case of $Cr(CO)_4L'_2$ was made uncertain by an off-center peak (see ref 5, Figure 2) attributed to a small amount of impurity. The calculated spectra for this compound were observed to be markedly changed by varying J_{PP} in the range of 0–10 cps by as little as 1 cps.

We find as previously stated[5] that J_{PP} appears to follow the order $Fe(CO)_3L'_2 > Mo(CO)_4L'_2 > W(CO)_4L'_2 > Cr(CO)_4L'_2 > Ni(CO)_2L'_2$ for the disubstituted complexes, which is also the order suggested by inspection of the methine proton resonances of the corresponding $P(OCH)_3(CH_2)_3$ complexes shown in Figure 4. Owing to line broadening from coupling to the adjacent methylene protons, a rigorous treatment is more difficult. The increasing intensity at the center of the methine multiplet in the series of complexes of $P(OCH)_3(CH_2)_3$ is qualitatively similar to the behavior of the $X_6AA'X'_6$ system of the corresponding $P(OCH_2)_3CCH_3$ complexes as J_{PP} increases. This is also in the order of tetrahedral < octahedral < trigonal bipyramidal for the geometry of both series of complexes. It is found within the octahedral geometry that P–P coupling follows the order Mo > W > Cr. The shapes of the methine resonances for the tetrahedral nickel compounds are found to progress from a doublet to a relatively broad single peak from di- to tetrasubstitution.

The methine proton is observed to exhibit an upfield shift from the mono- to the disubstituted complexes. Indeed within the $Ni(CO)_{4-x}L_x$ system this upfield shift is observed to continue with the tri- and tetrasubstituted complexes. With respect to σ-bonded compounds of $P(OCH)_3(CH_2)_3$, it is found that these carbonyl compounds and others in which π-bonding is postulated have abnormally high-field proton chemical shifts.[31] Similar trends with respect to chemical shifts and P–P coupling were also observed for the analogous complexes of $P(OCH_2)_3CCH_3$.[5]

Acknowledgment.—J. G. V. thanks the National Science Foundation for a grant (GP-2328) in partial support of this research. Mr. A. Vandenbroucke's experimental assistance is gratefully appreciated.

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Some Donor Properties of 1,4-Thioxane: Complexes with Transition Metal Halides

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Several complexes of 1,4-thioxane with transition metal halides have been prepared and their infrared spectra measured in the region 4000–265 cm^{-1}. By comparison with some analogous 1,4-dithiane and 1,4-dioxane complexes it is concluded that thioxane is sulfur-bonded rather than oxygen-bonded. Possible structures for these complexes are suggested on the basis of their far-infrared spectra. The magnetic susceptibilities and visible spectra of the copper complexes $CuCl_2$·2thioxane, $CuBr_2$·2thioxane, $CuCl_2$·dithiane, and $CuCl_2$·morpholine have been measured and are consistent with distorted octahedral structures.

Introduction

Several heterocyclic donor molecules of the type C_4H_8XY, such as 1,4-dioxane, 1,4-thioxane, 1,4-dithiane, and piperazine form a variety of complexes with transition and nontransition metal halides.[1–6] Infrared spectra measurements have shown[5,6] that the coordinated C_4H_8XY molecules invariably retain the "*chair*" conformation that is shown by the free ligands. Thus the infrared spectrum of 1,4-dioxane[7] and an X-ray analysis of 1,4-dithiane[8] show that these molecules have the "*chair*" rather than the "*boat*" conformation.

Of the above ligands 1,4-thioxane is particularly interesting since this molecule possesses oxygen and sulfur donor atoms in virtually identical, sterically unhindered positions. Several complexes of 1,4-thioxane with metal halides have therefore been prepared and their infrared spectra measured, and an attempt has been made to correlate the donor properties of 1,4-thioxane with the acceptor properties of the halides.

The relative affinities of ligand atoms for acceptor molecules and ions have been reviewed,[9] and it has been concluded that two types of acceptors exist: "class A, which form their most stable complexes with the first ligand atom of each group, *i.e.*, N, O, and F,

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* Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

[1] H. Rheinboldt, A. Luyken, and H. Schmittmann, *J. Prakt. Chem.*, **149**, 30 (1957).

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[4] F. G. Mann and H. R. Watson, *J. Chem. Soc.*, 2772 (1958).

[5] P. J. Hendra and D. B. Powell, *ibid.*, 5105 (1960).

[6] P. J. Hendra and D. B. Powell, *Spectrochim. Acta*, **18**, 299 (1962).

[7] D. A. Ramsay, *Proc. Roy. Soc.* (London), **A190**, 562 (1947).

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and class B, those which form their most stable complexes with the second or a subsequent ligand atom." A study of thioxane complexes should therefore enable class A and B acceptors to be differentiated if they are oxygen- and sulfur-bonded, respectively.

Experimental Section

The metal halides, 1,4-thioxane, and 1,4-dioxane were reagent grades and were used as supplied. Dr. G. W. A. Fowles kindly supplied a sample of 1,4-dithiane.

The purest available grades of methyl cyanide, nitromethane, and acetone were used for conductivity and spectral measurements.

Preparation of Complexes.—The titanium complexes $TiCl_4\cdot 2C_4H_8OS$, $TiBr_4\cdot 2C_4H_8OS$, and $TiCl_3\cdot C_4H_8OS$ have been reported elsewhere.[10,11] Complexes of the dihalides with thioxane, dithiane, dioxane, and morpholine precipitated on mixing ethanolic solutions of the reactants.[1-5] The complexes were filtered off and washed with ethanol and ether. Of the 1,4-dioxane and 1,4-dithiane complexes only $CdBr_2\cdot C_4H_8O_2$ has not previously been reported.

Anal. Calcd for $CdBr_2\cdot C_4H_8O_2$: C, 14.54; H, 2.44; O, 9.69. Found: C, 13.96; H, 2.48; O, 9.46.

The following thioxane complexes were prepared.

$CuCl_2\cdot 2C_4H_8OS$.—Lustrous green plates. *Anal.* Calcd for $CuCl_2\cdot 2C_4H_8OS$: C, 28.03; H, 4.71; S, 18.71. Found: C, 28.19; H, 4.84; S, 18.57.

