configuration of *R* at the secondary nitrogen, exhibit three Cotton effects in the first absorption band region; their signs are (−), (+), and (−). However, the peak heights of the corresponding CD bands are markedly different from one another. A similar disagreement is recognized in the RD curves. These results may be attributed to the antipodal character of the asymmetric carbon of these ligands. Moreover, it is difficult to consider that the CD or RD curve for $Co(NH_3)_4prol^{2+}$ is a composite curve of $Co(NH_3)_4ala^{2+}$ and $(+)_{436}$-*S*-$Co(NH_3)_4sar^{2+}$. This means that the environments of the asymmetric carbon and the secondary nitrogen in the L-proline complex differ somewhat from those of the other complexes owing to the five-membered structure, since the CD or RD curve is considered to reflect clearly the slight difference of the circumstances of cobalt(III) ion. The additive nature of two (or more) vicinal effects in the same chelate ligand will be restricted in similar cases.

Although Buckingham, *et al.*,[10] have pointed out that the sarcosinate chelate is coordinated stereoselectively in $Co(en)_2sar^{2+}$, the analogous complexes with other N-substituted amino acids have not been reported. Bis(ethylenediamine) complexes with optically active N-substituted amino acids should be restricted in the configuration about the cobalt(III) ion, and the $\Delta(C_2)$ or $\Lambda(C_2)$ isomer will be formed stereospecifically according to the absolute configuration of the asymmetric secondary nitrogen atom, *R* or *S*, respectively. An attempt to prepare the L-prolinatobis(ethylenediamine)-cobalt(III) ion was reported to be unsuccessful.[14] However, the bis(ethylenediamine) complexes containing N-methyl-L-alanine and D-pipecolic acid are now isolated, and evidence supporting the stereoselective formation of the $\Delta(C_2)$ or the $\Lambda(C_2)$ isomer, respectively, has been obtained; this will be reported in subsequent papers.

Acknowledgment.—This research was supported in part by a grant from Asahi Glass Foundation. The authors thank Aji-no-moto Co. for supplying L-alanine.

[14] D. A. Buckingham and J. P. Collman, *Inorg. Chem.*, **6**, 1803 (1967)

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY,[1]
UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA 46556

Mössbauer Spectra of Some Complexes of Tin(IV) Chloride and Tin(IV) Bromide with Organic Ligands

BY JOSE PHILIP, M. ANGELA MULLINS, AND COLUMBA CURRAN

Received February 8, 1968

Mössbauer data are reported for 25 complexes of tin(IV) halides with organic ligands. The effectiveness of the donor atom in the six-coordinate complexes in reducing the electron density at the tin nucleus follows the order O > N > S > P. Quadrupole splittings have been observed for nine complexes having oxygen or phosphorus as the donor atom. The largest splitting, 1.0 mm/sec, was observed for $[(n\text{-}C_4H_9)_3P]_2SnCl_4$, for which dielectric data suggest a *trans* configuration.

Previous reports[2,3] of Mössbauer spectra of complexes of tin(IV) halides with organic ligands, using tin(IV) oxide as a source, have failed to reveal quadrupole splittings in these complexes and no correlations have been found between isomer shifts and the donor atoms of the ligands. In the present investigation a palladium–tin alloy source was used having a narrower line width than tin(IV) oxide, and complexes having a variety of donor ligands were studied.

