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# H-bonded Chains and Networks: A Recurring Feature in the Solid State Structures of Manganese (III) Carboxylate Schiff Base Complexes

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## Abstract

Two new manganese(III) Schiff base complexes, [Mn(salen)(*m*-$NO_2$-$C_6H_4CO_2$)($H_2O$)] (**1**) and [Mn(msalen)(*p*-OH-$C_6H_4CO_2$)($H_2O$)] (**2**), where $H_2$salen = *N,N'*-bis(salicylidene)-1,2-diaminoethane, $H_2$msalen = *N,N'*-bis (3-methoxysalicylidene)-1,2-diaminoethane were synthesized from the manganese (II) carboxylates. Single crystal X-ray diffraction studies show that the Jahn-Teller distorted octahedral complexes are stabilized by H-bonded chains and networks in the solid state.

**Keywords:** Manganese (III), Carboxylate, Schiff base, H-bonds, Chains, Networks.

## 1. Introduction

The construction of a supramolecular assembly through specific recognition events, leading to a supermolecule like a single crystal, with well-defined shape and structure involves the establishment of specific and selective connections between two or more

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molecules through non-covalent interactions [1-4]. Electrostatic interactions arising from the presence of small directional and non-directional electrical charges on the interacting molecules play a major role in the formation of non-covalent bonds. A wide range of attractive and repulsive forces, such as ion-ion interactions, dipole-dipole interactions, ion-dipole interactions, van der Waals forces, and π-π stacking are classified as non-covalent interactions [5, 6a-6c, 7, 8, 9a & 9b]. Hydrogen bonding, a specific example of a dipole-dipole interaction corresponding to the attractive force between a hydrogen atom attached to an electronegative atom and a neighbouring dipole, has been extensively used in the construction of supramolecular entities. These bonds are relatively strong and directional, and offer a degree of control in the creation of a variety of molecular architectures through self-assembly process. Bond energies between 4-120 kJ $mol^{-1}$ are known and various bond lengths from 1.2 to 3.2 Å have been reported [10-11].

An area, where the coordination chemistry of high-valent manganese witnessed significant attention in recent decades, is complexes employing ligands like carboxylates and Schiff bases [12-20]. Manganese(III) carboxylate complexes with Schiff base ligands display a great deal of structural diversity and includes mononuclear, dinuclear, and polymeric species [14,16]. We have been exploring the chemistry of manganese(III) complexes with carboxylate and Schiff base ligands for some time. Some of the results have already been published as preliminary structure reports [21,22]. Herein we present a detailed analysis of these structures with a view to investigate the hydrogen bonding interactions present in these complexes.

## 2. Experimental

### 2.1 Materials and methods

All chemicals were purchased from E-Merck and used without further purification. The manganese(II) carboxylate precursors 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 [14].

### 2.2 Physical methods

IR spectra were recorded on a *Nicolet* 6700 spectrometer (KBr pellets, 4000-400 cm$^{-1}$) and elemental analyses were performed using a *Perkin-Elmer* 2400 CHNS analyzer.

### 2.3 Synthesis

#### 2.3.1 [Mn(salen)(*m*-$NO_2$-$C_6H_4CO_2$)($H_2O$)](1)

To a solution of Mn(*m*-$NO_2$-$C_6H_4CO_2$)$_2$.2$H_2O$ (1.00 g, 2.36 mmol) and salicylaldehyde (0.58 g, 4.72 mmol) in methanol (40 ml), 1,2-diaminoethane (0.14 g, 2.36 mmol) was added. The solution was stirred for 20 minutes, filtered and left to evaporation in an open conical flask. Brown crystals were deposited in 2–3 days. These were collected by filtration, washed with methanol, and dried in air. Yield 0.88 g (74.5 %). *Anal.* Calc. for $C_{23}H_{20}MnN_3O_7$ (505.36): C, 57.9; H, 3.9; N, 8.3; Mn, 10.8 %. Found: C, 57.6; H, 3.8; N, 7.9; Mn, 10.6 %. IR (KBr pellet): $\bar{\upsilon}$/cm$^{-1}$ = 3042 (*m,br*), 1622 (*vs*), 1597 (*vs*), 1537 (*s*), 1359 (*s*), 1274 (*m*), 1152 (*m*), 459 (*w*).