$CuBr_2\cdot 2C_4H_8OS$.—Dark brown crystals. *Anal.* Calcd for $CuBr_2\cdot 2C_4H_8OS$: C, 22.26; H, 3.74; S, 14.84; Br, 37.01. Found: C, 21.51, 22.49; H, 3.61; 3.94; S, 14.18; 14.14; Br, 36.01, 36.04. When boiled with acetone this complex rapidly turned to a dirty white crystalline solid which was shown to be $CuBr_2\cdot C_4H_8OS$. *Anal.* Calcd for $CuBr\cdot C_4H_8OS$: C, 19.40; H, 3.26; N, 12.94. Found: C, 19.49; H, 3.35; N, 12.90.

$HgCl_2\cdot 2C_4H_8OS$.—White feathery crystals. *Anal.* Calcd for $HgCl_2\cdot 2C_4H_8OS$: C, 20.03; H, 3.36; S, 13.36; Cl, 14.78. Found: C, 19.91; H, 3.14; S, 13.18; Cl, 14.89.

$CdBr_2\cdot 2C_4H_8OS$.—White crystals. *Anal.* Calcd for $CdBr_2\cdot 2C_4H_8OS$: C, 20.00; H, 3.36; S, 13.35. Found: C, 19.80; H, 3.29; S, 13.88.

$PdCl_2\cdot 2C_4H_8OS$.—Bright yellow solid. *Anal.* Calcd for $PdCl_2\cdot 2C_4H_8OS$: C, 24.90; H, 4.18; S, 16.62. Found: C, 24.97; H, 4.21; S, 16.68.

$PtCl_2\cdot 2C_4H_8OS$.—Pale yellow solid. *Anal.* Calcd for $PtCl_2\cdot 2C_4H_8OS$: C, 20.25; H, 3.40; S, 13.51. Found: C, 20.73; H, 3.44; S, 12.23.

$PtBr_2\cdot 2C_4H_8OS$.—Pale orange-yellow solid. *Anal.* Calcd for $PtBr_2\cdot 2C_4H_8OS$: C, 17.06; H, 2.86. Found: C, 17.65; H, 2.83.

$AgNO_3\cdot C_4H_8OS$.—White light-sensitive needles. *Anal.* Calcd for $AgNO_3\cdot C_4H_8OS$: C, 17.52; H, 2.94; S, 11.69. Found: C, 17.47; H, 3.61; S, 11.41. This complex was insoluble in nitromethane, nitrobenzene, and acetone but could be recovered unchanged from methyl cyanide. In this latter solvent a 3.43×10^{-3} *M* solution had a molar conductivity of 146 ohm^{-1} cm^2.

$AgClO_4\cdot 3C_4H_8OS$.—White light-sensitive crystals. *Anal.* Calcd for $AgClO_4\cdot 3C_4H_8OS$: C, 27.71; H, 4.65; S, 18.49. Found: C, 27.52; H, 4.52; S, 18.04. A 1.37×10^{-3} *M* solution of this complex in methyl cyanide had $\Lambda_M = 171$ ohm^{-1} cm^2.

$CuClO_4\cdot 3C_4H_8OS$.—The hydrate $Cu(ClO_4)_2\cdot xH_2O$ was dissolved in ethanol and a few milliliters of thioxane added. The green solution was evaporated to leave a sticky white crystalline solid. Ethanol was added, and the crystalline product was filtered off and washed with acetone, ethanol, and ether. *Anal.* Calcd for $CuClO_4\cdot 3C_4H_8OS$: C, 30.31; H, 5.09; S, 20.22. Found: 29.86; H, 5.08; S, 20.66. The complex could be recovered unchanged from acetone and a 1.96×10^{-3} *M* solution in nitromethane had $\Lambda_M = 69$ ohm^{-1} cm^1.

The morpholine complex $CuCl_2\cdot C_4H_9ON$ was precipitated as a yellow-green powder. *Anal.* Calcd for $CuCl_2\cdot C_4H_9ON$: C, 21.58; H, 4.09; N, 6.29. Found: C, 22.10; H, 4.30; N, 6.23.

The infrared spectrum of this complex showed bands at 3500 and 3390 cm^{-1} indicating a small amount of contamination with basic salts. In fact, addition of water to the complex gave a blue-green powder which was insoluble in all solvents tried and which contained only a trace of morpholine. *Anal.* Found: C, 0.7; H, 1.6; N, ~0.

Infrared Spectra.—These were measured on Nujol mulls using Perkin-Elmer 237 (4000–650 cm^{-1}) and Perkin-Elmer 221 (700–265 cm^{-1}) spectrophotometers equipped with sodium chloride and cesium bromide optics, respectively. In the latter region samples were studied between polythene plates.

Diffuse Reflectance and Solution Spectra.—These were measured in the region 2500–350 mμ on a Beckman DK2A spectrophotometer.

Conductivity.—Determinations were carried out at 25° using a Philips PR9500 bridge.

Magnetic Susceptibility.—Measurements were carried out at room temperature by the Gouy procedure. The susceptibility of $CuCl_2\cdot 2C_4H_8OS$ was measured over a temperature range using the apparatus described by Figgis and Nyholm.[12]

