726. *Phosphine Oxide Complexes. Part V.* Tetrahedral Complexes of Manganese*(II) *containing Triphenylphosphine Oxide, and Triphenylarsine Oxide as Ligands.*

By DAVID M. L. GOODGAME and F. A. COTTON.

Some complexes of manganese(II) salts with triphenylphosphine oxide and with triphenylarsine oxide have been prepared. Various lines of spectral evidence are adduced to show that several of these, particularly those of the general formula $[Mn(Ph_3PO)_2X_2]$ (X = halide) and their arsine oxide analogues, are tetrahedral. Some confirmatory *X*-ray evidence is also given.

PREVIOUS studies have shown that complexes of the type $[M^{II}(Ph_3PO)_2X_2]$ are frequently tetrahedral. This has been found to be true for the nickel(II) complexes where X = Cl,[1] Br,[1,2] or I[1], as well as for their triphenylarsine oxide analogues[3] with X = Cl or Br, for the cobalt(II) complexes[2,4] where X = Cl, Br, or I, and for the copper(II) compounds[5] where X = Cl or Br, although the arsine oxide analogues of these copper(II) compounds appear not to be tetrahedral.[5] These results suggested that the corresponding manganese(II) complexes might be tetrahedral, and accordingly the compounds $[Mn(Ph_3PO)_2X_2]$ where X = Cl, Br, and I as well as the triphenylarsine oxide analogues of two of them have been prepared and thoroughly investigated by various physical techniques. The results show that most, if not all, of these compounds do contain tetrahedrally co-ordinated manganese(II).

* Part IV, *J.*, 1961, 2298.

[1] Cotton and Goodgame, *J. Amer. Chem. Soc.*, 1960, **82**, 5771.

[2] Issleib and Mitscherling, *Z. anorg. Chem.*, 1960, **304**, 73.

[3] Goodgame and Cotton, *J. Amer. Chem. Soc.*, 1960, **82**, 5774.

[4] Holm and Cotton, *J. Chem. Phys.*, 1960, **32**, 1168.

[5] Goodgame and Cotton, *J.*, 1961, 2298.

The compounds studied in this work are listed in Table 1. All are well-defined crystalline substances with definite melting points. The attempt to prepare $[Mn(Ph_3AsO)_2I_2]$ failed, affording instead $[Mn(Ph_3AsO)_4]I_2$. As shown in Table 2, the electrolytic conductances and magnetic moments support the assigned formulæ and structures. Most of the effective magnetic moments are in excess of the expected spin-only moment (5·92 B.M.) by slightly more than the estimated experimental errors. This may be a consequence of weak ferromagnetic interactions but we did not deem this point to be of sufficient interest at present to warrant extending the susceptibility measurements to low temperatures. However, because it is to be expected theoretically that the spin–orbit coupled interaction between excited quartet states having orbital angular momentum and the $^6A_{1g}$ ground state [6] will be small, the interionic coupling mechanism seems more probable.

TABLE 1. *Formulæ and characteristics of the manganese*(II) *complexes.*

Compound	Colour	M. p.	Yield (%)	C (%) Found	C (%) Reqd.	H (%) Found	H (%) Reqd.	As or P (%) Found	As or P (%) Reqd.
$[Mn(Ph_3PO)_2Cl_2]$	Pale yellow	244°	58	63·4	63·4	4·6	4·4	9·2	9·1
$[Mn(Ph_3PO)_2Br_2]$	Pale green	243	60	56·25	56·1	4·05	3·9	8·2	8·0
$[Mn(Ph_3PO)_2I_2]$ ……	Pale yellow	230	39	50·0	50·0	3·5	3·5	7·3	7·2
$[Mn(Ph_3PO)_2(NO_3)_2]$	Pale yellow	236	69	58·7	58·8	4·0	4·1	8·15 [b]	8·4
$[Mn(Ph_3AsO)_2Cl_2]$	Very pale yellow	236	86·5	56·4	56·1	3·85	3·9	19·6	19·45
$[Mn(Ph_3AsO)_2Br_2]$	Pale yellow-green	214	79	50·6	50·3	3·7	3·5	17·8	17·4
$[Mn(Ph_3AsO)_4]I_2$	Pale cream	228	51 [a]	53·9	54·1	3·8	3·8	18·95	18·8

[a] Based on triphenylarsine oxide. [b] Found: N, 3·9. $C_{36}H_{30}MnN_2O_8P_2$ requires N, 3·8%.