#### 2.3.2 [Mn(msalen)(*p*-OH-$C_6H_4CO_2$)$H_2O$] (2)

To a solution of [Mn(*p*-OH-$C_6H_4CO_2$)$_2$($H_2O$)$_2$].$H_2O$ (1.00 g, 2.61 mmol), and 3-methoxysalicylaldehyde (0.76 g, 5.22 mmol) in methanol (40 ml), 1,2-diaminoethane (0.16 g, 2.61 mmol) was added. The solution was stirred for 20 minutes, filtered and left to evaporation in an open conical flask. Brown crystals were deposited in 2-3 days. These were collected by filtration, washed with methanol, and dried in air. Crystals for X-ray crystallography were grown from a DMF solution. Yield 1.00 g (72.0 %). *Anal.* Calc. for $C_{25}H_{25}MnN_2O_8$ (536.41): C, 55.9; H, 4.6; N, 5.2; Mn, 10.3 %. Found: C, 55.6; H, 4.4; N, 5.0; Mn, 9.9 %. IR (KBr pellet): $\bar{\upsilon}$/cm$^{-1}$ = 3051 (*m,br*), 1633 (*vs*), 1596 (*vs*), 1383(*s*), 1286 (*m*), 1151(*m*), 463 (*w*).

### 2.4 X-ray crystallography

Data were collected on a *Bruker* SMART APEX II diffractometer, equipped with a CCD area detector (Cu-*K*α radiation, graphite monochromator, $\lambda$ = 1.54178 Å) at 100(2) K. The crystal structures were 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 [23]. 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 MERCURY 2.0 [24].

## 3. Results and Discussion

### 3.1 Molecular structures of 1 and 2

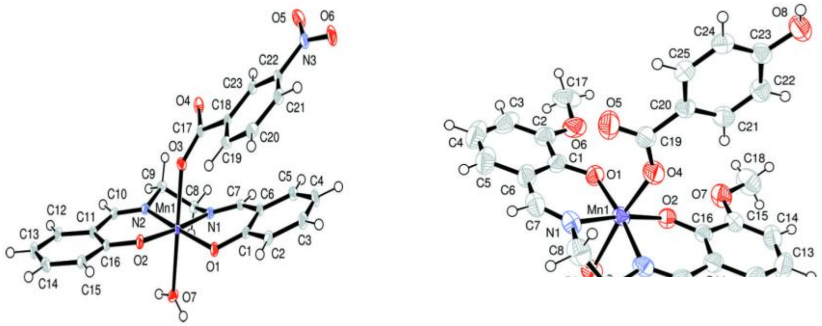

Figure 1: Molecular structures of [Mn(salen)($m$-$NO_2$-$C_6H_4CO_2$)($H_2O$)] (1) and [Mn(msalen)($p$-OH-$C_6H_4CO_2$)$H_2O$] (2).

Molecular structures of **1** and **2** consist of manganese (III) ions in distorted octahedral environments (Figure 1). Table 1 summarizes data collection and structure refinement for the complexes. The $N_2O_2$ donor set of the tetradentate Schiff base ligand bind the manganese(III) ion in a nearly planar square consisting of two Mn–$N_{imine}$ (1.97-1.99 Å) and two Mn−$O_{phenol}$ (1.88-1.91 Å) bonds (Table 2) leaving only the *trans* positions open for carboxylate linkage. In both complexes, the carboxylates adopt a unidentate coordination mode accommodating the aqua ligands along the opposite axial directions. Jahn-Teller distortions, which facilitate the removal of double degeneracy of the $e_g$ electron of the high-spin manganese (III) ion are apparent in complexes **1** and **2** with elongated axial bonds [Mn–$O_{aq}$ = 2.32 and 2.33 Å and Mn–$O_{carb}$= 2.12 and 2.15 Å].

