



SYNTHESIS AND CRYSTALLOGRAPHIC CHARACTERIZATION OF MANGANESE(III) SCHIFF BASE COMPLEXES WITH AXIAL CARBOXYLATE LIGATION

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Keywords: manganese(III); Schiff base; carboxylate; H-bond interactions; supramolecular assembly.

Two new complexes of manganese(III), [Mn(salen)(*p*-ClC₆H₄CO₂)H₂O] and [Mn(msalen)(C₆H₅CO₂)H₂O] have been synthesized from their manganese(II) carboxylate precursors [H₂salen=*N,N'*-bis(salicylidene)-1,2-diaminoethane and H₂msalen=*N,N'*-bis(3-methoxysalicylidene)-1,2-diaminoethane]. Single crystal X-ray diffraction studies show that the Jahn-Teller distorted octahedral complexes are stabilized by H-bonded chains in the solid state.

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Introduction

Ligands such as aliphatic, cyclic Schiff bases, polypyridyl systems, carboxylic acids, alcohols, oximes and so on, have been extensively employed in the development of the coordination chemistry of high-valent manganese over the past few decades.¹⁻² Application and relevance of high-valent manganese complexes of these ligand systems in areas like bioinorganic modeling³⁻⁵, molecular magnetism⁶⁻⁸ and asymmetric catalysis^{9,10}, have been well-documented. Complexes where Schiff bases in combination with carboxylates stabilize higher oxidation states of manganese, have also been in focus in recent times.¹¹⁻¹⁸ Factors like the flexibility of the Schiff base ligand and the *pK_b* values of the carboxylates could bring about a great deal structural diversity in manganese(III) carboxylate complexes with Schiff base ligands, and these include mononuclear, dinuclear, and polymeric species.^{12,13} *N,N'*-bis(salicylidene)-1,2-diaminoethane (H₂salen) and its derivatives are among the most widely used Schiff base ligands in manganese(III) coordination chemistry.^{12-13,19-23} Our interest in exploring the chemistry of manganese(III) with *salen* ligands in conjunction with aryl carboxylates has led to the isolation of two new complexes, and herein we report structural characterization these two, mainly on the basis of a crystallographic analysis.

Experimental

All chemicals were purchased from E-Merck and used without further purification. The manganese(II) carboxylates were prepared as reported earlier or alternatively by mixing hot aqueous solutions of sodium carboxylate and manganese(II) chloride (2:1 molar ratio), which gave pale

pink crystals of the compounds in yields greater than 70 % in a day's time.¹²

Measurements

IR spectra were recorded on a Nicolet 6700 spectrophotometer (KBr pellets, 4000-400 cm⁻¹) while UV-Vis spectra were taken on a Cary 100 Bio UV-Vis spectrophotometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHNS analyzer.

X-ray crystallography

Data were collected on a Bruker APEX II diffractometer, equipped with a CCD area detector [Mo *K* α radiation, $\lambda = 0.71073$ Å, graphite monochromator, at 296(2) K for complex **1**; (Cu-*K* α radiation, graphite monochromator, $\lambda = 1.54178$ Å, at 100(2) K for complex **2**]. The crystal structure was solved by direct methods and refined by full-matrix least squares methods based on *F*² values against all reflections including anisotropic displacement parameters for all non-H atoms, using SHELXS97 and SHELXL97.²⁴ All the non-hydrogen atoms were located from a Fourier map and refined anisotropically. Hydrogen site locations were inferred from neighbouring sites and were treated by a mixture of independent and constrained refinement. The molecular graphics were done with PLATON and MERCURY 2.0.²⁵⁻²⁶

Synthesis of [Mn(salen)(*p*-ClC₆H₄CO₂)H₂O] (**1**)

To a solution of Mn(*p*-ClC₆H₄CO₂)₂·2H₂O (1.00 g, 2.49 mmol) and salicylaldehyde (0.61 g, 4.98 mmol) in methanol (40 mL), 1,2-diaminoethane (0.15 g, 2.49 mmol) was added. The brown solution was stirred for 20 minutes, filtered and left to evaporation in an open conical flask. Greenish black crystals, deposited in 3-4 days were collected by filtration, washed with diethylether (10 mL) and dried in air. Yield: 0.91 g (74 %). *Anal. Calc.* for C₂₃H₂₀ClMnN₂O₅ (494.80): C, 55.8; H, 4.1; N, 5.6; Mn, 11.1 %. *Found:* C, 55.6; H, 4.0; N, 5.5, Mn, 10.9 %.

