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Triphenylarsine and Triphenylarsine Oxide Complexes of Cobalt(II)

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This paper reports spectral, magnetic, and X-ray powder data for several cobalt(II) complexes of triphenylarsine oxide, and the preparation and characterization of the triphenylarsine complex, $[\text{Co}((\text{C}_6\text{H}_5)_3\text{As})_2\text{I}_2]$. In addition to the compounds $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{Cl}_2]$, $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{Br}_2]$, and $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_4](\text{ClO}_4)_2$ previously reported by Phillips and Tyree, the new compounds $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{I}_2]$, $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_4]\text{I}_2$, and $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2(\text{NCS})_2]$ also were studied. The results are discussed in terms of ligand field theory. Points of particular interest are the formation of $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_4]\text{I}_2$, in which the neutral ligand has displaced an anionic ligand, the evidence that in the thiocyanate complex the thiocyanate ions are N-bonded, and the properties of $[\text{Co}((\text{C}_6\text{H}_5)_3\text{As})_2\text{I}_2]$, which is the only triphenylarsine complex which could be isolated, although several analogous triphenylphosphine complexes of Co(II) are known.

Introduction

The coordination compounds of triphenylphosphine oxide with a number of transition metals have been examined in some detail.²⁻¹¹ The information on complexes of triphenylarsine oxide is more limited, however. There have been a few isolated examples of complexes containing arsine oxides in the earlier literature¹²⁻¹⁴; more recently, Phillips and Tyree¹⁵ have made a general survey of the coordination chemistry of triphenylarsine oxide, reporting complexes with salts of eight transition metals and two non-transition metals, and previous papers from this Laboratory have reported in detail on the molecular and electronic structures of complexes of Cu(II) halides,¹⁰ Ni(II) halides,¹⁶ and Mn(II) halides.¹¹ In this paper we are reporting a similar detailed study of some Co(II) complexes of triphenylarsine oxide.

In addition, we have attempted to prepare triphenylarsine complexes of Co(II) analogous to

those formed by triphenylphosphine.^{17,18}

Experimental

Preparation of Compounds. Diiodobis(triphenylarsine)cobalt(II).—A hot solution of triphenyl arsine (4.08 g., 0.0133 mole) in nitromethane (20 ml.) was mixed with one of hexaaquo cobalt(II) iodide (2.81 g., 0.0067 mole) in the same solvent (5 ml.). The deep-green solution obtained yielded brown crystals on cooling. These were filtered, washed with a small quantity of diethyl ether, and dried *in vacuo* over sulfuric acid; yield, 2.07 g. (33%), m.p. 200°. *Anal.* Calcd. for $\text{C}_{36}\text{H}_{30}\text{As}_2\text{CoI}_2$: C, 46.73; H, 3.27; As, 16.19; I, 27.44. Found: C, 46.64; H, 3.23; As, 15.92; I, 27.43. The compound forms green solutions in cold chloroform, acetone, or acetonitrile, but a blue solution is formed with cold ethyl acetate. It is insoluble in cyclohexane, carbon tetrachloride, and chlorobenzene, and decomposed by methylene chloride or dioxane.

Dihalobis(triphenylarsine oxide)cobalt(II) Compounds.—These were all prepared by essentially the same method. A solution of triphenylarsine oxide (0.01 mole) in absolute ethanol (~6 ml.) was mixed with a solution of the cobalt salt (0.005 mole) in absolute ethanol (~5 ml.). For the chloro and bromo compounds the products separated immediately as blue crystals. For the thiocyanato compound the product separated from hot solution as a blue oil which subsequently was crystallized by cooling the mixture for 2 hr. in a refrigerator followed by warming and stirring. In preparing the iodo compound, as the CoI_2 solution was added to the $(\text{C}_6\text{H}_5)_3\text{AsO}$ solution a bright blue solid formed immediately but on completion of the addition of the CoI_2 the color of the solid tended to blue-green. The mixture was heated to boiling and then allowed to cool with stirring for an hour when the solid was entirely blue-green. The crystals of all complexes were filtered, washed once with cold absolute ethanol, and dried *in vacuo* over sulfuric acid. The yields, colors, melting points, and analyses of these compounds are given in Table I.

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TABLE I
 PROPERTIES AND ANALYTICAL DATA FOR $\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{X}_2$ COMPOUNDS

Compound	Color	Yield, %	M.P.	Analyses							
				C		H		Cl, Br, I, or N		Co	
				Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
$\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{Cl}_2$	Blue	82	232	55.6	55.84	3.91	3.91	9.21	9.16
$\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{Br}_2$	Blue	86	214	49.9	50.09	3.52	3.50	18.5	18.52
$\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{I}_2$	Blue-green	82	205	45.6	45.17	3.18	3.16	25.8	26.52
$\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2(\text{NCS})_2$	Blue	86	201	55.6	55.69	3.96	3.69	3.34	3.42	6.91	7.19

Tetrakis(triphenylarsine oxide)cobalt(II) Perchlorate.—This was prepared as were the dihalo complexes and precipitated immediately on mixing the reactants as blue crystals; yield, 85%; m.p. 334°. *Anal.* Calcd. for $\text{C}_{72}\text{H}_{60}\text{As}_4\text{Cl}_2\text{CoO}_{12}$: C, 55.91; H, 3.91. Found: C, 56.20; H, 3.95.

