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The Co-ordination Chemistry of Manganese. Part V.^{1,2} The Preparation and Spectroscopic Characterisation of some Manganese(II) Complexes of Arsenic and Antimony Donor Ligands

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Tetrahydrofuran has been found to be a convenient solvent for the preparation of complexes of manganese(II), the hardest '3d metal ion, with o-phenylenebis(dimethylarsine) (pdma) and o-phenylene(dimethylarsine) (dimethyl-stibine) (pdads), bidentate ligands containing 'soft 'arsenic and antimony donors. The i.r., electronic reflectance, and e.p.r. spectra indicate a *trans*-octahedral geometry for these $[Mn(L-L)_2X_2]$ (X = CI, Br, or I) species. E.p.r. evidence also suggests that trace amounts of moisture readily decompose these complexes with the formation of $[MnX_4]^{2-}$ ions.

PHOSPHINES and arsines form numerous complexes with 3d transition-metal halides,³ the only exception being manganese for which the well characterised complexes are derived from manganese carbonyl and usually contain the metal in a low formal oxidation state. Nyholm and Sutton ⁴ reported manganese(II) complexes of *o*-phenyl-enebis(dimethylarsine) (pdma) almost 20 years ago, but

due to the instability of these complexes few properties were reported. A recent preliminary communication ⁵ reported some manganese(II) complexes of *o*-phenylenebis(dimethylphosphine) (pdmp) and cast doubt on the existence of the pdma complexes. We have previously shown ¹ that the reported ⁶ manganese(II) complexes of triphenylphosphine and triphenylarsine are ligand oxide complexes, and that phenyl-substituted diphosphine and diarsine ligands do not complex with Mn^{II} . In the light

Part III, S. Casey, W. Levason, and C. A. McAuliffe, J.C.S. Dalton, 1972, 943.
 Part IV, W. Levason and C. A. McAuliffe, J. Inorg. Nuclear

 ² Part IV, W. Levason and C. A. McAuliffe, J. Inorg. Nuclear Chem., 1975, 37, 340.
 ³ K. K. Chow, W. Levason, and C. A. McAuliffe, in 'Transi-

³ K. K. Chow, W. Levason, and C. A. McAuliffe, in 'Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands,' ed. C. A. McAuliffe, MacMillan, London, 1973, ch. 2.

⁴ R. S. Nyholm and G. J. Sutton, J. Chem. Soc., 1958, 564. ⁵ L. F. Warren and M. A. Bennett, J. Amer. Chem. Soc.,

⁶ L. F. Warren and M. A. Bennett, J. Amer. Chem. Soc., 1974, 96, 3340.

⁶ L. Naldini, Gazzetta, 1960, 90, 1337.

of the more recent results a reinvestigation of the manganese(II) pdma complexes by spectroscopic techniques seems timely, and we have extended these studies to related diarsine, arsine-stibine, and distibine ligands.

EXPERIMENTAL

Physical measurements were made as described previously.7 Electron paramagnetic resonance spectra were recorded at ca. 115 K as frozen solutions in tetrahydrofuran (thf) on a Varian E9 spectrometer in the X-band between 0 and 8 500 G.*

Anhydrous manganese(II) halides were prepared by careful dehydration of the hydrated salts (B.D.H.) in vacuo at ca. 100 °C initially, the temperature being raised slowly to >200 °C over ca. 6 h, and the salts maintained at that temperature for 12 h at ca 10⁻¹ mmHg. The products were finely ground and manipulated in a dry-box. Tetrahydrofuran was dried by refluxing over sodium wire for 3 d and finally distilled from sodium diphenylketyl under nitrogen just prior to use. The ligands used in this study were prepared by literature methods: o-phenylenebis(dimethylo-phenylene(dimethylarsine)(dimethylstibine),9 arsine),8 1,3-bis(dimethylarsino)propane,10 1,2-bis(methylphenylarsino)ethane,¹¹ 1,3-bis(methylphenylarsino)propane,¹² 1,3bis(dimethylstibino)propane; 13 the synthesis of o-phenylenebis(dimethylstibine) will be described elsewhere.14 The complex preparations were carried out using Schlenktube techniques under a dry-nitrogen atmosphere and with precautions to exclude moisture. Manipulations and measurements were similarly made with the exclusion of atmospheric moisture.