IR (KBr pellet): $\nu/\text{cm}^{-1} = 3064$ (*w,br*), 1622 (*s*), 1597 (*s*), 1537 (*s*), 1359 (*s*), 1274 (*m*), 1152 (*m*), 459 (*s*). UV-Vis (MeOH); $\lambda/\text{nm} = 216$ ($\epsilon_{\text{max}} = 9851 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$), 250 ($\epsilon_{\text{max}} = 7811 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$), 292 ($\epsilon_{\text{max}} = 3861 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$), 322 ($\epsilon_{\text{max}} = 1985 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$), 415 ($\epsilon_{\text{max}} = 985 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$).

Synthesis of [Mn(msalen)(C₆H₅CO₂)H₂O] (2)

To a solution of Mn(C₆H₅CO₂)₂·2H₂O (1.00 g, 3.00 mmol) and 3-methoxysalicylaldehyde (0.87 g, 6.00 mmol) in methanol (40 mL), 1,2-diaminoethane (0.18 g, 3.00 mmol) was added. The brown solution was stirred for 20 minutes, filtered and left to evaporation in an open conical flask. Greenish brown crystals, deposited in 3-4 days were collected by filtration, washed with diethylether (10 mL) and dried in air. Yield: 1.19 g (77 %). *Anal. Calc.* for C₂₅H₂₅MnN₂O₇ (520.41): C, 57.7; H, 4.8, N, 5.4; Mn, 10.5 %. *Found:* C, 57.2; H, 4.7; N, 5.2; Mn, 10.1 %. IR (KBr pellet): $\nu/\text{cm}^{-1} = 3058$ (*w,br*), 1631 (*vs*), 1598 (*s*), 1538 (*s*), 1383 (*s*), 1259 (*m*), 1149 (*m*), 457 (*s*). UV-Vis (MeOH); $\lambda/\text{nm} = 215$ ($\epsilon_{\text{max}}=11968 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$), 233 ($\epsilon_{\text{max}}=11864 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$), 281 ($\epsilon_{\text{max}}=4845 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$), 314 ($\epsilon_{\text{max}}=2984 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$), 405 ($\epsilon_{\text{max}}=1187 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$).

Results and discussion

Molecular structures of 1 and 2

A summary of crystallographic data collection and structure refinement for complexes **1** and **2** is furnished in table 1. In both complexes (Figures 1 and 2), the bis-deprotonated ligands with their N₂O₂ donor set define the equatorial planes consisting of two Mn–N_{imine} (1.97 and 1.99 Å) and two Mn–O_{phenol} (1.87-1.90 Å) bonds, in the overall distorted octahedral geometries around the manganese(III) ions. The *trans* positions are now open for carboxylate binding and previous reports are replete with examples of different structural patterns like monomers with chelating carboxylates, polymers with bridging carboxylates, μ -phenoxy dimers with unidentate carboxylates or a monomer with a unidentate carboxylate and a neutral ligand like water occupying axial positions.¹²⁻¹⁴

The carboxylates adopt a unidentate coordination mode in **1** and **2**, accommodating the aqua ligands along the opposite axial directions. Jahn-Teller distortions which facilitate the removal of double degeneracy of the *e_g* electron at the metal centres are commonplace in high-spin manganese(III) complexes with polydentate Schiff-base ligands.

Both complexes typically undergo a Jahn-Teller distortion showing an elongation of the axial bonds [Mn–O_{aq} = 2.29-2.35 Å and Mn–O_{carb} = 2.11-2.14 Å]. The dihedral angles between the aromatic rings of the Schiff base ligands (5.87 and 12.03°) are indicative of substantial distortions around the Mn–N₂O₂ cores of the complexes. The deviation of the Mn(III) ion from the N,N',O,O' least-square planes along the Mn–O_{carb} directions in complex **1** is 0.048 Å, whereas the corresponding shift in complex **2** is more than twice at 0.101 Å.

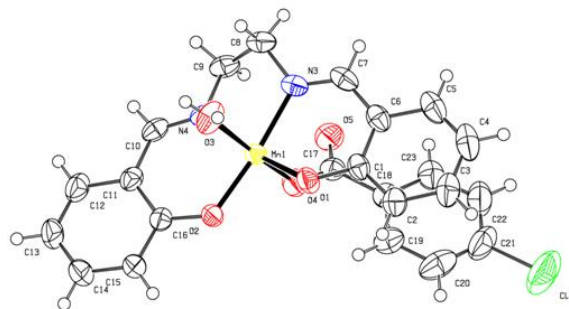


Figure 1. Molecular structure of **1**. Thermal ellipsoids are drawn at 50 % probability level.