| Complex | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{23}H_{20}Mn\ N_3O_7$ | $C_{25}H_{25}MnN_2O_8$ |
| Formula weight | 505.36 | 536.41 |
| $T$ ($K$) | 100(2) | 100(2) |
| Wavelength (Å) | 1.54178 | 1.54178 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/c$ |
| $a$ (Å) | 6.7297 (1) | 8.5988 (3) |
| $b$ (Å) | 10.5793 (2) | 13.5524 (5) |
| $c$ (Å) | 29.228 (5) | 21.1335 (8) |
| $\alpha$ (°) | 90 | 90.00 |
| $\beta$ (°) | 95.188 (1) | 93.280 (2) |
| $\gamma$ (°) | 90 | 90.00 |
| $V$(Å$^3$) | 2072.4 (4) | 2458.75 (16) |
| $Z$ | 4 | 4 |
| $\rho_{calc.}$ (g cm$^{-3}$) | 1.620 | 1.449 |
| $\mu$ (mm$^{-1}$) | 5.66 | 4.82 |
| $F$(000) | 1040 | 1112 |
| $\theta_{min/max}$ (°) | 9.7/70.5 | 9.7/72.7 |
| Total data | 21257 | 26252 |
| Unique data | 3640 | 4259 |
| $R_{int}$ | 0.046 | 0.033 |
| Restraints/ parameters | 0/308 | 0/329 |
| Goodness-of-fit (GOF) | 1.114 | 1.04 |
| Final R indices [I > 2σ(I)] | $R_1 = 0.0347$<br>$wR_2 = 0.0366$ | $R_1 = 0.0290$<br>$wR_2 = 0.0348$ |
| R indices (all data) | $R_1 = 0.0909$<br>$wR_2 = 0.0922$ | $R_1 = 0.0784$<br>$wR_2 = 0.0815$ |

Table 1: Crystal data and structure refinement for 1 and 2.

| Complex | **1** | **2** |
|---|---|---|
| Mn–$O_p$ | 1.8879 (15) | 1.8821 (11) |
| Mn–$O_p$ | 1.9113 (15) | 1.8848 (12) |

Oa = $O_{aqua}$, $O_c$ = $O_{carboxyate}$, $O_p$ = $O_{phenolic}$, $N_i$ = $N_{imine}$

Table 2: Selected bond angles (˚) and bond lengths (Å) of 1and 2.

The extent of angular distortions around the Mn-$N_2O_2$ cores of the complexes vary significantly the dihedral angles between the aromatic rings of the Schiff base ligands are 15.60 and 3.60°respectively and the corresponding *N,N',O,O'* least-square plane deviations from the manganese(III) ions, along the Mn--$O_{carb}$ directions are 0.016 and 0.083 Å.

### 3.2. Solid state structures of 1, 2

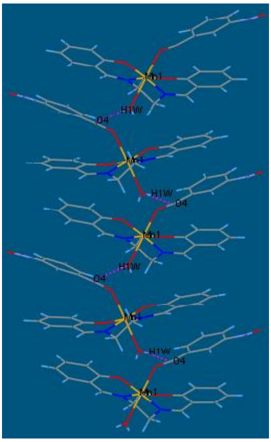

Figure 2: Helical chain of [Mn(salen)(*m*-$NO_2$-$C_6H_4CO_2$)($H_2O$)] (1) molecules along the *ab* plane; H-bonds (---).

