Metal Complexes of Hybrid Oxygen-Arsenic Ligands VII: IR, Reflectance and EPR Spectral Studies of Oxo-manganese (II)-Arsine Complexes Using Ligands from o-R₂AsC₆H₄CO₂H

S. S. PARMAR¹, A. AGGARWAL², M. L. SEHGAL³*, MIDAS TSAI² and S. MITTAL⁴

¹Department of Chemistry, G. N. D. U., Amritsar, 143005, India.
²Department 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, New York.
³Department of Chemistry, D.A.V. College, Jalandhar, 144008, India.
⁴School of Chemistry and Biochemistry, Thapar Institute of Engineering & Technology, Patiala, 147004, India.

*Corresponding author E-mail: manoharsehgal@hotmail.com

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ABSTRACT

This paper describes four oxo-manganese(II)-mono-tertiary arsine complexes: \([\text{Mn}_2\text{O}\{(\text{o-Ph}_2\text{AsC}_6\text{H}_4\text{CO}_2\text{H})_2(\text{H}_2\text{O})_5}\}(\text{H}_2\text{O})_4]\) (structure 4), \([\text{Mn}_2\text{O}(\text{o-Ph}_2\text{AsC}_6\text{H}_4\text{CO}_2\text{H})_2(\text{H}_2\text{O})_4]\), and two isomeric compounds of \([\text{Mn}_2\text{O}\{(\text{o-(p-tolyl)AsC}_6\text{H}_4\text{CO}_2\text{H})_2(\text{H}_2\text{O})_4}\}\) (structure 5) by reacting \(\text{Mn(OCMe)}_2\cdot \text{nH}_2\text{O}\), (where “n” represents the number of water molecules, \(n=0\) and \(n=4\)) with the ligands \(\text{o-R}_2\text{AsC}_6\text{H}_4\text{CO}_2\text{H}\) having only the aryl substituents \((\text{R=Ph}, \text{p-tolyl})\). This work extends the argument further that deoxygenated anhydrous conditions are not a prerequisite to stabilize As(III)-Mn(II) bond with the hybrid (As-O) chelates. The prepared complexes were characterized by IR, reflectance and EPR spectral studies and were confirmed by elemental analysis and thermogravimetric studies for their structures.

Keywords: Thermogravimetric analysis, Mono-tertiary arsine, Spin-lattice relaxation, Molar Conductance, Magnetic Moment.

INTRODUCTION

Transition metal complexes with organic ligands are of great interest of researchers since the discovery of first such complex compound of Ni(II) with azabenzenephene ligand in early 1960s.¹ Since then a wide variety of cyclometallated complex compounds of transition and post transition metal ions with ligands containing nitrogen, phosphorous, arsenic, oxygen, sulfur etc. as donor atoms has been investigated thoroughly.² The complexes of manganese (II) with arsines ligands are not very common as the arsines are very much susceptible to oxidation even in the presence of traces of moisture when reacted with Mn (II) salts like manganese (II) halides react with AsPh₃ to form complexes like \([\text{Mn(OCAsPh)}_2\text{X}_2]\)³⁴ where AsPh₃ would oxidize to arsine oxide.
Six manganese (II)-mono-tertiary arsine complexes had been reported in literature.\(^5\) Chiswell et al.,\(^6\) were able to stabilize two manganese (II)-arsine complexes \([\text{Mn(As-NX)}_2]\) (where, \(X=\text{Br or ClO}_4\)) with arsenic-nitrogen chelating agent-\(\text{o-dimethylarsinoaniline}\) even in the presence of both oxygen and water the latter was removed from the mixture azeotropically. Parmar et al.,\(^7\) reported four manganese (II)-mono-tertiary arsine complexes \([\text{Mn}\{(\text{o-Me}_2\text{AsC}_6\text{H}_4\text{CO}_3)\text{Cl}\}]\).\(^8\)\(^9\)\(^1\)\(^2\)\(^3\)\(^4\)\(^5\)\(^6\)\(^7\)\(^8\)\(^9\)\(^1\)\(^2\)\(^3\)\(^4\)\(^5\)\(^6\)\(^7\)\(^8\)\(^9\)\(^1\)\(^2\)\(^3\) of \([\text{Mn}(\text{o-R}_2\text{AsC}_6\text{H}_4\text{CO}_3)_{\text{p}}\text{H}_2\text{O}]\) \(\text{nH}_2\text{O}\) (\(R=\text{Ph, } \text{p-tolyl, } \text{n=0; and } R=\text{Et, } \text{n=1}\)) formed by reacting \(\text{MnCl}_2\cdot4\text{H}_2\text{O}\) with \(\text{o-R}_2\text{AsC}_6\text{H}_4\text{CO}_2\text{Na}\) (\(R=\text{Me, Et, Ph, } \text{p-tolyl}\)) in 1:2 molar ratio in 95% EtOH. All these four complexes were also isolated in the presence of both moisture and oxygen.