Tetrakis(triphenylarsine oxide)cobalt(II) Iodide.—A solution of cobalt iodide (1.04 g., 0.0033 mole) in absolute ethanol (5 ml.) was added dropwise to a vigorously stirred solution of triphenylarsine oxide (5.34 g., 0.0167 mole) also in absolute ethanol (7 ml.) cooled in ice. A bright blue solid separated and was filtered, washed with absolute ethanol, and dried *in vacuo* over sulfuric acid; yield, 4.17 g. (78%), m.p. 218°. *Anal.* Calcd. for $\text{C}_{72}\text{H}_{60}\text{As}_4\text{CoI}_2\text{O}_4$: C, 53.99; H, 3.78; I, 15.85. Found: C, 54.32; H, 3.92; I, 15.31.

Physical Measurements. Electrolytic Conductances.—These were measured using a Serfass bridge and a conventional cell, previously calibrated with an aqueous solution of potassium chloride. The results are shown in Table II.

Magnetic Measurements.—Magnetic measurements were carried out by the Gouy method, using tubes calibrated with $\text{HgCo}(\text{NCS})_4$, as previously described.^{18,19} The results are shown in Table II. In all cases the susceptibilities at ~ 300 , ~ 195 , and $\sim 75^\circ\text{K}$. could be fitted to a straight line on plotting $1/\chi_{\text{Mol}}^{\text{Corr}}$ against T and we quote here only the values of μ and θ as defined by the Curie-Weiss law, $\mu = 2.84 [\chi_{\text{Mol}}^{\text{Corr}} (T - \theta)]^{1/2}$. The $\chi_{\text{Mol}}^{\text{Corr}}$ values used were corrected for diamagnetism and for temperature independent paramagnetism (TIP) as previously described.¹⁹ For $[\text{Co}((\text{C}_6\text{H}_5)_3\text{As})_2\text{I}_2]$ the TIP was taken as 500×10^{-6} c.g.s. units; for the arsine oxide complexes TIP was calculated from the Δ value given in Table II. Diamagnetic corrections were estimated from Pascal's constants.²⁰ By inserting μ , T , and θ in the Curie-Weiss expression and deducting the two corrections (Table II) from the values of $\chi_{\text{Mol}}^{\text{Corr}}$ so obtained the experimental molar susceptibility values may be recovered to within the experimental uncertainties.

X-Ray Powder Diagrams.—Many of these were obtained for us by Miss R. Babineau of Arthur D. Little Co., to whom we express our appreciation. Table III lists the interplanar spacings and relative intensities for the stronger lines.

Measurements of Electronic Spectra.—The spectra were obtained using a Cary Model 14 recording spectrophotometer. The technique used for the mull spectra has been described previously.^{18,19} The data are shown in

Table IV and some representative spectra are illustrated in Fig. 1 and 2.

Discussion

Triphenylarsine Complexes.—We attempted the preparation of several, using the chloride, bromide, iodide, and thiocyanate of Co(II), but only with the iodide did we succeed. Using chloride or bromide no product was isolated, while with the thiocyanate, which was treated with triphenylarsine in CH_2Cl_2 , with free exposure of the reaction mixture to air, the only isolable product was dithiocyanatobis(triphenylarsine oxide)cobalt (II). Attempts to prepare the triphenylmethylarsonium and tetra-*n*-butylammonium salts of $[\text{Co}((\text{C}_6\text{H}_5)_3\text{As})\text{I}_3]^-$ using stoichiometric quantities of reactants gave, with the first cation, only $((\text{C}_6\text{H}_5)_3\text{CH}_2\text{As})_2\text{CoI}_4$ and with the second no product was isolated.

Thus diiodobis(triphenylarsine)cobalt(II) is the first and, so far, the only arsine complex of tetrahedral Co(II) to be prepared. A study of its properties and electronic structure therefore has special interest for the information it might provide about the reasons for the apparent instability of other triphenylarsine complexes. A series of triphenylphosphine complexes can be made rather easily¹⁷ and in various other classes of complexes arsine and phosphine are frequently similar in their properties.

Diiodobis(triphenylarsine)cobalt(II) is a brown solid. Its infrared spectrum had no bands attributable to an As-O group. In nitrobenzene it showed an equivalent conductance of 4.5 ohm^{-1} at 25° . This is well below the range ($18\text{--}30 \text{ ohm}^{-1}$) typical of 1:1 electrolytes in this solvent and may be considered to be in satisfactory accord with the postulated non-ionic structure. It has been found previously that analogous triphenylphosphine compounds also exhibit similar low conductances, which are attributable to slight solvolytic ionization.¹⁸

The electronic spectrum of solid $[\text{Co}((\text{C}_6\text{H}_5)_3\text{As})_2\text{I}_2]$ is clearly recognizable as that of a compound containing Co(II) tetrahedrally coordinated

