TABLE II

X-RAY POWDER DIFFRACTION DATA FOR $B_{12}S$

Obtained by use of 140 mm. camera and filtered CrKα radiation

h	*k*		*d*, Å.	I/I_1
0	0	3	3.97	20
0	1	2	3.84	70
1	1	0	2.90	10
1	0	4	2.566	100
0	2	1	2.454	100
0	1	5	2.159	10
2	1	1	1.875	10
1	1	6	1.641	10
3	0	3	1.545	5
1	2	5	1.486	30
2	2	0	1.449	20
2	0	3	1.413	20
1	0	8		
1	3	1	1.383	20
2	2	3	1.359	20
3	1	2		
2	0	8	1.283	50
3	0	6		
4	0	1	1.251	1
1	1	9	1.203	5
3	1	5		

With the discovery of $B_{12}S$ there appear to be three types of interstitial compounds of boron, namely, $B_{12}X$, $B_{12}X_3$ and $B_{13}X_2$.

The 2*c* positions in the structure are found to accommodate carbon, silicon, phosphorus and arsenic while the 1*b* position can accommodate boron, carbon, silicon and sulfur. A homogeneity range similar to that found in the boron–carbon system may also exist in some other boron systems. However, with the present methods of preparation they have not been observed.

Though the proposed mechanism explains satisfactorily the formation of a series of boron compounds involving elements of the third, fourth, fifth and sixth groups, a direct determination of the actual atomic arrangement would be desirable.[19] The X-ray scattering power of silicon, phosphorus, etc., is sufficiently different from that of boron to enable definite placement of these elements in the structure.

Acknowledgments.—The author wishes to express his appreciation for technical assistance provided by J. L. Peret, of this Laboratory, who prepared the samples of $B_{12}S$, and to R. G. Greenler for helpful discussions and the preparation of the manuscript.

[19] Such work is in progress at the Polytechnic Institute of Brooklyn by B. Post, on $B_{13}P_2$ crystals supplied by this Laboratory.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA]

The Donor Properties of Triphenylarsine Oxide

BY D. J. PHILLIPS AND S. Y. TYREE, JR.

RECEIVED SEPTEMBER 9, 1960

The coördination chemistry of triphenylarsine oxide with a variety of acceptors has been investigated. The new substances $CrCl_3\cdot4R$, $CrCl_2ClO_4\cdot4R$, $MnCl_2\cdot2R$, $Mn(ClO_4)_2\cdot4R$, $FeCl_3\cdot2R$, $Fe(ClO_4)_3\cdot4R$, $CoCl_2\cdot2R$, $CoBr_2\cdot2R$, $Co(ClO_4)_2\cdot4R$, $NiCl_2\cdot2R$, $Ni(ClO_4)_2\cdot4R$, $Cu(NO_3)_2\cdot4R$, $Zn(ClO_4)_2\cdot4R$, $HgCl_2\cdot2R$, $HgCl_2\cdot R$, $SnCl_4\cdot2R$, $SnBr_4\cdot2R$, $SbCl_3\cdot2R$, and $SbCl_5\cdot R$ (where R = triphenylarsine oxide) have been isolated and characterized by molecular conductance measurements in nitrobenzene, cryoscopic molecular weight measurements in freezing nitrobenzene, magnetic susceptibility measurements and infrared spectra. Most of the halides appear to be non-electrolytes, whereas the nitrate and perchlorates appear to be salt-like.

Introduction

In the course of some previous work we became aware of the class of compounds formed between triphenylphosphine oxide and metal halide acceptors.[1] Now we wish to report extensions of the earlier work to a wider variety of metal compounds and using triphenylarsine oxide. During the course of the work two other laboratories[2] reported analogous series of phosphine oxide compounds. Also Lindquist[3] has prepared and studied some additional similar phosphine oxide complexes in the interim. Workers in Prof. Hieber's laboratory at Munich also report addition compounds of iron and cobalt carbonyls with triphenylarsine oxide.[4,5]

We believe the first example of an arsine oxide complex to be $(C_3H_7)_3AsO\cdot2HgCl_2$, reported by Partheil and co-workers.[6] The only other examples we are aware of are $Cu[(C_6H_5)_2CH_3AsO]_4X_2$, reported by Nyholm,[7] and the chelates bis-(α-picolyldimethylarsine oxide)-copper(I) perchlorate and bis-(α-picolyldimethylarsine oxide)-copper(II) perchlorate, reported by Goodwin and Lions.[8]

Experimental

Reagents.—Reagent grade chemicals were used without further purification except in the cases noted.

Triphenylarsine oxide was prepared from Eastman "White Label" triphenylarsine,[9] m.p. 194.5–196°; literature values, 189°[10,11] and 191–193°.[12]

Anal. Calcd. for $(C_6H_5)_3AsO$: As, 23.25. Found[13]: As, 23.0.

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[1] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 262 (1906).

