# 109. *Studies in Co-ordination Chemistry. Part XVI.* Complexes of Bivalent and Tervalent Manganese with a Di(tertiary Arsine).*

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Complexes of bivalent and tervalent manganese halides with the di(tertiary arsine) chelate group, *o*-phenylenebisdimethylarsine, are described. The bivalent complexes have the general formula $Mn(Diarsine)_2X_2$ where X may be Cl, Br, or I. They are best prepared under anhydrous conditions in 1 : 4-dioxan, and are non-electrolytes and monomeric in nitrobenzene. Magnetic data indicate the presence of five unpaired electrons; hence they can be formulated as spin-free (outer-orbital) sexicovalent complexes of $Mn^{II}$. A red $Mn^{III}$ diarsine of the formula $[MnDiarsineCl_2,H_2O]ClO_4$ containing four unpaired electrons has also been isolated. These are the first complexes of manganese with tertiary arsines to be described. Owing to the case with which the compounds are hydrolysed they are difficult to obtain pure.

In the preceding paper it was shown that chromium(III) but not chromium(II) complexes of the di(tertiary arsine) (I) (p. 560) could be isolated. Special interest attaches to manganese-(II) and -(III) since the formation of any octahedral complex using two $3d_\gamma$ orbitals necessitates electron-pairing, which is very uncommon with the lower-valency states of manganese and has been reported previously only with the complex cyanide.[1] Excepting scandium, which forms no bivalent compounds, bivalent manganese has the lowest total ionisation potential of the first transition elements, and its effective electronegativity is thus the smallest in the series; hence its capacity to form covalent bonds (in the Pauling sense of producing a spin-paired complex) is relatively small. Thus we find that most $Mn^{II}$ complexes which have been described [2] involve co-ordination with ligands of high electronegativity such as oxygen in water and nitrogen in amines, the metal–ligand bond being strongly polar. We might expect difficulty, therefore, in attempting to substitute the di(tertiary arsine) for ligands such as the foregoing.

It was expected that co-ordination might be favoured by heating the reactants under pressure or by the use of a suitable solvent with a low affinity for the $Mn^{2+}$ ion. In the presence of water, methanol, ethanol, or acetone as solvent no evidence of co-ordination of diarsine with the $Mn^{2+}$ ion was observed, presumably owing to the strong bond between the metal and the solvent. Indeed, a large number of $Mn^{II}$ complexes with alcohols such as ethanol,[3] propanol,[4] and glycerol [5] are known. Dioxan was then tried as a possible reaction medium for, although it does form a complex with manganous halides, its low dielectric constant (2·2) and ethereal character suggested that the bond might not be very strong. Furthermore, it is a better solvent for $Mn^{II}$ halides than benzene, ether, or chloro form. In anhydrous dioxan co-ordination of the diarsine with $Mn^{II}$ takes place very readily and the yield is limited only by the low solubility of the manganous halide in this solvent. The manganese(II) halide forms a violet complex with dioxan; addition of diarsine causes an instantaneous loss of colour as the dioxan is displaced. Complexes of the type $Mn(Diarsine)_2X_2$ were thus obtained (in which X = Cl, Br, or I) as white crystalline compounds by keeping the solutions at about 5° for several hours. The chloro-complex was not obtained pure owing to the difficulty in preventing hydrolysis. Similar trouble occurred with the bromo- and the iodo-complex. The complexes can also be

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* Part XV, preceding paper.

[1] Goldenberg, *Trans. Faraday Soc.*, 1940, **36**, 847.

[2] Sidgwick, "The Chemical Elements and Their Compounds," Oxford Univ. Press, 1950, p. 1286.

[3] Druce, *J.*, 1937, 1407.

[4] Zvyaginstsev and Chkhenkelei, *J. Gen. Chem. U.S.S.R.*, 1941, **11**, 791 (*Chem. Abs.*, 1942, **36**, 3743).