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TABLE II: ELECTROLYTIC CONDUCTANCES, MAGNETIC MOMENTS, AND SPECTRAL DATA FOR THE COMPLEXES

Compound	solutions			Magnetic data			Spectral data and ligand field parameters					
	Temp. °C.	CH ₃ NO ₂	Temp. °C.	μ _B	θ, °K.	λ, cm. ⁻¹	Molar susc. corr. dia.	X 10 ⁶ TIP	ν ₂	ν ₃	Δ	B'
	°C.	°C.	°C.	B.M.	°K.	cm. ⁻¹	dia.		(cm. ⁻¹)			
[Co((C ₆ H ₅) ₂ AsO) ₂ Cl ₂]	4.5	25.0	...	4.62 ± 0.05	-9	...	-470	500
[Co((C ₆ H ₅) ₂ AsO) ₂ Cl ₂]	2.2	27.8	...	4.60	-6.5	149	-450	640	5700	15,400	3270	753
[Co((C ₆ H ₅) ₂ AsO) ₂ Br ₂]	2.6	28.1	...	4.63	-6.5	155	-470	645	5670	15,000	3250	727
[Co((C ₆ H ₅) ₂ AsO) ₂ Cl ₂]	5.9	26.9	...	4.68	-8	163	-485	650	5600	14,800	3210	717
[Co((C ₆ H ₅) ₂ AsO) ₂ (NCS) ₂]	4.1	31.1	...	4.54	-10	166	-480	525	6870	16,000	3976	729
[Co((C ₆ H ₅) ₂ AsO) ₂ (ClO ₄) ₂]	63.1	27.9	164	4.55	-6	158	-830	560	6450	16,000	3720	754
[Co((C ₆ H ₅) ₂ AsO) ₂ I ₂]	21.1	29.1	136	4.58	-6	174	-910	530	6800	16,000	3930	736