We previously\(^4\)\(^5\)\(^6\)\(^7\)\(^8\) were able to prove that McAuliffe’s emphasis\(^3\)\(^4\)\(^7\)\(^8\) on the use of strictly non-aryl anhydrous reaction medium for stabilizing As(III)-Mn(II) bond would hold good only for soft ligands and not for (As-O) hybrid ligands. We, now, extend this argument further by using both the anhydrous \(\text{Mn(O}_2\text{CMe)}_2\) and hydrated \(\text{Mn(O}_2\text{CMe)}_2\cdot4\text{H}_2\text{O}\) in 95% EtOH as well as ethanol with \(\text{o-R}_2\text{AsC}_6\text{H}_4\text{CO}_2\text{H}\) instead of \(\text{o-R}_2\text{AsC}_6\text{H}_4\text{CO}_2\text{Na}\). Our emphasis would also include studies of the effect of counter anion by replacing chloride ion by acetate ion.

**EXPERIMENTAL**

Details of spectral and other measurements, preparation of [(Structure 1, Fig. 1); \(M=\text{H, } \text{Na}\)] and estimation of arsenic (III) were published elsewhere.\(^9\)\(^-1\)\(^3\) A brief experimental details of spectral and magnetic moment measurements are shown below in 2.2 and 2.3. Analytical grade \(\text{Mn(O}_2\text{CMe)}_2\). 4\text{H}_2\text{O}\) was used for the preparation of the complexes. Anhydrous \(\text{Mn(O}_2\text{CMe)}_2\) was prepared by heating \(\text{Mn(O}_2\text{CMe)}_2\) \(\text{H}_2\text{O}\) in a dry gun for 3-4 h and the resulting mass was cooled in vacuo. The vacuum refers to distillation using a rotary evaporator attached to an efficient vacuum pump. The process was repeated till its IR shows no bands characteristic of water.

**Reaction 1-Preparation of Complexes of Manganese (II)**

**Preparation of \([\text{Mn}_2\text{O}((\text{o-Ph})\text{AsC}_6\text{H}_4\text{CO}_3)_{\text{p}}\text{H}_2\text{O})_2]\) (Structure 4)**

Addition of a hot ethanolic solution (18-20 cm\(^3\)) of [(Structure 1, Fig. 1); \(R=\text{Ph and } M=\text{H}\)] (8 mmol) and anhydrous \(\text{Mn(O}_2\text{CMe)}_2\) (0.692 g, 4 mmol) in ethanol (30-35 cm\(^3\)) gave a white solid. The reaction mass was further refluxed for 12 hours. The solid was filtered and washed with EtOH, Et\(_2\)O and dried in vacuo. Yield: 50-55%.

**Reaction 2-Preparation of \([\text{Mn}_2\text{O}((\text{o-Ph})\text{AsC}_6\text{H}_4\text{CO}_3)_{\text{p}}\text{H}_2\text{O})_2]\) (Structure 5)**

The solution of [(Structure 1, Fig. 1); \(R=\text{Ph and } M=\text{H}\)] (8 mmol) and \(\text{Mn(O}_2\text{CMe)}_2\cdot4\text{H}_2\text{O}\) (0.98 g, 4 mmol) in 95% EtOH (40 cm\(^3\)) was refluxed for 2 h and resulted into a clear solution. The addition of Et\(_2\)O to this clear solution gave a white solid which was filtered, washed with Et\(_2\)O and dried in vacuo. Yield: 50-60%.

**Reaction 3-Preparation of \([\text{Mn}_2\text{O}((\text{o-p-tolyl})\text{AsC}_6\text{H}_4\text{CO}_3)_{\text{p}}\text{H}_2\text{O})_2]\) (Structure 5)**

The reaction mass obtained by the dropwise addition of \(\text{Mn(O}_2\text{CMe)}_2\) (0.692 g, 4 mmol) in 95% EtOH (25-35 cm\(^3\)) to a solution of [(Structure 1, Fig. 1); \(R=\text{p-Tolyl and } M=\text{H}\)] (8 mmol) in the same solvent (18-20 cm\(^3\)) and was refluxed for 12 hours. The reaction mixture was cooled to 0-5°C. The solid, thus, obtained was filtered, washed with 95% EtOH, Et\(_2\)O and dried in vacuo. Yield: 40-50%.