Results and Discussion

(1) **Infrared Spectra (4000–500 Cm.$^{-1}$).**—The infrared spectra of 1,4-thioxane and its metal halide complexes were recorded in the region 4000–500 cm^{-1} and the principal absorption bands between 1350 and 500 cm^{-1} were as follows. **1,4-Thioxane:** 1320 m, 1286 s, 1270 w, 1214 m, 1201 m, 1178 m, 1105 vs, 1052 wm, 1012 s, ~995 sh, 975 ms, ~960 sh, 834 s, 815 w, 693 m, 664 s, 613 vw, 588 s. **$CuCl_2\cdot 2C_4H_8OS$:** 1350 sh, 1312 w, 1303 w, 1272 ms, 1254 w, 1202 w, 1183 m, 1154 m, 1095 s, 1043 m, 1000 sh, 991 s, 965 m, 819 vw, 808 sh, 658 m, 562 s. **$CuBr_2\cdot 2C_4H_8OS$** 1350 sh, 1313 m, 1300 sh, 1276 m, 1271 s, 1247 w, 1203 m, 1188 w, 1176 ms, 1156 w, 1147 m, 1096 vs, 1040 m, 1008 sh, 998 ms, 991 m, 985 ms, 963 ms, 940 w, 819 m, 810 sh, 652 w, 563 m. **$PdCl_2\cdot 2C_4H_8OS$:** 1350 vw, 1313 wm, ~1300 vw, 1280 m, 1271 m, 1262 m, 1214 mw, 1196 m, 1192 m, 1160 m, 1095 s, 1050 m, 1003 sh, 999 m, 992 m, 975 m, 970 m, 822 m, 813 sh, 690 vw, 649 w, 571 s. **$PtCl_2\cdot 2C_4H_8OS$:** 1350 vw, 1309 m, 1290 vw, 1279 s, 1250 w, 1203 m, 1178 s, 1147 s, 1099 vs, 1044 s, 999 s, 986 s, 968 s, 942 w, 822 ms, 810 sh, 694 vvw, 649 w, 575 mw, 567 ms. **$PtBr_2\cdot 2C_4H_8OS$:** 1350 sh, 1312 m, 1272 s, 1250 w, 1205 m, 1180 s, 1148 s, 1100 vs, 1046 s, 1002 s, 990 s, 968 w, 945 w, 823 ms, 815 sh, 647 vw, 573 m. **$HgCl_2\cdot 2C_4H_8OS$:** 1340 sh, 1316 m, 1293 vw, 1278 s, 1254 w, 1210 m, 1186 m, 1153 m, 1100 vs, 1086 sh, 1047 wm, 1007 m, 1001 s, 996 m, 990 sh, 963 s, 948 w, 822 m, 810 w, 685 vvw, 647 w, 562 m. **$CdBr_2\cdot 2C_4H_8OS$:** ~1350 sh, 1318 m, ~1300 vw, 1280 ms, 1256 w, 1210 m, 1186 m, 1155 m, 1100 vs, 1071 w, 1048 wm, 1006 m, 1002 s, 996 m, 990 sh, 962 s, 948 w, 822 ms, 810 w, 683 w, 648 w, 561 ms. **$TiCl_3\cdot C_4H_8OS$:** 1332 m, 1310 w, 1291 m, 1278 m, 1258 w, 1218 m, 1168 m, ~1100 w, 1057 s, 1013 s, 984 s, 958 s, 858 m, 818 vs, 804 vs, 680 wm, 653 wm, 615 wm, 567 s. **$TiX_4\cdot 2C_4H_8OS$** (X = Cl or Br): 1316 m, 1281 s, 1259 m, 1212 m, 1196 m, 1161 s,

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(10) G. W. A. Fowles, R. A. Hoodless, and R. A. Walton, *J. Chem. Soc.*, 5873 (1963).

(11) G. W. A. Fowles and R. A. Walton, *ibid.*, 4330 (1964).

(12) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 331 (1959).

1105 s, 1050 m, 1007 s, 977 s, 898 vw, 840 m, 830 m, 818 w, 690 w, 653 m, 563 s.

The spectra of $MCl_2 \cdot 2C_4H_8OS$ (M = Cu, Hg, and Pt) agree well with those previously reported,[5] except that in the present work several bands were found to be split. Georgieff and Dupré have reported[13a] the infrared spectrum of 1,4-thioxane and this is identical with the spectrum obtained here except that no band was observed at 865 cm^{-1} in the present study.

With the exception of $TiCl_3 \cdot C_4H_8OS$, all the thioxane complexes had spectra which were similar to that of the free ligand.[13b] With 1,4-dioxane and its complexes, the formation of the less symmetrical "boat" conformer should lead to a more complex spectrum.[5,7] However, the "boat" and "chair" conformations of 1,4-thioxane have the same basic symmetry (C_s), so at first sight we would expect their spectra to be more complex than the more symmetrical dioxane analogs. A ready distinction between the "boat" and "chair" conformers of 1,4-thioxane is unlikely because of their low symmetry. The tendency of ligands of the type C_4H_8XY to have the "chair" conformation and the stoichiometry of the thioxane complexes reported here suggests that this conformation is retained.

For comparison purposes the spectra of several metal halide complexes of 1,4-dioxane and 1,4-dithiane were recorded. In the case of $HgCl_2 \cdot C_4H_8O_2$ and $CdBr_2 \cdot C_4H_8O_2$, the spectra were virtually identical with those reported by other workers[5,14a] and are not recorded here. However, dithiane and the complexes $MCl_2 \cdot C_4H_8S_2$ (M = Cu, Pt, and Hg) had spectra which were slightly different from those reported by Hendra and Powell;[5] in particular bands at 1294 w, 1273 m, and ~975 w, br for dithiane were not reported by these workers. The spectrum of $PtCl_2 \cdot C_4H_8S_2$ differed significantly from that of 1,4-dithiane and its other complexes, suggesting that in this molecule dithiane may be in the "boat" conformation.[14b] It has been proposed that the analogous complexes of platinum(II) and palladium(II) halides with 1,4-diselenane[15,16] have a similar structure.

By comparison with the infrared spectra of 1,4-dioxane and 1,4-dithiane complexes it should be possible to gain some information on the bonding of 1,4-thioxane in its complexes with metal halides (*i.e.*, oxygen- or sulfur-bonded). These two possibilities are now considered separately.

(a) **Oxygen Bonded.**—The antisymmetric and symmetric C–O–C stretching frequencies of 1,4-thioxane are assigned to the very strong sharp bands at 1105 and 834 cm^{-1}, respectively. In the complexes $TiX_4 \cdot C_4H_8O_2$, bands associated with ν_{C-O-C} are split and lowered in frequency (Figure 1) compared with the free ligand.[10,17] We would therefore expect that when thioxane is oxygen-bonded these bands (1105 and 834 cm^{-1}) should be similarly modified. In all the thioxane complexes reported, except $TiCl_3 \cdot C_4H_8OS$,[10] these bands are virtually unaltered (Figure 2) although they both suffer a slight decrease in frequency (10 cm^{-1} or less). This is good evidence that thioxane is not oxygen bonded.