TABLE III: X-RAY POWDER DATA FOR [M(P(C₆H₅)₂XO)₂Y₂] COMPOUNDS^{a,b}

M X Y	Co			Ni			Mn			Co			Ni			Mn			Ni			
	As Cl	P Cl	As Br	As Br	P Br	As Br	P Br	As Br	P Br	As Br	P Br	As Br	P Br	As Br	P Cl	As Cl	As Cl	P Cl	As Cl	P Cl	As Cl	
8.90 (50)	8.80 (48)	8.80 (90)	8.80 (62)	9.60 (26)	9.50 (22)	9.00 (14)	9.05 (16)	8.79 (26)	10.2 (14)	8.80 (18)	9.30 (15)	8.80 (18)	8.80 (18)	8.80 (18)	8.80 (18)	8.80 (18)	8.80 (18)	8.80 (18)	8.80 (18)	8.80 (18)	8.80 (18)	8.80 (18)
8.60 (59)	8.60 (78)	8.50 (66)	8.60 (53)	8.75 (100)	8.80 (89)	8.70 (24)	8.85 (28)	8.25 (100)	9.40 (11)	8.60 (47)	8.70 (65)	8.60 (47)	8.60 (47)	8.60 (47)	8.60 (47)	8.60 (47)	8.60 (47)	8.60 (47)	8.60 (47)	8.60 (47)	8.60 (47)	8.60 (47)
6.95 (68)	7.00 (63)	6.85 (104)	6.95 (90)	8.30 (89)	8.20 (100)	...	8.61 (18)	7.00 (7)	8.90 (9)	7.80 (60)	8.50 (100)	7.80 (60)	7.80 (60)	7.80 (60)	7.80 (60)	7.80 (60)	7.80 (60)	7.80 (60)	7.80 (60)	7.80 (60)	7.80 (60)	7.80 (60)
6.43 (72)	6.45 (48)	6.45 (35)	6.30 (22)	7.80 (21)	7.78 (20)	8.35 (100)	8.25 (100)	5.50 (11)	8.40 (3)	7.35 (57)	7.60 (11)	7.35 (57)	7.35 (57)	7.35 (57)	7.35 (57)	7.35 (57)	7.35 (57)	7.35 (57)	7.35 (57)	7.35 (57)	7.35 (57)	7.35 (57)
5.62 (21)	5.60 (21)	5.60 (28)	5.60 (17)	7.20 (38)	7.20 (30)	7.10 (24)	7.00 (14)	4.20 (78)	8.10 (12)	6.95 (31)	6.80 (16)	6.95 (31)	6.95 (31)	6.95 (31)	6.95 (31)	6.95 (31)	6.95 (31)	6.95 (31)	6.95 (31)	6.95 (31)	6.95 (31)	6.95 (31)
5.05 (59)	5.00 (47)	5.01 (76)	5.05 (27)	6.80 (31)	6.78 (29)	5.68 (12)	5.65 (14)	3.66 (97)	6.50 (6)	6.40 (43)	6.00 (9)	6.40 (43)	6.40 (43)	6.40 (43)	6.40 (43)	6.40 (43)	6.40 (43)	6.40 (43)	6.40 (43)	6.40 (43)	6.40 (43)	6.40 (43)
5.01 (89)	4.95 (76)	4.97 (134)	4.98 (67)	5.84 (15)	5.82 (15)	5.50 (25)	5.43 (22)	3.60 (22)	6.35 (4)	6.15 (18)	6.00 (9)	6.15 (18)	6.15 (18)	6.15 (18)	6.15 (18)	6.15 (18)	6.15 (18)	6.15 (18)	6.15 (18)	6.15 (18)	6.15 (18)	6.15 (18)
4.44 (43)	4.40 (38)	4.40 (110)	4.40 (62)	5.28 (26)	5.28 (24)	5.18 (17)	5.16 (12)	3.48 (60)	5.62 (12)	5.84 (24)	5.80 (13)	5.84 (24)	5.84 (24)	5.84 (24)	5.84 (24)	5.84 (24)	5.84 (24)	5.84 (24)	5.84 (24)	5.84 (24)	5.84 (24)	5.84 (24)
4.33 (68)	4.30 (48)	4.30 (97)	4.30 (95)	5.15 (16)	5.10 (11)	5.08 (23)	5.00 (20)	3.15 (54)	5.10 (100)	5.57 (100)	5.32 (9)	5.57 (100)	5.57 (100)	5.57 (100)	5.57 (100)	5.57 (100)	5.57 (100)	5.57 (100)	5.57 (100)	5.57 (100)	5.57 (100)	5.57 (100)
4.15 (100)	4.15 (100)	4.15 (100)	4.17 (100)	4.82 (15)	4.84 (12)	4.47 (40)	4.42 (32)	...	4.44 (4)	5.38 (40)	5.18 (12)	5.38 (40)	5.38 (40)	5.38 (40)	5.38 (40)	5.38 (40)	5.38 (40)	5.38 (40)	5.38 (40)	5.38 (40)	5.38 (40)	5.38 (40)
3.83 (25)	3.82 (10)	4.67 (41)	4.64 (26)	4.44 (36)	4.39 (48)	...	4.34 (11)	4.94 (20)	5.05 (23)	4.94 (20)	4.94 (20)	4.94 (20)	4.94 (20)	4.94 (20)	4.94 (20)	4.94 (20)	4.94 (20)	4.94 (20)	4.94 (20)	4.94 (20)
3.66 (48)	3.66 (22)	3.65 (41)	3.66 (35)	4.46 (15)	4.42 (15)	4.33 (51)	4.31 (31)	...	4.17 (12)	4.75 (31)	4.80 (33)	4.75 (31)	4.75 (31)	4.75 (31)	4.75 (31)	4.75 (31)	4.75 (31)	4.75 (31)	4.75 (31)	4.75 (31)	4.75 (31)	4.75 (31)
3.64 (23)	3.62 (24)	3.63 (41)	3.63 (25)	4.22 (24)	4.24 (27)	4.25 (27)	4.22 (31)	...	4.00 (9)	4.58 (60)	4.62 (25)	4.58 (60)	4.58 (60)	4.58 (60)	4.58 (60)	4.58 (60)	4.58 (60)	4.58 (60)	4.58 (60)	4.58 (60)	4.58 (60)	4.58 (60)
3.45 (16)	3.47 (8)	...	3.49 (17)	4.16 (38)	4.15 (29)	4.18 (41)	4.15 (26)	...	3.40 (3)	4.44 (50)	4.44 (11)	4.44 (50)	4.44 (50)	4.44 (50)	4.44 (50)	4.44 (50)	4.44 (50)	4.44 (50)	4.44 (50)	4.44 (50)	4.44 (50)	4.44 (50)
3.35 (13)	3.34 (8)	...	3.32 (9)	4.11 (38)	4.10 (33)	3.70 (32)	3.31 (4)	4.30 (30)	4.85 (9)	4.30 (30)	4.30 (30)	4.30 (30)	4.30 (30)	4.30 (30)	4.30 (30)	4.30 (30)	4.30 (30)	4.30 (30)	4.30 (30)	4.30 (30)
3.30 (18)	3.28 (24)	3.27 (52)	3.27 (21)	4.04 (18)	4.04 (16)	3.66 (26)	3.66 (30)	...	3.14 (4)	4.23 (15)	4.24 (14)	4.23 (15)	4.23 (15)	4.23 (15)	4.23 (15)	4.23 (15)	4.23 (15)	4.23 (15)	4.23 (15)	4.23 (15)	4.23 (15)	4.23 (15)

^a The entries record interplanar spacings and, in parentheses, relative intensities of the more prominent lines. ^b There is considerable similarity of the patterns for [Mn((C₆H₅)₂PO)₂Br₂] and [Ni((C₆H₅)₂PO)₂Br₂] out to *d* values of ~4.2; isomorphism might well be assumed on the basis of these data alone. However, there are enough differences outside this range that we have hesitated to draw this conclusion definitely.