TABLE 2. *Some further characteristic properties of the complexes.*

			Molar conductance (Λ_M) in ohm^{-1} for 10^{-3}M-solutions				Magnetic data [a]			
			Ph·NO$_2$		Me·NO$_2$					
Compound	Fluorescent	Triboluminescent	Λ_M	Temp. (c)	Λ_M	Temp. (c)	Temp. (K)	$10^6\chi_M$ (corr.)	Diamagnetic correction (× 10^6)	μ (B.M.) ±0·06
$[Mn(Ph_3PO)_2Cl_2]$	No	At 80° K	~0	26·2°	—	—	298·3°	14,544	408	5·92
$[Mn(Ph_3PO)_2Br_2]$	Yes	Yes	1·2	24·2	—	—	298·3	15,045	429	6·02
$[Mn(Ph_3PO)_2I_2]$	Yes	Yes	3·3	25·8	—	—	298·4	15,081	457	6·02
$[Mn(Ph_3PO)_2(NO_3)_2]$	No	No	1·8	26·6	—	—	299·3	15,402	408	6·10
$[Mn(Ph_3AsO)_2Cl_2]$	No	No	2·2	26·6	—	—	298·6	15,098	452	6·03
$[Mn(Ph_3AsO)_2Br_2]$	At 80° K	At 80° K	2·4	25·0	—	—	299·8	15,023	473	6·03
$[Mn(Ph_3AsO)_4]I_2$	No	No	32·3	27·2	136	26·4°	295·4	15,074	899	5·99

[a] Values of the corrected molar susceptibility, χ_M (corr.), and the diamagnetic corrections are in c.g.s. units.

The complexes have been further characterized by their infrared spectra. The more significant observations are collected in Table 3. For all of the phosphine oxide complexes, the P–O frequencies are lowered by complex-formation, in accord with previous observations and with theoretical expectation [7,8,9] on the assumption of partial multiple-bond character for the P–O bonds as well as for the comparable S–O bonds in dialkyl sulphoxides. In the compound $[Mn(Ph_3PO)_2(NO_3)_2]$ the infrared spectrum shows that the nitrate groups are co-ordinated through oxygen as in the analogous cobalt(II), nickel(II), copper(II), and zinc(II) complexes,[10] on the criteria first developed by Gatehouse, Livingstone, and Nyholm.[11]

---

[6] Figgis, *Trans. Faraday Soc.*, 1960, **56**, 1553.

[7] Sheldon and Tyree, *J. Amer. Chem. Soc.*, 1958, **80**, 4775.

[8] Cotton, Barnes, and Bannister, *J.*, 1960, 2199.

[9] Cotton, Francis, and Horrocks, *J. Phys. Chem.*, 1960, **64**, 1534.

[10] Bannister and Cotton, *J.*, 1960, 2276.

[11] Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.

For the two arsine oxide complexes, [Mn(Ph$_3$AsO)$_2$Cl$_2$] and [Mn(Ph$_3$AsO)$_2$Br$_2$], however, we obtain the surprising result that the As–O frequencies appear to be shifted upwards by some 20—30 cm.$^{-1}$. This result is in sharp disagreement with some previous observations [5,13,14] on triphenylarsine oxide complexes of other metal salts in which the expected frequency decreases were found. We are not at present able to offer any well-founded explanation for these results, but further studies have been undertaken and will be reported later.