The complexes were prepared by the same general method exemplified by that of [Mn(pdma)₂Cl₂]. Anhydrous manganese(11) chloride (0.504 g, 4 mmol) was dissolved in thf (150 cm³) with gentle heating; the solution was filtered and treated immediately with pdma (2.3 g, ca. 8 mmol). After stirring for 1 h the solution was concentrated under reduced pressure to ca. 15 cm³ and the white crystalline product which separated was filtered off, rinsed with thf (5 cm³), and dried in vacuo, yield ca. 1.3 g (42%).

RESULTS AND DISCUSSION

The reaction of anhydrous manganese(II) halides with o-phenylenebis(dimethylarsine) and o-phenylene-(dimethylarsine)(dimethylstibine) (pdads) in thf yielded $[Mn(L-L)_2X_2]$ (L-L = pdma or pdads; X = Cl, Br, or I) as white or cream crystalline solids (Table 1). Tetrahydrofuran is superior to dioxan 4 as a solvent since the managanese(II) salts are more soluble in it, whilst benzene, halogenocarbons, or diethyl ether are useless due to the very low solubility of both MnX₂ and the products. The complexes dissolve slightly in thf and nitrobenzene, and decompose in alcohols, acetone, or nitromethane, so

* 1 G = 10^{-4} T, 1 mmHg $\approx 13.6 \times 9.8$ Pa, 1 B.M. \approx $9.27~\times~10^{-24}$ A m².

E.p.r. spectra of thf solutions of the complexes exposed to moist air suggest that [MnX₄]²⁻ ions are present, presumably arising from hydrolysis of the complexes.

⁷ L. Baracco and C. A. McAuliffe, J.C.S. Dalton, 1972, 943.
⁸ R. D. Feltham, R. S. Nyholm, and A. Kasenally, J. Organometallic Chem., 1965, 7, 285.
⁹ B. R. Cook, C. A. McAuliffe, and D. W. Meek, Inorg. Chem.,

1971, 10, 2676. ¹⁰ D. J. Thornhill and A. R. Manning, *J.C.S. Dalton*, 1973, 2086.

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that the reported failure ⁵ to prepare $[Mn(pdma)_2Cl_2]$ in isopropanol is not surprising. Moisture rapidly hydrolyses the complexes; † on exposure to air they develop the repulsive odour of the free ligands within a few minutes, and rigorously dry solvents must be used if pure products are to be obtained and erroneous measurements avoided. The [Mn(pdads)₂Cl₂] complex is particularly sensitive in this respect, the iodides generally least rapidly affected. Manganese(II) thiocyanate in refluxing the did not appear to react with either ligand, and no complexes were obtained with manganese(II) perchlorate, $[Mn(OH_2)_6][ClO_4]_2$, even in the presence of triethyl orthoformate or 2,2-dimethoxypropane. Attempts to prepare either $[Mn(L-L)_2X][BPh_4]$ or $[Mn(L-L)X_2]$ generally yielded only impure $[Mn(L-L)_2X_2]$ species.

In ca. 10⁻³ mol dm⁻³ nitrobenzene solution the complexes are non-electrolytes and the room-temperature magnetic moments are ca. 6 B.M., consistent with a highspin d^5 configuration. Examination of the i.r. spectra of the complexes in the range 500-4 000 cm⁻¹ revealed only absorptions attributable to co-ordinated ligands, 15, 16 ruling out any possibility that complexes of ligand oxides are present.¹ The far-i.r. spectra of the chloro- and bromo-complexes exhibited a single $\nu(Mn-X)$ vibration consistent with a trans-octahedral structure for the $[Mn(L-L)_{2}X_{2}]$ complexes. Insufficient solubility. coupled with the very low absorption coefficients expected for a high-spin d^5 ion, prevented electronic spectra in solution being obtained, but the diffuse-reflectance spectra consisted of a number of relatively weak bands at $<30\ 000\ \mathrm{cm}^{-1}$ and ill defined intense absorptions, presumably charge-transfer bands, at $\geq 33\ 000\ \text{cm}^{-1}$. We have been able to assign the spectra satisfactorily on the basis of essentially O_h geometry.¹⁷ Transitions from the ${}^{6}A_{1g}$ ground state occurring at *ca.* 19 000 ($\rightarrow^{4}T_{1g}$), *ca.* 22 000 ($\rightarrow^{4}T_{2g}$), *ca.* 23 000 ($\rightarrow^{4}E_{g}$, ${}^{4}A_{1g}$), and *ca.* 27 000 cm^{-1} ($\rightarrow^{4}T_{2g}$), the ${}^{4}T_{1g} \leftarrow {}^{6}A_{1g}$, and transitions expected at higher energies were obscured by the charge-transfer bands.

