Oxomanganese(II)-Arsine Oxide Complexes from o-R₂AsC₆H₄CO₂H Ligands: Role of Inductive Effect and Reaction Conditions in Stabilizing Manganese(II)-Arsine Complexes

S. S. PARMAR[1], A. AGGARWAL[2]*, M. L. SEHGAL[3]*, SUNAINA SINGH[2] and MIDAS TSAI[2]

[1]Department of Chemistry, G. N. D. U., Amritsar, 143005, India.
[2]Department of Natural Sciences, LaGuardia Community College of the City University of New York, 31-10 Thomson Avenue, Long Island City, New York, NY 11101, United States.
[3]Department of Chemistry, D.A.V. College, Jalandhar, 144008, India.
*Corresponding author E-mail: manoharsehgal@hotmail.com, aaggarwal@lagcc.cuny.edu

ABSTRACT

Reactions of $Mn(O_2CMe)_2 \cdot nH_2O$ (n = 0 and 4) with the ligand $o\text{-}R_2AsC_6H_4CO_2H$ (where, R = alkyl substituent such as $-CH_3$ (Me), $-C_2H_5$ (Et), and $-C_6H_{11}$) formed nine oxomanganese (II)-arsine oxide complexes: $[Mn_2O\{(o\text{-}R_2As(O)C_6H_4CO_2)_2(H_2O)n\} \cdot n' H_2O]$ {R = -Me, n = 3; n' = 0 (three isomers); R = -Et, n = 3, n' = 0; n = 5, n' = 1, 2; R = $-C_6H_{11}$, n = 5, n' = 0 (two isomers), n = 1, n' = 0} in the presence of both moisture and oxygen. The prepared complexes were characterized by IR, UV-Vis, and EPR spectroscopic techniques and were further confirmed by measuring their magnetic susceptibility, thermal and molar conductance. The formation of two different types of complexes was due to the difference in the inductive effect of aryl and the alkyl substituent and the change of the counter-anion, i.e., chloride and acetate and their role significantly helped in deciding the formation of oxomanganese(II)-arsine oxide or oxomanganese(II)-arsine complexes.

Keywords: Thermogravimetric, Mono-tertiary arsine, Counter–anion, Isoelectronic.

INTRODUCTION

Complexation of organoarsinic ligand with a wide range of transition metal ions continues to play a vital role in the synthesis and application of organometallic chemistry.[1] However, the binding of organoarsinic ligand via coordinate bond with manganese(II) ion is not very common, as the former tends to oxidize easily from arsenic(III) to arsenic(V) even in the presence of traces of moisture and oxygen.[1,2]

To the best of our knowledge, only ten manganese(II)-mono-tertiary arsine complexes has been reported in literature.[3-5] Chiswell *et al.*,[3] reported two complexes: $[Mn(As-N)X_2]$, where (X= Br or ClO$_4$) formed by the reaction between manganese(II) salts and o-dimethylarsinoaniline an arsenic-nitrogen

chelating agent in the presence of both oxygen and water; the water being removed azeotropically with a stable As(III)→Mn(II) bond. We previously reported[4,5] eight complexes of manganese(II) ion with hybrid arsenic-oxygen chelating agents (As-O) in the presence of both oxygen and water. Four out of eight complexes consisted of manganese(II)-mono-tertiary arsine complexes[4]: $[Mn\{(o\text{-}Me_2AsC_6H_4CO_2)$ Cl\}. ½$H_2O]$, $[Mn\{(o\text{-}R_2AsC_6H_4CO_2)_2(H_2O)_2\}. nH_2O]$ (R = -Ph, p-tolyl, n = 0; R = -Et, n = 1) prepared by reacting $MnCl_2$. $4H_2O$ with $o\text{-}R_2AsC_6H_4CO_2Na$ (R = -Me, -Et, -Ph, *p*-tolyl) in 1:2 molar ratio in 95% EtOH. The other four complexes belonged to oxomanganese(II)-mono-tertiary arsine[5] type: $[Mn_2O\{(o\text{-}Ph_2AsC_6H_4CO_2)_2(H_2O)_4\}]$, $[Mn_2O\{(o\text{-}Ph_2AsC_6H_4CO_2)_2(H_2O)_5\}. (H_2O)]$, $[Mn_2O\{(o\text{-}(p\text{-}tolyl)_2AsC_6H_4CO_2)_2(H_2O)_4]$(two isomers) that were obtained by reacting $[Mn(O_2CMe)_2.nH_2O]$ (where n = 0 and 4) salts with the ligand $o\text{-}R_2AsC_6H_4CO_2H$ having only the aryl substituents (R = -Ph and p-tolyl) in 1:2 molar ratio both in 95% EtOH solvents.

We had previously[4,5] supported Chiswell *et al.,*[3] in contravention to McAuliffe's view[6-9], that the presence of water and oxygen in reactions of manganese(II) salts with (As-O) hybrid ligands did not inhibit the formation of As(III)→Mn(II) bond with hybrid ligand $o\text{-}R_2AsC_6H_4CO_2H$ having aryl substituent (R = -Ph, *p*-tolyl) using $[MnCl_2.4H_2O]$[4] and $[Mn(O_2CMe)_2.nH_2O]$ (where n = 0, 4)[5]; no matter $MnCl_2$. $4H_2O$ also formed As(III)→Mn(II)

bond with the ligands having alkyl substituent (R = -Me, -Et)[4] while R = -C_6H_{11} always formed the arsine oxide complexes. The presented work is aimed to study the effect of changing both the substituent from aryl (R = -Ph, *p*-tolyl) to alkyl (R = -Me, -Et, -C_6H_{11}) and, thereby, the inductive effect and also of the counter anion from chloride to acetate in stabilizing manganese (II)-arsine complexes.