[2] (a) F. A. Cotton, *et al.*, *Proc. Chem. Soc.* (*London*), 158 (1958); (b) F. A. Cotton, *et al.*, *J. Chem. Soc.*, 1873 (1960); (c) 1878 (1960); (d) 1959 (1960); (e) 2265 (1960); (f) K. Issleib and B. Mitscherling, *Z. anorg. allgem. Chem.*, **304**, 73 (1960).

[3] I. Lindquist, private communication.

[4] W. Hieber and A. Lipp, *Chem. Ber.*, **92**, 2075 (1959).

[5] G. Franz, Doctoral Dissertation, Technischen Hochschule Munchen, 1959.

[6] A. Partheil, *et al.*, *Archiv. Pharm.*, **237**, 136 (1899).

[7] R. S. Nyholm, *J. Chem. Soc.*, 1767 (1951).

[8] H. A. Goodwin and F. Lions, *J. Am. Chem. So.*, **81**, 311 (1959).

[9] R. L. Shriner and C. N. Wolf, *Org. Syn.*, **30**, 97 (1950).

[10] A. Michaelis, *Ann.* (*Liebig*), **201**, 244 (1880).

[11] F. Zuckerkandl and M. Sinai, *Ber.*, **54**, 2485 (1921).

[12] F. G. Mann, *J. Chem. Soc.*, 970 (1932).

Chromium(III) chloride 4.25-hydrate was supplied by Dr. J. T. Yoke[14] and used as received.

Nickel perchlorate 7-hydrate was prepared according to the method of Goldblum and Terlikowski.[15]

Anal. Calcd. for $Ni(ClO_4)_2 \cdot 7H_2O$: Ni, 15.3. Found: Ni, 15.3.

Zinc perchlorate was prepared by the reaction of $ZnCO_3$ and the equivalent amount of 1:1 $HClO_4$. The product was recrystallized twice from water and used without analysis.

Tin(IV) bromide was obtained from student preparations and redistilled, b.p. 203–204°; literature value,[16] 207°.

Nitrobenzene (for conductance and cryoscopic work): Baker and Adamson "Purified" nitrobenzene was fractionally crystallized, retaining approximately one half of each batch. The frozen samples were dried over $CaCl_2$ and redistilled at reduced pressure, retaining the middle 3/4 fractions.

Nitromethane.—The Eastman "Spectro Grade" product was dried over $CaCl_2$ and distilled at 760 mm., retaining the fraction boiling at 100.5–101.5°.

Analyses.—The complexes generally were decomposed by warming with concentrated nitric acid before titration for metal, although this was found to be unnecessary with the manganese, cobalt and nickel halogen complexes. Metal titrations were made by the chelometric EDTA method of Reilley and co-workers.[17] Manganese and iron were determined directly using Eriochrome Black T and copper PAN indicators, respectively. Back titrations with magnesium sulfate and Eriochrome Black T were used for cobalt and nickel. A direct titration with PAN indicator was used for copper. Halogen analyses on the manganese, cobalt, nickel, tin and antimony complexes were performed potentiometrically using silver and calomel electrodes. Preliminary decomposition by digestion with strong aqueous potassium hydroxide was necessary for the tin and antimony complexes. With all other complexes halogen was determined gravimetrically in the presence of 1:1 nitric acid. With the mercury complexes a preliminary reduction with ethanolamine was necessary.[18] Carbon and hydrogen analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Preparation of the Complexes.—Details of typical experiments only will be given, since all of the complexes have been prepared a number of times and, in several cases, identical procedures suffice for different complexes.

$MnCl_2 \cdot 2(C_6H_5)_3AsO$.—0.462 g. of Merck reagent $MnCl_2 \cdot 4H_2O$ in 15 ml. of absolute ethanol was added to 1.5 g. of the arsine oxide in 15 ml. of absolute ethanol. The resulting solution was evaporated to approximately one half of its original volume. On standing in a vacuum desiccator over $CaCl_2$ the solution deposited 1.4 g. of pale greenish yellow needles. These were recrystallized from absolute ethanol. The final product was washed first with absolute ethanol, than with ether and dried *in vacuo* over $CaCl_2$. The complex is soluble in ethanol, nitrobenzene and warm nitromethane, very slightly soluble in hot acetone and insoluble in benzene, chloroform and ether. It is decomposed by cold water, immediately turning colorless.

Anal. Calcd. for $MnCl_2 \cdot 2(C_6H_5)_3AsO$: C, 56.1; H, 3.93; Mn, 7.13; Cl, 9.21. Found: C, 55.8; H, 4.17; Mn, 7.09; Cl, 9.21.