TABLE 3. *Infrared absorption spectra.*

	P–O stretching frequency (cm.$^{-1}$)		Shift (cm.$^{-1}$)	Ref.		As–O stretching frequency (cm.$^{-1}$)		Shift (cm.$^{-1}$)
Ph$_3$PO		1195	—	8	Ph$_3$AsO		880	—
[Mn(Ph$_3$PO)$_2$Cl$_2$]		1155	−40		[Mn(Ph$_3$AsO)$_2$Cl$_2$]	923sh	892	+28
[Mn(Ph$_3$PO)$_2$Br$_2$]	1163sh	1151	−38(av)		[Mn(Ph$_3$AsO)$_2$Br$_2$]	911	883	+17
[Mn(Ph$_3$PO)$_2$I$_2$]	1161	1148	−41(av)		[Mn(Ph$_3$AsO)$_4$]I$_2$		872	−8
[Mn(Ph$_3$PO)$_2$(NO$_3$)$_2$]	1189	1165	−18(av)					

Data for nitrate group:	Absorption maxima (cm.$^{-1}$)	Ref.
[Mn(Ph$_3$PO)$_2$(NO$_3$)$_2$]	1499ms, 1292s, 1031m, 821mw	
Co-ord. nitrate (M–ONO$_2$)	1530—1480(s—ms), 1290—1253s, 1035—970s, 820—780(w—m)	10, 11
Ionic nitrates	1450—1350(s—vs), ~1050(vw or absent), 840—880(vw—m)	11, 12

The spectral properties of these complexes are of special interest. There is much experimental evidence to show that Mn(II) ions in tetrahedral surroundings tend to cause fluorescence and that the fluorescence has a pale yellow-to-green hue. Thus, many commercial luminescent materials are Mn(II)-doped zinc compounds such as ZnO, ZnS, or Zn$_2$SiO$_4$, in which the cations are tetrahedrally co-ordinated.[15,16] It is also known that the tetrahedral tetrahalogenomanganese(II) ions,[17-20] *e.g.*, [MnCl$_4$]$^{2-}$, [MnBr$_4$]$^{2-}$, [MnI$_4$]$^{2-}$, and various mixed ones [20] are generally fluorescent.[17,18,20] There is also evidence that when octahedrally co-ordinated manganese(II) ions do cause fluorescence the colour is pink, salmon, or red in contrast to the yellow-green colour characteristic of the fluorescence of tetrahedral manganese(II).[15,16,21] As shown in Table 2, two of the compounds reported here, [Mn(Ph$_3$PO)$_2$X$_2$] ($X =$ Br and I), fluoresce at room temperature, and one, [Mn(Ph$_3$AsO)$_2$Br$_2$], does so when cooled to ~80° K. The remaining four compounds exhibited no fluorescence at either temperature. In the three cases of fluorescence, the colour was yellow-green. On the basis of the empirical correlations summarized above, this constitutes good evidence that these three compounds contain tetrahedrally co-ordinated manganese(II) ions. The failure to observe fluorescence in the remaining compounds is not, of course, to be construed as evidence against their containing tetrahedrally co-ordinated manganese(II), for fluorescence can be quenched by various mechanisms having no relation to the gross symmetry of the co-ordination sphere.[15,16] In particular, vibrational excitation of lattice modes can provide a path for non-radiative escape from a potentially fluorescent excited state. The fact that dibromobis(triphenylarsine oxide)manganese(II) becomes fluorescent at 80° K emphasizes the temperature-dependence of the phenomenon and requires recognition of the possibility that one or more of the remaining complexes might fluoresce at still lower temperatures.

[12] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

[13] Goodgame and Cotton, unpublished observations on Ph$_3$AsO complexes of nickel(II).

[14] Phillips and Tyree, *J. Amer. Chem. Soc.*, 1961, **83**, 1806.

[15] Kröger, *Ergebn. exakt. Naturwiss.*, 1956, **29**, 61.

[16] Leverenz, " An Introduction to Luminescence of Solids," John Wiley and Sons, Inc., New York, 1950.

[17] Cotton, Goodgame, and Goodgame, unpublished results.

[18] Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 53.