The e.p.r. spectra of the bromo- and iodo-complexes of both ligands are characterised by lines at $g_{\text{eff.}}$ ca. 6 and ca. 2 together with other lines (Table 3). The lowest-field lines were split further by nuclear hyperfine coupling to manganese (line spacing ca. 107 G for pdads and 97 G for pdma complexes). Comparison of the experimental spectra with the published graphs of Dowsing and Gibson ¹⁸ suggests that for each of these four complexes D is ca. 0.21 cm⁻¹ and λ ca. 0.033.

¹¹ B. Bosnich and S. B. Wild, J. Amer. Chem. Soc., 1970, 92,

459. ¹² W. Levason, C. A. McAuliffe, and S. G. Murray, *Inorg.* Chim. Acta, in the press.

¹³ R. J. Dickinson, W. Levason, C. A. McAuliffe, and R. V. Parish, *J.C.S. Chem. Comm.*, 1975, 272.
 ¹⁴ W. Levason and C. A. McAuliffe, unpublished work.

¹⁵ J. H. S. Green, W. Kynaston, and G. A. Rodley, Spectrochim. Acta, 1968, A24, 853.

 B. K. W. Baylis and J. C. Bailar, *Inorg. Chem.*, 1970, 9, 641.
 A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, Amsterdam, 1968.

¹⁸ R. D. Dowsing and J. F. Gibson, J. Chem. Phys., 1969, 50, 294.

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The e.p.r. spectra of the chloro-complexes are characterised by a broad single line at $g_{\text{eff.}}$ ca. 2 with shoulders (Table 3). Probably, for the chlorides, λ is ca. 0.033 and D < 0.05 cm⁻¹. We conclude that all these complexes have near-axial symmetry with a small distortion from octahedral. The low values of λ are consistent with a *trans*-octahedral structure with little departure from axial symmetry, although this does not necessarily = 2 or 3) were unsuccessful; complex formation appeared to occur but the products were always contaminated with manganese(II) halide, and due to their poor solubility in all solvents in which they did not decompose purification of these complexes was not possible. In the cases of the two ditertiary stibines, $Me_2Sb(CH_2)_3$ -SbMe₂ and C₆H₄(SbMe₂-o)₂, no reaction with MnX₂ salts was evident in thf. These results show that 'soft'

TABLE 1

Analytical data and some	e physical	properties of	of the complexes
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Complex Colour		Uaff C	λ^{d}			
	Colour	С	H	X ^b	B.M.	S cm ² mol ⁻¹
[Mn(pdma),Cl.]	White	34.4(34.4)	4.9(4.7)	10.4(10.2)	6.00	0.5
[Mn(pdma),Br,]	White	29.8 (30.5)	4.0 (4.1)	20.6(20.4)	5.96	0
[Mn(pdma),I,]	Cream	27.1 (27.2)	3.7 (3.6)	29.1 (28.8)	5.99	0.3
[Mn(pdads),Cl,]	White	30.4 (30.2)	4.1(4.1)	9.2(9.0)	6.03	1.0
[Mn(pdads)2Br2]	Cream	26.9 (27.3)	3.5(3.6)	18.1(18.2)	6.00	0.5
$[Mn(pdads)_2I_2]^{-1}$	Fawn	24.2(24.6)	3.6 (3.4)	26.3(26.2)	6.12	0.5
				3 2 0 - 0 3 5 1 1 - 2	· · ·	

⁶ Calculated values are given in parentheses. ^b Halogen. ^c ± 0.05 B.M. ^d 10^{-3} Mol dm⁻³ solutions in nitrobenzene; 1:1 electrolytes have values in the range 20-30 S cm² mol⁻¹ in this solvent.

TABLE 2

Electronic a	and infra	red spectra	of the	manganese(II)	complexes
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Complex		Electronic-reflectance spectra $(10^3 \text{ cm}^{-1})^{b}$					
	ν (Mn-X) ^a /cm ⁻¹	$4T_{1g} \leftarrow 6A_{1g}$	⁴ T ₂₉ ← ⁶ A ₁₉	$\overset{4}{4}A_{1g}, \overset{4}{E}_{g} \xleftarrow{6}A_{1g}$	⁴ T _{2g} ← ⁶ A _{1g}		
[Mn(pdma),Cl ₂]	305	19.6	22.8	23.6	27.4		
[Mn(pdma),Br,]	210	19.1	22.5	ca. 23.8	27.3		
[Mn(pdma),I.]		18.5	21.5	23.0	27.0		
[Mn(pdads), Cl.	287	ca. 19.6	22.0	23.2	26.4		
[Mn(pdads)2Br2]	215	19.1	21.8	ca. 23.4	26.0		
$[Mn(pdads)_2I_2]$		ca. 18.7	21.0	22.4, 23.8			

^a Nujol mull. ^b Diffuse-reflectance spectra; assignments based essentially on O_h symmetry.

