Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2019, 8 (3): 1012-1023

(International Peer Reviewed Journal)

Syntheses, Structures and Characterizations of some Manganese(III) Carboxylates in Combination with some Tetradentate N_2O_2 Donor Schiff Bases-A Review

Somnath Choubey*

Department of Chemistry, Government General Degree College, Manbazar-II,
Susunia, Purulia, PIN-723131, West Bengal, **INDIA**
Email: somnathchoubey@gmail.com

Accepted on 25th April, 2019

ABSTRACT

Manganese(III) carboxylate complexes with tetradentate N_2O_2 donor Schiff base ligands have been found to exhibit rich structural diversity. The syntheses, characterizations and structural variations of such complexes by simply altering the substituents on the carboxylate ligands and/or backbone of the Schiff bases has been discussed in this short review.

Highlights

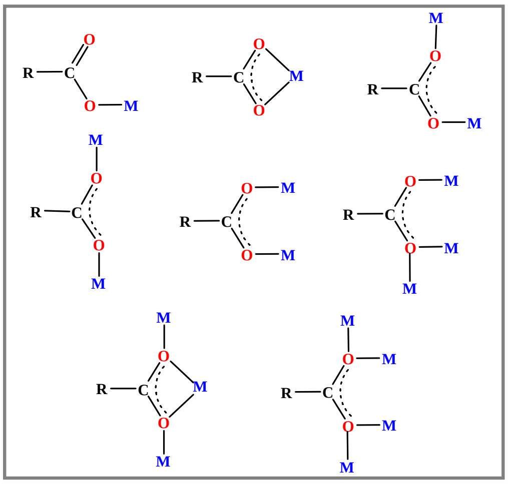
- Syntheses of some novel Manganese(III) carboxylate complexes with tetradentate N_2O_2 donor Schiff bases are described.
- Their detailed and systematic characterizations are highlighted.
- Structural variations of such compounds by simply changing the substituents on the carboxylate ligands and/or backbone of the Schiff bases are outlined.

Keywords: Manganese(III) Complex, Carboxylates, Schiff base, Structural diversity.

INTRODUCTION

The last few decades have witnessed a remarkable growth in the interest in mono-, di- and polynuclear manganese carboxylate compounds in combination with oxygen- and nitrogen-based ligands. This has been mainly due to their application to two major fields, bioinorganic chemistry and molecular magnetism, as well as to the architectural beauty and aesthetically pleasing structures they possess. Manganese(II/III) ions and biological carboxylate ligands are found at the active sites of several redox enzymes, the most interesting of which is the water-oxidizing complex (WOC) on the donor side of photosystem II in green plants and cyanobacteria [1-4], thus, bioinorganic chemists have been trying to rebuild with synthetic models the structure, spectroscopic properties and/or function of the active sites of such enzymes [5-7], and especially so of the $\{Mn_4CaO_x\}$ cluster unit that is present in the WOC. In the molecular magnetism arena, manganese carboxylate clusters containing manganese(III) have been found to often have large ground state spin (S) values, which combined with a large and negative magneto-anisotropy (as reflected in a large and negative zero-field splitting parameter, D) have led to some of these complexes being able to function as single-molecule magnets

(SMMs) [8-15]. SMMs are individual molecules or ions that behave as nanoscale magnets below a certain ("blocking") temperature, and thus represent a molecular, 'bottom-up' approach to nanomagnetism. Scientists around the world are currently seeking to raise the blocking temperature in SMMs and extend this phenomenon as far as possible [16-17]. The metal carboxylates are also interesting because they form open-framework structures [18-21] resulting from the presence of the carboxylate function itself, but also where the carboxylate group acts as a linker between inorganic moieties (Scheme 1). Herein, we present a concise review of the syntheses, structures and characterizations of the families of manganese carboxylates complexes in combination with some N_2O_2 donor Schiff bases [22-26].



Scheme 1. Possible coordination modes of the simple carboxylate ligands.