**Spectroscopic Measurements**

**Infrared Spectra**

The infrared spectra of the prepared complexes were recorded PYE UNICAM Sp3-300 IR Spectrophotometer in the range 4000-200 cm\(^{-1}\) on KBr pellets.

**Electronic Absorption Spectra**

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

**Electron Paramagnetic Resonance (EPR) Spectra**

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; 0-10000 G). The g values were calculated by using the formula \(h v=g |H|\) where \(H\) is the magnetic field in gauss measured at the point where the peak appears.
Conductance Measurements
The molar conductance of millimolar solutions of the complexes in PhNO₂ or CH₂Cl₂ were measured on Toshniwal Conductivity Bridge Type CLOI/02A using conventional dip type platinum electrode.

Thermogravimetric Analysis
The thermogravimetric analyses of the complexes were carried out on a manual thermobalance (FCI) at the heating rate of 10°C/min and %loss in weight was plotted against temperature.

Magnetic Susceptibility Measurements
Magnetic susceptibilities of the powdered samples of the complexes were measured at room temperature using Gouy’s method. Diamagnetic corrections for the ligand anions (o-R₂AsC₆H₄CO₂)₆ were calculated using Pascal’s Law constants (R=Me, -113.6 x 10⁻⁶/mole; Et, -137.3 x 10⁻⁶/mole; C₆H₄, -210.4 x 10⁻⁶/mole; Ph, -188.1 x 10⁻⁶/mole and p-tolyl, -205.9 x 10⁻⁶/mole).

**RESULTS AND DISCUSSION**

Elemental [C, H, N, Mn] (Table 1) and thermogravimetric data (Table 2) authenticated the correctness of formulae of the oxomanganese (II)-arsine complexes which behaved as nonelectrolytes in PhNO₂ or CH₂Cl₂. Their molecular weights could not be determined as the complexes got separated as solids under cryoscopic conditions.

### Table 1: Elemental Data of Manganese (II) Complexes

| Formula of Complex Compound (M. P°C) | Color* of the Complex Compound | C Found (Calcd)% | H Found (Calcd)% | As(III) Found (Calcd)% | Mn(II) Found (Calcd)% |
|-------------------------------------|--------------------------------|------------------|------------------|------------------------|-----------------------|
| [MnO{(o-Ph₂AsC₆H₄CO₂)₆(H₂O)}] | Dirty White (175°C) | 50.2(50.9) | 3.8(4.0) | 16.3(16.6) | 12.8(12.3) |
| [MnO{(o-Ph₂AsC₆H₄CO₂)₆(H₂O)}] | Light Pink (212°C) | 47.8(48.9) | 4.1(4.3) | 15.8(16.1) | 12.1(11.8) |
| [MnO{(o-p-tolyl)₆AsC₆H₄CO₂)₆(H₂O)}] | Light Pink (300°C) | 52.2(52.9) | 4.7(4.6) | 16.0(15.8) | 12.0(11.6) |
| [MnO{(o-p-tolyl)₆AsC₆H₄CO₂)₆(H₂O)}] | Light Pink (300°C) | 52.2(52.9) | 4.2(4.6) | 15.2(15.8) | 11.9(11.6) |

*A white compound may change to dirty white or light pink on drying.*

### Table 2: Thermal Analysis and Molar Conductance Data of Manganese (II) Complexes

| Formula of Complex Compound | Thermal Analysis | λ(S cm⁻² mol⁻¹) in PhNO₂(CH₂Cl₂) | PhNO₂(CH₂Cl₂) |
|----------------------------|------------------|---------------------------------|--------------|
| [MnO{(o-Ph₂AsC₆H₄CO₂)₆(H₂O)}] | 100-240, 8.0(8.0; 4H₂O) | --- | --- |
| [MnO{(o-Ph₂AsC₆H₄CO₂)₆(H₂O)}] | 80-120, 1.75(1.91; H₂O) | 0.2 | |
| [MnO{(o-p-tolyl)₆AsC₆H₄CO₂)₆(H₂O)}] | 120-200, 9.25(9.64; 5H₂O) | --- | --- |
| [MnO{(o-p-tolyl)₆AsC₆H₄CO₂)₆(H₂O)}] | 100-160, 3.75(3.75; 2H₂O) | --- | --- |
| [MnO{(o-p-tolyl)₆AsC₆H₄CO₂)₆(H₂O)}] | 160-215, 3.75(3.75; 2H₂O) | --- | --- |

### Presence of bent Mn(II)-O-Mn(II) system in the complexes
Contrary to our previous study of reacting same ligands with [MnCl₂·4H₂O], a strong new band always appeared in 560-610 cm⁻¹ region for all the four synthesized complexes (Table 3) that indicates the presence of a bent Mn(II)-O-Mn(II) system in the complexes.