$CrCl_3 \cdot 4(C_6H_5)_3AsO$ (lavender), **$CoCl_2 \cdot 2(C_6H_5)_3AsO$** (blue), **$CoBr_2 \cdot 2(C_6H_5)_3AsO$** (blue) and **$HgCl_2 \cdot (C_6H_5)_3AsO$** (White), were made in a similar way, starting from $CrCl_3 \cdot 4.25H_2O$, Baker "Analyzed Reagent" $CoCl_2 \cdot 6H_2O$, Amend C.P. $CoBr_2 \cdot 6H_2O$, and B and A Reagent $HgCl_2$, respectively. Reactions were carried out in absolute ethanol, using the oxide in appropriate proportions. The mercury complex is soluble in ethanol, acetone, nitrobenzene, nitromethane, chloroform and benzene but only sparingly soluble in ether. The chromium and cobalt complexes are soluble in ethanol, nitrobenzene and nitromethane and insoluble in ether and chloroform. In acetone the cobalt complexes are sparingly soluble and the chromium complex is insoluble.

Anal. Calcd. for $CrCl_3 \cdot 4(C_6H_5)_3AsO$: C, 59.8; H, 4.18; Cl, 7.35. Found: C, 59.7; H, 4.35; Cl, 6.97. Calcd. for $CoCl_2 \cdot 2(C_6H_5)_3AsO$: C, 55.8; H, 3.91; Co, 7.61; Cl, 9.16. Found: C, 55.9; H, 4.15; Co, 7.5; Cl, 9.08. Calcd. for $CoBr_2 \cdot 2(C_6H_5)_3AsO$: C, 50.1; H, 3.50; Co, 6.83; Br, 18.52. Found: C, 49.8; H, 3.75; Co, 6.7; Br, 18.3; Calcd. for $HgCl_2 \cdot (C_6H_5)_3AsO$: C, 36.4; H, 2.55; Cl, 11.9. Found: C, 36.6; H, 2.77; Cl, 12.1.

$Cr[(C_6H_5)_3AsO]_4Cl_2ClO_4$.—One g. of $CrCl_3 \cdot 4(C_6H_5)_3AsO$ in 100 ml. of absolute ethanol was treated with 0.7 g. of $LiClO_4$ dissolved in 10 ml. of absolute ethanol. A pink crystalline precipitate formed slowly. It was allowed to stand overnight, then was filtered, washed with absolute ethanol and ether and dried *in vacuo*. The complex is soluble in nitrobenzene and nitromethane, moderately soluble in ethanol and acetone and insoluble in benzene. It appears to be unaffected by several hours contact with cold water.

Anal. Calcd. for $CrCl_3O_4 \cdot 4(C_6H_5)_3AsO$: C, 57.2; H, 4.00; Cl (excluding ClO_4^-), 4.69. Found: C, 55.9; H, 4.53; Cl, 5.02.

$HgCl_2 \cdot 2(C_6H_5)_3AsO$.—0.84 g. of B and A reagent $HgCl_2$ in 50 ml. of hot ether was added to 2.0 g. of the arsine oxide in 150 ml. of hot ether to which had been added 5 ml. of ethanol. The coloriess platelets which deposited on standing were filtered and washed with ether. The complex is soluble in ethanol, acetone, nitrobenzene, nitromethane, benzene and hot water.

Anal. Calcd. for $HgCl_2 \cdot 2(C_6H_5)_3AsO$: C, 47.2; H, 3.30; Cl, 7.74. Found: C, 47.5; H, 3.78; Cl, 7.59.

$FeCl_3 \cdot 2(C_6H_5)_3AsO$.—0.25 g. of $FeCl_3$ was extracted with 100 ml. of hot, dry benzene. The extract was filtered directly into 70 ml. of hot benzene containing 2 g. of the arsine oxide. The residue of the $FeCl_3$ which was insoluble in the first portion of benzene was extracted with a second portion of hot benzene. This extract was filtered directly into the same solution of arsine oxide. The resulting solution was left in a vacuum desiccator over $CaCl_2$, yellow needles being deposited after a few hours. The product was washed with benzene, then ether and finally dried *in vacuo*. The complex is soluble in alcohol, acetone, nitrobenzene and nitromethane, slightly soluble in benzene and insoluble in chloroform and ether. On contact with water it slowly dissolves giving a yellowish solution. The undissolved crystals are not changed in color.

Anal. Calcd. for $FeCl_3 \cdot 2(C_6H_5)_3AsO$: C, 53.6; H, 3.75; Fe, 6.92; Cl, 13.2. Found: C, 53.5; H, 3.84; Fe, 6.6; Cl, 13.1.

$NiCl_2 \cdot 2(C_6H_5)_3AsO$.—3.0 g. of the arsine oxide dissolved in 15 ml. of absolute ethanol was added to 1.0 g. of Merck Reagent $NiCl_2 \cdot 6H_2O$ dissolved in 15 ml. of absolute ethanol containing 3 drops of 12 *N* hydrochloric acid. Blue crystals deposited from the green solution after the solution had stood in a partially evacuated desiccator for several days. The crystals were washed with small portions of absolute ethanol and ether and transferred immediately to a vacuum desiccator. The complex is soluble in alcohol, nitrobenzene and nitromethane but insoluble in acetone, chloroform, ether and benzene. It is decomposed by cold water, turning colorless after several minutes of contact.