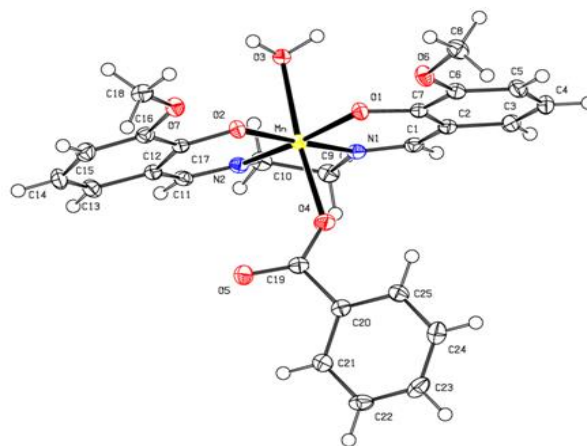


Figure 2. Molecular structure of **2**. Thermal ellipsoids are drawn at 50 % probability level.

Table 1. Crystal data and structure refinement for **1**, **2**.

Complex	1	2
Empirical formula	C ₂₃ H ₂₀ ClMnN ₂ O ₅	C ₂₅ H ₂₅ MnN ₂ O ₇
Formula weight	494.80	520.41
<i>T</i> (K)	296 (2)	100(2)
Wavelength (Å)	0.71073	1.54178
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 21/ <i>n</i>	<i>P</i> -1
<i>a</i> (Å)	6.8060(4)	8.3366(1)
<i>b</i> (Å)	10.6760(6)	11.6426(2)
<i>c</i> (Å)	29.1458(16)	12.3893(2)
α (°)	90.00	100.064(1)
β (°)	90.451 (1)	97.230(1)
γ (°)	90.00	103.937(1)
<i>V</i> (Å ³)	2117.7 (2)	1131.26(3)
<i>Z</i>	4	2
ρ_{calc} (g cm ⁻³)	1.552	1.528
μ (mm ⁻¹)	0.79	5.187
<i>F</i> (000)	1016	540
$\theta_{\text{min/max}}$ (°)	1.4/28.1	3.68 /67.36
Total data	19400	9369
Unique data	5135	3694
<i>R</i> _{int}	0.023	0.016
Restraints/parameters	0/297	0/319
Goodness-of-fit (GOF)	1.12	1.085
Final <i>R</i> indices	<i>R</i> ₁ = 0.0520	<i>R</i> ₁ = 0.0286
[<i>I</i> > 2σ(<i>I</i>)]	<i>wR</i> ₂ = 0.0583	<i>wR</i> ₂ = 0.0299
<i>R</i> indices (all data)	<i>wR</i> ₂ = 0.1232	<i>R</i> ₁ = 0.0849
	<i>R</i> ₁ = 0.1283	<i>wR</i> ₂ = 0.086

$$R_1 = \frac{\sum (|F_o| - |F_c|) / \sum (|F_o|)}{\sum (|F_o|)}, wR_2 = \left\{ \frac{\sum [w(F^2 - F_c^2)^2] / \sum [w(F_o^2)^2]}{w} \right\}^{1/2}$$

$$w = 1 / [\sigma^2(F_o^2) + (0.0306P)^2 + 2.7747P], \text{ where } P = (F_o^2 + 2F_c^2) / 3$$

Solid state structures 1 and 2

Occupation of the *trans* coordination sites by carboxylate and water enable molecules of complexes **1** and **2** to recognize one another and spontaneously generate supramolecular architectures in the solid state through non-covalent interactions like hydrogen bonding. Carboxylate and water of adjacent [Mn(salen)(*p*-ClC₆H₄CO₂)H₂O] molecules meet in a nearly end on fashion along a screw (2₁) axis, in the crystal structure of complex **1**, resulting in hydrogen bonding interactions (O5---H1A = 1.95 Å; O3---O5 = 2.70 Å) that beget a helical chain parallel to the (001) plane (Figure 3). The intra-chain Mn---Mn distance is 6.49 Å.