### Table 3: IR Spectral (cm⁻¹) and Magnetic Moments Data of Manganese (II) Complexes

| Formula of Complex Compound | γ_Cν (cm⁻¹) | ν(asym CO₂) (cm⁻¹) | ν(sym CO₂) (cm⁻¹) | ν(Mn-O-Mn) (cm⁻¹) | Structure |
|----------------------------|-------------|-------------------|-------------------|--------------------|-----------|
| [MnO{(o-Ph₂AsC₆H₄CO₂)₆(H₂O)}] | 3610 w, 3430 brm, [1610 sh] | 1595 vs | 1390 vs | 560 s | 5 |
| [MnO{(o-Ph₂AsC₆H₄CO₂)₆(H₂O)}] | 3430 brm, [1615 sh] | 1602 vs | 1405 vs | 610s | 4 |
| [MnO{(o-p-tolyl)₆AsC₆H₄CO₂)₆(H₂O)}] | 3360 brm, [1620 sh] | 1589 vs | 1378 vs | 590s | 5 |
| [MnO{(o-p-tolyl)₆AsC₆H₄CO₂)₆(H₂O)}] | 3400 brm, [1630 sh] | 1580 s | 1395 s | 570s | 5 |

Brm = broad medium intensity; s = strong; vs = very strong; w = weak; sh = shoulder

**Bonding mode of carboxylate ion in oxomanganese (II)-arsine complexes**
The IR spectra of the complexes resembled with those of ([Structure 1, Fig. 1]17; M=H) in 700-900 cm⁻¹ region which possessed strong ν(C=O) bands at 740 and 690 cm⁻¹ respectively and were
always accompanied by a weak $\delta_{OCO}$ band at 835 cm$^{-1}$. Application of direction shift (d.s.) criterion$^{6,15,16}$ to the IR data (Table 3) of the four complexes in the carboxylate region would suggest (structure 2; Fig. 1)$^{17}$ involving the simultaneous coordination of As(III) and carboxylato oxygen to Mn(II) to rule out (structure 3, Fig. 1)$^{18}$. The widely different values of the marked bands in the two compounds with molecular formula $[\text{Mn}_2\text{O}((\sigma-(p-tolyl))_{3}\text{AsC}_6\text{H}_4\text{CO}_2\text{H}(\text{H}_2\text{O})_2)]$ is confirmation of their isomeric forms. The presence of oxo-bridged $\text{H}_2\text{O}$ molecule in three of the four studied complexes, though difficult to ascertain only with vibrational spectral studies, yet the presence of broad band in the range of 930-50 cm$^{-1}$ points towards the presence of water in their structures.

**Presence of water in complexes**

Surprisingly, the complexes obtained under anhydrous conditions shown in Reaction 1 possessed either the same number of water molecules or even more than the corresponding complexes isolated from the hydrated conditions shown in Reactions 2 and 3. This could only be explained based on the absorption of moisture during the manipulations of Reaction 1. The presence of water molecules in the prepared complexes was indicated by the appearance of a strong band $\nu_{\text{OH}} (\text{H}_2\text{O})$ at $\approx 3350$-3400 cm$^{-1}$ and $\delta_{\text{H}_2\text{O}}$ at $\approx 1600$-1630 cm$^{-1}$. Rocking mode of coordinated water $\rho_{\text{H}_2\text{O}}$ found at $\approx 800$-900 cm$^{-1}$ was obscured by $\delta_{\text{OCO}}$ and $\nu_{\text{As}=\text{O}}$ bands at 835-870 cm$^{-1}$ region. The water molecules present in the complexes lost up to 100°C (T.G.A. data; Table 2) were regarded as lattice or loosely coordinated while the remaining water molecules were strongly coordinated to the metal ion (Table 2).$^{22}$ In the complex compound $[\text{Mn}_2\text{O}(\sigma-\text{Ph}\text{AsC}_6\text{H}_4\text{CO}_2\text{H}(\text{H}_2\text{O})_2)\text{H}_2\text{O}]$, one water molecule that is present outside the bracket (i) is lost below 120°C indicates that it is a either a loosely bound lattice water molecule. On the other hand, the stoichiometric loss of other five water molecules (% loss = 1.75 : 9.25 = 1 : 5) in this complex beyond 120°C points towards the presence strongly bound coordinated bond with Mn(II) metal ion in the complex (Table 2).$^{20}$