TABLE IV
SPECTRAL DATA FOR THE COMPLEXES

Compound	Medium	$m\mu$	cm.^{-1}	ϵ_{molar}	Compound	Medium	$m\mu$	cm.^{-1}	ϵ_{molar}		
[Co{(C ₆ H ₅) ₃ -AsO} ₂ Cl ₂]	C ₄ Cl ₆ mull	2000	5,000	..	[Co{(C ₆ H ₅) ₃ -AsO} ₄ I ₂]	C ₄ Cl ₆ mull	~578sh	~17,300	..		
		1730	5,780	..			564	17,730	..		
		1550	6,450	..		CH ₂ Cl ₂	~1650 ^a	~6,100 ^a	70		
		682	14,660	..			0.001 M	~729sh	~13,700	..	
		~650sh	~15,400	..		675	14,810	349			
		~620sh	~16,100	..		621	16,100	381			
	CH ₂ Cl ₂	1910	5,240	60		~585sh	~17,100	..			
		0.001 M	1730	5,780		65	[Co{(C ₆ H ₅) ₃ -AsO} ₂ (NCS) ₂]	C ₄ Cl ₆ mull	(broad absorption centering at		
			1525	6,560		67			~1450	~6,900	..)
			675	14,810		536			(broad absorption centering at		
			~645sh	~15,500		..			~625	~16,000	..)
			~625sh	~16,000		..			~510sh	~19,600	..
~602sh	~16,600		..	CH ₂ Cl ₂	~1550sh	~6,450			..		
~590sh	~16,950	..	0.005 M		1400	7,140		133			
[Co{(C ₆ H ₅) ₃ -AsO} ₂ Br ₂]	C ₄ Cl ₆ mull	2060	4,850		..	~1290sh		~7,750	..		
		1740	5,750		..	640		15,630	835		
		1530	6,530		..	610		16,390	825		
		704	14,200		..	~575sh		~17,400	..		
		656	15,240	..	[Co{(C ₆ H ₅) ₃ -AsO} ₄ -(ClO ₄) ₂]	C ₄ Cl ₆ mull		(broad absorption centering at			
		~635sh	~15,750	..			~1550	~6,450	..)		
	~605sh	~16,500	..	654			15,290	..			
	~2000sh	~5,000	..	600			16,670	..			
	CH ₂ Cl ₂	1740	5,750	75			~565sh	~17,700	..		
		1540	6,490	75			CH ₂ Cl ₂	1750	5,710	66	
		698	14,330	518		0.001 M	1540	6,490	72		
		652	15,360	462		1350	7,410	70			
~633sh		~15,800	..	646		15,480	415				
~620sh		~16,100	..	~623sh		~16,050	..				
~605sh	~16,500	..	600	16,670		395					
[Co{(C ₆ H ₅) ₃ -AsO} ₂ I ₂]	C ₄ Cl ₆ mull	(broad absorption centering at				~578sh	~17,300	..			
		~1790	~5,590	..)	557	17,950	260				
		747	13,400	..	[Co{(C ₆ H ₅) ₃ -As ₂ I ₂]	C ₄ Cl ₆ mull	1882	5,310	..		
		675	14,800	..			1530	6,540	..		
		~646sh	~15,480	..			1167	8,570	..		
		635	15,750	..			~850sh	~11,800	..		
	615	16,260	..	790			12,660	..			
	~633sh	~15,800	..	~766sh			~13,050	..			
	CH ₂ Cl ₂	619	16,160	394		~732sh	~13,700	..			
		(broad absorption centering at				702	14,250	..			
		~1750	~5,710	93)		~660sh, w	~15,150	..			
		736	13,590	457		~615sh, w	~16,300	..			
670		14,930	461	~508		19,700	..				
~633sh		~15,800	..	CHCl ₃		~1880sh	~5,320	..			
[Co{(C ₆ H ₅) ₃ -AsO} ₄ I ₂]	C ₄ Cl ₆ mull	1750	5,710		..	0.001 M	1715	5,830	47		
		1640	6,100		..	1400	7,140	70			
		1500	6,670		..	705	14,180	335			
		~1350sh	~7,410		..	658	15,200	425			
		650	15,380		..	~615sh	~16,300	..			
		~625sh	~16,000	..							
	600	16,670	..								

^a Very broad band with no resolved structure.

nated but with considerable broadening and splitting of the observed absorption bands, attributable to the presence of ligands making grossly different contributions to the ligand field, *i.e.*, of a pronounced C_{2v} component to the basic tetrahedral field; the spectrum is similar to that of [Co-

((C₆H₅)₃P)₂I₂].^{17,21} Because of the great breadth and complexity of the bands, no attempt was

(21) In reference 17 the appearance of ν_2 was not reported because at that time we did not have a spectrometer which covered the 1.2-2.0- μ region. We now have studied the ν_2 absorption of [Co-((C₆H₅)₃P)₂I₂] and find the following bands, given in cm.⁻¹: ~5560 (sh), 6850, 8890.