Methodology
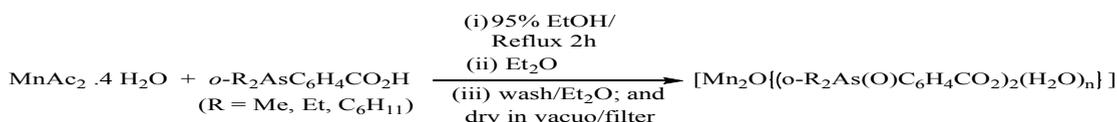
Details of the experimental method for the preparation of ligand (Structure 1, Fig. 1; M = H, Na), anhydrous $Mn(O_2CMe)_2$, and the various studied spectral measurements of the complexes were reported elsewhere.[5,10-14]

Preparation of complexes of manganese(II)
Reaction 1: Preparation of $[Mn_2O\{(o\text{-}R_2As(O)C_6H_4CO_2)_2(H_2O)n\}]$ (R = -Me and -Et, n = 3; R = -C_6H_{11}, n = 5)

A reaction mixture of [(Structure 1, Fig. 1); M = H] (8 mmol) and $Mn(O_2CMe)_2$. $4H_2O$ (0.98 g, 4 mmol) in 95% EtOH (40 cm^3) were refluxed for 2 h to the formation of a clear solution. Upon addition of diethyl ether, Et_2O to this clear solution, a white solid was formed that was filtered, washed with Et_2O and dried in vacuo. Yield: 50-60% (R = -Me, -Et) and 30-35% (R = -C_6H_{11}). The chemical reaction for the formation of these three complexes (I-III) is shown below in scheme 1.
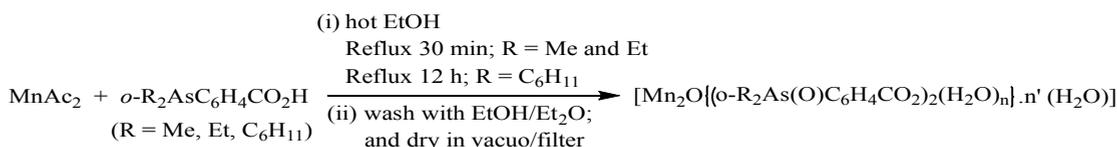
$$\text{MnAc}_2 \text{ .4 H}_2\text{O } + \text{ } o\text{-R}_2\text{AsC}_6\text{H}_4\text{CO}_2\text{H} \xrightarrow[\substack{\text{(iii) wash/Et}_2\text{O; and} \\ \text{dry in vacuo/filter}}]{\substack{\text{(i) 95\% EtOH/} \\ \text{Reflux 2h} \\ \text{(ii) Et}_2\text{O}}} [\text{Mn}_2\text{O}\{(\text{o-R}_2\text{As(O)C}_6\text{H}_4\text{CO}_2)_2(\text{H}_2\text{O})_n\}]$$
$$(\text{R = Me, Et, C}_6\text{H}_{11})$$

Scheme 1. Preparation of the three complexes (I-III) of manganese(II)

Reaction 2: Preparation of $[Mn_2O\{(o\text{-}R_2As(O)C_6H_4CO_2)(H_2O)n\}. n'(H_2O)]$ (R = -Me, n = 3, n' = 0; R = -Et, n = 5, n' = 1 ; R = -C_6H_{11}, n = 5, n' = 0)

A white solid separated on refluxing (30 min for R = -Me, -Et) a mixture of hot ethanolic solution (18-20 cm^3) of (Structure 1, Fig. 1; M = H) (8 mmol) and anhydrous $Mn(O_2CMe)_2$ {0.692 g, 4 mmol} in the same solvent (30-35 cm^3). However,

for R = -C_6H_{11}, a white solid separated only on the concentration of the solution after refluxing for 12 hours. The complex formed in each case was filtered, washed with EtOH, Et_2O and dried in vacuo. Yield: 75-80% (R = -Me, -Et) and 50-55% (R = -C_6H_{11}). The chemical reaction for the formation of these three complexes (IV-VI) is shown below in Scheme 2.
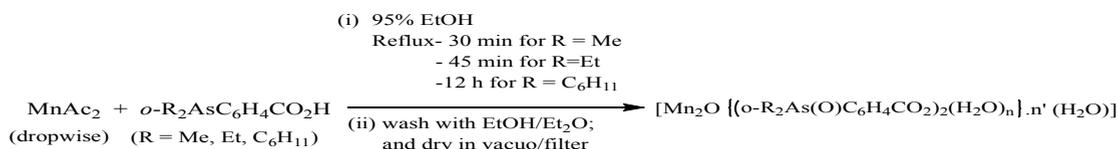
$$\text{MnAc}_2 \text{ + } o\text{-R}_2\text{AsC}_6\text{H}_4\text{CO}_2\text{H} \xrightarrow[\substack{\text{(ii) wash with EtOH/Et}_2\text{O;} \\ \text{and dry in vacuo/filter}}]{\substack{\text{(i) hot EtOH} \\ \text{Reflux 30 min; R = Me and Et} \\ \text{Reflux 12 h; R = C}_6\text{H}_{11}}} [\text{Mn}_2\text{O}\{(\text{o-R}_2\text{As(O)C}_6\text{H}_4\text{CO}_2)_2(\text{H}_2\text{O})_n\}.n' (\text{H}_2\text{O})]$$
$$(\text{R = Me, Et, C}_6\text{H}_{11})$$

