

Manganese(III) Complexes of Phenylarsonic Acid & Its Derivatives

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Nine manganese(III) complexes of molecular formula $[Mn(PAA)(OH)(H_2O)_3] \cdot nH_2O$ (where $PAA = C_6H_5AsO_3H_2$ or its derivatives, and $n = 0, 1$ or 2) have been prepared and characterized on the basis of IR and electronic spectral data, oxidimetric titrations, conductivity and magnetic measurements, and thermogravimetric analyses. An octahedral environment around the metal ion has been proposed. The complexes are non-electrolytes. The complexes show subnormal magnetic moment values at room temperature; four of the complexes studied upto liquid air temperature indicate magnetic interactions.

Recently Sandhu and coworkers¹⁻⁵ reported the isolation of complexes of first series transition metals and lanthanides with phenylarsonic acid, *o*-arsanilic acids and substituted phenylarsonic acids. A literature survey revealed lack of information on Mn(III) complexes with these ligands. We report here the isolation and characterization of Mn(III) complexes with phenylarsonic acid and its derivatives.

Materials and Methods

Hydrated Mn(III) acetate was prepared following Brauer⁶. Phenylarsonic acid derivatives were prepared by the reported method⁷. All the chemicals and solvents were either BDH (AR) or E Merck (GR) reagents. The IR spectra of complexes were recorded in KBr or nujol on a Beckmann IR 12 spectrophotometer. The diffuse reflectance spectral data were recorded on a Cary 17D spectrophotometer.

Preparation of the complexes:

Hydroxo(phenylarsonato)triquomanganese(III);
 $[Mn(C_6H_5AsO_3)(OH)(H_2O)_3]$

Hydrated manganese(III) acetate (2.6 g, 10 mmol) and phenylarsonic acid (3.0 g, 15 mmol) were separately dissolved in methanol, mixed and their mixture was stirred with a magnetic stirrer. A grey precipitate appeared after about half an hour. The precipitation could be enhanced by the addition of a few drops of water. The mixture was filtered and washed with ethanol and dried *in vacuo* over fused $CaCl_2$.

The other complexes were prepared by a method similar to that used for the phenylarsonic acid complex except that 0.5-1.0 ml of glacial acetic acid was added in these preparations. In the case of *p*-methoxy derivative the reaction was carried out in methanol-dioxane (2 : 1) solvent.

In the above complexes, manganese was determined spectrophotometrically. Arsenic was estimated as arsenic sulphide^{8,9}. Nitrogen was estimated by Dumas semimicro method. The analytical data are recorded in Table 1.

Results and Discussion

The complexes are grey to brown in colour. These are stable towards dilute mineral acids other than hydrochloric acid and are sparingly soluble in polar organic solvents. The oxidation state of the complexes was determined by treating the weighed complexes with a known excess of standard Mohr salt solution; excess Fe(II) was back titrated with potassium dichromate solution using diphenylamine as indicator. The oxidation state was found to be in the range 2.83-3.10. The very low conductance values ($1.1-2.6 \text{ mho cm}^2 \text{ mol}^{-1}$) indicate the non-ionic nature of the complexes.

The arylarsonate ion may be coordinated to the manganese ion in a variety of ways (Ia-e).

The assignments of the bands in IR spectra of the complexes reported here are based on earlier