[19] Gill and Nyholm, *J.*, 1959, 3997.

[20] Sacco and Naldini, *Gazzetta*, 1960, **89**, 2258.

[21] Linwood and Weyl, *J. Opt. Soc. Amer.*, 1942, **32**, 443.

In addition to the fluorescence under ultraviolet excitation, triboluminescence has been observed in several of these compounds. Dibromobis(triphenylphosphine oxide)manganese(II) and di-iodobis(triphenylphosphine oxide)manganese(II), both of which fluoresce at room temperature, also triboluminesce at room temperature, while dibromobis(triphenylarsine oxide)manganese(II), which fluoresces only on cooling, also triboluminesces only on cooling. In addition, dichlorobis(triphenylphosphine oxide)manganese(II), which was not observed to fluoresce even on cooling to 80° K, does triboluminesce when cooled. In all four cases the colour of the triboluminescence, which is difficult to detect in an illuminated room but very easily observed in the dark, is indistinguishable by eye from the colour of the fluorescence, suggesting that the emitting species is the same in both cases. Triboluminescence has been previously observed in various commercial phosphors of the types referred to earlier,[22] and may be attributed to excitation of the tetrahedrally co-ordinated manganese(II) ions by electric discharges through high local potentials at fracture faces.

Unfortunately, all of the new compounds reported here were insufficiently soluble in suitable solvents to allow measurement of their electronic absorption spectra in the visible region. In a thorough study of the electronic spectra of the $[MnX_4]^{2-}$ ions [17] it has been established that the molar absorbance values at the peaks are 10^2—10^3 times higher than those for octahedral complexes; nevertheless, they are only of the order of 2—25 l. mole^{-1} cm.$^{-1}$ and since all of these complexes have rather high molecular weights (700—1600) solutions of sufficiently high molar concentrations could not be prepared. However, the reflectance spectra provide good evidence of tetrahedral co-ordination in four cases. The wavelengths of the absorption maxima for all these compounds are collected in Table 4 and the spectra of the five dihalogenobis[triphenylphosphine (or arsine) oxide]manganese(II) complexes are shown in the Figure.

TABLE 4. *Reflectance spectra of the complexes.*

Compound	Position of absorption bands (mμ)								
$[Mn(Ph_3PO)_2Cl_2]$		330	350	~375sh		~430sh	443	~470sh	
$[Mn(Ph_3PO)_2Br_2]$		~330sh	352	375		~430sh	445	465	
$[Mn(Ph_3PO)_2I_2]$		~330sh		375				~475sh	~550sh
$[Mn(Ph_3PO)_2(NO_3)_2]$	320	340	~357sh		~410sh, br				
$[Mn(Ph_3PO_4)](ClO_4)_2$	320 [a]								
$[Mn(Ph_3AsO)_2Cl_2]$ ...		330		375		430	445	~485sh	
$[Mn(Ph_3AsO)_2Br_2]$ ...		330	~347sh	~375sh		430	448	~475sh	
$[Mn(Ph_3AsO)_4]I_2$		330	~345sh	~365sh					

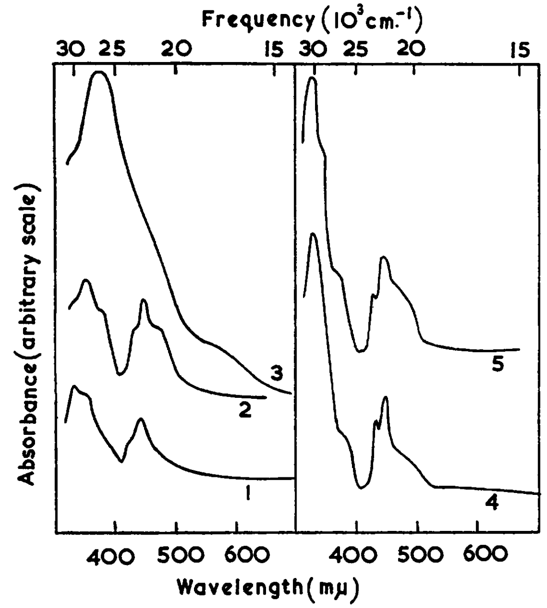
[a] Data of Bannister and Cotton.[24]