Experimental Section

Preparation and Purification of Compounds.—Hexamethylphosphoramide $\{[(CH_3)_2N]_3PO\}$, pyrrolidine (C_4H_8N), tetrahydrothiophene (C_4H_8S), tetramethylammonium chloride $[(CH_3)_4NCl]$, tetraethylammonium bromide $[(C_2H_5)_4NBr]$, and 1,2-dimethoxyethane $[CH_3O(CH_2)_2OCH_3]$ were obtained from Eastman Organic Chemicals; the 1,2-dimethoxyethane was dried by shaking with potassium carbonate. Pyridine (C_5H_5N), stannic chloride, N,N,N′,N′-tetramethylethylenediamine $[(CH_3)_2N(CH_2)_2N(CH_3)_2]$, and 1,4-dioxane were J. T. Baker products; the tetramethylethylenediamine was purified by distilling over sodium and the dioxane was purified according to Fieser.[4] Tetramethylurea $\{[(CH_3)_2N]_2CO\}$ and α,α-dipyridyl ($C_{10}H_8N_2$) were obtained from Matheson Coleman and Bell. Tetramethylthiourea $\{[(CH_3)_2N]_2CS\}$ and triphenylphosphine $[(C_6H_5)_3P]$ were products of Chemical Intermediates and Research Corp. Tri-*n*-butylphosphine $[(C_4H_9)_3P]$ and thiophosphoryl chloride ($PSCl_3$) were from K & K Laboratories. Stannic bromide was obtained from City Chemical Corp. Piperidine ($C_5H_{10}N$) was obtained from Fisher Scientific Co. Triphenylphosphine oxide $[(C_6H_5)_3PO]$ was purchased from Aldrich Chemical Co. The 1,2-di(methylthio)ethane was synthesized in this laboratory by the method of Morgan and Ledbury.[5] Carbon tetrachloride was reagent grade and was dried over phosphorus pentoxide. All solvents were CP grade or better.

Tripiperidinophosphine sulfide $[(C_5H_{10}N)_3PS]$ and tripyrrolidinophosphine sulfide $[(C_4H_8N)_3PS]$ were prepared by the general

---

[1] The Radiation Laboratory is operated by the University of Notre Dame under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-419.

[2] V. I. Goldanski, E. F. Makarov, R. A. Stukan, T. N. Sumarokova, V. A. Trukhtanov, and V. V. Krapov, *Dokl. Akad. Nauk SSSR*, **156**, 400 (1964).

[3] N. N. Greenwood and J. N. R. Ruddick, *J. Chem. Soc.*, *A*, 1679 (1967).

[4] L. F. Fieser, "Experiments in Organic Chemistry, 2nd ed, D. C. Heath and Co., New York, N. Y., 1941.

[5] G. T. Morgan and W. Ledbury, *J. Chem. Soc.*, **121**, 2882 (1922)

method of Audrieth and Toy,[6] using piperidine (or pyrrolidine) and thiophosphoryl chloride in a 6:1 ratio to form the phosphine sulfide and the amine hydrochloride. The phosphine sulfide was then isolated from the mixture.

All preparations of complexes were carried out in a drybox. The complexes precipitated from solution, were filtered, washed with the solvent in which they were prepared, and dried under vacuum, ordinarily at about 100°, except the triphenylphosphine and tri-*n*-butylphosphine complexes which were dried under vacuum at room temperature. The dimethoxyethane complexes were dried at room temperature and purified by sublimation.

Tetrachloro- and tetrabromotin(IV) mono complexes of tripiperidinophosphine sulfide, tripyrrolidinophosphine sulfide, α,α-dipyridyl, tetramethylethylenediamine, dimethoxyethane, dimethylthioethane, and triphenylphosphine (chloride only) were prepared by mixing carbon tetrachloride solutions of the stannic halide and the ligand in a 1:1 ratio.

Tetrachloro- and tetrabromotin(IV) bis complexes of pyridine, hexamethylphosphoramide, and tetrahydrothiophene (bromide only) were prepared by adding 0.001 mol of the stannic halide to excess of the ligand. The precipitated complexes were washed with petroleum ether (bp 30–60°) before being dried under vacuum at 100°.

Tetrachloro- and tetrabromotin(IV) bis complexes of the following ligands were prepared by mixing solutions of the stannic halide and the ligand in a 1:2 ratio in the solvent specified: **triphenylphosphine oxide, tetramethylurea, tetramethylthiourea, and triphenylphosphine (bromide only)** complexes were formed using carbon tetrachloride as the solvent; the **tri-*n*-butylphosphine (chloride only)** complex was formed in petroleum ether medium; **dimethyl sulfoxide** complexes were prepared using chloroform solutions according to the method of Cotton and Francis.[7]

Hexabromobis(tetraethylammonium)tin(IV) and hexachlorobis(tetramethylammonium)tin(IV) were prepared by mixing chloroform and methanol solutions, respectively, of the stannic halide and tetraethyl- or tetramethylammonium chloride in a 1:2 ratio.