Anal. Calcd. for $NiCl_2 \cdot 2(C_6H_5)_3AsO$: C, 55.85; H, 3.91; Ni, 7.58; Cl, 9.16. Found: C, 56.1; H, 4.20; Ni, 7.41; Cl, 9.35.

In the preceding preparation it was observed that occasionally some yellow crystals formed on the walls of the flask just above the surface of the solution. What appeared to be the same crystals could be obtained sometimes in larger quantity by rapid evaporation of the solution containing the reactants.

$Mn(ClO_4)_2 \cdot 4(C_6H_5)_3AsO$.—0.123 g. of Merck Reagent $MnCl_2 \cdot 4H_2O$ and 1.0 g. of the arsine oxide were dissolved in 60 ml. of hot absolute ethanol. A few ml. of absolute ethanol saturated with $NaClO_4$ were added to this solution. Upon standing, sparkling, colorless plates were deposited. They were washed with ethanol and ether and dried *in vacuo*. The complex is soluble in ethanol, acetone, nitrobenzene and nitromethane. It is insoluble in benzene. It is apparently unaffected by several hours contact with cold water.

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(13) Kindly done by Mrs. Betty P. Herring, U. S. Public Health Service, Chapel Hill, N. C.

(14) Department of Chemistry, University of Arizona, Tucson.

(15) H. Goldblum and F. Terlikowski, *Bull. soc. chim. France*, (IV) **11**, 103 (1912).

(16) L. L. Quill, Ed., "The Chemistry and Metallurgy of Miscellaneous Materials," McGraw-Hill Book Co., New York, N. Y., 1950, p. 205.

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(18) W. H. Rauscher, *Anal. Chem.*, **10**, 331 (1938).

Anal. Calcd. for $Mn(ClO_4)_2\cdot 4(C_6H_5)_3AsO$: C, 56.1; H, 3.92; Mn, 3.56. Found: C, 56.0; H, 4.11; Mn, 3.45.

$Fe(ClO_4)_3\cdot 4(C_6H_5)_3AsO$ (white) and **$Co(ClO_4)_2\cdot 4(C_6H_5)_3AsO$** (blue) were prepared in a manner identical with that used for the previous complex, Baker "Analyzed" Reagent $Fe(NO_3)_3\cdot 6H_2O$ and B and A Reagent $Co(NO_3)_2\cdot 6H_2O$ being used as starting materials. The solubilities of these two complexes are similar to those of the manganese perchlorate complex.

Anal. Calcd. for $Fe(ClO_4)_3\cdot 4(C_6H_5)_3AsO$: C, 52.6; H, 3.68; Fe, 3.40. Found: C, 52.2; H, 3.71; Fe, 3.40. Calcd. for $Co(ClO_4)_2\cdot 4(C_6H_5)_3AsO$: C, 55.9; H, 3.91; Co, 3.81. Found: C, 56.2; H, 4.16; Co, 3.78.

$Ni(ClO_4)_2\cdot 4(C_6H_5)_3AsO$.—5 ml. of absolute ethanol containing 1.0 g. of the arsine oxide was added to 2 ml. of absolute ethanol containing 0.236 g. of $Ni(ClO_4)_2\cdot 7H_2O$. A yellow precipitate formed immediately. It was washed with absolute ethanol and ether. The complex is soluble in ethanol and nitromethane, but only slightly soluble in acetone and nitrobenzene. It is apparently unaffected by several hours contact with cold water.

Anal. Calcd. for $Ni(ClO_4)_2\cdot 4(C_6H_5)_3AsO$: C, 55.9; H, 3.91; Ni, 3.80. Found: C, 55.9; H, 4.19; Ni, 3.70.

$Cu(NO_3)_2\cdot 4(C_6H_5)_3AsO$.—35 ml. of hot absolute ethanol containing 0.56 g. of Baker "Analyzed" Reagent $Cu(NO_3)_2\cdot 3H_2O$ and six drops of 15 *N* HNO_3 were added in small portions, with shaking, to a hot solution of 3.0 g. of the arsine oxide in 50 ml. of absolute ethanol. The resulting pale blue precipitate was washed many times with ethanol and ether and dried *in vacuo*. The complex is sparingly soluble in ethanol and nitromethane and insoluble in acetone, nitrobenzene and benzene. It is apparently unaffected by several hours contact with cold water.

Anal. Calcd. for $Cu(NO_3)_2\cdot 4(C_6H_5)_3AsO$: C, 58.6; H, 4.10; Cu, 4.30. Found: C, 58.6; H, 4.25; Cu, 4.31.

$Zn(ClO_4)_2\cdot 4(C_6H_5)_3AsO$.—A solution of 0.58 g. of $Zn(ClO_4)_2\cdot 6H_2O$ in 100 ml. of absolute ethanol was added to a warm solution of 3.0 g. of the arsine oxide in 400 ml. of the same solvent. Colorless crystals deposited slowly. After standing overnight in the refrigerator the crystals were filtered, washed with cold ethanol and ether and dried *in vacuo*. The product is soluble in nitrobenzene and ethanol.