The reflectance spectra of the chloro- and bromo-complexes provide evidence of their tetrahedral structures in three ways. (1) The fact that the triplet in the 400—500 mμ range is clearly observed indicates that their extinction coefficients are much higher than those for octahedrally co-ordinated manganese(II). The corresponding bands for octahedral manganese(II) are extremely difficult and generally impossible to detect in ordinary reflectance spectra whereas salts of the tetrahedral tetrahalogeno-anions always give the same well-developed reflectance spectra as we have observed here. (2) Further indications of the much stronger absorption in the 400—500 mμ range by tetrahedral than by octahedral manganese(II) are the fairly pronounced yellow to green colours of the tetrahedral tetrahalogeno-complexes as well as those reported here, whereas octahedral manganese(II) compounds usually have very pale pink tints. This simple visual criterion seems to provide a very reliable distinction, especially when the compound is available in crystalline form. Finely powdered tetrahedral complexes often look completely colourless, or very nearly so, but when crystals even only about 0·1 mm. thick are examined the yellow-to-green colour is unmistakable. (3) The energy-level diagram for manganese(II) is qualitatively the same for both tetrahedral and octahedral fields, and the triplet in the

---

[22] Ref. 16, pp. 171—172.

400—500 mμ range can be assigned to transitions from the ^6S ground state to the excited states, in increasing order of energy, $^4T_1$, $^4T_2$, (^4E, $^4A_1$), which originate from the ^4G term of the free ion. The separation between these states is dependent upon the ligand field strength, but not linearly, because there are higher-lying T_1 and T_2 states which interact with those considered here. For our purpose here, a sufficiently accurate idea of the dependence in these compounds may be obtained from the diagram published by Heidt, Koster, and Johnson.[23] While the three peaks constituting this triplet are separated by ~4000 ($^4T_{2g}$ — $^4T_{1g}$) and ~2000 ($^4A_{1g}$,^4E_g — $^4T_{2g}$) wave numbers, in the octahedral hexa-aquo-ion, the separations observed in our compounds are ~1700 ($^4T_2$ — $^4T_1$) and ~600 ($^4A_1$,^4E — $^4T_2$) wave numbers. Since oxygen, bromide, and chloride are all closely placed in the spectrochemical series we should expect $10Dq$ in these tetrahedral complexes to be ~4/9 of that (~8000 cm.$^{-1}$) in the hexa-aquo-ion. Using the diagram of Heidt *et al.*[23] we find that for $10Dq = 3600$ cm.$^{-1}$ the expected separations are ~1600 ($^4T_2$ — $^4T_1$) and ~500 ($^4A_1$,^4E — $^4T_2$) wave numbers, in excellent agreement with the observations.



Reflectance spectra of: (1) [Mn(Ph$_3$PO)$_2$Cl$_2$]; (2) [Mn(Ph$_3$PO)$_2$Br$_2$], (3) [Mn(Ph$_3$PO)$_2$I$_2$], (4) [Mn(Ph$_3$AsO)$_2$Cl$_2$], *and* (5) [Mn(Ph$_3$AsO)$_2$Br$_2$]. *Absorbance values are relative within spectra and arbitrary from one spectrum to another.*