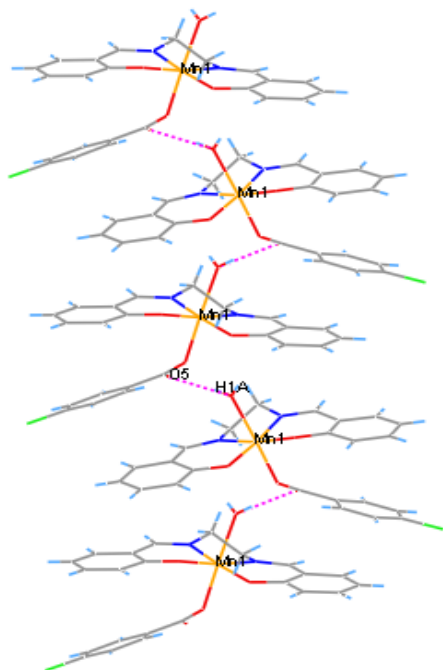


Figure 3. Helical chain of [Mn(salen)(*p*-ClC₆H₄CO₂)H₂O] (**1**) molecules parallel to the (001) plane; H-bonds (---).

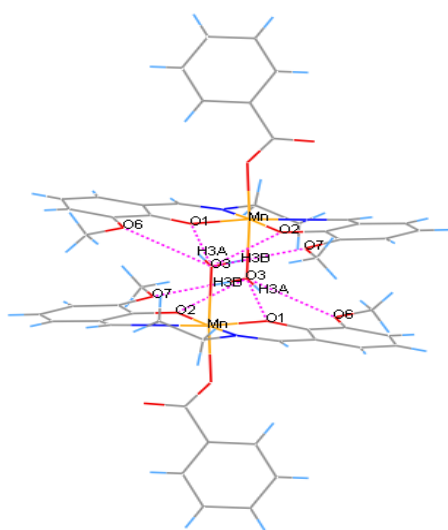


Figure 4. Section of the crystal structure of **2** showing the formation of a μ -aqua dimer; H-bonds (---)

The presence of extra methoxy groups on the Schiff base in complex **2**, afford four proximate recognition sites for each water molecule on the nearby asymmetric unit in the solid state structure. A face on approach of the coordinated water molecules in adjacent [Mn(msalen)(C₆H₅CO₂)H₂O] molecules help the aqua hydrogens, H3A (O3---O1 = 2.86 Å; O3---O6 = 3.03 Å) and H3B (O3---O2 = 2.66 Å; O3---O7 = 2.95 Å), to connect with the methoxy and phenoxy oxygens of the Schiff base through bifurcated hydrogen bonds generating a discrete supramolecular μ -aqua dimer with a Mn---Mn distance of 4.81 Å (Figures 4 and 5). The Schiff base aryl rings are involved in face-to-face (offset) π - π stacking interactions with a centroid to centroid distance of 3.99 Å and a dihedral angle (α) of 12.03°, that offer extra stabilization to the crystal structure. A survey of literature confirm that the formation of such dimers, stabilized by non-covalent interactions is not a rare feature in manganese(III)-Schiff base chemistry.^{14,27-28}

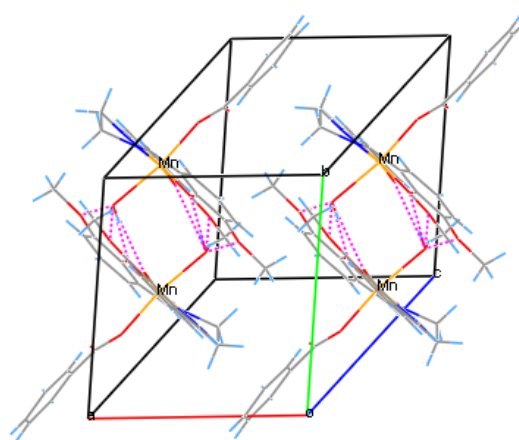


Figure 5. Crystal structure of **2** showing the close packing of μ -aqua dimers.

Conclusions

Manganese(II) carboxylate and Schiff bases generated *in situ* under aerobic conditions gave manganese(III) Schiff base complexes with supporting carboxylate ligands. The template reactions offer an easy route for the introduction of carboxylate and water as capping ligands in the octahedral complexes of manganese(III). Solid state structures reveal that the presence of these ligands at axial positions, leads to significant levels of non-covalent interactions in these complexes.

Acknowledgements

The authors are grateful to Prof. M. V. Rajasekharan, University of Hyderabad, India and Prof. R. Lalancette, Rutgers University, Newark, USA, for X-ray diffraction analysis.

Supplementary material

CCDC 914840 and CCDC 896929 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from

the Cambridge Crystallographic Data Centre (CCDC), 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; email: [http://deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Appendices A and B contain infra red and UV-Vis spectra of the complexes.

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Received: 30.03.2014.

Accepted: 17.04.2014.