RESULTS AND DISCUSSIONS

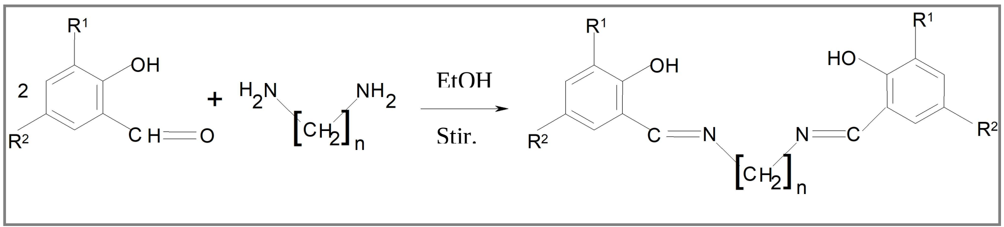
Preparation of Manganese(II) carboxylate salts, $Mn(O_2CR)_2$: From detailed literature survey it is found that all the Manganese(II) carboxylate salts have been prepared in an analogous manner by the reaction of an excess of the appropriate acid with manganese carbonate in water. Here this is exemplified by the preparation of $Mn(O_2CEt)_2$. Manganese carbonate (11.5 g, 0.1 mol) was added to round-bottomed flask (500 cm^3) containing water (250 cm^3). Propionic acid (22.2 g, 0.3 mol) was added. The mixture was refluxed with stirring for 6 h. The reaction mixture was cooled, filtered to remove unchanged manganese carbonate and the aqueous phase washed with diethyl ether (100 cm^3×2). The resultant aqueous solution was evaporated to dryness, resulting in a pale pink solid. This was ground in a pestle and mortar, dried *in vacuo* over P_2O_5 and finally dried *in vacuo* at 160°C for 4 h. For manganese(II) phenylacetate $Mn(O_2CCH_2Ph)_2$ yields were improved by using a 2 : 1 acid : carbonate ratio.

Characterization of manganese(II) carboxylate salts: All the manganese(II) carboxylate salts have been formed in an analogous manner [other than the commercially available $Mn(O_2CMe)_2.4H_2O$] by the reaction of the appropriate acid with manganese carbonate in aqueous solution. The compounds isolated by this method can be used in subsequent syntheses satisfactorily. The infrared spectra of all salts are dominated by bands which can be assigned to the asymmetric and symmetric stretching modes of the carboxylate ligand (Table 1) and are otherwise essentially featureless (although aliphatic and aromatic C-C and C-H stretches are observed, they yield little information as to the structure of the salts). The relatively low yields (<60%) of some of the salts appear to be a direct result of the increased hydrophobicity of the corresponding acid. Despite them, this method does provide a satisfactory synthetic route to these salts, since the starting materials are relatively inexpensive.

Table 1. IR data and Yield for the manganese(II) carboxylate salts

Salts	IR/cm^{-1}		Yield (%)
	ν_{asym} (CO_2)	ν_{sym} (CO_2)	
$Mn(O_2CEt)_2$	1572	1415	67
$Mn(O_2CPr^n)_2$	1558	1415	56
$Mn(O_2CBu^n)_2$	1558	1410	49
$Mn(O_2CBu^t)_2$	1555	1412	47
$Mn(O_2CCH_2Ph)_2$	1562	1400	55
$Mn(O_2CPr^i)_2$	1555	1409	49

Preparation of the Schiff bases: All the Schiff bases were prepared as previously reported [22, 23] by the reaction of the appropriately substituted aldehyde with either 1,2-diaminoethane or 1,3-diaminopropane in ethanol as shown in scheme 2. They were isolated in virtually quantitative yield and satisfactorily characterized by using different microanalytical and spectroscopic methods.



H_2salen: $n=2$, $R^1 = H$, $R^2 = H$; H_2saltn: $n=3$, $R^1 = H$, $R^2 = H$; H_2bsalen: $n=2$, $R^1 = H$, $R^2 = Br$
H_2bsaltn: $n=3$, $R^1 = H$, $R^2 = Br$; H_2msalen: $n=2$, $R^1 = OMe$, $R^2 = H$;H_2msaltn: $n=3$, $R^1 = OMe$, $R^2 = H$

Scheme 2. General method of preparations of the Schiff bases.