The colour, fluorescence, and triboluminescence of di-iodobis(triphenylphosphine oxide)manganese(II) leave little doubt of its tetrahedral structure, although its reflectance spectrum does not provide positive evidence. Whether the unique appearance of this spectrum is due to the occurrence of charge-transfer absorption, which is not infrequently encountered in iodo-complexes in this region, to some anomalously high reflectivity of the crystal surfaces or to still other causes, we do not know. Tetrakis(triphenylarsine oxide)-manganese(II) iodide has a cream or light tan colour, different to the eye from the yellow-to-green colours of the other complexes, shows no fluorescence or triboluminescence, and its reflectance spectrum shows only a rising absorption toward the ultraviolet region with several ill-resolved shoulders and possibly a peak at about 330 mμ. It seems probable that this complex, like the similar compound,[24] tetrakis(triphenylphosphine oxide)-manganese(II) perchlorate, contains [Mn(OAsPh$_3$)$_4$] groups in which the MnO$_4$ moieties are planar or nearly so. For dinitratobis(triphenylphosphine oxide)manganese(II) the yellow colour is suggestive of a tetrahedral structure, but the compound does not fluoresce or

---

[23] Heidt, Koster, and Johnson, *J. Amer. Chem. Soc.*, 1958, **80**, 6471.

[24] Bannister and Cotton, *J.*, 1960, 1878.

triboluminesce under any conditions we have tried, nor does the reflectance spectrum provide any confirmatory evidence. It shows some structure, but none which is characteristic of tetrahedral complexes.

The *X*-ray powder diffraction patterns of two of these compounds show them to be isomorphous with their nickel(II) and cobalt(II) analogues which have previously been shown to be tetrahedral. Thus dichlorobis(triphenylphosphine oxide)manganese(II) is isomorphous with its cobalt(II) analogue,[4] and dibromobis(triphenylphosphine oxide)manganese(II) is isomorphous with its nickel(II) analogue.

In summary, the evidence supporting the assignment of a tetrahedral structure and the conclusions we believe may be drawn from it for each of the new complexes are collected in Table 5.

TABLE 5. *Summary of evidence for tetrahedral structure of the complexes.*

Compound	Colour	Reflectance spectrum	Fluorescence	Tribo-luminescence	*X*-Ray	Conclusion
$[Mn(Ph_3PO)_2Cl_2]$	+	++	0	+	++	Tetrahedral
$[Mn(Ph_3PO)_2Br_2]$	+	++	+	+	++	Tetrahedral
$[Mn(Ph_3PO)_2I_2]$	+	0	+	+	0	Tetrahedral
$[Mn(Ph_3AsO)_2Cl_2]$	+	++	0	0	0	Tetrahedral
$[Mn(Ph_3AsO)_2Br_2]$	+	++	+	+	0	Tetrahedral
$[Mn(Ph_3PO)_2(NO_3)_2]$	+	—	0	0	0	Probably not tetrahedral
$[Mn(Ph_3AsO)_4]I_2$	—	—	0	0	0	Probably not tetrahedral

+ Positive evidence; ++ very strong positive evidence; — negative evidence; 0 indecisive.

EXPERIMENTAL

Triphenylarsine Oxide.—This compound was prepared by the method of Shriner and Wolf.[25]

Complexes of Manganous Halides with Triphenylphosphine and Triphenylarsine Oxides.—The compounds $[Mn(Ph_3PO)_2X_2]$ where X = Cl, Br, I, and $[Mn(Ph_3AsO)_2X_2]$ where X = Cl, Br were prepared by the following general method. The phosphine or arsine oxide and manganous halide were mixed in 2·2 : 1 molar ratio in hot absolute ethanol solution (20—40 ml.). On cooling, crystals were obtained, which were filtered off, washed with cold absolute ethanol, and dried *in vacuo*. Details concerning the individual compounds are given in Table 1. The complexes were slightly soluble in acetone, acetonitrile, nitrobenzene, and nitromethane but very little soluble in other organic solvents.

An attempt to prepare the compound $MnI_2,2Ph_3AsO$, by the general method described above, yielded cream-coloured crystals, m. p. 225°. Carbon and hydrogen analyses indicated that the compound had formula $MnI_2,4Ph_3AsO$. On recrystallization from chlorobenzene (3·5 g. in 25 ml.; 61% recovery), the product had m. p. 228° (analysis in Table 1). The *complex* was soluble in the cold in methanol, nitrobenzene, and nitromethane and in the hot higher alcohols, acetone, and chlorobenzene, forming yellow solutions in each case. It was insoluble in benzene and cyclohexane and decomposed by hot dioxan.