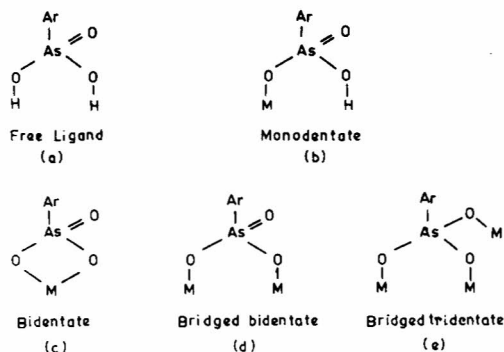


Table 1—Physical and Analytical Data of the Complexes

Complexes (colour)	Found (Calc.), %			μ_{eff} (B.M.) (28°C)	λ_{max} (cm ⁻¹)
	Mn	N	As		
Mn(C ₆ H ₅ AsO ₃)(OH)(H ₂ O) ₃ (Grey)	16.81 (16.90)	—	22.80 (23.05)	4.51	19,680 22,020
Mn(<i>o</i> -NO ₂ C ₆ H ₄ AsO ₃)(OH)(H ₂ O) ₃ .2H ₂ O (Grey)	13.56 (13.50)	3.42 (3.44)	18.69 (18.41)	4.34	19,490 21,800
Mn(<i>m</i> -NO ₂ C ₆ H ₄ AsO ₃)(OH)(H ₂ O) ₃ (Grey)	14.90 (14.81)	3.77 (3.77)	20.12 (20.19)	4.58	19,530 22,320
Mn(<i>p</i> -NO ₂ C ₆ H ₄ AsO ₃)(OH)(H ₂ O) ₃ (Grey)	14.78 (14.81)	3.78 (3.77)	20.25 (20.19)	4.36	— —
Mn(<i>p</i> -ClC ₆ H ₄ AsO ₃)(OH)(H ₂ O) ₃ .H ₂ O (Greyish brown)	14.34 (14.52)	—	19.92 (19.79)	4.68	19,420 22,120
Mn(<i>p</i> -BrC ₆ H ₄ AsO ₃)(OH)(H ₂ O) ₃ (Greyish brown)	13.36 (13.56)	—	18.11 (19.49)	4.62	19,340 21,930
Mn(<i>p</i> -CH ₃ OC ₆ H ₄ AsO ₃)(OH)(H ₂ O) ₃ (Brown)	15.19 (15.44)	—	20.56 (21.05)	4.40	19,350 22,000
Mn(<i>o</i> -CH ₃ OC ₆ H ₄ AsO ₃)(OH)(H ₂ O) ₃ (Brown)	15.14 (15.44)	—	20.60 (21.05)	4.38	—
MN(<i>p</i> -CH ₃ OC ₆ H ₄ AsO ₃)(OH)(H ₂ O) ₃ .H ₂ O (Grey)	15.30 (15.35)	—	20.45 (20.92)	4.55	19,540 22,320

assignments of the spectra of phenylarsonic acid and some of its known metal complexes^{1-5,10,11}.

The bands due to —OH groups around ~2700 and 2260 cm⁻¹ disappear from the spectra of Mn(III) complexes indicating complex formation with deprotonation of both the OH groups, thus ruling out mode (Ib) of complexation. The bands at 775 and 885 cm⁻¹ due to AsO₃ group are shifted towards lower wave numbers by 15 cm⁻¹, whereas the ν As-aromatic mode is shifted towards higher wave numbers indicating participation of As—O group in coordination with the metal ion.

The ν As=O band (880 cm⁻¹) of *m*-nitrophenylarsonic acid, which is lowered by 5 cm⁻¹ from that of phenylarsonic acid, is further lowered by 15 cm⁻¹ on complexation. The As-aromatic stretch shows a red shift in *m*-nitrophenylarsonic acid, while in *p*-nitroderivative, the band is blue shifted (~25 cm⁻¹).

In the case of *o*-tolylarsonic acid complex, the ν As=O band registers a fall of 10 cm⁻¹ and appears at 850 cm⁻¹. The ν As-aromatic frequency shows an increase of 15 cm⁻¹ on complexation.

The AsO₃ bands for *p*-chloro- and *p*-bromophenylarsonic acids split up into three and five peaks respectively. The As-aromatic stretch is, however, coupled with Cl-aromatic stretch and appears at 1090 cm⁻¹ in *p*-chlorophenylarsonic acid. This coupled band registers a fall of 20 cm⁻¹ on complexation. For *p*-bromophenylarsonic acid, ν As-aromatic is observed at 1070 cm⁻¹ and the ν Br-aromatic at 1055 cm⁻¹. On complexation only one peak at 1055 cm⁻¹ is observed. For the *o*-methoxyphenylarsonic acid (*o*-CH₃OPAA), ν As=O appears at 900 cm⁻¹. The increase in ν As=O

frequency in methoxy, chloro and bromo derivatives follows the order of electronegativities of oxygen, chlorine and bromine. However, on complex formation the AsO₃ band is lowered by 15-40 cm⁻¹ for these halo and methoxy derivatives.

The band due to As—O appears at 760, 720, 750 and 740 cm⁻¹ for *p*-ClPAA, *p*-BrPAA, *p*-CH₃OPAA and *o*-CH₃OPAA respectively. After complexation with Mn(III) this band appears at 755, 720, 740 and 740 cm⁻¹ respectively. This little or no change in band position indicates negligible influence of methoxy group attached to aromatic ring in the complexes.

The appearance of a broad band in almost all the complexes at ~3380 cm⁻¹ has been tentatively assigned to water which seems to be coordinated to the central metal ions; this is supported by thermogravimetric analyses of the complexes.

The M—N—O group exhibits the MOH bending mode below 1200 cm⁻¹, whereas the characteristic

$$\begin{array}{c} \text{H} \\ | \\ \text{bridged OH group (M—O—M)} \end{array}$$

appears at ~1100 cm⁻¹. Since the ligand bands overlap with the

$$\begin{array}{c} \text{H} \\ | \\ \text{bands due to M—OH/M—O—M} \end{array}$$

it is difficult to ascertain whether OH group is terminal or bridged. Since the magnetic moment values of the complexes are subnormal at room temperature, it may be assumed that the phenylarsonic acid acts as a bidentate bridge (Id). The ν Mn—O band in all the complexes appears at ~480 cm⁻¹.