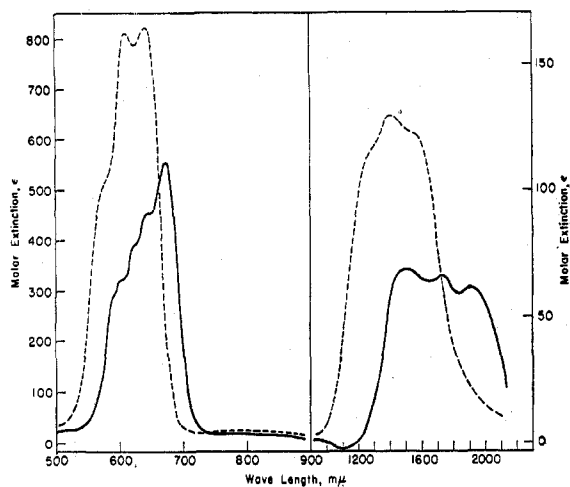


Fig. 1.—The spectra of $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO}_2)\text{Cl}_2]$, 0.001 M in CH_2Cl_2 (—) and $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2(\text{NCS})_2]$, 0.001 M in CH_2Cl_2 (- - -).

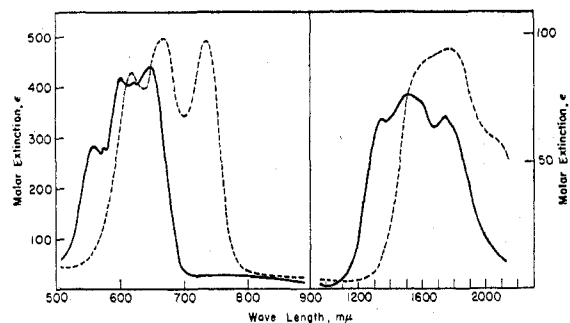


Fig. 2.—The spectra of $[(\text{C}_6\text{H}_5)_3\text{AsO}_4\text{Co}](\text{ClO}_4)_2$, 0.001 M in CH_2Cl_2 (—) and $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{I}_2]$, 0.001 M in CH_2Cl_2 (- - -).

made to estimate band centers and then to calculate the Δ value. However, it can be inferred by direct comparison of the spectra that strength of the tetrahedral field is about the same in $[\text{Co}((\text{C}_6\text{H}_5)_3\text{As})_2\text{I}_2]$ as it is in $[\text{Co}((\text{C}_6\text{H}_5)_3\text{P})_2\text{I}_2]$. This conclusion is given quantitative support by the fact that the magnetic moments of both compounds are 4.62 ± 0.05 B.M.

It also should be recorded that $[\text{Co}((\text{C}_6\text{H}_5)_3\text{As})_2\text{I}_2]$ gives green solutions in all solvents tested, whereas the solid compound is brown. The spectral data for a green solution in chloroform are summarized in Table II and may be compared with the data for the solid. It appears that this color change is not due to any changes in the ν_2 and ν_3 bands except those of the sort frequently observed on going from the solid to solution (mainly a narrowing of bands and disappearance of some shoulders). The color change instead is due mainly to relatively small variations in the absorption rising steeply into the ultraviolet and

TABLE V
COMPARISON OF SPECTROSCOPICALLY DERIVED Δ VALUES AND MAGNETIC MOMENTS FOR ANALOGOUS $(\text{C}_6\text{H}_5)_3\text{PO}$ AND $(\text{C}_6\text{H}_5)_2\text{AsO}$ COMPLEXES

Compounds	Reference	μ , B.M.	Δ , cm^{-1}
$[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_4]^{2+}$		4.56	~ 3800
$[\text{Co}((\text{C}_6\text{H}_5)_3\text{PO})_4]^{2+}$	19	4.53	3680
$[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{Cl}_2]$		4.60	3270
$[\text{Co}((\text{C}_6\text{H}_5)_3\text{PO})_2\text{Cl}_2]$	19	4.58	3270
$[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{Br}_2]$		4.63	3250
$[\text{Co}((\text{C}_6\text{H}_5)_3\text{PO})_2\text{Br}_2]$	19	4.63	3180
$[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{I}_2]$		4.68	3210
$[\text{Co}((\text{C}_6\text{H}_5)_3\text{PO})_2\text{I}_2]$		4.79 ^a	3056 ^a
$[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2(\text{NCS})_2]$		4.54	3976
$[\text{Co}((\text{C}_6\text{H}_5)_3\text{PO})_2(\text{NCS})_2]$	19	4.46	4030

^a The moment of 4.82 B.M. previously reported¹⁷ for this compound was computed using an estimated TIP of 500×10^{-6} c.g.s. units. The moment listed above has been recalculated from the same susceptibility data with a TIP value of 684×10^{-6} c.g.s. units obtained from the Δ value also given in this table. The Δ value, 3056 cm^{-1} , has been calculated from experimental data (using a mull in hexachlorobutadiene) not previously reported, *viz.*, for the visible band, ν_3 , 632 $m\mu$, 681 $m\mu$, 727 $m\mu$, and for the infra-red band, ν_2 , 1670 $m\mu$, 1880 $m\mu$, 2135 $m\mu$. From these data we estimate the band energies as 14,500 cm^{-1} (ν_3) and 5340 cm^{-1} (ν_2) and using equations previously given¹⁹ we calculate $\Delta = 3056 \text{ cm}^{-1}$, $B' = 711 \text{ cm}^{-1}$.

other small changes, but does not seem to imply any gross change in the nature of the absorbing species.