Scheme 2. Preparation of three complexes (IV-VI) of manganese(II)

Reaction 3: Preparation of [Mn$_2$O{(*o*-R$_2$As(O)C$_6$H$_4$CO$_2$)$_2$(H$_2$O)n}. n'(H$_2$O)] (R = -Me, n = 3, n' = 0; R = -Et, n = 5, n' = 2; R = -C$_6$H$_{11}$, n=1, n' = 0)

A white solid was separated on refluxing (30 min for R = -Me; 45 min for R = -Et; and 12 h for R = -C$_6$H$_{11}$) the reaction mixture obtained by the drop wise addition of anhydrous Mn(O$_2$CMe)$_2$ {0.692 g,

4 mmol} in 95% EtOH (25-35 cm^3) to a solution of (Structure 1, Fig. 1; M = H) (8 mmol) in the same solvent (18-20 cm^3). The complex (white solid) so formed was filtered, washed with 95% EtOH, Et$_2$O and dried in vacuo. Yield: 75-80% (R = -Me, -Et); 40-50% (R = -C$_6$H$_{11}$). The chemical reaction for the formation of these three complexes (VII-IX) is shown below in Scheme 3.

$$\text{MnAc}_2 \ + \ \textit{o}\text{-R}_2\text{AsC}_6\text{H}_4\text{CO}_2\text{H} \xrightarrow[\substack{\text{(ii) wash with EtOH/Et}_2\text{O;}\\ \text{and dry in vacuo/filter}}]{\substack{\text{(i) 95\% EtOH}\\ \text{Reflux- 30 min for R = Me}\\ \text{- 45 min for R=Et}\\ \text{-12 h for R = C}_6\text{H}_{11}}} [\text{Mn}_2\text{O }\{(\textit{o}\text{-R}_2\text{As(O)C}_6\text{H}_4\text{CO}_2)_2(\text{H}_2\text{O})_n\}.\text{n' (H}_2\text{O)}]$$

(dropwise)   (R = Me, Et, C$_6$H$_{11}$)

Scheme 3. Preparation of three complexes (VII-IX) of manganese(II)

Thus, the above given three reactions enabled us to prepare nine oxomanganese(II)-arsine oxide complexes: {R= -Me, n =3; n'=0 (three isomers); R = -Et, n = 3, n' = 0; n = 5, n' = 1, 2; R = -C$_6$H$_{11}$, n = 5, n' = 0 (two isomers), n = 1, n' = 0}

Spectroscopic Measurements
Infrared (IR) Spectral Studies: IR spectra of the prepared nine complexes were recorded in the range 4000-200 cm^{-1} on a PYE UNICAM SP3-300 IR Spectrophotometer using potassium bromide (KBr) pellets.

Electronic Absorption Spectral Studies: The electronic absorption spectra of the complexes were recorded using a VSU-2P (DDR) spectrophotometer in the range 10000-30000 cm^{-1} in solid-state using magnesium oxide as the standard reflector.

Molar Conductance Measurements: The molar conductance values of millimolar solutions of prepared complexes in PhNO$_2$ or CH$_2$Cl$_2$ were measured on a Toshniwal Conductivity Bridge Type CLOI/O2A using conventional dip type platinum electrode.

Thermogravimetric Analysis: The thermogravimetric analysis of the complexes was carried out on a manual thermo-balance (FCI) at the heating rate of 100°C/min and % loss in weight was plotted against temperature.

Electron Paramagnetic Resonance (EPR) Spectral Studies: The powder pattern EPR of the complexes at room temperature were recorded at R.S.I.C., I.I.T., Madras using Varian Spectrophotometer having a constant microwave frequency of 9.3 GHz (X-band;

0-10000G). The Lande's splitting factor, g values were calculated using the formula: hν = gβH, here H is the applied magnetic field in gauss where the peak appears.

Magnetic Susceptibility Measurements: Magnetic susceptibilities of the powdered samples of the complexes were measured at room temperature using Gouy's Magneto balance. Diamagnetic corrections for the ligand monovalent anions (*o*-R$_2$AsC$_6$H$_4$CO$_2$) were calculated by using Pascal's constants (R = -Me, -113.6 x 10^{-6}/mole; -Et, -137.3 x 10^{-6}/mole; -C$_6$H$_{11}$, -210.4 x 10^{-6}/mole; Ph , -188.1 x 10^{-6}/mole and p-tolyl, -205.9 x 10^{-6}/mole).

Elemental (Mn and As) Analysis:
(i)   Mn^{2+} was estimated volumetrically by EDTA method[12].
(ii)   As(III) could not be estimated because of its spontaneous oxidation to As(V) in all the 9 complexes.