The visible region spectra of all the complexes exhibit bands at 19,800 and 22,220 cm⁻¹ in almost all

Table 2—Variable Temperature Magnetic Moment Data

T(°K)	$\mu_{\text{eff.}}$ (B.M.)	T(°K)	$\mu_{\text{eff.}}$ (B.M.)
Mn(PAA)(OH)(H₂O)₃ $\theta = -25^\circ\text{K}$		Mn(<i>m</i>-NO₂PAA)(OH)(H₂O)₃ $\theta = -26.5^\circ\text{K}$	
304	4.51	303	4.58
285	4.44	278	4.56
261	4.40	57	4.45
239	4.38	238	4.4
223	4.36	209	4.49
201	4.35	180	4.44
168	4.22	151	4.35
140	4.16	130	4.31
115	4.06	113	4.21
96	4.02	92	4.11
Mn(<i>p</i>-ClPAA)(OH)(H₂O)₃ H₂O		Mn(<i>o</i>-NO₂PAA)(OH)(H₂O)₃ $\theta = -40.6^\circ\text{K}$	
302	.68	304	4.34
278	4.52	281	4.38
258	4.41	256	4.42
231	4.30	232	4.36
208	4.23	210	4.22
184	4.17	183	4.14
148	4.10	152	4.05
132	4.06	130	3.94
104	4.02	108	3.86
89	3.99	90	3.79

the complexes indicating the same environment in all the compounds.

The ground term 5E_g is subject to strong Jahn-Teller distortion in Mn(III) complexes¹²⁻¹³. Splitting due to Jahn-Teller effect has been observed for the complexes under investigation. A weak shoulder at $38,000\text{ cm}^{-1}$ in the UV region has been assigned to $\pi\text{-}\pi^*$ transition of aromatic ring and the nitro group.

All the complexes show low magnetic moments at room temperature (Table 1). Magnetic behaviour of four of these complexes has been studied up to liquid nitrogen temperature (Table 2). The magnetic moment values decrease with lowering of temperature. Plot of the reciprocal of molar susceptibilities ($1/\chi_A'$), corrected for diamagnetism, against the absolute temperature (T, K) is linear (Fig. 1) except in the case of *p*-chloro derivative. On the other hand, the plots of μ_{eff} versus T are non-linear except in the case of the complex of phenylarsonic acid. The plots of χ_A' versus T have uniformly curved shapes. All these results point towards the existence of magnetic interaction in these complexes.

The thermal analyses in the temperature range 30–800°C gave two peaks—one endothermic and the other exothermic. The endothermic transformation starts from 50°C with peaks in the range 105°C–160°C for *p*-chloro and *o*-nitro derivatives, and in the range

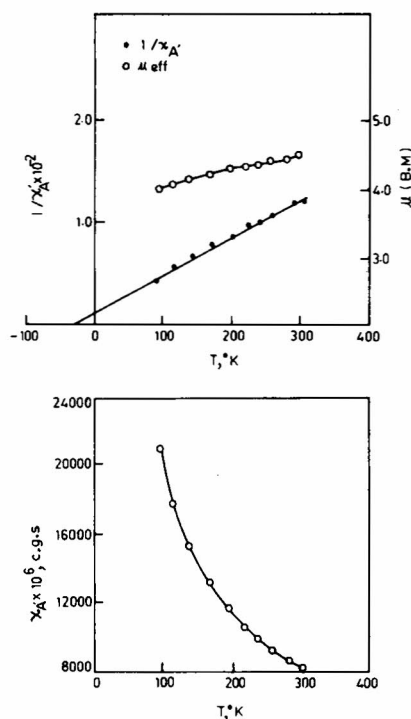
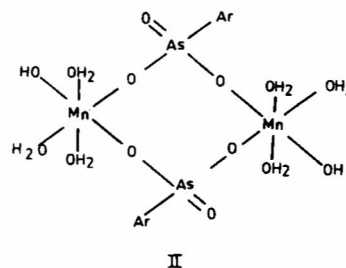


Fig. 1—Variation of magnetic moment and susceptibility values of Mn(PAA)(OH)(H₂O)₃ with temperature.



105–165°C for *p*-bromo, *m*-nitro and *p*-nitro complexes. The mass loss corresponds to 4 and 5 mole of water in the former cases and 3 mole in the rest of the complexes.

The second transformation step is highly exothermic and is due to complete decomposition of the complexes into MnO₂ and Mn₂O₃ in each case.

The magnetic moments of the complexes are subnormal, but not low enough to be attributed to any strong interaction. The bridging appears to occur through arsonic acid rather than oxo or hydroxo groups, giving rise to weak interaction. Considering the tetrahedral nature of the arsonic acid group and stoichiometry of the complexes, the following distorted octahedral structure (II) can be proposed for the present Mn(III) complexes.

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