Dielectric constant and density measurements on some of these compounds dissolved in dioxane were carried out as in previous investigations,[8] using an oscillator similar to that described by Estok.[9] The results of interest are listed in Table II. $\Delta\epsilon/X_2$ and $\Delta d/X_2$ are the changes in dielectric constant and density with mole fraction and MRD is the molar refraction, assuming that the refractions of the donor molecules and SnX_4 are additive. The distortion polarization was taken as 1.2MRD. The value obtained for $\Delta\epsilon/X_2$ for $SnBr_4$ in dioxane is 50.

Mössbauer Spectra.—These were obtained by means of a Nuclear Science and Engineering Corp. (NSEC) Model AM-1 Mössbauer effect spectrometer which drives an electromechanical transducer with constant acceleration. The transducer supports a Pd–Sn^{119m} source, containing 12% tin by weight, obtained from New England Nuclear Corp. The Model AM-1 spectrometer was used in conjunction with a Reuter–Stokes X-ray proportional counter tube with xenon–nitrogen fill gas, Model RSG-30A, an RIDL preamplifier, Model 31-24, and single-channel analyzer, Model 33-13A, a modified Tetronix oscilloscope, Model RM-503, which obviated the need for a time-base generator, a Nuclear Data 512 channel memory unit, Model ND-180 M, and indicator unit, Model ND-180 I, and a Teletype tally tape readout. Recent measurements were made with both source and absorber at 80°K, using a Texas Instruments Cryoflask, Model CLF-3, modified and adapted by NSEC for use with the Model AM-1. The per cent absorption was greatly improved by means of a Pd filter (57 mg/cm^2), obtained from NSEC, in connection with the counting tube, which reduced the number of transmitted X-rays by 50%. Only 0.07–0.03 g of finely divided absorber, placed between two sheets of collodion-coated aluminum foil, was required for the sample holder provided with the Cryoflask.

The method of analyzing the earlier samples, the computer program used, and the calibration of the AM-1 spectrometer were described previously.[10] All values are reported to an accuracy of ±0.07 mm/sec with a relative precision of ±0.05 mm/sec.

Discussion of Results

An isomer shift of −1.52 mm/sec was obtained for tin(IV) oxide relative to the palladium–tin source. Isomer shifts reported in Table I can be compared with those reported by other investigators relative to tin(IV) oxide by adding 1.52 to their values. The average isomer shift for tin(IV) chloride listed by Zuckerman,[11] 0.8, is −0.7 mm/sec on the palladium–tin scale. A mean value for tin(IV) bromide is −0.4 mm/sec. The isomer shifts for the last two compounds in Table I, $(R_4N)_2SnX_6$, are −1.01 and −0.66 mm/sec for the chloride and bromide, respectively. The changes from the tetrahalides appear to the authors larger than would be expected from the 3% increase in the covalent radius of tin.[12] Assuming sp^{3}d^2 hybridization in these complexes, these values indicate a greater polarity for the Sn–X bonds in the SnX_6^- anion than in the corresponding SnX_4 molecule. With the exception of $(C_4H_9)_3P)_2SnCl_4$, all of the complexes show greater negative isomer shifts than the corresponding SnX_4, indicating that the formation of two dative bonds to give octahedral complexes results in a decrease in the electron density at the tin nucleus. Any back-bonding (π bonds) involving the tin 4d electrons would result in a *smaller* negative isomer shift because of decreased shielding of the tin s electrons. The general order of donor atoms in promoting a large negative isomer shift is seen from Table I to be $O > N > S > P$ (in $(C_4H_9)_3P$). This is the expected reverse order of σ-electron release, but it may be associated partly with Sn=P and Sn=S double-bond character.