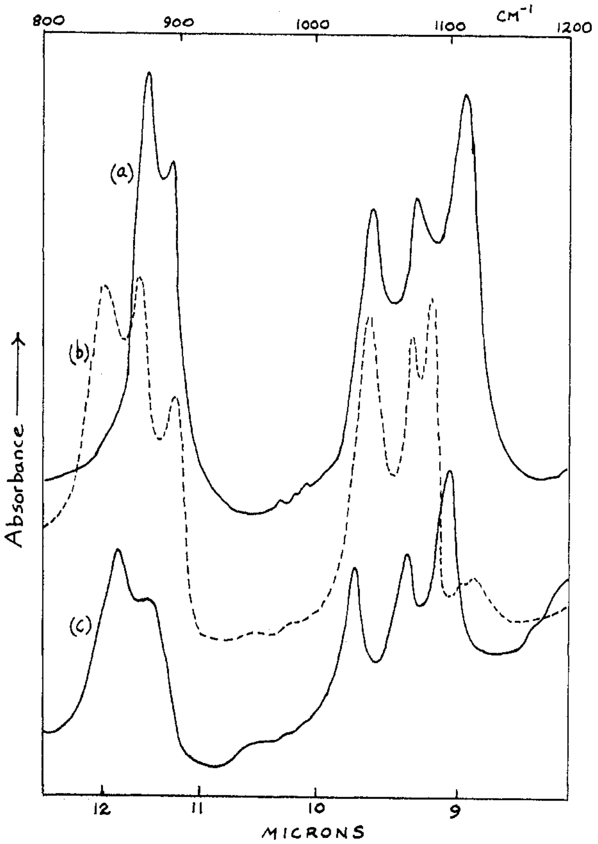

Figure 1.—Infrared spectra (1200–800 cm^{-1}) of: (a) 1,4-dioxane as a liquid film; (b) $TiCl_4 \cdot C_4H_8O_2$ in Nujol mull; (c) $HgCl_2 \cdot C_4H_8O_2$ in Nujol mull.

However, in $HgCl_2 \cdot C_4H_8O_2$ and some other 1,4-dioxane complexes[5,14a] the bands associated with ν_{C-O-C} are only slightly modified compared with the free ligand [ν_{sym}(C–O–C) is lowered by 20–30 cm^{-1} on complex formation] even though $HgCl_2 \cdot C_4H_8O_2$ is known to be polymeric with dioxane bridging.[18] This may arise from the presence of a longer, weaker metal–oxygen bond in these complexes. Thus an unambiguous assignment is not possible in all cases and a further complicating feature is that although an ether group may not be bonded to a metal, interactions in the solid state may modify the C–O–C vibrations of the "free" ether and so give the effect of a bonded group. Figure 1 shows the infrared spectra in the region 1200–800 cm^{-1} of the polymeric complexes $TiCl_4 \cdot C_4H_8O_2$ and $HgCl_2 \cdot C_4H_8O_2$.

(b) **Sulfur Bonded.**—Both the Raman[19] and infra-

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[13] (a) K. K. Georgieff and A. Dupré, *Can. J. Chem.*, **37**, 1104 (1959). (b) In their study of the infrared spectra of complexes of metal halides with 1,4-dioxane, 1,4-dithiane, and 1,4-thioxane, Hendra and Powell[5] were principally concerned with the conformation of the donor molecules on complex formation. The possibility that 1,4-thioxane was oxygen- or sulfur-bonded was not investigated.

[14] (a) P. Tarte and P. A. Laurent, *Bull. Soc. Chim. France*, 403 (1957). (b) The spectra of 1,4-dithiane and its complexes are illustrated in ref 5 and are essentially the same as those recorded in the present work.

[15] P. J. Hendra and D. B. Powell, Abstracts, 7th International Conference on Coordination Chemistry, 1962, p 220.

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[19] P. A. Akishin and N. G. Rambidi, *Dokl. Akad. Nauk SSSR*, **102**, 745 (1955).

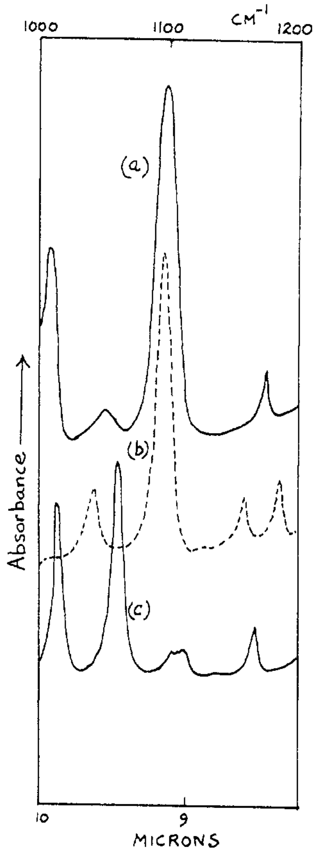

Figure 2.—Infrared spectra (1200–1000 cm^{-1}) of: (a) 1,4-thioxane as a liquid film; (b) CuCl$_2$·2C$_4$H$_8$OS in Nujol mull; (c) TiCl$_3$·C$_4$H$_8$OS in Nujol mull.