Anal. Calcd. for $Zn(ClO_4)_2\cdot 4(C_6H_5)_3AsO$: C, 55.7; H, 3.89; Zn, 4.21. Found: C, 54.0; H, 3.78; Zn, 4.19.

$SnCl_4\cdot 2(C_6H_5)_3AsO$.—A solution of 0.20 g. of Baker "Analyzed" Reagent $SnCl_4$ in 30 ml. of warm, dry CCl_4 was filtered into a warm solution of 0.5 g. of the arsine oxide in 35 ml. of dry CCl_4, the operation being carried out in an atmosphere of dry nitrogen. The resulting white precipitate was filtered, triturated several times with absolute ethanol and washed finally with ether. The complex is soluble in acetone and nitromethane, slightly soluble in ethanol and nitrobenzene and insoluble in benzene. It is slowly hydrolyzed by cold water.

Anal. Calcd. for $SnCl_4\cdot 2(C_6H_5)_3AsO$: C, 47.8; H, 3.34; Cl, 15.7. Found: C, 47.6; H, 3.48; Cl, 15.6.

$SnBr_4\cdot 2(C_6H_5)_3AsO$.—0.509 g. of $SnBr_4$ in 60 ml. of absolute ethanol was added to 2.5 g. of the arsine oxide in 60 ml. of absolute ethanol. A cream precipitate resulted which was washed with ethanol and ether. The operations were carried out under dry nitrogen. The complex is soluble in nitrobenzene and nitromethane, slightly soluble in ethanol and acetone and insoluble in benzene. It is slowly hydrolyzed by cold water.

Anal. Calcd. for $SnBr_4\cdot 2(C_6H_5)_3AsO$: C, 39.9; H, 2.79; Br, 29.5. Found: C, 39.9; H, 2.97; Br, 29.5.

$SbCl_3\cdot 2(C_6H_5)AsO$.—0.5 g. of the arsine oxide dissolved in 25 ml. of warm benzene was added to a solution of 0.177 g. of Baker "Analyzed" Reagent $SbCl_3$ in 25 ml. of benzene. A milky suspension resulted which cleared on shaking. Upon standing overnight colorless crystals were deposited from the solution. They were filtered and washed with benzene and ether. The complex is soluble in nitromethane and slightly soluble in ethanol, acetone, nitrobenzene and benzene. It is hydrolyzed by cold water.

Anal. Calcd. for $SbCl_3\cdot 2(C_6H_5)_3AsO$: C, 49.6; H, 3.47; Cl, 12.19. Found: C, 49.6; H, 3.71; Cl, 11.9.

$SbCl_5\cdot(C_6H_5)_3AsO$.—A warm solution of 1.0 g. of the arsine oxide in 80 ml. of dry CCl_4 was added, in small portions, with shaking, under an atmosphere of dry nitrogen, to a solution of 0.93 g. of Baker "Analyzed" Reagent $SbCl_5$ in 50 ml. of dry CCl_4 saturated with chlorine. An immediate white precipitate formed. After standing overnight in a vacuum desiccator, it was filtered and washed with dry CCl_4 in a dry nitrogen atmosphere. The complex is soluble in ethanol, acetone, nitrobenzene and nitromethane and slightly soluble in benzene. It is slowly hydrolyzed by cold water.

Anal. Calcd. for $SbCl_5\cdot(C_6H_5)_3AsO$: C, 34.8; H, 2.43; Cl, 28.5. Found: C, 32.3; H, 2.42; Cl, 26.4.

Conductance measurements were made at 25° using conventional dip type platinum blacked electrodes. The bridge used was assembled in this Laboratory, balance being indicated ultimately on an RCA electron ray tube No. 1629. The balance arm of the bridge consisted of a 1000 ohm precision Helipot potentiometer of $\pm$ 0.5% linearity. Cell constants were determined in the usual manner with 0.1 *N* KCl.

Molecular weight mesurements were made cryoscopically in nitrobenzene using a Beckmann thermometer in an enclosed glass apparatus fitted with a magnetic stirrer. Means of several measurements on pure solvent and solution were taken in each case. The procedure used gave a molecular weight of 124 for naphthalene (theor., 128).

Magnetic susceptibility measurements were made on finely powdered samples in a conventional Gouy apparatus assembled by Coffey.[19] The electromagnet with a pole gap of 1.76 cm. gave a field strength of approximately 6.7×10^3 oersteds. Determinations were made at room temperature only. A gram susceptibility of 5.92×10^{-6} c.g.s. units at 19° was assumed for $CuSO_4\cdot 5H_2O$, the standard used.

Infrared spectra were obtained of the complexes in paraffin oil mulls between NaCl plates in a Baird Associates recording spectrophotometer, serial No. AB2-193. Duplicate spectra were taken upon samples prepared at widely spaced time intervals.