Manganese carboxylate complexes with Schiff bases: From detailed literature survey on manganese carboxylate complexes with different N, O-donor Schiff bases many new notable complexes were observed, within them syntheses and characterization [22-26, 28, 29] some of the interesting compounds are described in this part.

A number of manganese (III) complexes of tetradentate N_2O_2 Schiff-base ligands have been prepared with various additional carboxylate anions. Many of these compounds have been crystallographically characterized [28, 29] revealing that a remarkable array of structural chemistry is available. Mono-, di- and polymeric structures are formed by proper tuning of the carboxylate anions and Schiff bases [22-26]. $[\{Mn(saltn)\ (O_2CMe)\}_{2n}].3nH_2O$, is the first example [22] of a manganese(III) Schiff base polymer containing a dimeric repeating unit (Figure 2). Complex $[Mn(saltn)(O_2CEt)]_n$ was also found to consist of a polymer (Figure 3) which unlike $[\{Mn(saltn)(O_2CMe)\}_{2n}].3nH_2O$ contains a monomeric repeating unit. In complete contrast to the aforementioned polymeric structures $[\{Mn(saltn)(O_2CMe)\}_{2n}].3nH_2O$ and $[Mn(saltn)(O_2CEt)]_n$, $[Mn(saltn)\ (O_2CBu^n)]$ has a monomeric structure (Figure 4). Structures of $[Mn(saltn)(O_2CBu^t)]$ and $[Mn(salpn)(O_2CPr^i)]$ found to consists of the monomeric species like $[Mn(saltn)(O_2CBu^n)]$ with a *cis*-chelated carboxylate ligand (Figure 5 and 6). The complex $[Mn_2(salen)_2\ (O_2CPr^n)\ (EtOH)(H_2O)]\ [O_2CPr^n]$ crystallized as the dinuclear form (Figure 7).

The structure of $[Mn(msalen)(O_2CMe)(H_2O)].\ 2H_2O$ is found to consist of a monomeric manganese(III) centre (Figure 8) which is ligated in the *xy* plane by the tetradentate Schiff base ligand. The structure of $[\{Mn(msalen)(O_2CEt)\}_2]$.EtOH, found to be a dimer in which the manganese centers are linked by phenoxy bridges between one phenolic oxygen atom of each ligand (Figure 9). $[\{Mn(msalen)(O_2CBu^n)\}_2]$ (Figure 10) is found to have analogous to that of $[\{Mn(msalen)(O_2CEt)\}_2]$.EtOH. The coordination sphere of $[Mn(msalen)(O_2CCH_2Ph)(H_2O)].H_2O$ (Figure 11) consists of the tetradentate Schiff base ligand, msalen in the *xy* plane, with the axial sites filled with the unidentate carboxylate O(5) and a water molecule O(1w). Both complexes $[Mn(msaltn)(O_2CPr^i)]$

and [Mn(msaltn)(O_2CBu^t)] were found to exist as monomeric species (Figure 12) in which the Schiff base ligand, msaltn affords *cis* sites at the manganese(III) centre for bidentate chelation of the carboxylate ligands.

[{Mn(bsaltn)(O_2CCH_2Ph)}$_n$] found to consist of a polymeric complex, (Figure 13) Unlike the other polymeric complexes of this type the $[Mn(bsaltn)]^+$ units are linked by the carboxylate binding in the relatively rare *syn-anti* rather than *anti-anti* mode. In contrast to [{Mn(bsaltn)(O_2CCH_2Ph)}$_n$], [Mn(msaltn)(O_2CCH_2Ph) (H_2O)] is a mononuclear complex and here the carboxylate is behaving as a unidentate ligand (Figure 14).