Among the oxygen donors, the dimethyl ether of ethylene glycol (see **11** and **12**) is seen to be the best (in terms of electron release), followed by dimethyl sulfoxide and tetramethylurea (**5** and **7**). Tetramethylethylenediameine (**22**) is an appreciably better donor than pyridine (**20**) or dipyridyl (**18**), indicating that Sn=N bonding involving tin 4d electrons cannot be important in the complexes of the latter two ligands. The thioethers and tetramethylthiourea are seen to be about equal in their donor properties, superior to the phosphine sulfides. The lack of quadrupole splitting for compounds **23**, **24**, and **25** suggests six-coordination about tin, with Sn–S–Sn sulfur bridging in these 1:1 complexes, similar to that reported in dithiocyanatobis(thiourea)cadmium.[13] The absorptions associated with the P=S stretching vibrations in these complexes are at lower frequencies than those observed in the spectra of

---

(6) E. F. Audrieth and A. D. Toy, *J. Am. Chem. Soc.*, **64**, 1553 (1942).

(7) F. A. Cotton and R. Francis, *ibid.*, **82**, 2986 (1960).

(8) C. Curran, P. A. McCusker, and H. S. Makowski, *ibid.*, **79**, 5188 (1957).

(9) G. K. Estok, *J. Chem. Educ.*, **39**, 478 (1962).

(10) M. A. Mullins and C. Curran, *Inorg. Chem.*, **6**, 2017 (1967).

(11) J. J. Zuckerman, *J. Inorg. Nucl. Chem.*, **29**, 2191 (1967).

(12) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 251.

(13) M. Nardelli, L. Cavalia, and A. Braibanti, *Gazz. Chim. Ital.*, **86**, 876 (1956).