RESULTS AND DISCUSSION

Elemental [C, H, and Mn] analysis data (Table 1) and thermogravimetric and molar conductance data of the nine oxomanganese(II)-arsine oxide complexes shown below in Table 2 corroborated with the stoichiometry of the prepared complexes. All the studied compounds here behaved as nonelectrolytes in both nitrobenzene (C$_6$H$_5$NO$_2$) and dichloromethane (CH$_2$Cl$_2$) solvents. The non-electrolytic behavior of the complexes was confirmed with their measured molar conductance values (Table 2). Since the solid complexes would separate under cryogenic conditions, it was not possible to determine their molecular weights.

Table 1: Elemental Analysis Data of Oxomanganese(II)-arsine oxide Complexes

Formula of the Complex	M.p.t°C	Color*	Elemental composition Found (Calcd.)%		
			C	H	Mn
$[Mn_2O\{(o\text{-}Me_2As(O)C_6H_4CO_2)_2(H_2O)_3\}]$	(300°C)	White	33.8(32.6)	3.8(3.9)	17.3(16.6)
$[Mn_2O\{(o\text{-}Et_2As(O)C_6H_4CO_2)_2(H_2O)_3\}]$	(300°C)	Dirty White	36.6(36.8)	4.4(4.7)	15.8(15.3)
$[Mn_2O\{(o\text{-}(C_6H_{11})_2As(O)C_6H_4CO_2)_2(H_2O)_5\}$	(290°C)	Light Pink	46.1(47.0)	6.5(6.4)	10.8(11.3)
$[Mn_2O\{(o\text{-}Me_2As(O)C_6H_4CO_2)_2(H_2O)_3\}]$	(300°C)	Dirty White	32.0(32.6)	4.5(3.9)	16.5(16.6)
$[Mn_2O\{(o\text{-}Et_2As(O)C_6H_4CO_2)_2(H_2O)_5. H_2O]$	(300°C)	White	33.7(34.2)	4.7(5.2)	15.2(14.3)
$[Mn_2O\{(o\text{-}(C_6H_{11})_2As(O)C_6H_4CO_2)_2(H_2O)_5\}]$	(245°C)	Light Pink	47.6(47.0)	6.9(6.4)	11.4(11.3)
$[Mn_2O\{(o\text{-}Me_2As(O)C_6H_4CO_2)_2(H_2O)_3\}]$	(218°C)	Dirty White	31.7 (32.6)	3.3(3.9)	17.5 (16.6)
$[Mn_2O\{(o\text{-}Et_2As(O)C_6H_4CO_2)_2(H_2O)_5\}.2H_2O]$	(300°C)	Dirty White	32.7(33.4)	4.8(5.3)	13.9(13.9)
$[Mn_2O\{(o\text{-}(C_6H_{11})_2As(O)C_6H_4CO_2)_2(H_2O)\}]$	(235°C)	Light Pink	51.3(50.8)	6.5(6.0)	11.4(12.2)

Table 2: Thermal Analysis and Molar Conductance Data of Oxomanganese(II)-arsine oxide Complexes

Formula of the Complex	Temp. Range (°C)	Thermal Analysis Loss % Found (Calcd.) No. of Lattice (L) and Coordinated (C) H_2O molecules	Λ (S cm^2 mol^{-1}) in PhNO$_2$ or CH$_2$Cl$_2$
$[Mn_2O\{(o\text{-}Me_2As(O)C_6H_4CO_2)_2(H_2O)_3\}]$	60-180	8.0(8.1;3 H_2O), C=3	Insoluble in PhNO$_2$ or CH$_2$Cl$_2$
$[Mn_2O\{(o\text{-}Et_2As(O)C_6H_4CO_2)_2(H_2O)_3\}]$	60-100 140-180	2.5(2.53; H_2O), L=1 5.0(5.06; 2H_2O), C=2	Insoluble in PhNO$_2$ or CH$_2$Cl$_2$
$[Mn_2O\{(o\text{-}(C_6H_{11})_2As(O)C_6H_4CO_2)_2(H_2O)_5\}]$	80-110; 120-230	8.0 (7.4; 4H_2O), L=4 1.7 (1.82; H_2O), C=1	Insoluble in PhNO$_2$ or CH$_2$Cl$_2$
$[Mn_2O\{(o\text{-}Me_2As(O)C_6H_4CO_2)_2(H_2O)_3\}]$	60-180	8.0(8.1;3 H_2O), C=3	2.8
$[Mn_2O\{(o\text{-}Et_2As(O)C_6H_4CO_2)_2(H_2O)_5\}.H_2O]$	80-120 120-210	2.25(2.0; H_2O), L=1 11.25(1183; 5H_2O), C=5	Insoluble in PhNO$_2$ or CH$_2$Cl$_2$
**$[Mn_2O\{(o\text{-}(C_6H_{11})_2As(O)C_6H_4CO_2)_2(H_2O)_5\}$	120-200	9.70(9.60: 5H_2O), C=5	3.2
**$[Mn_2O\{(o\text{-}Me_2As(O)C_6H_4CO_2)_2(H_2O)_3\}]$	60-180	8.0 (8.1; 3H_2O), C=3	2.9
$[Mn_2O\{(o\text{-}Et_2As(O)C_6H_4CO_2)_2(H_2O)_5\}.2H_2O]$	60-100	4.7 (4.6; 2H_2O), L=2 11.9(11.6; 5 H_2O), C=5	0.3
$[Mn_2O\{(o\text{-}(C_6H_{11})_2As(O)C_6H_4CO_2)_2(H_2O)\}]$	80-100	3.5(3.44; H_2O), C=1	Insoluble in PhNO$_2$ or CH$_2$Cl$_2$