**Magnetic moments of complexes**

The formation of the bent Mn(II)-O-Mn(II) system was expected to result only a marginal lowering of magnetic moment values in contrast to the linear bridging which would cause a drastic lowering. Probably, no bent Mn(II)-O-Mn(II) systems were known whereas in the analogous isoelectronic Fe(III)-O-Fe(III) systems, the formation of $\sigma$ and $\pi$ bonds was invoked to explain the spin exchange coupling between M-3d and O-2p orbitals.$^{23-26}$ The experimental $\mu_{\text{eff}}$ values of these oxo-manganese (II) complexes would lie in the range of 5.12-5.90 B.M. and, thus, indicated the presence of high spin Mn(II) with $^{6}A_{1g}$ ground having no contribution from TIP (Temperature Independent Paramagnetism).
Reflectance Spectra of complexes

The room temperature magnetic moment values of the four Mn (II) complexes suggest that they have octahedral stereochemistry. This is further, corroborated by their reflectance electronic spectra which showed very week bands due to their doubly forbidden nature as neither they obey the multiplicity rule nor the symmetry (Laporte) rule. 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 6A1g where ‘g’ stands for gerade in octahedral stereochemistry. The spectroscopic state immediately higher to 6S state is 4G which splits up into 1T1g, 4T2g, 4A1g, 4Eg in an octahedral field. Three spectral bands arising from 4A to 4G are assigned to as 6A1g → 1T1g (4G), 6A1g → 4T2g (4G) and 6A1g → 4A1g = 4Eg (4G) as the last two terms do not differ very largely in their energies. The fourth band occurs by the transition between the ground 6A1g term to 4T2g obtained by the splitting of 4F which is immediately higher in energy to 4G (Table 4).

| Complex | ν1 (cm⁻¹) | ν2 (cm⁻¹) | ν3 (cm⁻¹) | ν4 (cm⁻¹) | ν5 (cm⁻¹) | μB (B.M.) |
|---------|-----------|-----------|-----------|-----------|-----------|------------|
| [Mn2O(ο-Ph,AsC6H5CO2)3(H2O)] | 18182, 17000 | 21050 | 24390 | 25600 | 5.12 |
| [Mn2O(ο-Ph,AsC6H5CO2)3(H2O)] | 18182, 17000 | 21252 | 24352 | 25640 | 5.74 |
| [Mn2O(ο-(p-toly1),AsC6H5CO2)3(H2O)] | 16625 | -- | -- | 25640 | 5.53 |
| [Mn2O(ο-(p-toly1),AsC6H5CO2)3(H2O)] | 16625 | 20000 | 22471 | 25640 | 5.90 |

EPR Spectra of complexes

Only [Mn2O(ο-Ph,AsC6H5CO2)3(H2O)] complex gave EPR signal at room temperature in the form of a broad peak with g = 2.0 which indicated its nearly axial symmetry having small distortion from octahedral stereochemistry with 6A1g ground term. It was quite likely that the lines of the system had their EPR resonance broadened beyond distinction due to spin-lattice relaxation. Further, this might also, be due to magnetic exchange between manganese (II) ions in the oxo-complexes, i.e., coupling between Mn-3d and O-2p orbitals as had already been predicted based on the magnetic data.

Structures of the four oxomanganese (II)-arsine complexes

The IR spectra of the complexes indicated the presence of bent Mn(II)-O-Mn(II) unit. The electronic absorption, EPR spectra and magnetic data complemented one another to confirm their almost octahedral stereochemistry around Mn(II). The thermal data showed the presence of four coordinated water molecules in three complexes: [MnO2{ο-R,AsC6H5CO2}2(H2O)] (R=Ph, p-toly1 (two isomers)) and five coordinated water molecules and one loosely bound lattice water molecule in the fourth complex:[MnO2{ο-Ph,AsC6H5CO2}2(H2O)]. Thus, all the techniques used in this study corroborated well to assign them the tentative structures 4, 5; Fig. 1 (Table 3).

CONCLUSION

Though we obtained oxomanganese(II)-mono-tertiary arsine complexes and not the manganese(II)-mono-tertiary complexes, yet As(III) was not oxidized to As(V) oxide contrary to McAuliffe's emphasis on the use of strictly deoxygenated anhydrous reaction medium for stabilizing As(III)-Mn(II) bond which highlighted the importance of inductive effect in restricting the oxidation of As(III) to As(V) in ligands with aryl substituents (R=Ph or p-toly1). It, also, justified the effect of counter anion as chloride would affect neither As(III) nor Mn(II) while the acetate ion would change manganese (II) to oxo-manganese (II) without oxidizing As(III) to As(V) oxide.

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Conflict of interest

The authors declare that they have no conflict of interest.
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