[5] Gomer and Tyson, *J. Amer. Chem. Soc.*, 1944, **66**, 1331.

formed in diethyl ether, but the method is impracticable owing to the low solubilities of the halides in this solvent. The properties of the various complexes of manganese(II) are given in the Table. The low molecular conductivities in nitrobenzene indicate that the complexes are practically non-electrolytes in this solvent and hence that the $Mn^{II}$ atom is sexicovalent. The molecular weights of the bromide and iodide confirm this. It is apparent from the magnetic moments ($\mu_{eff} \sim 5{\cdot}9$ B.M.) that no electron-pairing occurs and hence that no 3*d* orbitals are involved in the octahedral binding. This is important, because in every previous case where complexes of this di(tertiary arsine) have been prepared spin-pairing with $3d_\gamma$ orbital binding occurs.* We attribute this to the high stability of the half-filled 3*d* sub-shell in the $Mn^{II}$ atom *and* the low electronegativity of the $Mn^{2+}$ ion. The complexes of the isoelectronic tervalent iron atom do show electron-pairing but in this case the higher valency state means that the iron atom has a higher effective electronegativity. This means a greater tendency to draw the lone-pair electrons of the arsenic atoms into the $3d_\gamma$ orbitals.

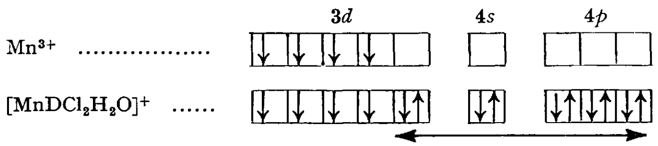
*Properties of manganese diarsine complexes.*

| Compound * | Colour | Molecular conductivity in $Ph{\cdot}NO_2$ at 25° | | Magnetic susceptibility at 20° | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $\Lambda_M$ | Concn. ($10^{-3}$M) | $\chi_g \times 10^{-6}$ | $\chi_m \times 10^{-6}$ | Diamag. corrn. | $\chi_m' \times 10^{-6}$ | $\mu_{eff.}$ (B.M.) |
| $MnD_2Cl_2$ † ......... | White | 3·1 † | 0·54 | 21·9 | 15,300 | 426 | 15,726 | 6·1 † |
| $MnD_2Br_2$ ............ | White | 0·6 | 1·79 | 18·56 | 14,600 | 447 | 15,047 | 5·95 |
| $MnD_2I_2$ ............ | Pale yellow | 1·1 | 1·61 | 16·60 | 14,600 | 467 | 15,067 | 5·96 |
| $[MnDCl_2H_2O]ClO_4$ | Purple-red | 18·2 | 2·27 | 20·6 | 10,920 | 270 | 11,190 | 5·13 |
| $[MnDBr_2H_2O]ClO_4$ | Green | 21·2 | 0·36 | — | — | — | — | — |

* D = Diarsine.

† Impure.

Attempts to oxidise these bivalent manganese complexes to the tervalent state were unsuccessful. Addition of various oxidising agents such as chlorine or bromine yielded fleeting pink colours suggestive of a higher oxidation state but the complexes immediately decomposed. Hence it was decided to try to cause the diarsine to react directly with suitable anhydrous manganese(III) compounds. The diarsine rapidly reduced both manganic acetate and manganic acetylacetone to the bivalent state even in anhydrous dioxan or in acetic anhydride, but in the presence of a small amount of water a small yield of a red crystalline precipitate of composition $[MnDiarsineCl_2H_2O]ClO_4$ is formed. Since the reduction is the principal reaction, the amount of water required has to be kept to a minimum; it is added by using 70% perchloric acid in conjunction with acetic anhydride and glacial acetic acid as solvent. No loss in weight occurred when this compound was stored over phosphoric oxide for one month, hence it appears that the water is co-ordinated and not zeolitic. All attempts to oxidise or reduce the complex $[MnDiarsineCl_2H_2O]ClO_4$ resulted in loss of diarsine by decomposition. A molecular-weight determination in nitrobenzene gave a result indicating that two ions were formed. Conductivity measurements in nitrobenzene were in agreement with this formulation as a uni-univalent electrolyte. The magnetic moment of 5·1 B.M. indicates four unpaired electrons, as shown in the diagram. This indicates that only one vacant $3d_\gamma$ orbital is left for bond formation.



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* Complexes of $Cr^{III}$ are excluded from this generalisation because in this case two $3d_\gamma$ orbitals are available *without* spin-pairing.

The co-ordination number of 5 for the $Mn^{III}$ ion suggests the possibility that the bonding orbitals may be $3d4s4p^3$.

By using dry hydrogen bromide in place of hydrogen chloride, very small amounts of a green compound having similar properties to the above were obtained. This is probably the analogous bromo-complex $[MnDiarsineBr_2H_2O]ClO_4$.