Note: The two complexes marked ** are of 'a' type while the remaining seven are of 'b' type oxide complexes

Presence of bent Mn(II)-O-Mn(II) system in complexes

The presence of a strong band at 590-610 cm^{-1} region (Table 3) in all these nine complexes was assigned to ν_{sym}(Mn-O-Mn) to indicate the presence of bent Mn(II)-O-Mn(II) system. This band was, also, invariably present in the four oxomanganese(II)–arsine complexes[5] as there would occur magnetic exchange between Mn(II)-3d and O-2p orbital in the oxo-complexes. Of course, it was always found missing in manganese(II)–arsine complexes[4].

Bonding mode of carboxylate ion in oxomanganese(II)-arsine oxide complexes

IR spectra of two oxomanganese(II)-arsenic oxide complexes $[Mn_2O\{o\text{-}R_2As(O)C_6H_4CO_2)_2(H_2O)n\}]$ (R = -Me, n = 3; R = -C$_6$H$_{11}$, n = 1) obtained from Reaction-III resembled with (Structure 2, Fig. 1; M = H) and were termed as a-type of oxides where the 740 cm^{-1} p$_{C\text{-}H}$ band of (Structure 1, Fig. 1; M = H) would shift to 765±5 cm^{-1} and the δ_{OCO} band at 835 cm^{-1} was observed to be much weaker than $\nu_{C\text{-}H}$

band. Moreover, absence of bands due to $\nu_{(As\text{-}OH)}$[15, 16] at 2360, 2370 cm^{-1} (R = -Me) and 2385, 2360 cm^{-1} (R = -C$_6$H$_{11}$) and in 865-870 cm^{-1} region $\nu_{As=O}$[11] in the two a-type of oxomanganese(II) oxide complexes indicated the formation of As-O-Mn group implying the absence of As=O species.

In the remaining seven oxomanganese(II)-arsine oxide complexes, the aforesaid intensity pattern was reversed. An abnormally strong band appeared at 830±10 cm^{-1} which obscured the δ_{OCO} band and was assigned to $\nu_{As=O}$[11] because the appearance of the two bands, i.e. $\nu_{As=O}$ and δ_{OCO} at almost the same region resulted in increased intensity. These observations could be rationalized if these seven arsine oxides were assumed to contain carboxylato-arsine moiety derived from the structure (Structure 3, Fig. 1; M = H); called b-type arsine oxides. Lowering of $\nu_{As=O}$ from 865 cm^{-1} in this structure to 830±10 cm^{-1} in these b-type arsine oxide complexes (Table 3) was attributed to the coordination of oxygen[17,18] of As=O group to Mn (II).

Formula of the Complex	ν(OH)	ν_{asym} (CO_2)	ν_{sym} (CO_2)	ν_{sym} (Mn-O-Mn)	$\nu_{(As=O)}$	δ_{HOH}
[Mn$_2$O{(o-Me$_2$As(O)C$_6$H$_4$CO$_2$)$_2$(H$_2$O)$_3$}]	3390 br	1597 vs	1390 vs	610 w	820 s	1620 sh
[Mn$_2$O{(o-Et$_2$As(O)C$_6$H$_4$CO$_2$)$_2$(H$_2$O)$_3$}]	3400 br	1605 vs	1390 vs	595 w	830 s	1620 sh
[Mn$_2$O{(o-(C$_6$H$_{11}$)$_2$As(O)C$_6$H$_4$CO$_2$)$_2$(H$_2$O)$_5$}]	3400 br	1605 vs	1380 vs	610 w	830 s	1620 sh
[Mn$_2$O{(o-Me$_2$As(O)C$_6$H$_4$CO$_2$)$_2$(H$_2$O)$_5$}]	3380 brm	1600 vs	1392 vs	610 w	820 vs	1620 sh
[Mn$_2$O{(o-Et$_2$As(O)C$_6$H$_4$CO$_2$)$_2$(H$_2$O)$_5$}. H$_2$O]	3400 brm	1605 vs	1392 vs	590 w	822 vs	1620 sh
**[Mn$_2$O{(o-(C$_6$H$_{11}$)$_2$As(O)C$_6$H$_4$CO$_2$)$_2$(H$_2$O)$_5$}]	3400 brm	1602 vs	1397 vs	610 w	----	1620 sh
**[Mn$_2$O{(o-Me$_2$As(O)C$_6$H$_4$CO$_2$)$_2$(H$_2$O)$_3$}]	3380 brm	1597 vs	1410 s	610 w	----	1625 sh
[Mn$_2$O{(o-Et$_2$As(O)C$_6$H$_4$CO$_2$)$_2$(H$_2$O)$_5$}.$_2$H$_2$O]	3400 brm	1602 vs	1402 s	595 w	823 vs	1630 sh
[Mn$_2$O{(o-(C$_6$H$_{11}$)$_2$As(O)C$_6$H$_4$CO$_2$)$_2$(H$_2$O)}]	3400 brm	1605 vs	1380 s	610 w	840 vs	1600 sh

br = broad; brm = broad medium; s = strong; vs = very strong; w = weak; sh = shoulder. Note: The two complexes marked ** are of 'a' type while the remaining seven are of 'b' type oxide complexes.