Occupation of the *trans* coordination sites by carboxylate and water in complex **1** facilitate the spontaneous generation of supramolecular architectures, in the solid state through hydrogen bonding. Adjacent [Mn(salen)(*m*-$NO_2$-$C_6H_4CO_2$)($H_2O$)] molecules meet in a nearly end on fashion along a screw ($2_1$) axis so that the carboxylate and water engage in hydrogen bonding interactions (O4---H1W = 1.89 Å; O4---O7 = 2.71 Å) to generate helical chains progressing along the *ab* plane (Figure 2 and Table 3). The Mn---Mn distance in the chain is 6.24 Å, whereas the repeat distance is 10.58 Å.

| *D* –H…*A* | *D* –*H* | *H*…*A* | *D*… *A* | *D* –*H*…*A* |
|---|---|---|---|---|
| O7–H2W…O2$^{i}$ | 0.77 | 2.31 | 3.074 (2) | 172 |
| O7–H1W…O4$^{ii}$ | 0.84 | 1.89 | 2.710 (2) | 166 |

Symmetry codes: (i) – x– , y + , – z + ; (ii) – x + , y + , – z +

Table 3: Hydrogen-bond geometry of complex 1 (Å, °).

Asymmetric units in complex **2** are much closer to one another than those in complex **1** (Mn---Mn = 4.85 Å). Approach of the coordinated water molecules is face on. This together with the presence of extra methoxy groups on the Schiff base provides four proximate recognition sites for every axial water molecule.

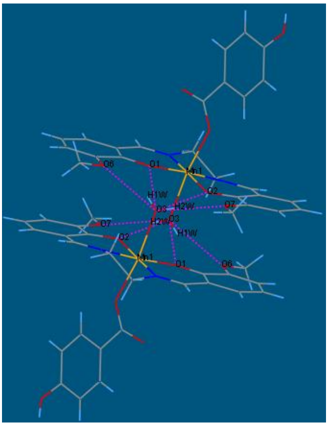

Figure 3: Section of the crystal structure of [Mn(msalen)(*p*-OH-$C_6H_4CO_2$)$H_2O$] (**2**) showing the formation of a $\mu$-aqua dimer; H-bonds (---).

Bifurcated hydrogen bonds are formed between the aqua hydrogens, H1W (O3---O6 = 3.00 Å; O3---O1 = 2.95 Å), H2W (O3---O7 = 3.00 Å; O3---O2 = 2.87 Å) and the methoxy/phenoxy oxygens of the Schiff base giving rise to a supramolecular $\mu$-aqua dimer (Figure 3).

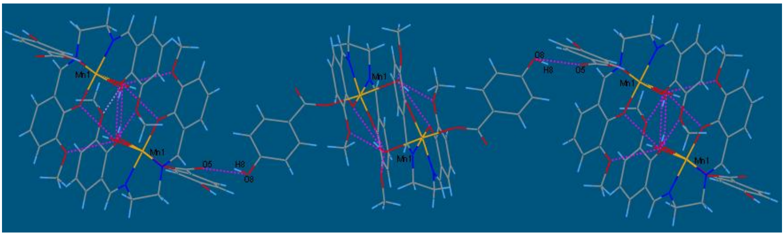

Figure 4: Section of the crystal structure of 2 showing dimer-dimer self assembly through H-bonds.

Adjacent $Mn_2$ dimers are further linked through hydrogen bonds utilizing the non-bonded oxygens of the carboxylate and the hydrogens of the *p*-hydroxy group (H8---O5 = 1. 79 Å, O8---O5 =

2.59 Å) producing a supramolecular chain extending along the (103) plane (Figure 4). Two such chains are connected through identical supplementary H-bond interactions between non-bonded oxygens of the carboxylate and the hydrogens of the *p*-hydroxy group (H8---O5 = 1. 79 Å, O8---O5 = 2.59 Å) producing a 2-dimensional network progressing nearly parallel to the (103) plane (Figures 5 and 6). Formation of $\mu$-aqua dimers stabilized by non-covalent interactions like H-bonds are occasionally encountered in manganese(III)-Schiff base chemistry [16,25,26].