Preparation of Manganese(III) carboxylate complexes with N_2O_2-donor-set Schiff-base ligands: From literature study it is established that all the complexes have been prepared in an analogous manner by the reaction of the appropriate salt with the Schiff base in ethanol; complexes of all salen ligands are brown whilst those of saltn ligands are green. This is illustrated by the preparation of [Mn(bsaltn)(O_2CMe)]. To a solution of manganese acetate (1.23 g, 0.005 mol) in ethanol (50 cm^3) was added H_2bsaltn (2.19 g, 0.005 mol) in ethanol (50 cm^3). This mixture was refluxed for 2.5 h and filtered. The filtrate was reduced in volume (*ca.* 25 cm^3) and added dropwise to diethyl ether (200 cm^3) resulting in the formation of a green precipitate. This precipitate was isolated, washed with diethyl ether and dried *in vacuo*. Yields are frequently low for the complexes of saltn ligands. This is due to the large quantity of an insoluble material produced in these reactions, which was removed by filtration. This is compounded by the relatively high solubility of the isolated complexes in diethyl ether. Many synthetic attempts to characterize this insoluble material of stoichiometry $Mn_4L_3(O_2CR)_3.nH_2O$ (n = 0–3); this has established to be an intractable problem.

Characterization of manganese(III) carboxylate complexes with Schiff bases: All the complexes have been prepared in an analogous manner by the reaction in air of the appropriate manganese(II) carboxylate with Schiff base ligand in ethanol and also have been characterized [28, 29] by using different spectroscopic and microanlytical techniques. The infrared spectra of the complexes generally show shifts in ν(C=N) to lower energy compared with the free ligand values, indicative of co-ordination to manganese. The ν(C=N) value lie in the range 1605-1635 cm^{-1}. Two bands can be assigned to the asymmetric and symmetric stretching modes of the carboxylate group in all complexes [22-27] are in the range 1520-1575 and 1380-1469 cm^{-1} respectively (Table 2). The co-ordination of the ligand to manganese is further substantiated by two weak bands in the far-infrared region which we assign to ν(Mn-N). The UV-Vis spectra of the complexes in methanol are also essentially identical (Figure 1 and Table 3) and are typical of high spin d^4 manganese(III) complexes. The complexes of the msalen ligand all show five bands in the spectra [25]. The wavelengths at which these bands occur are virtually identical, as are the absorption coefficients, implying that the manganese(III) carboxylate complexes of msalen are identical in methanolic solution.

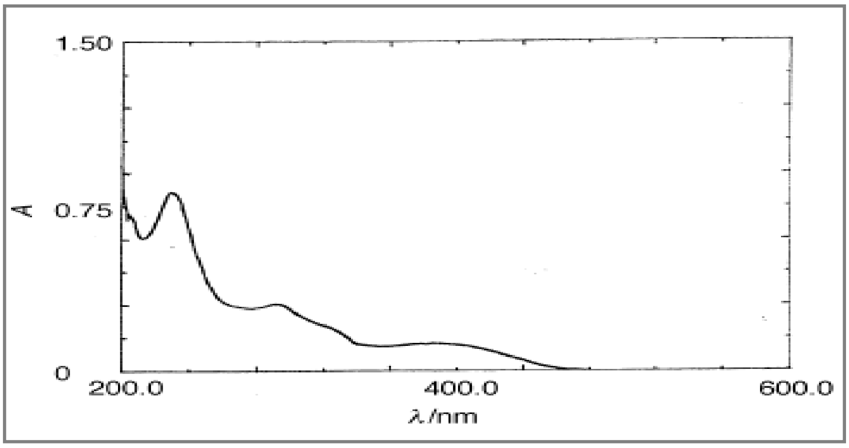


Figure 1. The UV-Vis spectrum of a methanolic solution of [{Mn(msalen)(O_2CPr^n)}$_2$].