In two *a*-type arsine oxide complexes [Mn$_2$O{o-R$_2$As(O)C$_6$H$_4$CO$_2$)$_2$(H$_2$O)n}] (R = -Me, n = 3; R = -C$_6$H$_{11}$, n = 1),a symmetric chelation of Mn(II) with the carboxylate ions was observed (Structure 4, Fig. 1) as both ν_{asym}(CO_2) and ν_{sym}(CO_2) values were found to be higher than those of the sodium salts of the ligands (Table 3). The direction shift (d.s) criterion[11,14,19] when applied to IR spectra (Table 3) of the seven *b*-type arsine oxide complexes favored uni-dentate mode because their ν_{asym}(CO_2) were raised and ν_{sym}(CO_2) was lowered from those of values of sodium salts of the ligands. This, accompanied by the coordination of oxygen of As=O group to Mn(II), implied the formation of (Structure: 3, Fig. 1) because a very strong new band appeared at 820-840 cm⁻¹ due to the lowering of $\nu_{As=O}$[11] on coordination with Mn(II) with no band in 260-280 cm⁻¹ region of ν_{M-As}[20] to indicate the absence of Mn(II)-As(III) bond.
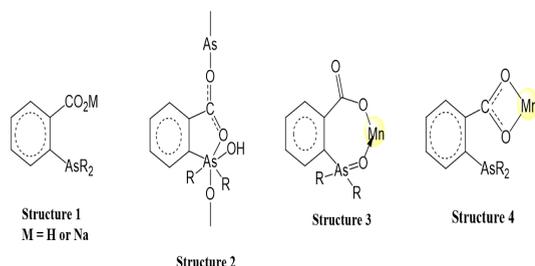

Fig. 1. Structure 1: *o*-Diarylarsinobenzoic acids with M=H or Na(R= alkyl or aryl). **Structure 2:** Type-a oxide of *o*-Dialkyl/ aryl arsinobenzoic acids with M=H. **Structure 3:** Simultaneous uni-dentate carboxylate and O of As=O coordination with Mn (II) in Type-b oxide. **Structure 4:** Chelation of Mn(II) with carboxylate of ligands(R= alkyl/ aryl)

Presence of water in complexes

The complexes obtained under hydrated conditions in Reaction-I and Reaction-III possessed either the same number of water molecules or more than the corresponding complexes isolated from the anhydrous conditions in Reaction-II because they would absorb moisture very strongly. The presence of water in the complexes was indicated by the appearance of a strong band ν_{OH}(H$_2$O)[21] at ≈ 3350-3400 cm⁻¹ and δ_{HOH}(sh)[22] ≈ 1600-1630 cm⁻¹ (Table 3). The rocking mode of coordinated water ρ(H$_2$O)[23] found at ≈ 800-900 cm⁻¹ was obscured by [δ_{OCO}][24]/ [$\nu_{As=O}$][11] at ≈ 850-70 cm⁻¹. The strongly coordinated water molecules were lost after 100°C while the lattice or loosely bound water molecules were lost up to 100°C (T.G.A. data; Table 2).[25] These studies show that out of the 9 oxide complexes, there are three isomers for R = -Me; two for R = -C$_6$H$_{11}$.

Magnetic moments of the complexes

Formation of the bent system would result in only a marginal lowering of magnetic moment values while the linear bridging caused drastic lowering. Since no Mn(II)-O-Mn(II) systems were previously known like those of isoelectronic Fe(III)-O-Fe(III) systems, the formation of σ and π bonds were involved to explain the spin-exchange between Mn(II)-3d and O-2p orbital.[26-29] The experimental μ_{eff} values of the nine oxomanganese(II)–arsine oxide complexes were found to lie in the range of 5.0-5.98 B.M. (Table 4) indicating the presence of high spin Mn(II) having $^6A_{1g}$ ground term.

Reflectance Spectra of the complexes

Reflectance electronic spectra of the complexes showed very weak bands due to their doubly forbidden nature as neither they obey the multiplicity rule nor the symmetry (Laporte) rule that favored their octahedral stereochemistry.[30] With

five unpaired electrons, these Mn(II) complexes have six multiplicity with ^6S ground state and the symmetry symbol ^6A. The ground term is represented by $^6A_{1g}$ where 'g' stands for *gerade* in octahedral stereochemistry. The spectroscopic state immediately higher to ^6S state is ^4G which splits up into $^4T_{1g}$, $^4T_{2g}$, $^4A_{1g}$, ^4E_g in an octahedral field. Three

spectral bands arising from ^6A to ^4G are assigned to as $^6A_{1g} \rightarrow ^4T_{1g}$ (^4G), $^6A_{1g} \rightarrow ^4T_{2g}$ (^4G) and $^6A_{1g} \rightarrow ^4A_{1g}$ = ^4E_g (^4G) as the last two terms do not differ very largely in their energies. The fourth band occurs by the transition between the ground $^6A_{1g}$ term to $^4T_{2g}$ obtained by the splitting of ^4F which is higher in energy to ^4G (Table 4).