TABLE 3

Electron paramagnetic resonance results *

Complex			Fi	ield positions	(G)		
[Mn(pdma) ₂ Cl ₂]	<i>~</i>	1 750w 2 300w	3 375s	4 000w	5 000w		-1
[Mn(pdma),Br.]	1 050s	1450w	3 350m	4 100w	5 375m		8 050m
[Mn(pdma), I,]	1.100s	1 650w	3 400m	$4100\mathrm{w}$	5 650m	7 200 w	8 700w
$[Mn(pdads)_2Cl_2]$		1 450w 1 900w	3 450s	4 500w	4 800w		
[Mn(pdads),Br.]	1 075s	1450w	3 100s	3500w	5 400m		7 850m
$[Mn(pdads)_2I_2]$	1 100s	1.550w	3 350s	4 100w	5 550m	7 300w	

* Approximate observed line positions. The field position was taken to be where the first derivative spectrum crossed the baseline. Hyperfine splitting was ignored. s = Strong, m = medium, and w = weak.

eliminate a *cis*-octahedral structure. The order of increasing D (Cl < Br \sim I) is the same as that of the expected ligand strengths and size. The latter effect is probably dominant since D for the bromides and iodides are quite similar. When this solutions of these complexes were allowed to stand at room temperature, open to the air, each sample subsequently exhibited similar e.p.r. spectra. At 115 K the spectra comprised a nearly isotropic line at $g_{\rm eff.}$ ca. 2 with fine structure. These spectra are identical to those we have obtained from [PPh₄]₂-[MnX₄] (X = Cl, Br, or I) species, suggesting that moist air hydrolyses the complexes resulting in formation of [MnX₄]²⁻ species in the e.p.r. tube.

Repeated attempts to isolate pure complexes with the ligands $Me_2As(CH_2)_3AsMe_2$ or $PhMeAs(CH_2)_nAsMePh$ (*n*

diarsine or arsine-stibine bidentate chelates can be coordinated to Mn^{II} , the 'hardest' of the $3d M^{II}$ ions, provided rigorously anhydrous conditions (and the absence of any other strong oxygen donors) are employed. However, the complexes reported here are considerably less stable than those of *o*-phenylenebis(dimethylphosphine)⁵ (pdmp) consistent with the greater σ -donor power of phosphorus.

Warren and Bennett⁵ also report complexes of Mn^{III} and Mn^{IV} with pdmp, but all our attempts to oxidise $[Mn(pdma)_2X_2]$ or $[Mn(pdads)_2X_2]$ using halogens, concentrated nitric acid, or $[CPh_3][BF_4]$ were unsuccessful, although very transient purple or green colours were sometimes observed. However, even at -78 °C these colours persisted for only a few seconds. Starting with

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' $MnCl_3$ '² and pdma or pdads, no manganese(III) complexes were isolated, although deep green or red solutions, the colours of which persisted for several hours at -20 °C, were formed. In this context it is interesting that $[Mn(pdma)(OH_2)X][ClO_4]$ (X = Cl or Br) complexes are claimed ⁴ to have been obtained from the reaction of $Mn(O_2CMe)_3$, HX, pdma, HClO₄, and 'a trace of water ' in acetic acid-acetic anhydride solution. It seems probable that these complexes contain the diarsine dioxide ligand (cf. $[Mn(OAsPh_3)_2Cl_3]^{19}$). Elemental analyses (C, H, X) for $[Mn\{C_6H_4(AsMe_2O-o)_2\}X_2][ClO_4]$ are closely similar to those expected for [Mn(pdma)-(OH₂)X][ClO₄], and the trace amount of water necessary is quite obvious, since its function is to convert the C_6H_4 -(AsMe₂Cl₂-o)₂ formed initially into C_6H_4 (AsMe₂O-o)₂.

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¹⁹ E. Contreras, V. Riera, and R. Uson, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 287.