Dinitratobis(triphenylphosphine oxide)manganese(II).—A solution of triphenylphosphine oxide (4·59 g., 0·0165 mole) in absolute ethanol (15 ml.) was added to 2·7 g. of a 50% aqueous solution of manganous nitrate [0·0075 mole of $Mn(NO_3)_2$] in absolute ethanol (5 ml.). After being heated to the b. p. and then cooled, the solution was placed in a partially evacuated desiccator over sulphuric acid for 3 days. The resulting pale pink solid recrystallized from chlorobenzene (5·37 g. in 50 ml.) as pale yellow crystals. These were filtered off, washed with chlorobenzene, then with benzene, and dried *in vacuo* (recovery 71·5%). The compound gradually decomposed, becoming brown during 2 months. It was soluble in the cold in alcohols, acetone, chloroform, dioxan, acetonitrile, nitromethane, and nitrobenzene and in hot chlorobenzene, but insoluble in ethyl acetate, benzene, toluene, cyclohexane, ligroin, and carbon tetrachloride.

Fluorescent Properties of the Complexes.—The compounds $[Mn(Ph_3PO)_2X_2]$ (X = Br, I) showed a marked green fluorescence under ultraviolet light at room temperature. The compound $[Mn(Ph_3AsO)_2Br_2]$ did not fluoresce at room temperature, but did so on strong cooling, *e.g.*, in liquid nitrogen. The compounds $[Mn(Ph_3PO)_2X_2]$ (X = Br,I) were triboluminescent at

---

[25] Shriner and Wolf, *Org. Synth.*, 1950, **30**, 97.

room temperature, as were $[Mn(Ph_3AsO)_2X_2]$ (X = Cl, Br) on strong cooling only. Although $[Mn(Ph_3PO)_2Cl_2]$ was triboluminescent on cooling it was not fluorescent under ultraviolet light in the temperature range ~77° to ~300° K. The compounds $[Mn(Ph_3PO)_2(NO_3)_2]$, $[Mn(Ph_3AsO)_2Cl_2]$, and $[Mn(Ph_3AsO)_4]I_2$ were neither fluorescent nor triboluminescent at room temperature or at liquid nitrogen temperature. The above results are summarized in Table 2.

Electrolytic Conductance.—Measurements of electrolytic conductance were made with a Serfass bridge. A conventional cell was used, previously calibrated with aqueous solutions of potassium chloride. The results are shown in Table 2.

Magnetic Measurements.—Determinations of magnetic susceptibilities were made at room temperature by the Gouy method as previously described.[26] Mohr's salt and copper sulphate pentahydrate were used to calibrate the Gouy tubes. Duplicate determinations were carried out over a range of field strengths. The results are shown in Table 2. The diamagnetic corrections were calculated with Pascal's constants [27] and the value recorded by Foex [28] for triphenylarsine oxide.

Electronic Spectra.—The reflectance spectra of the solid compounds were measured by using a Beckman DU spectrophotometer with the standard Beckman reflectance accessory, and magnesium carbonate as the reference sample. The results are shown in Table 4.

Infrared Absorption Spectra.—These were obtained with a Perkin–Elmer Model 21 spectrophotometer, fitted with a rock-salt prism. Nujol mulls were used. The relevant data from the spectra are shown in Table 3, together with reference data from the literature.

X-*Ray Powder Diagrams.*—These were obtained for us by Miss R. Babineau of Arthur D. Little Co., to whom we express our appreciation.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE 39, MASS., U.S.A.

[*Received, February* 20*th*, 1961.]

---

[26] Holm and Cotton, *J. Chem. Phys.*, 1959, **31**, 788.

[27] Selwood, " Magnetochemistry," 2nd edn., Interscience Publ. Inc., New York, 1956.

[28] Foex, " Constantes Selectionées Diamagnetisme et Paramagnetisme," Masson et Cie, Paris, 1957.