Table 4: Electronic Spectral (cm^{-1}) and Tentative Structures of Oxomanganese(II)-arsine oxide Complexes

Formula of the Complex, Complex number	$\rightarrow ^4T_{1g}$	$\rightarrow ^4T_{2g}$	$\rightarrow ^4A_{1g}$, ^4E_g	$\rightarrow ^4T_{2g}$	μ_{eff}(B.M.)	Structure
$[Mn_2O\{(o\text{-}Me_2As(O)C_6H_4CO_2)_2(H_2O)_3\}]$,I	20000	21000	23529	26666	5.50	5
$[Mn_2O\{(o\text{-}Et_2As(O)C_6H_4CO_2)_2(H_2O)_3\}]$, II	17857	21045	----	----	5.35	7
$[Mn_2O\{(o\text{-}(C_6H_{11})_2As(O)C_6H_4CO_2)_2(H_2O)_5\}]$, III	19230, 17070	----	----	25000	5.00	8
$[Mn_2O\{(o\text{-}Me_2As(O)C_6H_4CO_2)_2(H_2O)_3\}]$, IV	19320, 17194	----	23809	27397	5.98	5
$[Mn_2O\{(o\text{-}Et_2As(O)C_6H_4CO_2)_2(H_2O)_5\}. H_2O]$, V	----	21376	----	25640	5.96	6
**$[Mn_2O\{(o\text{-}(C_6H_{11})_2As(O)C_6H_4CO_2)_2(H_2O)_5\}]$, VI	17857	----	23809	27027	5.70	6
**$[Mn_2O\{(o\text{-}Me_2As(O)C_6H_4CO_2)_2(H_2O)_3\}]$, VII	17857	21739	24100	27027	----	5
$[Mn_2O\{(o\text{-}Et_2As(O)C_6H_4CO_2)_2(H_2O)_5\}. 2H_2O]$, VIII	19417, 17241	22471	24096	27777	5. 75	6
$[Mn_2O\{(o\text{-}(C_6H_{11})_2As(O)C_6H_4CO_2)_2(H_2O)\}]$, IX	17857	----	23809	27027	5.97	8

Note: The two complexes marked ** are of 'a' type while the remaining seven are of 'b' type oxide complexes.

EPR Spectra of the complexes

Only $[Mn_2O\{(o\text{-}R_2As(O)C_6H_4CO_2)_2(H_2O)n\}]$ (R = -Me, -Et, n = 3; R = -C$_6$H$_{11}$, n = 5) complexes gave an EPR signal at room temperature in the form of a broad single peak with Lande's splitting factor value, g ≈ 2.0 to indicate their nearly axial symmetry with a small distortion from octahedral stereochemistry having $^6A_{1g}$ ground term[31] as the lines were broadened due to spin-lattice relaxation and the magnetic exchange between manganese(II) ions because of the presence of intervening oxo group, i.e. Mn(II)-3d and O-2p orbital.[32]

Structures of the oxomanganese(II)-arsine oxide complexes

The IR spectra of all the studied complexes indicated the presence of bent Mn(II)-O-Mn(II) unit; the uni-dentate coordination of Mn(II) with one carboxylato oxygen and also with the oxygen of As=O in the seven *b*-type arsine oxide complexes while the symmetric chelation of Mn(II) with carboxylate ion in the remaining two *a*-type arsine oxides was indicated. Electronic and EPR spectra and magnetic data complemented one another to confirm the presence of octahedral stereochemistry around Mn(II). Thermal data (Table 2) showed the presence of both the coordinated and lattice water molecules as indicated in their respective stoichiometries in the complexes. These studies corroborated with one another to assign them structures 5-8 as mentioned

in (Table 4) and were represented in Fig. 2. We also generate the ball and stick model for these compounds (5-7) that helped us to provide different points of view for 3D images. We were not able to generate a ball and stick model Image for structure 8 due to the complexity of the structure. We used Gaussian 98 program to generate the ball and stick model for these complexes.

Role of inductive effect and reaction conditions in stabilizing As(III)→ Mn(II) bond

The complexes prepared by the reactions of MnCl$_2$. 4H$_2$O and Mn(O$_2$CMe)$_2$.nH$_2$O (n = 0 and 4) 4, 5 with five arsenic-oxygen hybrid chelating agents derived from *o*-R$_2$AsC$_6$H$_4$CO$_2$M [(1), R= -Me, -Et, -C$_6$H$_{11}$, -Ph, p-tolyl; M= H or Na], were categorized into three types as follows:

(a) Ligands with aryl substituents (R = -Ph and *p*-tolyl) on reaction with MnCl$_2$.4H$_2$O and Mn(O$_2$CMe)$_2$.nH$_2$O (n = 0 and 4)[4] as well as the ligands having alkyl substituents (R = -Me, -Et) with MnCl$_2$.4H$_2$O formed manganese(II)-arsine complexes[4].

(b) Ligands with aryl substituents (R = -Ph and *p*-tolyl) when reacted with [Mn(O$_2$CMe)$_2$. nH$_2$O][5] resulted in the formation of oxomanganese(II)-arsine complexes.

(c) Ligands with alkyl substituents (R = -Me, -Et, -C$_6$H$_{11}$) when reacted with [Mn(O$_2$CMe)$_2$.