Our studies of $[\text{Co}((\text{C}_6\text{H}_5)_3\text{As})_2\text{I}_2]$ have not provided any clues to the seeming instability, or at least difficulty of preparation, of triphenylarsine complexes relative to their triphenylphosphine analogs.

X-Ray Powder Patterns.—Comparison of the X-ray powder diffraction patterns of $[\text{Co}((\text{C}_6\text{H}_5)_3\text{P})_2\text{I}_2]$, $[\text{Co}((\text{C}_6\text{H}_5)_3\text{As})_2\text{I}_2]$, and $[\text{Ni}((\text{C}_6\text{H}_5)_3\text{P})_2\text{I}_2]$ shows that the cobalt phosphine and the nickel phosphine complexes are isomorphous. The cobalt arsine complex has a pattern which is very similar but not exactly identical with those of the other two compounds. The chief differences are (a) in certain relative intensities and (b) in the presence of a few additional, relatively weak lines in the arsine compound. It seems likely that the arsine compound has a structure which is either exactly the same or very nearly the same as those of the phosphine complexes, with the small differences in the powder patterns being due chiefly to the fact that arsenic will make considerably greater contributions to certain structure factors (F_{hkl}) than does phosphorus. In view of the fact that the nickel complex has been shown to

have a tetrahedral structure,²² it follows that the two cobalt complexes also have such a structure.

Triphenylarsine Oxide Complexes.—Six complexes of this class have been prepared and studied. They are listed, together with some of their properties, in Table I. Three of them, $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{Cl}_2]$, $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{Br}_2]$, and $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_4](\text{ClO}_4)_2$ already have been reported by Phillips and Tyree.¹⁵ Our observations on these compounds are in agreement with theirs insofar as comparisons can be made. Their magnetic moments are significantly higher than those we record in Table II, but this probably is due to the fact that theirs are based only on room-temperature measurements and are calculated without correction for temperature independent paramagnetism and without allowance for θ values of $\sim -6^\circ$ in the Curie-Weiss equation ($\mu = 2.84 [\chi_{\text{Mol}}^{\text{Corr}}(T-\theta)]^{1/2}$).

The isolation of green $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{I}_2]$ completes the series of dihalobis(triphenylarsine oxide)cobalt(II) complexes. This compound has properties expected in comparison with those of the chloro and bromo analogs.

The blue compound $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_4]\text{I}_2$ is, so far as we know, unique in that neutral ligands have completely displaced from the tetrahedral coordination sphere anions which are capable of functioning as donors. It seems quite possible, and perhaps likely, that this compound is only metastable relative to the neutral, green $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{I}_2]$. Thus when a finely powdered specimen of the blue compound was left standing on the bench overnight it turned green, and when a slurry of the blue compound was stirred with a solution of cobalt iodide in absolute ethanol it turned green after 3–4 hr. It also gives a green solution in nitrobenzene which has a molar conductance well below the normal range for 1:2 electrolytes in this solvent, although the conductance in nitromethane, a somewhat more ionizing solvent, is nearly normal. In addition, the visible spectra (ν_3 absorption region) in both nitrobenzene and chloroform (see Table IV) differ from each other and from the reflectance and mull spectra of the solid. While there is no evidence of the formation of $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{I}_2]$, although some may be formed when $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_4]\text{I}_2$ turns green, either in solution or under the other conditions mentioned, the conductance data suggest that the color change is caused by iodide ions entering the coordination sphere. The green

color is to be attributed to charge transfer absorption in the very near ultraviolet, which always is found in tetrahedral complexes of this type^{10, 11, 16, 17, 19, 23} containing coordinated iodide ions.

An attempt was made to isolate $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_4]\text{Br}_2$ but this was unsuccessful, only $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{Br}_2]$ being obtained.

The isolation of $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_4]\text{I}_2$ was accomplished by running a cold solution of CoI_2 into a cold solution of $(\text{C}_6\text{H}_5)_3\text{AsO}$, whereupon the blue compound precipitates instantly. On the assumption that it is the maintenance of an excess of $(\text{C}_6\text{H}_5)_3\text{AsO}$ and low temperature which permits the isolation of this metastable compound, an attempt was made to isolate the analogous $(\text{C}_6\text{H}_5)_3\text{PO}$ compound by the same technique. When the CoI_2 solution first was added to the $(\text{C}_6\text{H}_5)_3\text{PO}$ solution a bright blue color was observed but this gradually turned purple. On standing in a refrigerator overnight, green-blue $[\text{Co}((\text{C}_6\text{H}_5)_3\text{PO})_2\text{I}_2]$ was formed. Evidently the low solubility of the arsine oxide compound is a critical factor. Quite generally, we have observed that the arsine oxide complexes are significantly less soluble than their phosphine oxide analogs.

In Table V the data for the triphenylarsine oxide complexes are compared with data for analogous triphenylphosphine oxide complexes. It will be seen that in all cases the analogous pairs have virtually identical magnetic moments, the differences being within experimental error. The Δ values tend, with one exception, to be slightly higher for the arsine oxide complexes, which is in line with a previous inference from the spectra of some tetrahedral nickel(II) complexes²³ that triphenylarsine oxide provides a stronger ligand field than does triphenylphosphine oxide.