Table 2. Selected infrared data (cm^{-1}) for the manganese(III) carboxylate complexes

Complexes	υ(C=N)	$\upsilon_{asym}(CO_2)$	$\upsilon_{sym}(CO_2)$	υ(Mn-N)
$[\{Mn(saltn)(O_2CEt)\}_n]$	1620	1535	1403	372
$[Mn(saltn)(O_2CBu^t)]$	1622	1544	1448	384
$[\{Mn(bsaltn)(O_2CCH_2Ph)\}_n]$	1620	1532	1380	380
$[Mn(msaltn)(O_2CBu^t)]$	1614	1526	1376	378
$[Mn(saltn)(O_2CBu^n)]$	1615	1548	1469	387
$[Mn(saltn)(O_2CPr^i)]$	1618	1545	1448	390
$[\{Mn(msalen)(O_2CBu^n)\}_2]$	1622	1550	1410	377
$[\{Mn(msalen)(O_2CEt)\}_2]$.EtOH	1626	1548	1410	375
$[\{Mn(saltn)(O_2CMe)\}_{2n}].3nH_2O$	1623	1544	1404	372
$[Mn_2(salen)_2(O_2CPr)(EtOH)(H2O)][O_2CPr]$	1624	1558,1542	1403,1388	376
$[Mn(msaltn)(O_2CPr^i)]$	1616	1541	1401	372
$[Mn(msaltn)(O_2CCH_2Ph)(H_2O)]$	1616	1543	1404	378
$[Mn(msalen)(O_2CCH_2Ph)(H_2O)].H_2O$	1624	1546	1399	390
$[Mn(saltn)(O_2CPr^n)]$	1614	1542	1393	393

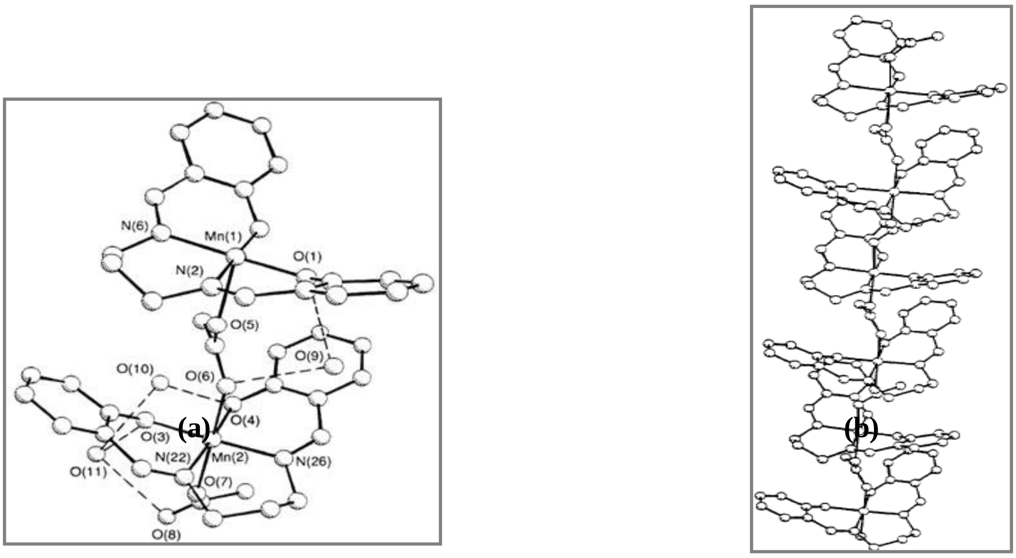
Table 3. The UV-Vis data for the manganese(III) carboxylate complexes of msalen in methanol

Complexes	λ/nm	*A*	$\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$
$[Mn(msalen)(O_2CMe)]$	203.5	0.956	32 081
	233.5	1.212	40 671
	298.0	0.323	10 839
	328.0	0.331	11 107
	403.5	0.117	3 926
$[Mn(msalen)(O_2CEt)]$	203.0	0.161	32 984
	233.5	0.404	41 543
	301.0	0.397	11 689
	328.0	1.411	11 895
	404.0	1.096	4 740
$[Mn(msalen)(O_2CPr^n)]$	203.5	0.986	32 984
	234.0	1.244	41 615
	297.0	0.354	11 842
	328.0	0.364	12 043
	407.0	0.138	4 616
$[Mn(msalen)(O_2CBu^n)]$	203.5	1.096	34 550
	233.5	1.370	43 187
	298.5	0.376	11 842
	328.5	0.387	12 199
	404.0	0.144	4 539

Structures of manganese(III) carboxylate complexes with Schiff bases: During literature review some very interesting Manganese(III) carboxylate complexes in combination with a variety of Schiff bases have been identified. Structural details of some of such fascinating complexes are discussed here.