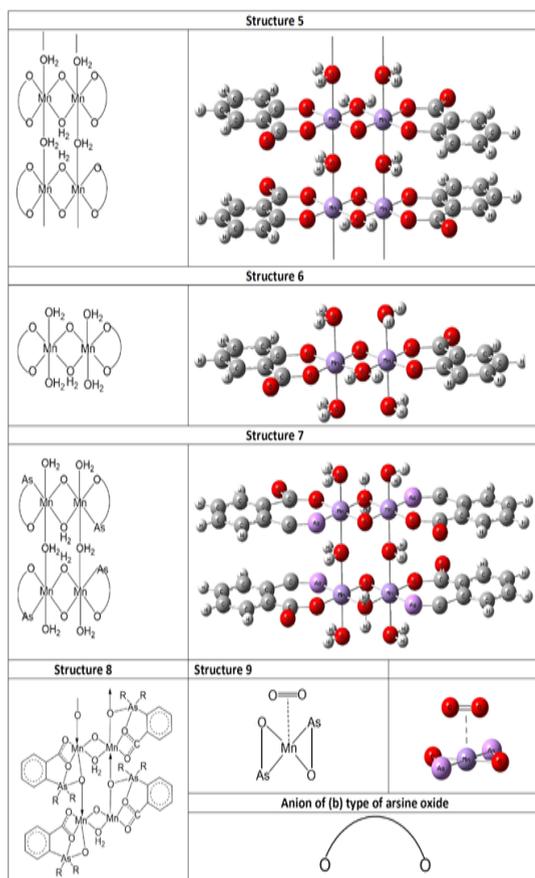nH$_2$O] formed oxomanganese(II)–arsine oxide complexes.

Fig. 2. Left side column: Structure 5: Represents complex numbers I, IV & VII each containing 1.5 coordinate H$_2$O molecules/Mn; Structure 6: Represents complex numbers V, VI &VIII each containing 2.5 coordinate H$_2$O molecules/ Mn; Structure 7: Represents complex number II; with 2.0 coordinate H$_2$O molecules/Mn; Structure 8: Represents complex number III & IX; each with 0.5 coordinated H$_2$O molecule/Mn; Structure 9; Intermediate formed before the resultant 'b-type' Arsenic oxide complex. Right side column: The right-side column represents the ball and stick model for structures 5,6,7 and 9 respectively

Whether an arsine complex would form or an arsine oxide complex would result depends both upon the inductive effect of the substituent (aryl or alkyl) and the presence of the counter anion (chloride or acetate) as follows:

(i)   Chloride would restrict the oxidation of arsine in the presence of manganese(II) while acetate would facilitate it. It was supported by the fact that when the manganese(II)-

arsine complexes obtained from MnCl$_2$.4H$_2$O were treated with a few drops of MeCO$_2$H in 95% EtOH[14], they got converted into *b*-type arsine oxide complexes to infer that it was the MeCO$_2$H formed in situ which had brought about the oxidation of initially formed manganese(II)-arsine complexes into b-type manganese(II)-arsine oxide complexes.

(ii)   The -C$_6$H$_{11}$ group, being the best electron releasing among the three alkyl groups would always form manganese(II)-arsine oxide complex while the ligands with two other alkyl groups (R = -Me, -Et) and two aryl groups (R = - Ph, p-tolyl) formed manganese(II)-arsine complexes with [MnCl$_2$.4H$_2$O][4] (coordinated water) in presence of 95% EtOH (water in medium) to prove that neither the coordinated water nor water in the medium nor the presence of atmospheric oxygen inhibits the formation of manganese(II)-arsenic(III) bond. This fact enabled us to prepare four manganese(II)-arsine complexes.[4]

(iii) During the reaction of MnX$_2$ with PR$_3$ to form complexes like [Mn(OPR$_3$)X$_2$], McAuliffe's[9] mechanism suggested that such complexes were formed through an intermediate[Mn PR$_3$(O$_2$)X$_2$] where it was not the coordinated phosphine but the one present in excess would get oxidized to phosphine oxide. In our case, the 7 out of the 9 manganese(II)-arsine oxide complexes, it was the coordinated arsine that got oxidized to b-type arsine oxide complexes due to the hydrolysis the intermediate [Mn{*o*-R$_2$AsC$_6$H$_4$CO$_2$)$_2$(O$_2$)}] (Structure 9) in presence of H$_2$O/MeCO$_2$H. The formation of two a-type of arsenic oxide complexes was considered to take place when the oxidation of arsine preceded the coordination.

CONCLUSION

(i)   McAuliffe's[6-9] emphasis on strictly anhydrous and deoxygenated conditions for the preparation of manganese(II)-phosphine/ arsine complexes might hold good for soft ligands because the present investigation and two of our previous studies[4,5] corroborated with Chiswell *et al.,*[3] to prove that the presence of water and oxygen in reactions of manganese(II) salts with (As-O) hybrid ligands did not inhibit the formation of

manganese(II)–arsine complexes if group-R and counter anion were suitably selected.

(ii) The Mn(II)-O-Mn(II) system looked unprecedented in the literature, the final word about its existence in these complexes could be said with a certainty only after single-crystal X-ray investigation. We were unable to develop their crystals because of the virtual insolubility of all the nine complexes in almost all the common solvents.

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