Results

The new complexes are listed in Table I together with some physical properties. Calculation of the effective magnetic moments involves large diamagnetic corrections.[19,20] In the worst case, $Cu(NO_3)_2\cdot 4(C_6H_5)_3AsO$, the correction amounts to 780 parts out of approximately 1900 in the value of χ_M'. In addition the magnetic pulls were small, being about 2 mg. for the same case. However, even for this complex three separate determinations of μ_{eff} gave values of 1.91, 1.91 and 1.92 B.M.

Molar conductances are reported for 0.001 *M* solutions in nitrobenzene solvent at 25° unless otherwise noted. Under the conditions used, 1:1 electrolytes generally exhibit conductances in the range 20–30 ohm^{-1}; 2:1 fall in the range 40–60 ohm^{-1}.[21]

The infrared spectra of $(C_6H_5)_3AsO$ and $(C_6H_5)_3As$ are very similar except for a strong peak in the former at 879 cm.$^{-1}$. We tentatively attribute this peak to the As–O stretching frequency. The only previous assignment of an As–O stretching frequency is the 811 cm.$^{-1}$ peak in $AsOF_3$.[22] Absorptions in the 880 cm.$^{-1}$ region only are reported in Table II, inasmuch as this is the only region where the complexes differ substantially from the free arsine oxide.

Discussion

Chromium(III).—The molar conductance of $CrCl_3\cdot 4(C_6H_5)_3AsO$ is in the range for 1:1 electrolytes. Its molecular weight is consistent with

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[21] C. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 4375 (1956).

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TABLE I

Complex		ΛM in $C_6H_5NO_2$ (10^{-3} *M*), mhos at 25°	Mol. wt.		μ_{eff} (B.M.)
			Calcd.	Found	
$[CrR_4Cl_2]Cl$	pink	21.4	1447	796	3.83
$[CrR_4Cl_2]ClO_4$	pink[a]	25.6	..	..	4.00
$[MnCl_2 \cdot 2R]^0$	yel. green	1.5	770	557	5.90
$[MnR_4](ClO_4)_2$	white	43.8	..	..	6.02
$FeCl_3 \cdot 2R$	yellow	11.9	807	493	5.92
$[FeR_4](ClO_4)_3$	white	52.4	..	..	6.11
$[CoCl_2 \cdot 2R]^0$	blue	2.0	774	539	4.77
$[CoBr_2 \cdot 2R]^0$	blue	2.3	863	836	4.76
$[CoR_4](ClO_4)_2$	blue	50.8	..	..	4.73
$[NiCl_2 \cdot 2R]^0$	blue	2.8	..	..	3.69
$[NiR_4](ClO_4)_2$	yellow	45.8	..	..	3.50
$[CuR_4](NO_3)_2$	pale blue	149.3 (DMF)[b]	..	..	1.91
$[ZnR_4](ClO_4)_2$	white	54.0	..	..	..
$[HgCl_2 \cdot 2R]^0$	white	1.2	916	570	..
$HgCl_2 \cdot R$	white	0.9	594	583	..
$[SnCl_4 \cdot 2R]^0$	white	0.9	..	..	..
$[SnBr_4 \cdot 2R]^0$	white	2.4	1083	646	..
$SbCl_3 \cdot 2R$	white	10.4	..	..	..
$[SbCl_5 \cdot R]^0$	white[a]	0.6	621	375	..

R = $(C_6H_5)_3AsO$

[a] Impure complexes, we believe. [b] In a subsequent communication we will report the measurements of conductances of a number of complexes in DMF (dimethylformamide). At dilutions of M/1000 1:1, 2:1 and 3:1 electrolytes exhibit molar conductances of 70–80, 135–175 and 200–250, respectively, in DMF at 25°.

TABLE II

Compound	Arsenyl frequency (cm.$^{-1}$)	Shift due to coördination (cm.$^{-1}$)
Ph_3AsO	879	–
$CrCl_3 \cdot 4R$	865	−14
$CrCl_2ClO_4 \cdot 4R$	874	− 5
$MnCl_2 \cdot 2R$	930 → 950 broad.	?
$Mn(ClO_4)_2 \cdot 4R$	872	− 7
$FeCl_3 \cdot 2R$	884, 871 shldr., 858	−21
$Fe(ClO_4)_3 \cdot 4R$	825	−54
$CoCl_2 \cdot 2R$	882, 862	−17
$CoBr_2 \cdot 2R$	880 shldr., 860	−19
$Co(ClO_4)_2 \cdot 4R$	860	−19
$NiCl_2 \cdot 2R$	841	−38
$Ni(ClO_4)_2 \cdot 4R$	858	−21
$Zn(ClO_4)_2 \cdot 4R$	867	−12
$Cu(NO_3)_2 \cdot 4R$	855 shldr., 841	−38
$HgCl_2 \cdot 2R$	880, 870, 860 shldr.	− 9
$HgCl_2 \cdot R$	810	−69
$SnCl_4 \cdot 2R$	885, 850	−29
$SnBr_4 \cdot 2R$	875, 840	−39
$SbCl_3 \cdot 2R$	846wk, 840wk, 822, 808	−64 av.
$SbCl_5 \cdot R$	835	−44