$[\{Mn(saltn)(O_2CMe)\}_{2n}].3nH_2O$: Compound, $[\{Mn(saltn)(O_2CMe)\}_{2n}].3nH_2O$, is the first example of a manganese(III) Schiff base polymer [22] containing a dimeric repeating unit $[Mn(saltn)(O_2CMe)]_2.3H_2O$ with acetate bridges. The repeating dimeric unit contains two distorted octahedral manganese(III) ions, two saltn ligands orientated at 180° with respect to each other and three hydrogen-bonded water molecules (Figure 1a). The two bridging acetate groups adopt an *anti-anti* configuration along the symmetry axis and produce a linear Mn-OAc-Mn-OAc chain propagated [22] along the central axis as is illustrated by figure 1b.

$[Mn(saltn)(O_2CEt)]_n$: Complex $[Mn(saltn)(O_2CEt)]_n$ was found to consist of a polymer [25] (Figure 3) which unlike $[\{Mn(saltn)(O_2CMe)\}_{2n}].3nH_2O$ contains a monomeric repeating unit. The presence of such a monomeric repeating unit, rather than a dimeric unit, can be attributed to the stabilizing



(a) (b)

Figure 2(a). [Mn(saltn)(O_2CMe)]$_2$.3H_2O, where broken lines indicate intramolecular hydrogen bonds (all other atoms shown are carbon); and **(b).** [Mn(saltn)(O_2CMe)]$_n$, showing the orientation of ligands and *anti-anti* configuration of the acetate groups.

effect of the π…π interactions between the Schiff-base ligands. The structure indicates that, in absence of the hydrogen-bonded solvent or water molecules, such polymers are preferred. It is to note that the dimeric repeating unit in [{Mn(saltn) (O_2CMe)}$_{2n}$].3nH_2O, forms as a direct result of such hydrogen bonding. The structure consists of a distorted octahedral manganese(III) centre which is bridged by a carboxylate coordinated in the *anti-anti* mode [25]. The planar coordination of the Schiff-base ligand is symmetric due to the manganese and oxygen atoms of the carboxylate lying in a mirror plane. The planar coordination of the Schiff base ligand leaves *trans* sites open for carboxylate coordination resulting the linear chains of the polymer.

[Mn(saltn)(O_2CBu^n)]: In complete contrast to the aforementioned polymeric structures of [{Mn(saltn) (O_2CMe)}$_{2n}$].3nH_2O and [Mn(saltn)(O_2CEt)]$_n$, [Mn(saltn)(O_2CBu^n)] has a monomeric structure (Figure 4). This is only the second monomeric manganese complex with nitrogen donor and carboxylate ligands to be crystallographically characterized. The chelation of the valerate anion necessarily involves considerable distortion of the manganese centre from ideal octahedral geometry.

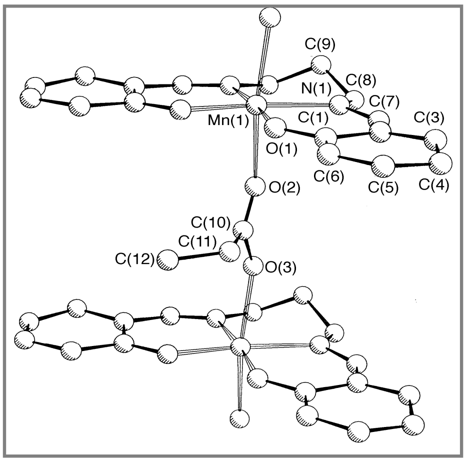


Figure 3. Coordination environment of [Mn(saltn)(O_2CEt)]$_n$.