TABLE I

MÖSSBAUER DATA OBTAINED AT 80°K WITH A PALLADIUM–TIN ALLOY SOURCE

No.	Compound	% C		% H		% absorption	Line width, mm/sec	Isomer shift, mm/sec	Quadrupole splitting, mm/sec
		Calcd	Found	Calcd	Found				
1	$SnCl_4 \cdot 2[(CH_3)_2N]_3PO$	23.28	23.52	5.82	6.08	9.5	...	−1.21	0.70
2	$SnBr_4 \cdot 2[(CH_3)_2N]_3PO$	18.08	19.27	4.53	4.84	7	...	−0.96	0.76
3	$SnCl_4 \cdot 2(C_6H_5)_3PO^a$	52.90	52.34	3.67	3.68	5	...	−1.17	0.50
4	$SnBr_4 \cdot 2(C_6H_5)_3PO^a$	43.45	42.10	3.01	3.02	2.6	...	−0.89	0.61
5	$SnCl_4 \cdot 2(CH_3)_2SO$	11.52	12.30	2.88	3.02	16	1.07	−1.15	...
6	$SnBr_4 \cdot 2(CH_3)_2SO$	8.07	8.62	2.01	2.10	9.4	1.05	−0.86	...
7	$SnCl_4 \cdot 2[(CH_3)_2N]_2CO^a$	24.39	24.56	4.87	4.97	5	...	−1.17	0.75
8	$SnBr_4 \cdot 2[(CH_3)_2N]_2CO^a$	17.91	18.36	3.58	3.72	2.7	...	−0.82	0.85
9	$SnCl_4 \cdot 2[(CH_3)_2N]_2CS$	22.89	22.69	4.57	4.72	15	0.97	−0.82	...
10	$SnBr_4 \cdot 2[(CH_3)_2N]_2CS$	17.09	17.32	3.41	3.51	9.7	0.92	−0.58	...
11	$SnCl_4 \cdot CH_3O(CH_2)_2OCH_3^a$	13.69	13.98	2.85	2.99	7	...	−1.01	0.80
12	$SnBr_4 \cdot CH_3O(CH_2)_2OCH_3^a$	9.09	9.28	1.89	1.93	2.5	1.61	−0.71	...
13	$SnCl_4 \cdot CH_3S(CH_2)_2SCH_3$	12.54	13.63	2.61	2.73	13	0.87	−0.82	...
14	$SnBr_4 \cdot CH_3S(CH_2)_2SCH_3$	8.57	8.90	1.79	1.79	11	0.89	−0.55	...
15	$SnBr_4 \cdot 2C_4H_8S$	15.63	15.76	2.60	2.81	10.5	0.84	−0.53	...
16	$SnCl_4 \cdot 2(C_4H_9)_3P$	43.33	43.41	8.12	8.15	4.7	...	−0.65	1.0
17	$SnBr_4 \cdot 2(C_6H_5)_3P$	44.88	43.34	3.11	3.06	4	...	−0.89	0.66
18	$SnCl_4 \cdot C_{10}H_8N_2^a$	28.81	28.59	1.92	1.97	8.4	0.96	−1.05	...
19	$SnBr_4 \cdot C_{10}H_8N_2$	20.19	19.98	1.34	1.44	11	0.88	−0.79	...
20	$SnCl_4 \cdot 2C_5H_5N$	28.66	29.28	2.38	2.27	16	0.91	−1.01	...
21	$SnBr_4 \cdot 2C_5H_5N$	20.12	20.45	1.67	1.91	9.3	0.87	−0.78	...
22	$SnCl_4 \cdot (CH_3)_2N(CH_2)_2N(CH_3)_2$	19.14	19.59	4.25	4.48	12.7	1.04	−0.91	...
23	$SnCl_4 \cdot (C_5H_{10}N)_3PS^a$	31.27	30.76	5.21	5.61	2	1.05	−1.03	...
24	$SnCl_4 \cdot (C_4H_8N)_3PS$	27.00	26.51	4.50	5.01	10	1.06	−1.09	...
25	$SnBr_4 \cdot (C_4H_8N)_3PS$	20.24	20.30	3.27	3.41	5.6	1.20	−0.90	...
26	$[(CH_3)_4N]_2 \cdot SnCl_6$	20.02	20.30	5.00	5.01	3.6	0.88	−1.01	...
27	$[(C_2H_5)_4N]_2 \cdot SnBr_6$	22.37	22.59	4.66	4.92	4.7	1.12	−0.66	...

[a] These measurements were made with the source at room temperature; all others were made with the source at 80°K, using a Pd filter.

TABLE II

DIELECTRIC AND DENSITY DATA FOR DIOXANE SOLUTIONS AT 25°

Compound	10^4X_2	$\Delta\epsilon/X_2$	$\Delta d/X_2$, g/ml	MR_D, ml	μ, D
$SnCl_4 \cdot 2(C_4H_9)_3P$	3.7–4.1	11.3	0.6	169	2.4
$SnCl_4 \cdot 2(C_6H_5)_3PO$	2.3–2.7	133	2.9	214	9.5
$SnBr_4 \cdot 2(C_6H_5)_3PO$	2.3–2.4	164	4.7	226	10.1
$SnBr_4 \cdot 2C_4H_8S$	7.4–7.6	107	3.9	97	8.0
$SnCl_4 \cdot 2[(CH_3)_2N]_2CO$	5.0–8.6	83	1.8		a
$SnBr_4 \cdot 2[(CH_3)_2N]_2CO$	3.9–5.4	130	4.6		a

[a] Infrared absorption measurements indicated appreciable dissociation of these complexes.