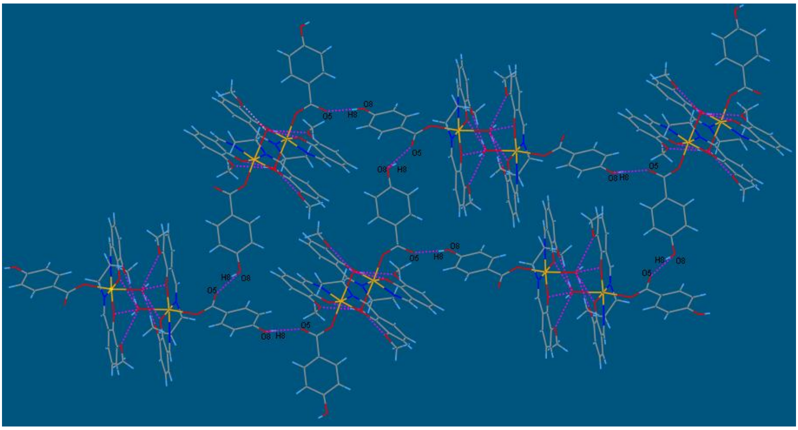

Figure 5: Section of the crystal structure of 2 showing H-bonded 2D-network.

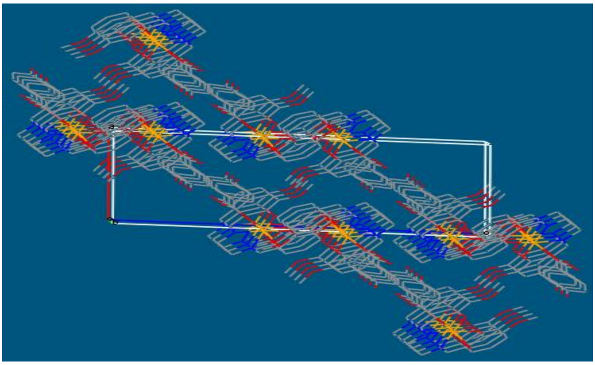

Figure 6: Close-packing of 2 showing H-bonded 2D-network parallel to the (103) plane.

| *D* − *H*…*A* | *D* − *H* | *H*…*A* | *D*… *A* | *D* − *H*…*A* |
|---|---|---|---|---|
| O8 − H8…O5$^{i}$ | 0.84 | 1.79 | 2.599 (2) | 161 |
| O3 − H2W…O7$^{ii}$ | 0.84 | 2.32 | 3.002 (2) | 139 |
| O3 − H2W…O2$^{ii}$ | 0.84 | 2.11 | 2.871 (2) | 150 |
| O3 − H1W…O6$^{ii}$ | 0.84 | 2.29 | 3.000 (2) | 142 |
| O3 − H1W…O1$^{ii}$ | 0.84 | 2.21 | 2.948(2) | 147 |

Symmetry codes: (i) $-x+1, y+\ \ , -z+\ \ $; (ii) $-x, -y+1, -z+1$.

Table 4: Hydrogen-bond geometry of complex 2 (Å, °).

## 4. Conclusion

X-ray diffraction analysis reveal a great deal of information about non-covalent interactions like hydrogen bonds in the solid state structures of manganese(III) carboxylate complexes with symmetric $N_2O_2$ Schiff base ligands. It is obvious that the use of carboxylate and water as capping ligands in these complexes facilitates the formation of H-bonded chains and networks in the solid state. Natural systems are abound with examples of chains and networks arising from non-covalent interactions and are vital for the catalytic functioning of many metallo-biomolecules. As there are several manganese-containing biomolecules in biological systems, it may be worthwhile to pursue structural level studies as discussed in the paper, in areas like bioinorganic modeling.

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## Supplementary materials

Supplementary data for this paper is available from the IUCr electronic archives (References: SI2096 and BT5032). http://journals.iucr.org/services/earchive.html

## References

[1] J. D. Dunitz, “Phase transitions in molecular crystals from a chemical viewpoint”, *Pure Appl. Chem.*, vol. 63, No. 2, pp. 177-185, 1991. doi:10.1351/pac199163020177

[2] J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995.

[3] G. M. Whitesides and B. Grzybowski, “Self-Assembly at All Scales”, *Science*, vol. 295, pp. 2418-2421, 2002. doi:10.1126/science.1070821.