1:1 dissociation. The compound thus appears to have the structure $Cr[(C_6H_5)_3AsO]_4Cl_2{}^+Cl^-$. The low molecular weight also can be attributed to displacement of arsine oxide ligands by nitrobenzene solvent molecules, an effect discussed below under the non-electrolyte complexes. The isolation of the perchlorate salt, $Cr[(C_6H_5)_3AsO]_4Cl_2ClO_4$ (in an impure state), by the route described under experimental, is corroborative evidence. The latter complex functions as a 1:1 electrolyte also. Both complexes have magnetic moments close to the theoretical "spin only" value of 3.87 B.M. for three unpaired spins. As usual with Cr(III) the 3d electrons are spin free. We presume, then, that the complexes are octahedral.

Manganese(II).—The low molar conductance of the chloride complex indicates the non-electrolyte structure $[MnCl_2 \cdot 2(C_6H_5)_3AsO]$. The molecular weight of the substance is substantially less than the monomeric value. The same effect is observed for nearly all of the halide complexes we have prepared. Ionic dissociation is ruled out by the molar conductances. We feel that the most likely explanation is displacement of donor arsine oxide molecules by nitrobenzene solvent coördination. The perchlorate complex is thought to have the ionic structure, $Mn[(C_6H_5)_3AsO]_4{}^{++}$ $2ClO_4{}^-$, on the basis of its molar conductance. Both of these complexes have magnetic moments close to the "spin only" value of 5.92 B.M.

Iron(III).—The 11.9 ohm^{-1} molar conductance value for the chloride complex can be doubled, of course, if the dimeric molecular weight is used in the calculation. An ionic structure such as $Fe[(C_6H_5)_3AsO]_4Cl_2{}^+$ $FeCl_4{}^-$ would explain the data. Attempts at the isolation of the perchlorate salt, as was done in the Cr(III) case, yielded only poorly defined products, however. The perchlorate, $Fe[(C_6H_5)_3AsO]_4{}^{+3}$ $3ClO_4{}^-$, is presumably a 3:1 electrolyte, although the molar conductance is somewhat low, being in the range for a 2:1 electrolyte. (In DMF it is well within the range of 3:1 electrolytes.) We are aware of a conductance value for only one other 3:1 electrolyte in nitrobenzene, 86 ohm^{-1} for $Co(dipy)_3{}^{+3}3ClO_4{}^-$ at a dilution of 0.2×10^{-3} *M*.[23] Both complexes have magnetic moments close to the spin only value for 5 unpaired spins.

Cobalt(II).—The low molar conductances of the halide adducts indicate non-electrolyte structures, albeit with dissociation in polar solvents, in the case of the chloride adduct, as was observed with the manganese chloride complex and as is indicated again by the low apparent molecular weight in nitrobenzene. The perchlorate, $Co[(C_6H_5)_3AsO]_4{}^{++}2ClO_4{}^-$, behaves as a 2:1 electrolyte. The μ_{eff} values for the three complexes lie between 4.73 and 4.77 B.M., indicative of three unpaired spins. In addition they are all blue, a color usually associated with tetrahedral Co(II) complexes. Figgis and Nyholm point out that tetrahedral Co(II) complexes usually have values of μ_{eff} between 4.3 and 4.7 B.M., whereas the range for spin-free octahedral complexes is 4.8–5.6 B.M.[24] It is possible that the compounds are of the 4-coördinate type reported recently by Cotton and Holm in which the donor groups are oxygen and the proposed stereochemistry is tetrahedral.[25]

Nickel(II).—The chloride complex resembles the manganese and cobalt halide complexes. It dissolves in alcohol to give a green solution from which the blue crystals can be recovered. Such behavior may be due to dissociation and solvent coordination, although a simple increase in coördination number through solvent coördination is an alternate explanation. The perchlorate appears to be a 2:1 electrolyte. The magnetic moment of the perchlorate complex is similar to that reported for the analogous triphenylphosphine oxide complex by Cotton.[2b]

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(23) N. S. Gill, private communication.

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

(25) F. A. Cotton and R. H. Holm, *J. Chem. Phys.*, **32**, 1168 (1960).