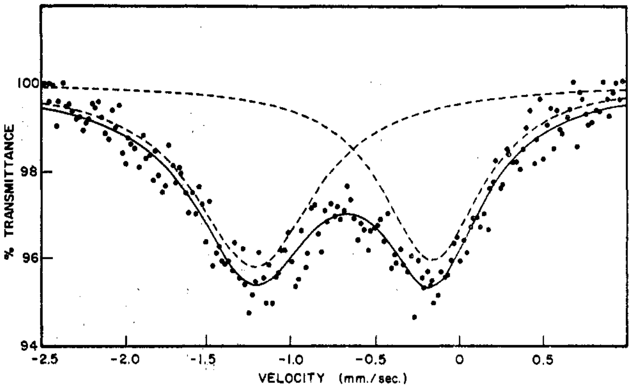

Figure 1.—Mössbauer spectrum of $SnCl_4 \cdot 2(n\text{-}C_4H_9)_3P$.

any 2:1 complex of tripiperidinophosphine sulfide or tripyrrolidinophosphine sulfide, again suggesting sulfur bridging (with increased $^+P–S^-$ character).[14] Bridging sulfur atoms are expected to be poorer electron donors than those forming only one dative bond. The isomer shifts are from 0.24 to 0.35 mm/sec less negative for the tetrabromide complexes than for the corresponding tetrachlorides; no correlation with donor atoms is evident.

Quadrupole Splittings.—The Mössbauer spectra of nine complexes listed in Table I indicate quadrupole splittings, small compared to those observed for complexes of dibutyltin dihalides.[10] In each of these spectra the splitting is evident from the experimental points; the spectrum of the complex of tri-*n*-butylphosphine with tin(IV) chloride is illustrated in Figure 1. These results do not conform to the empirical generalizations of Greenwood and Ruddick,[3] who postulate that electric field gradients and quadrupole interactions are observed only when there is an imbalance of π interactions. On this basis the tetramethylethylenediamine complex should show the greatest splitting, but none is observed. It is interesting that none of the complexes listed in Table I having nitrogen or sulfur as the donor ligand shows a quadrupole splitting. An explanation in terms of π interactions is not evident. If the tin share of the electrons of the σ bonds follows the order $Sn–P(C_4H_9)_3 > Sn–Br > Sn–Cl > Sn–O$, and $Sn–Br > Sn–P(C_6H_5)_3$, the observed splittings could be effected by the resulting asymmetries; the greater splittings observed for the bromides than for the chlorides are consistent with this order. The lack of splitting for the complexes containing nitrogen and sulfur may be an

---

(14) J. Philip, Ph.D. Thesis, University of Notre Dame, Sept 1965.

indication of the lack of a sufficient difference in the tin share of the electrons of the N–Sn and S–Sn dative bonds and the tin–halogen bonds. The above order and suggested similarities are reasonable, but the relative polarities of donor-atom-to-metal dative bonds and metal-to-halogen bonds have not been clearly established to date.

The large half-width of the absorption for $SnBr_4 \cdot CH_3O(CH_2)_2OCH_3$, 1.61 mm/sec (which compares with 1.8 mm/sec for the absorption envelope for the corresponding chloride), strongly suggests an unresolved doublet. This complex and those of dimethyl sulfoxide are the only oxygen-donor complexes that failed to show quadrupole splittings. The infrared spectra of $SnCl_4 \cdot 2DMSO$ and $SnBr_4 \cdot 2DMSO$[15] indicate abnormally high O–Sn and Sn–halogen stretching frequencies. It is evident that a number of line widths do not differ significantly from the value 0.88 mm/sec observed for $[(CH_3)_4N]_2SnCl_6$, for which no appreciable deviation from spherical symmetry of the tin electron cloud is expected.

If there are significant differences between the tin share of the electrons of the dative bond and the tin–halogen bonds, larger quadrupole splittings are expected for *trans* than for *cis* complexes. The electric dipole moment of $SnCl_4 \cdot 2(C_4H_9)_3P$, 2.4 D, indicates that this complex, which shows the largest quadrupole splitting, is chiefly *trans* in solution. The large moments of the triphenylphosphine oxide complexes, Table II, indicate a *cis* configuration, and the large values for $\Delta\epsilon/X_2$ for the partially dissociated tetramethylurea complexes, compared to values of 22 and 50 for solvated $SnCl_4$[16] and $SnBr_4$ and 19 for tetramethylurea, indicate a *cis* configuration for these complexes. The moment of $SnBr_4 \cdot 2C_4H_8S$, 8.0 D, indicates a *cis* configuration for this compound in solution, compared to a *trans* configuration reported for the solid from X-ray diffraction studies.[17]

[15] T. Tanaka, *Inorg. Chim. Acta*, **1**, 217 (1967).