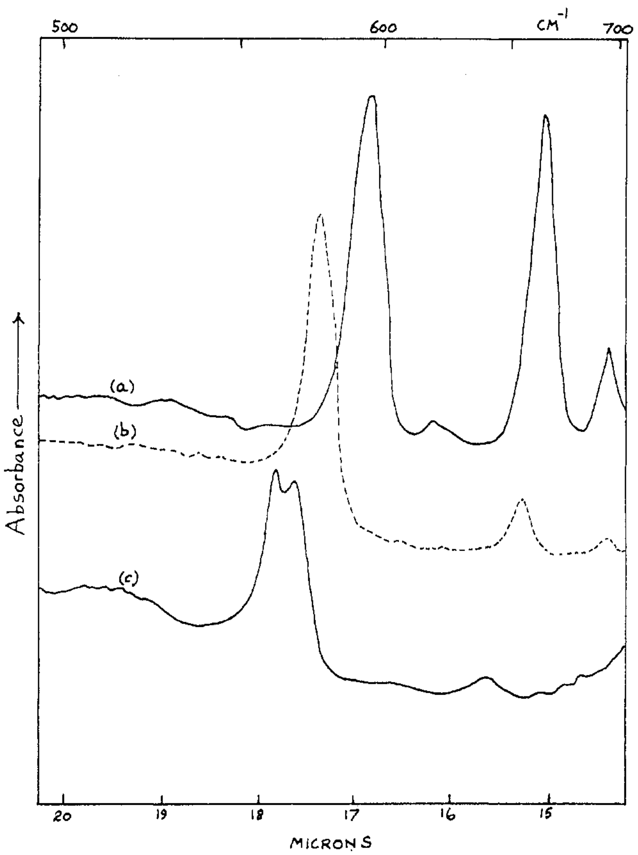

Figure 3.—Infrared spectra (700–500 cm^{-1}) of: (a) 1,4-thioxane as a liquid film; (b) PdCl$_2$·2C$_4$H$_8$OS in Nujol mull; (c) PtCl$_2$·2C$_4$H$_8$OS in Nujol mull.

red spectra of 1,4-thioxane show fairly strong bands at 693 and 664 cm^{-1} which are assigned to the C–S stretching modes. In all the thioxane complexes studied both bands suffer a lowering in frequency and decrease in intensity, and in several cases the 693 cm^{-1} band is not observed.

With 1,4-dithiane complexes a strong band at 665 cm^{-1} in the free ligand is lowered by about 10 cm^{-1} on complex formation and in PtCl$_2$·C$_4$H$_8$S$_2$ is observed very weakly although a stronger band occurs at 623 cm^{-1}. In the case of dithiane complexes these band modifications must be typical of the coordinated C–S–C group. This suggests that the spectra of the thioxane complexes in the 700–600 cm^{-1} region (Figure 3) are characteristic of sulfur-bonded thioxane.

Nuclear magnetic resonance measurements[11] on TiX$_4$·2C$_4$H$_8$OS and a crystal structure determination of dichlorobis(phenoxathiin)mercury[20] show that in these molecules the ligand is sulfur- rather than oxygen-bonded. In the present work a study of ligand vibrations in the 1300–500 cm^{-1} region provides evidence that the thioxane molecules are probably only sulfur-bonded (except in TiCl$_3$·C$_4$H$_8$OS).[10]

The infrared spectra of the complexes AgNO$_3$·C$_4$H$_8$OS and MClO$_4$·3C$_4$H$_8$OS, where M = Cu or Ag, showed bands typical of other thioxane complexes. For example, the perchlorate complexes had bands at 685 (w), 654 (w), and 559 (m) cm^{-1} which indicated that in these complexes 1,4-thioxane was sulfur-bonded. In addition both complexes showed a band at 1100–1110 cm^{-1}, assigned to ν_{C-O-C}, close to the perchlorate absorption at 1070 cm^{-1} in AgClO$_4$·3C$_4$H$_8$OS and at 1100 cm^{-1} in CuClO$_4$·3C$_4$H$_8$OS. Below 700 cm^{-1}, a strong band (ν_4) at 620 cm^{-1} confirmed the presence of ionic perchlorate since coordinated perchlorates of the type –O–ClO$_3$ generally have two bands in this region (ν_3, ν_5).[21]

The conductivity and infrared spectral data of the perchlorate complexes clearly show their ionic nature. The analogous dioxane complex, AgClO$_4$·3C$_4$H$_8$O$_2$, is known,[22] and a crystal structure determination has shown[23] that silver atoms, at the corners of a cube, are each surrounded by a regular octahedron of dioxane oxygen atoms. A similar structure is possible for the thioxane complexes MClO$_4$·3C$_4$H$_8$OS.

The thioxane complex of silver nitrate behaves as a 1:1 electrolyte in methyl cyanide and its infrared spectrum has a strong band at 1380 cm^{-1} typical of the nitrate ion.[24] An equally intense band at 1300 cm^{-1} may arise from some lowering in symmetry of the planar NO$_3{}^-$ ion in the crystal.

General Discussion.—Metal halides have been divided into classes A and B, depending upon their ac-

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TABLE I

FAR-INFRARED SPECTRA OF 1,4-THIOXANE AND RELATED COMPLEXES (500–265 cm^{-1})

Compound	Ligand vibrations	ν(M–X)	ν(M–L)	Ref
1,4-Thioxane	389 s, 340 w	. . .	. . .	*a, b*
$TiCl_4 \cdot 2C_4H_8OS$	433 w, 364 w	385 vs, 311 wm	. . .	*a, b*
$TiBr_4 \cdot 2C_4H_8OS$	392 w, 368 mw, 358 mw	~300 vs, br	. . .	*a, b*
$CuCl_2 \cdot 2C_4H_8OS$	368 vw	332 s	. . .	*c*
$CuBr_2 \cdot 2C_4H_8OS$	402 w, 377 w	~265 s, br[e]	. . .	*c*
$HgCl_2 \cdot 2C_4H_8OS$	406.5 mw, 366 mw, 356 sh	<250	. . .	*c*
$CdBr_2 \cdot 2C_4H_8OS$	405 m, 366 m	<250	. . .	*c*
$PdCl_2 \cdot 2C_4H_8OS$	416 m, 382 m	353 s	275 ms, 267 sh	*c*
$PtCl_2 \cdot 2C_4H_8OS$	455 m, 430 m	332 vs, 320.5 vs, 305 sh?	289 w	*c*
$PtBr_2 \cdot 2C_4H_8OS$	416 w, ~391 w	<250	. . .	*c*
$CuClO_4 \cdot 3C_4H_8OS$	372 w	. . .	. . .	*c*
$AgClO_4 \cdot 3C_4H_8OS$	399 w, ~360 vw, br	. . .	. . .	*c*
$AgNO_3 \cdot C_4H_8OS$	409 vw	. . .	. . .	*c*
1,4-Dioxane	283 m, 273 m	. . .	. . .	*d*
$TiCl_4 \cdot C_4H_8O_2$	329 w, 316.5 w, ~303 w	391 s, 340 m	. . .	*b*
$HgCl_2 \cdot C_4H_8O_2$[f]	. . .	286 vs	~373 sh, 351.5 vs	*c*
$CdBr_2 \cdot C_4H_8O_2$	305 sh	<250	286 vs[g]	*c*
1,4-Dithiane	470 w	. . .	. . .	*c*
$CuCl_2 \cdot C_4H_8S_2$	485 vw, 306 vw	329 s, <270 br[e]	. . .	*c*
$HgCl_2 \cdot C_4H_8S_2$	483 m	<270 br[e]	. . .	*c*
$PtCl_2 \cdot C_4H_8S_2$	~375 w, br	319 s, 305 w, sh	. . .	*c*