[4] J. M. Lehn, “From supramolecular chemistry towards constitutional dynamic chemistry and adaptive chemistry”, *Chem. Soc. Rev.,* vol. 36, pp. 151-160, 2007. doi: 10.1039/b616752g

[5] D. J. Hoffart, J. Tiburcio, A. de la Torre, L. K, Knight and S. J. Loeb, “Cooperative Ion-Ion Interactions in the Formation of Interpenetrated Molecules”, *Angew. Chem. Int. Ed.*, vol. 47 (1), pp. 97-101, 2007. doi: 10.1002/anie.200703019

[6] (6a)S. Adhikari, A. Uren and R. Roy, *J. Biol. Chem.*, vol.*283*, pp. 1334-1339, 2008.

(6b) Y. Mu and Y. Q. Gao, “Effects of hydrophobic and dipole-dipole interactions on the conformational transitions of a model polypeptide”, *J. Chem. Phys.,* vol. 127, pp. 105102-105111, 2007.

(6c) B. N. J. Persson and R. Ryberg, “Vibrational interaction between molecules adsorbed on a metal surface: The dipole-dipole interaction”, *Phys. Rev. B,* vol 24 (12), pp. 6954-6970, 1981.

[7] J. O' M. Bockris, K. N. Reddy and M. Gamboa-Aldeco, *Modern Electrochemistry 1*, Springer, Berlin, 2000.

[8] I. Kitaigorodski, *Molecular Crystals and Molecules*, Academic Press: New York, 1973.

[9] (9a) A. Sygula, F. R. Fronczek, R. Sygula, P. W. Rabideau and M. M. Olmstead, “A Double Concave Hydrocarbon Buckycatcher”, *J. Am. Chem. Soc.,* vol. 129 (13), pp. 3842-3843, 2007.

(9b) A. Petitjean, R. G. Khoury, N. Kyritsakas and J. -M. Lehn, “Dynamic Devices. Shape Switching and Substrate Binding in Ion Controlled Nanomechanical Molecular Tweezers”, *J. Am. Chem. Soc.*, vol. 126, pp. 6637-6647, 2004.

[10] M. Albrecht, “Supramolecular chemistry-general principles and selected examples from anion recognition and metallosupramolecular

chemistry", *Naturwissenschaften*, vol. 94, pp. 951-966, 2007. doi:10.1007/s00114-007-0282-7

[11] J. W. Steed, D. R. Turner, and K. J. Wallace, *Core Concepts in Supramolecular Chemistry and Nanochemistry*, John Wiley & Sons, Ltd, 2007.

[12] N. Aurangzeb, C. E. Hulme, C. A. McAuliffe, R. G. Pritchard, M. Watkinson, A. Garcia-Deibe, M. R. Bermejo and A. Sousa, "The crystal structure of [Mn(salpn)(acetate)]$_2$(H$_2$O)$_3$; the first example of a manganese(III) Schiff base polymeric complex containing a dimeric repeat unit [salpn =*N,N'*-bis(salicylidene)-1,3-diaminopropane]", *J. Chem. Soc. Chem. Commun*., (20), pp. 1524-1526, 1992.

[13] N. Aurangzeb, C. E. Hulme, C. A. McAuliffe, R. G. Pritchard, M. Watkinson, M. R. Bermejo and A. Sousa, "Structurally diverse manganese(III) carboxylate complexes of N$_2$O$_2$ donor set symmetrical Schiff base ligands", *J. Chem. Soc. Chem. Commun*., (18), pp. 2193-2195, 1994. doi:10.1039/C39940002193

[14] C. E. Hulme, M. Watkinson, M. Haynes, R. G. Pritchard, C. A. McAuliffe, N. Jaiboon, B. Beagley, A. Sousa, M. R. Bermejo and M. Fondo, "Structurally diverse manganese(III) complexes of tetradentate N$_2$O$_2$ Schiff-base ligands with ancillary carboxylate donors", *J. Chem. Soc. Dalton Trans*., (11), pp. 1805-1814, 1997. doi:10.1039/A701216K

[15] C. Zhang and C. Janiak, "A carboxylato-supported alkoxo-bridged dimanganese(III) complex:bis(µ-benzoato-*O*:*O*')bis[3-(3-methoxysalicylideneamino) propanolato-*O*,*N*,*O*':*O*']dimanganese(III)" , *Acta Cryst.* C37, pp. 719-720, 2001.