[16] T. J. Lane, P. A. McCusker, and C. Curran, *J. Am. Chem. Soc.*, **64**, 2076 (1942).

[17] I. R. Beattie, R. Hulme, and L. Rule, *J. Chem. Soc.*, 1581 (1965).

CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
BATH UNIVERSITY OF TECHNOLOGY, BATH, ENGLAND

Oxochloro Complexes of Rhenium(VI)

BY B. J. BRISDON AND D. A. EDWARDS

Received February 29, 1968

The magnetic and spectroscopic properties of the oxopentachlororhenate(VI) ion have been examined and compared with the closely related $MOCl_5^{2-}$ d^1 (M = Mo or W) and d^2 (M = Re) systems. Partial hydrolysis of this ion results in the formation of an oxygen-bridged dimeric rhenium(VI) species, which has also been characterized.

Introduction

The chemistry of rhenium(V) oxohalide complexes has been thoroughly investigated. Thus the $ReOX_5^{2-}$ and $ReOX_4^-$ ions and neutral adducts of rhenium(V) oxotrichloride have been prepared and examined by several groups of workers,[1–5] and a complete X-ray determination was carried out on $(C_6H_5)_4As[ReOBr_4 \cdot CH_3CN]$.[6] However the theoretically more interesting d^1 systems derived from rhenium oxotetrahalides have received scant attention. The magnetic properties of $ReOCl_4$[7] and $ReOF_4$[8] have been examined, but little has been reported on the reactions or spectra of these compounds or the related $ReOX_5^-$ ions. Ippolitov and Nikolaev[9] first prepared the oxofluoride ion $ReOF_5^-$ by partial hydrolysis of octafluororhenate(VI) complexes and reported room-temperature magnetic susceptibilities, and the corresponding complex chloride ion was prepared and briefly reported by the present authors.[10]

Here, we report in full the preparation and physical properties as well as some of the reactions of the oxopentachlororhenate(VI) ion and compare this ion with the $ReOCl_5^{2-}$, $MoOCl_5^{2-}$, and $WOCl_5^{2-}$ systems.

Experimental Section

Analyses.—Rhenium was determined as tetraphenylarsonium perrhenate after dissolution of the sample in dilute sodium hydroxide solution containing a little hydrogen peroxide. Halogen and oxidation state determinations were carried out as previously described.[11]

Physical Measurements.—Electronic spectra were recorded on the solid or in solution on an SP500 spectrophotometer in the range 10,000–30,000 cm^{-1}. Cells adapted for vacuum line operation were used for obtaining the solution spectra of air-sensitive compounds.

Magnetic susceptibilities were measured at room temperature

---

[1] R. J. Mawby and L. M. Venanzi, *J. Chem. Soc.*, 4447 (1962).

[2] J. Chatt, J. D. Garforth, N. P. Johnson, and G. A. Rowe, *ibid.*, 601 (1964).

[3] N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *ibid.*, 1054 (1964).

[4] D. E. Grove and G. Wilkinson, *ibid.*, 1224 (1966).

[5] F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, **4**, 1621 (1965).

[6] F. A. Cotton and S. J. Lippard, *ibid.*, **5**, 416 (1966).

[7] W. Klemm and H. Steinberg, *Z. Anorg. Allgem. Chem.*, **210**, 33 (1933).

[8] G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 1099 (1960).

[9] E. G. Ippolitov and N. S. Nikolaev, *Russ. J. Inorg. Chem.*, **7**, 940 (1962).

[10] B. J. Brisdon and D. A. Edwards, *Chem. Commun.*, 278 (1966).

[11] B. J. Brisdon and R. A. Walton, *J. Chem. Soc.*, 2274 (1965).