All attempts to obtain manganese complexes of the diarsine with the anions cyanide, thiocyanate, sulphate, perchlorate, oxalate, fluoride, and nitrate were unsuccessful. Attempted substitution in the phenanthroline complex $Mn\,phenan_2Cl_2$ was also unsuccessful.

## EXPERIMENTAL

*Dichlorodi-(*o*-phenylenebisdimethylarsine)manganese*(II).—Anhydrous manganous chloride was treated with 1 : 4-dioxan (400 ml.) which had been dried (Na) and redistilled. The mixture was stirred, warmed to 50°, and set aside. The anhydrous manganous chloride gradually dissolved owing to the progressive formation of the purple $MnCl_2$–dioxan complex. The solution was then filtered, the amount of residue showing that only a little manganous chloride had dissolved. Diarsine (0·2 g.), dissolved in 5 ml. of dioxan, was added to the filtrate, and the mixture stirred. The colour faded to a white opalescence as diarsine gradually replaced the dioxan, a white precipitate of the complex settling out when the solution was placed in a refrigerator. The substance was separated by decantation and centrifuging, washed with dioxan and ether, and dried *in vacuo*. The white crystalline solid which resulted was deliquescent and always gave analytical figures for carbon and chlorine which were low. The molecular conductivity (see Table) indicated a non-electrolyte with some slight impurity.

*Dibromodi-(*o*-phenylenebisdimethylarsine)manganese*(II).—Anhydrous manganous bromide was prepared by dissolving manganous carbonate in hydrobromic acid, evaporating the solution, and heating the residue. The procedure as for the chloride was then repeated with use of manganous bromide, diarsine, and dioxan. The white *complex* (0·1 g.), in the form of rhombic crystals, decomposed at 196° (Found: C, 29·5; H, 3·9; Br, 20·95%; *M*, in 1·6% solution in nitrobenzene, 720. $C_{20}H_{32}Br_2As_4Mn$ requires C, 30·5; H, 4·06; Br, 20·35%; *M*, 787).

*Di-iododi-(*o*-phenylenebisdimethylarsine)manganese*(II).—Manganese carbonate was dissolved in iodine-free hydriodic acid. The anhydrous iodide was obtained by driving off the water of hydration in the absence of air. The iodide was treated with diarsine as for the bromide. The pale yellow crystals (0·1 g.) decomposed on heating at 194° (Found: C, 26·3; H, 3·8; I, 29·6%; *M*, in 1·74% solution in nitrobenzene, 770. $C_{20}H_{32}I_2As_4Mn$ requires C, 27·2; H, 3·63; I, 28·8%; *M*, 881).

*Dichloromonoaquo-*o*-phenylenebisdimethylarsinemanganese*(III) *Perchlorate*.—Manganic acetate (1 g.), dissolved in the minimum of absolute alcohol, was cooled to 0°, and 70% perchloric acid (1 ml.) added, together with acetic anhydride (0·2 ml.), giving little more than the stoicheiometric proportion of water required. The solution was saturated with dry hydrogen chloride, and diarsine (0·2 g.) in a little ethanol added cautiously with intermittent shaking until a scarlet colour had developed and silky purplish-red crystals settled out. The mixture was set aside until settling was complete (1 hr.), and the liquid was then separated by centrifuging, and the crystals (0·05 g.), after being washed with a little ethanol and ether, were dried ($CaCl_2$) in a vacuum desiccator. Since the diarsine also reduced the manganese(III) to manganese(II), excess of perchlorate ion was added rapidly to precipitate the complex. The *complex* was soluble in acetone and fairly soluble in ethanol, the latter reducing it on warming to 50°. It is insoluble in common solvents other than nitrobenzene. The crystals had m. p. 202° (decomp.) (Found: C, 22·8; H, 3·5; Cl, 19·8%; *M*, in 0·24% solution in nitrobenzene, 240. $C_{10}H_{18}O_5ClAs_2Mn$ requires C, 22·70; H, 3·43; Cl, 20·2%; *M*, 530). The substance lost no detectable weight over phosphoric oxide in one month.

*Dibromomonoaquo-*o*-phenylenebisdimethylarsinemanganese*(III) *Perchlorate*.—This was prepared as for the chloride, hydrogen bromide being used instead of hydrogen chloride. A very small amount of the complex was isolated as green crystals insufficient for analysis. Qualitative tests established the presence of the various constituents, and the molecular conductivity in nitrobenzene solution was that expected for a univalent electrolyte.

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