The spectral data for $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2(\text{NCS})_2]$ lead to a Δ value (ligand field strength parameter) of $\sim 4000 \text{ cm.}^{-1}$ and the magnetic moment is 4.54 B.M. These are virtually the same as the corresponding parameters for $[\text{Co}((\text{C}_6\text{H}_5)_3\text{PO})_2(\text{NCS})_2]$ and on the basis of arguments previously given for the phosphine oxide complex¹⁸ they lead to the conclusion that the thiocyanate ions are bonded to cobalt through their nitrogen atoms.

X-Ray Powder Patterns.—X-Ray powder patterns have been obtained for the following twelve compounds: $[\text{M}((\text{C}_6\text{H}_5)_3\text{XO})_2\text{Y}_2]$ in which $\text{M} = \text{Co, Ni, or Mn}$, $\text{X} = \text{P or As}$, and $\text{Y} = \text{Cl or Br}$.

(22) L. M. Venanzi, *J. Chem. Soc.*, 7119 (1958).

(23) D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).

The observations are summarized in Table III. Systematic intercomparison of all possible pairs (66) showed that only in the following three groups does isomorphism definitely appear to exist

1. $\{[\text{Mn}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{Cl}_2], [\text{Mn}((\text{C}_6\text{H}_5)_3\text{PO})_2\text{Cl}_2],$
 $[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{Cl}_2], [\text{Co}((\text{C}_6\text{H}_5)_3\text{PO})_2\text{Cl}_2]\}$
2. $\{[\text{Co}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{Br}_2], [\text{Ni}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{Br}_2]\}$
3. $\{[\text{Mn}((\text{C}_6\text{H}_5)_3\text{PO})_2\text{Br}_2], [\text{Ni}((\text{C}_6\text{H}_5)_3\text{PO})_2\text{Br}_2]\}$

Included in these results are some previously mentioned.¹¹ Since the cobalt compounds can be assigned tetrahedral configurations with cer-

tainty, it follows that those isomorphous with them thus are proved to have tetrahedral configurations. This provides good independent support for such assignments previously made on the basis of spectral and magnetic data for $[\text{Ni}((\text{C}_6\text{H}_5)_3\text{PO})_2\text{X}_2]$ ⁹ and $[\text{Ni}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{X}_2]$ ¹⁰ compounds, and on the basis of spectral data for $[\text{Mn}((\text{C}_6\text{H}_5)_3\text{PO})_2\text{X}_2]$ ¹¹ and $[\text{Mn}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{X}_2]$ ¹¹ compounds.

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Compounds of Osmium and Rhenium with the Ordered Perovskite Structure

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A description is given of the preparation and characterization of a number of compounds of the type $\text{A}_2\text{BB}^1\text{O}_6$ where $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$; $\text{B}^1 = \text{Re}$ or Os ; and B represents a variety of univalent, divalent, and trivalent cations. Evidence is obtained for the existence of heptavalent osmium in the compound $\text{Ba}_2\text{LiOsO}_6$. The structure of many of these compounds is of the ordered perovskite type, but the hexagonal barium titanate structure is adopted in the osmium compounds when A is barium and B is a transition metal cation having d electrons. This structure also is found with the compounds $\text{Ba}_3\text{Cr}_2\text{ReO}_9$ and $\text{Ba}_3\text{Fe}_2\text{ReO}_9$. Preliminary measurements of the magnetic properties of some of the compounds are reported.

The discovery of thermally stable compounds of hexavalent and heptavalent rhenium having the ordered perovskite structure^{1,2} led us to inquire whether similar compounds of other elements with high oxidation states could be obtained. The obvious choice among the metallic elements was osmium. This paper describes a number of quaternary phases containing osmium in oxidation states extending up to heptavalent osmium. A comparison is made between these and systems containing rhenium.

The general formula for the type of compound sought in these experiments is $\text{A}_2\text{BB}^1\text{O}_6$ where A is a large divalent cation capable of 12-fold coordination with oxygen. The sum of the valences of B and B^1 must be eight and the size must be suitable for octahedral coordination with oxygen. The oxidation state of B^1 , which represents osmium or rhenium in this instance, thus may be controlled

by appropriate selection of the B cation.

For the preparation of crystalline compounds of this kind, the most usual procedure has been to heat stoichiometric mixtures of the oxides in a closed system. In many instances, suitable compounds of osmium were not available for the application of this method. It was found, however, that many of the compounds could be obtained by heating in air mixtures of osmium powder and the oxides or carbonates of the A and B metals. The temperatures at which these reactions were carried out lay in the range of 600 to 1000°. It is a testimony to the stability of these compounds that little or no osmium was lost from the samples. Apparently the reactions proceed by means of some gaseous species for many of the reactions were virtually complete in a few minutes.

The products were characterized by means of their X-ray powder diffraction patterns using a General Electric XRD-5 diffractometer. Chemical analyses, magnetic susceptibility measure-

(1) A. W. Sleight and R. Ward, *J. Am. Chem. Soc.*, **83**, 1088 (1961).

(2) J. Longo and R. Ward, *ibid.*, **83**, 2816 (1961).