[a] G. W. A. Fowles and R. A. Walton, *J. Chem. Soc.*, 4953 (1964). [b] I. R. Beattie and M. Webster, *ibid.*, 3507 (1964). [c] This work. [d] F. E. Halherbe and H. J. Bernstein, *J. Am. Chem. Soc.*, **74,** 4408 (1952). [e] At limit of the measurements (38 μ). [f] Previously measured by P. Tarte and P. A. Laurent, *Bull Soc. Chim. France*, 403 (1957). [g] Probably a doublet.

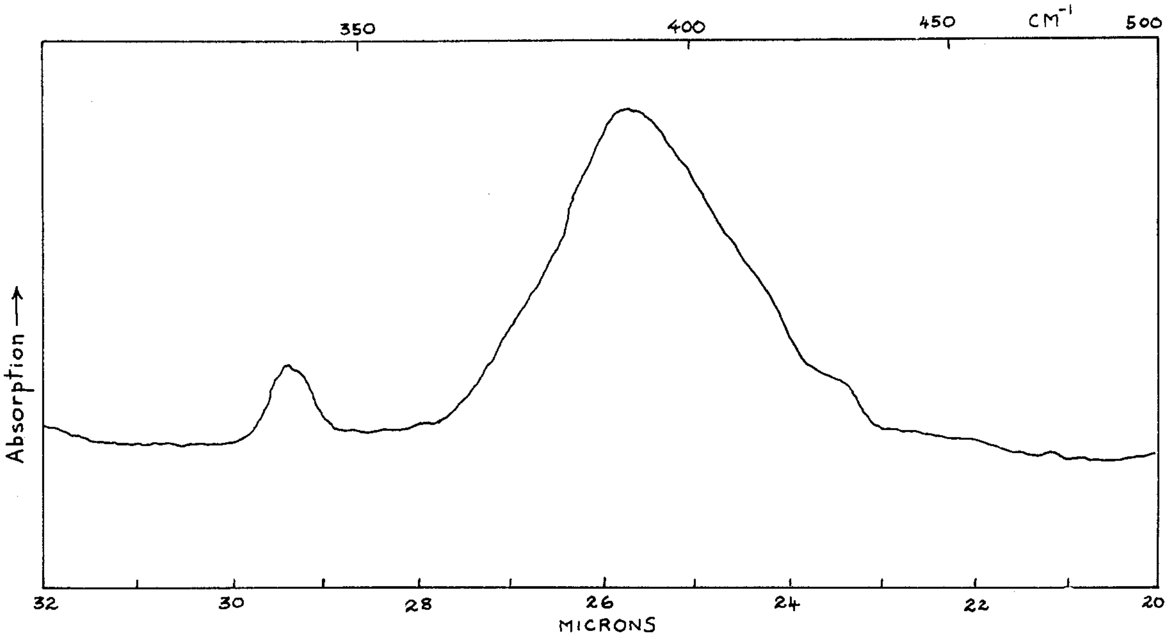

Figure 4.—Infrared spectrum (500–310 cm^{-1}) of 1,4-thioxane as a liquid film.

ceptor properties.[9] π bonding between the metal halide and the donor atom is believed to largely determine whether the metal halide shows class A or B character. Thus while titanium(IV) should show class A behavior and palladium(II), silver(I), platinum(II), and mercury(II) belong to class B, copper(II) and cadmium(II) should be of intermediate type, *i.e.*, A or B possible.

1,4-Thioxane would be expected to be sulfur-bonded to all the above halides except titanium(IV), if π bonding between the metal and sulfur is the main factor which determines preferential bond formation. The formation of stable sulfur-bonded complexes with titanium(IV) halides suggests that polarization of the sulfur lone pair by the metal ion may be an important factor in determining whether thioxane is sulfur- rather than oxygen-bonded. Titanium(IV) halides in fact form a variety of complexes with sulfur ligands.[25, 26]

(2) **Far-Infrared Spectra.**—The infrared spectral data in the region 500–265 cm^{-1} are listed in Table I and typical spectra are shown in Figures 4–6. In Table I assignments have been made of the ν(M–X) and ν(M–L) modes, although the latter are regarded as tentative and probably involve only partial metal–ligand stretching character. The ligand vibrations are usually the less intense bands in this region, but

(25) K. Baker and G. W. A. Fowles, *Proc. Chem. Soc.*, 362 (1964).

(26) K. Baker and G. W. A. Fowles, *J. Less-Common Metals*, **8**, 47 (1965).