Copper(II).—It should be noted that Cotton reports a very different product formed between copper(II) nitrate and triphenylphosphine oxide, specifically $[Cu(NO_3)_2 \cdot 2(C_6H_5)_3PO]$. While his preparative details differ from ours sufficiently to account for the difference in stoichiometry, it is also possible that the two ligands are sufficiently different to account for the difference. We will report shortly a comparative study of the donor behavior of $(C_6H_5)_3PO$, $(C_6H_5)_3AsO$ and C_5H_5NO toward most of the first row transition elements. No infrared absorption bands were observed for this compound in the 1531–1481 cm.$^{-1}$, 1290–1253 cm.$^{-1}$, 1034–970 cm.$^{-1}$ and 800-781 cm.$^{-1}$ regions which were not observed in both the $(C_6H_5)_3AsO$ and $(C_6H_5)_3As$ spectra, such as were reported for Cotton's adduct,[2e] indicative of nitrate coördination. $(C_6H_5)_3As$ and $(C_6H_5)_3AsO$ have strong peaks at 1370–1375 cm.$^{-1}$, but an additional strong peak is observed in this compound at 1345 cm.$^{-1}$ which may be due to the ν_3 NO_3^- absorption. The expected ionic nitrate peak at 800–840 cm.$^{-1}$ is difficult to assess in view of its proximity to the very strong As–O band at 841 cm.$^{-1}$ There is a very slight shoulder on the latter band on the low frequency side. While the evidence is not conclusive, we feel that the structure is ionic. The molar conductance in DMF supports the ionic structure, but we realize that this may result from substitution by the solvent. The magnetic moment is in the usual range for planar copper(II).

Mercury(II).—The 2:1 adduct, similar to some of the previous halide complexes, has an apparent molecular weight little above half the monomeric value. It is probably the monomeric structure $[HgCl_2 \cdot 2(C_6H_5)_3AsO]$ in the crystalline state, with partial replacement of arsine oxide ligand by solvent upon solution in nitrobenzene. The 1:1 adduct is monomeric in solution. It is possible that the three-covalent complex, $[HgCl_2 \cdot (C_6H_5)_3AsO]$, exists in solution, although solvent coordination resulting in tetrahedral coördination seems more likely. It is interesting that with only one arsine oxide ligand per acceptor atom there is no apparent displacement of the ligand by the solvent.

Tin(IV).—Both tin(IV) halide complexes are essentially non-electrolytes in nitrobenzene. Slight solubility precluded a molecular weight determination on the chloride. The non-electrolytic structure, $[SnX_4 \cdot 2(C_6H_5)_3AsO]$, is presumed.

Antimony(III).—The complex appears to ionize partially in nitrobenzene. It is not sufficiently soluble for a molecular weight determination. A similar situation was found among some five-covalent trihalide adducts of phosphorus, arsenic, antimony and bismuth with *o*-phenylenebisdimethylarsine ("diarsine") by Sutton.[26] Molecular weight determinations and the isolation of the complex, $[As(diarsine)I_2]^+ClO_4^- \cdot H_2O$, suggest that simple ionic dissociation occurs: $[M(diarsine)X_3]^0 = [M(diarsine)X_2]^+ \ X^-$. Such an effect may also occur in our complex resulting in the partial dissociation of the complex to $Sb[(C_6H_5)_3AsO]_2Cl_2^+$ ion.

Antimony(V).—The adduct is presumed to have the non-electrolytic structure, $[SbCl_5 \cdot (C_6H_5)_3AsO]$. Despite recrystallization this complex was only obtained in an impure state.

The qualitative strength of the arsine oxide as a donor can be inferred from the preparative and analytical work reported here. It is certainly strong enough to displace water from the coördination sphere of some metal ions, when the water is present at an activity level roughly comparable to that of the arsine oxide. On the other hand water and nitrobenzene, when either is present at high activity, *i.e.*, acting as a solvent, are capable of at least partially displacing the arsine oxide from the coördination sphere.

Infrared Spectra.—On coördination the As–O stretching frequency generally is lowered, the absorption maximum at 879 cm.$^{-1}$ usually being absent and fresh peaks appearing at lower frequencies. We assume that these peaks are due to the As–O stretching frequencies in the complexes. In some cases the As–O peaks are broad, sufficiently so with $MnCl_2 \cdot 2(C_6H_5)_3AsO$ to preclude a specific assignment of the frequency. It is reasonable to assume some double bond character for the As–O bond in the arsine oxide as arising from $p\pi$-$d\pi$ overlap of filled $p\pi$ orbitals on the oxygen with appropriate empty $d\pi$ orbitals on the arsenic. $(C_6H_5)_3AsO$ presumably can coördinate only through the oxygen atom which should tend to reduce the electron density in the π orbital. If the As–O σ bond is affected to a smaller extent, the As–O frequency will be lowered. With a number of 2:1 adducts the As–O frequency appears to be split, with one peak in the region of the uncoördinated As–O frequency and another at a lower frequency. We have observed this before.[27] It could be explained by the presence of non-equivalent ligand molecules held in the lattice. The crystal structure of $SnCl_4 \cdot 2POCl_3$ (in which the splitting is observed) shows equivalent ligand molecules, however, ruling such an explanation out in at least one case.[28] Coupling between the As-O vibrations of two ligands coördinated to the same acceptor atom may be the explanation.

A detailed discussion of the infrared spectra of the analogous triphenylphosphine oxide complexes has been published by Cotton.[29]

Acknowledgment.—This work was supported in part by the Office of Naval Research.

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