data are interpreted as evidence for equilibria between the solid phase and solutions containing Bi^{3+} , BiBr^+ , BiBr_2^+ , BiBr_4^- , BiBr_5^{2-} , and BiBr_6^{3-} . $\beta_1 = 1500$, $\beta_2 = 9.50 \times 10^4$, $\beta_4 = 6.2 \times 10^8$, $\beta_5 = 9.2 \times 10^{10}$, $\beta_6 = 9.6 \times 10^9$. The spectra of BiBr_5^{2-} and BiBr_6^{3-} show a nearly identical band, $\lambda_{\text{max}} 376 \text{ m}\mu$, $\epsilon_5 \approx 16,000$, $\epsilon_6 \approx 16,900$. No evidence of ion-pair formation between negative BiBr_n^{3-n} complexes and $(\text{CH}_3)_4\text{N}^+$ or H^+ was obtained. The evidence for BiBr_6^{3-} is tenuous, and the existence of this species must be considered still in doubt.

Previous study³ of the solubility of $[(\text{CH}_3)_4\text{N}]_3\text{Bi}_2\text{Cl}_9$ as a function of $[\text{Cl}^-]$ indicated that only BiCl_4^- and BiCl_6^{3-} are present at high $[\text{Cl}^-]$. On finding that only $[(\text{CH}_3)_4\text{N}]_3\text{Bi}_2\text{Br}_9$ precipitates when $(\text{CH}_3)_4\text{NBr}$ is added to solutions of BiOBr in HBr , a study of BiBr_n^{3-n} complex equilibria was undertaken for purposes of comparison with BiCl_n^{3-n} .

Experimental Section

Preparation of $[(\text{CH}_3)_4\text{N}]_3\text{Bi}_2\text{Br}_9$.—Seven grams of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was treated with 5 ml of $8.8 M \text{HBr}$. The mixture was hydrolyzed with 1 l. of H_2O . BiOBr was filtered, washed, and redissolved in $8.8 M \text{HBr}$. $(\text{CH}_3)_4\text{NBr}$ (3.2 g) dissolved in 25 ml of $4 M \text{HBr}$ was slowly added to give hexagonal crystals of $[(\text{CH}_3)_4\text{N}]_3\text{Bi}_2\text{Br}_9$ in 70% yield. The salt, which is stable in air, was dried *in vacuo* at room temperature.

Analysis of the salt for C, H, and N was made by the Clark Microanalytical Laboratory. Analysis for Bi and Br was made by hydrolyzing the salt according to the equation



BiOBr was filtered, dried, and weighed. H^+ was titrated with standard NaOH , and Br^- titrated with Ag^+ .

Anal. Calcd for $[(\text{CH}_3)_4\text{N}]_3\text{Bi}_2\text{Br}_9$: C, 10.5; H, 2.67; N, 3.09; Bi, 30.7; Br, 53.0; H^+ , 2.94 mequiv/g. Found: C, 10.9; H, 2.55; N, 2.94; Bi, 30.9; Br, 53.2; H^+ , 2.92 mequiv/g.

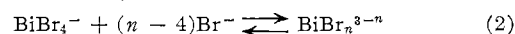
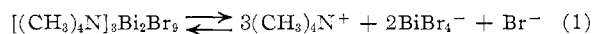
Solubility studies on the salt were done as before³ using a Brønsted saturator in a thermostat regulated at $25.0 \pm 0.1^\circ$. Stock $4 M \text{H}_2\text{SO}_4$ and $4 M \text{HBr}$ were prepared by dilution of concen-

trated acids and standardized against anhydrous sodium carbonate. Mixtures of the stock solutions covering the entire range $0 \leq [\text{Br}^-] \leq 4.0 M$ were prepared as solvents and used immediately. No oxidation of Br^- by $4 M \text{H}_2\text{SO}_4$ was ever observed. Saturated solutions were diluted to give $\sim 10^{-4} M \text{Bi}(\text{III})$ in $6 M \text{HCl}$. Analysis of the dilute solutions was made by measuring absorbance at $328 \text{ m}\mu$ as recommended by Merritt, Hershenson, and Rogers.⁴ Dilutions were so great as to eliminate any interference from Br^- in the original solvent.

The spectra of BiBr_n^{3-n} complexes in HBr were also studied. All spectrophotometric measurements were made with a Beckman D.U. spectrophotometer using 1.000-cm Corex cells.

Working Equations and Definitions of Terms

For purposes of data analysis, the chemical equilibria are assumed



If no polynuclear complexes are formed and the law of mass action holds, the following equations may be derived

$$10.4S^{5/2}[\text{Br}^-]^{1/2} = \frac{K_s^{1/2}}{\beta_4} \sum_0^N \beta_n [\text{Br}^-]^{n-4} \quad (3)$$

$$[\text{Br}^-] = \frac{[\text{Br}^-]_0}{1 + 5 \frac{dS}{d[\text{Br}^-]}} \quad (4)$$

$$\frac{d \log S}{d \log [\text{Br}^-]} = \frac{2\bar{n} - 9}{5} \quad (5)$$

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