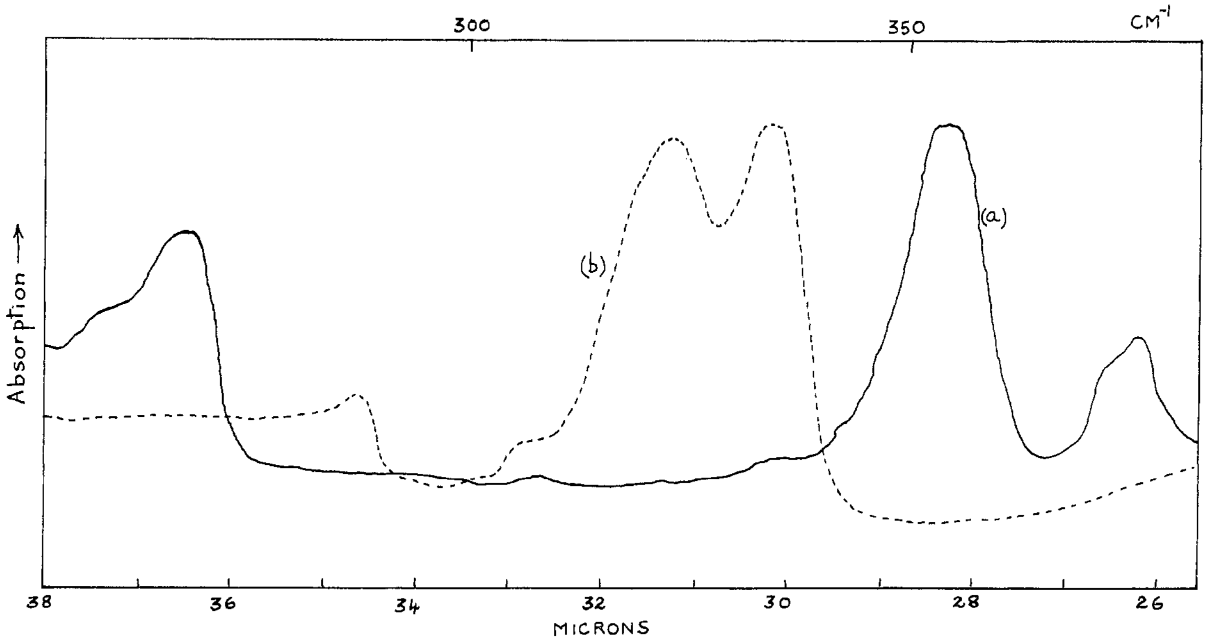

Figure 5.—Infrared spectra (385–265 cm^{-1}) of: (a) $PdCl_2{\cdot}2C_4H_8OS$ and (b) $PtCl_2{\cdot}2C_4H_8OS$ in Nujol mulls.

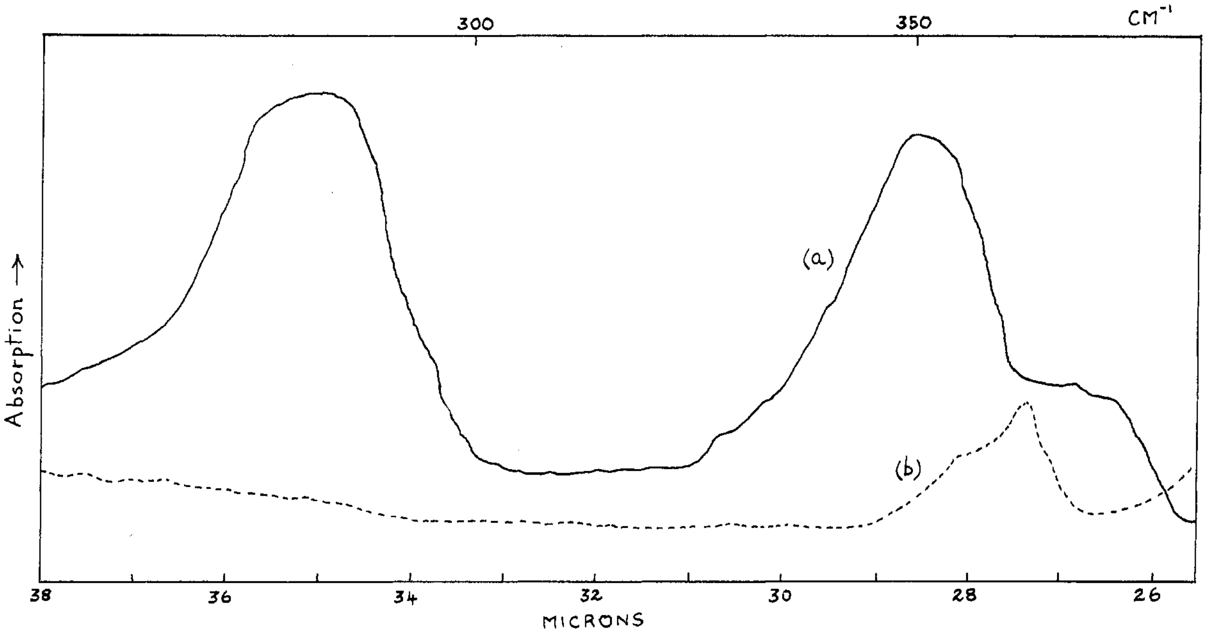

Figure 6.—Infrared spectra (385–265 cm^{-1}) of: (a) $HgCl_2{\cdot}C_4H_8O_2$ and (b) $HgCl_2{\cdot}2C_4H_8OS$ in Nujol mulls.

in the case of free 1,4-thioxane a strong band is observed at 389 cm^{-1}, although this is considerably reduced in intensity in the complexes. The ring bending vibrations of 1,4-dioxane (B_u symmetry) at 273 (ν_{19}) and 283 (ν_{28}) cm^{-1} occur very weakly in the complexes and should not interfere with the assignment of the ν(M–X) and ν(M–L) vibrations.

As expected the complexes $MClO_4{\cdot}3C_4H_8OS$ (M = Cu and Ag) and $AgNO_3{\cdot}C_4H_8OS$ only show bands associated with modified ligand vibrations in this region. The remaining complexes usually had bands due to ν(M–X) and are best considered separately.

$CuCl_2{\cdot}C_4H_8S_2$ and $CuX_2{\cdot}2C_4H_8OS$.—The former complex shows two ν(Cu–Cl) modes separated by ~60 cm^{-1}. It is reasonable to assign these to terminal (329 cm^{-1}) and bridging (~270 cm^{-1}) Cu–Cl units, respectively, by analogy with other complexes of copper(II) halides.[27] Similarly strong bands at 332 and ~265 cm^{-1} for the chloride and bromide complexes of $CuX_2{\cdot}2C_4H_8OS$ are assigned to the ν(Cu–X) vibrations associated with nonbridging Cu–X units, *i.e.*, ν(Cu–Br)/ν(Cu–Cl) ~ 0.8.