[16] M. R. Bermejo, M. I. Ferna´ndez, A. M. Gonza´lez-Noya, M. Maneiro, R. Pedrido, M. J. Rodrı´guez, J. C. Garcı´a-Monteagudo and B. Donnadieu, "Novel peroxidase mimics: µ-Aqua manganese-Schiff base dimers", *J. Inorg. Biochem*., vol.100 (9), pp. 1470-1478, 2006.

[17] S. Biswas, A. K. Dutta, K. Mitra, M. C. Dul, S. Dutta, C. R. Lucas and B. Adhikary, "Synthesis, characterization, electrochemical and magnetic studies on manganese(III) complexes involving bridging carboxylates", *Inorg. Chim. Acta,* vol. 377 (1), pp. 56-61, 2011.

[18] P. Kar, R. Biswas, M. G. B. Drew, Y. Ida , T. Ishida and A. Ghosh, "Structure and magnetic properties of an unprecedented *syn-anti μ*-nitrito-1κ*O*:2κ*O*' bridged Mn(III)-salen complex and its isoelectronic and isostructural formate analogue", *Dalton Trans*., vol. 40, pp. 3295-3304, 2011. doi:10.1039/C0DT01521K

[19] P. Mukherjee, P. Kar, S. Ianelli and A. Ghosh, "Isolation of a novel intermediate during unsymmetrical to symmetrical rearrangement of a tetradentate Schiff base ligand in a manganese(III) complex: Catalytic activity of the rearranged product towards alkene epoxidation", *Inorg. Chim. Acta*, vol. 365 (1), pp. 318-324, 2011.

[20] F. Benetollo, V. Peruzzo, S. Tamburini and P. A. Vigato, "Manganese complexes with acyclic compartmental Schiff bases", *Inorg. Chem. Commun.,* vol.15, pp. 84-87, 2012.

[21] V. S. Thampidas, T. Radhakrishnan and R. D. Pike, "Aqua{2,2-[ethane-1,2-diylbis(nitrilomethylidyne)] diphenolato}(3-nitrobenzoato) manganese(III)", *Acta Cryst.* E64, pp. m990-m991", 2008. doi:10.1107/S1600536808019715

[22] R. Reshma, P. V. Soumya, S. M. Simi, V. S. Thampidas and R. D. Pike, "Aqua{6,6'-dimethoxy-2,2'-[ethane-1,2-diylbis(nitrilomethylidyne)] diphenolato}(4-hydroxy benzoato) manganese(III)" *Acta Cryst.* E65, pp. m1110-m1111, 2009. doi:10.1107/ S1600536809032553

[23] G. M. Sheldrick, "Programs for Crystal Structure Analyses", SHELX-97 (SHELXS 97 and SHELXL 97), University of Göttingen, Germany, 1998.

[24] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, "Mercury: visualization and analysis of crystal structures", *J. Appl. Cryst.*, 39, pp. 453-457, 2006. doi:10.1107/S002188980600731X

[25] M. Á. Vázquez-Fernández , M. I. Fernández-García , A. M. González-Noya, M. Maneiro , M. R. Bermejo and M. J. Rodríguez-Doutón, "Supramolecular networks of Mn(III)–Schiff base complexes assembled by nitrate counterions: X-ray crystal structures of 1D chains and 2D networks", *Polyhedron*, vol. 31(1), pp 379, 2012.

[26] P. Bhowmik, H. P. Nayek, M. Corbella, N. Aliaga-Alcalde and S. Chattopadhyay, "Control of molecular architecture by steric factors: mononuclear vs polynuclear manganese(III) compounds with tetradentate $N_2O_2$ donor Schiff bases", *Dalton Trans.,* vol. 40, pp. 7916-7926, 2011. doi:10.1039/C0DT01723J