$PtCl_2{\cdot}C_4H_8S_2$, $PdCl_2{\cdot}2C_4H_8OS$, and $PtX_2{\cdot}2C_4H_8OS$.—From a study of the ligand vibrations, $PtCl_2{\cdot}C_4H_8S_2$ has been suggested to have a *cis*-planar configuration with 1,4-dithiane in the "boat" conformation. We would therefore expect two ν(Pt–Cl) bands[28] below 400

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[27] M. Goldstein, E. F. Mooney, A. Anderson, and H. A. Gebbie, *Spectrochim. Acta*, **21**, 105 (1965).

[28] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964).

cm^{-1} and those at 319 and 305 (shoulder) cm^{-1} are accordingly assigned to these modes, although the latter is rather weak.

A strong band at 353 cm^{-1} for $PdCl_2 \cdot 2C_4H_8OS$ suggests a *trans*-planar configuration, whereas $PtCl_2 \cdot C_4H_8OS$ is probably *cis* with ν(Pt–Cl) at 332 and 320.5 cm^{-1}.

$HgCl_2 \cdot C_4H_8S_2$, $HgCl_2 \cdot C_4H_8O_2$, and $CdBr_2 \cdot C_4H_8O_2$.—For $HgCl_2 \cdot C_4H_8S_2$, ν(Hg–Cl) is assigned to a broad absorption below ~270 cm^{-1}. A six-coordinate polymeric structure with halogen and dithiane bridges is likely. The pyridine complex $HgCl_2 \cdot 2py$, which is known[29] to have bridging chlorines, has ν(Hg–Cl) at 292 cm^{-1}.[30]

The polymeric complex of 1,4-dioxane with mercuric chloride has strong bands at 351.5 (shoulder at ~373 cm^{-1}) and 286 cm^{-1} which are probably associated with ν(Hg–Cl) and/or ν(Hg–O). Since r(Hg–Cl) = 2.34 A in $HgCl_2 \cdot C_4H_8O_2$ and for the two short Hg–Cl distances of $HgCl_2 \cdot 2py$,[29] the strong band at 286 cm^{-1} is accordingly assigned to ν(Hg–Cl). The alternative assignment of ν(Hg–Cl) to the 351.5 cm^{-1} band is ruled out since this mode is unlikely to occur at such a high frequency.

$CdBr_2 \cdot 2C_4H_8OS$ and $HgCl_2 \cdot 2C_4H_8OS$.—Dichlorobis(thioxane)mercury showed no bands associated with ν(Hg–Cl) above 265 cm^{-1} and may have a polymeric structure with chlorine bridging; *cf.* dichlorobis(phenoxathiin)mercury.[20]

(3) **Magnetic Susceptibilities.**—The magnetic moments of the copper(II) complexes $CuCl_2 \cdot C_4H_9ON$, $CuCl_2 \cdot C_4H_8S_2$, $CuCl_2 \cdot 2C_4H_8OS$, and $CuBr_2 \cdot 2C_4H_8OS$ were 1.97, 1.81, 1.84, and 1.88 BM, respectively, at room temperature, typical of octahedral copper(II).[31]

The magnetic susceptibility of $CuCl_2 \cdot 2C_4H_8OS$ was measured over a temperature range (298–78°K), and the moment was found to be virtually independent of temperature, falling from 1.84 to 1.81 BM over this range. As expected this confirmed the absence of any tetrahedral species since an unperturbed $^2T_2$ ground term should give rise to a variation of μ_{eff} with temperature. With a large distortion the moment should become temperature independent. A plot of $1/\chi^1m$ against temperature gave a straight line with $\theta = +8°$ and showed the absence of any significant magnetic exchange in this complex.

(4) **Visible Spectra.**—The diffuse reflectance and solution spectra of the copper(II) complexes (Table II) are typical of distorted octahedral copper(II).[32,33]

TABLE II

VISIBLE ABSORPTION SPECTRA OF COPPER(II) COMPLEXES

Compound	State	Peak positions, mμ ($\epsilon_{\max}$)
$CuCl_2 \cdot 2C_4H_8OS$	Solid	640, 488, 412
$CuCl_2 \cdot 2C_4H_8OS$	Acetone	860 (59), 474 (370), <350
$CuBr_2 \cdot 2C_4H_8OS$	Solid	~725 sh, 494, 380
$CuCl_2 \cdot C_4H_9ON$	Solid	845, 745, ~430 sh, 356
$CuCl_2 \cdot C_4H_9ON$	Acetone	850 (253), 755 (233)
$CuCl_2 \cdot C_4H_8S_2$	Solid	~720 sh, ~600 sh, 475 br

The 640 mμ band of $CuCl_2 \cdot 2C_4H_8OS$ is presumably associated with the $^2E_g \rightarrow {}^2T_{2g}$ transition, and its somewhat broad nature probably arises from a ligand field of symmetry lower than O_h.[33] With $CuBr_2 \cdot 2C_4H_8OS$ this band shifts to ~725 mμ, as expected in view of the ligand field order Cl > Br. The rather more intense bands at 490 and 380–410 mμ are presumably charge-transfer in character. The copper(II) chloride complex appears to react with acetone since the 640 mμ band shifts to 860 mμ, and the 412 mμ charge-transfer band is no longer observed. Some reaction with the solvent is also suggested by the small but significant molar conductivity values observed in acetone and methyl cyanide (19 and 32 ohm^{-1} cm^2, respectively, for ~10^{-3} *M* solutions).

In all cases the visible absorption spectra of these complexes are consistent with a distorted octahedral model. This is also in keeping with their magnetic susceptibility data.

Acknowledgment.—The award of a D.S.I.R. Fellowship is gratefully acknowledged.

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[29] D. Grdenić and I. Krstanović, *Arhiv Kem.*, **27**, 143 (1955).

[30] R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

[31] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 211 (1964).

[32] D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 2298 (1961).

[33] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, p 268.