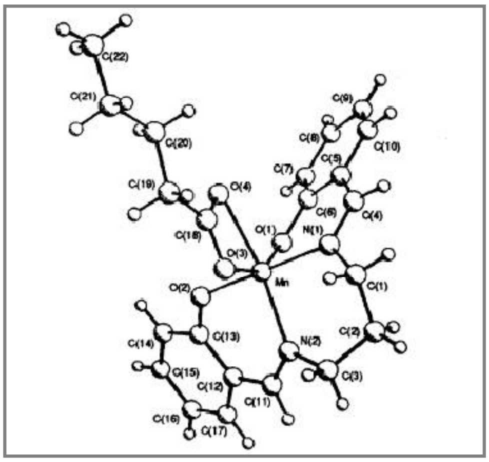


Figure 4. Molecular structure of [Mn(saltn)(O_2CBu^n)].

[Mn(saltn)(O_2CBu^t)]: Structure of [Mn(saltn)(O_2CBu^t)] found to consists of the monomeric species (Figure 5), rather than polymers previously observed for the acetate derivative [^-O_2CMe and ^-O_2CEt]. The increased steric bulk associated with the *tert*-butyl substituent on the acid, may serve to prevent polymer formation. The compound possesses essentially the same structure as [Mn(saltn)(O_2CBu^n)] and represents a further rare example of a monomeric complex with nitrogen and carboxylate donor ligands. The flexibility of the trimethylene backbone of the saltn ligands affords *cis* sites at the metal centre open for carboxylate chelation, in complete contrast to the *trans* sites in the analogous polymers. The chelation of the carboxylate necessarily involves distortion of the manganese centre from idealized octahedral geometry.

[Mn(saltn)(O_2CPr^i)]: Crystals suitable for single crystal X-ray diffraction studies of [Mn(salpn)(O_2CPr^i)] were found to consist, as expected, of a monomeric manganese(III) Schiff base complex with a *cis*-chelated carboxylate ligand (Figure 6). The distorted N_2O_4 octahedral coordination sphere of the manganese(III) centre is essentially identical to other related monomers [Mn(saltn)(O_2CBu^n)] and [Mn(saltn)(O_2CBu^t)]. The distortion of the manganese centre is as a result of the chelation of the carboxylate.

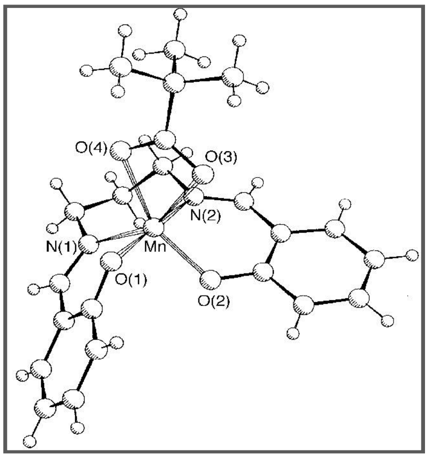


Figure 5. Molecular structure of [Mn(saltn)(O_2CBu^t)].

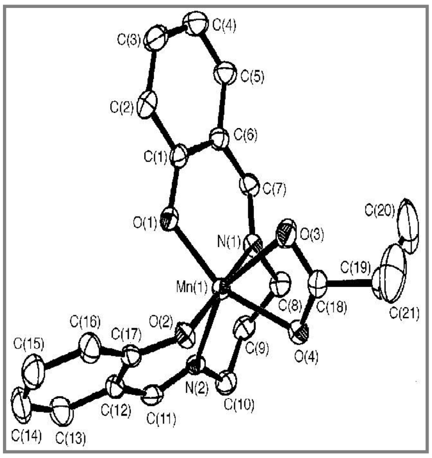


Figure 6. Molecular structure of [Mn(saltn)(O_2CPr^i)].

[Mn_2(salen)$_2$(O_2CPr^n)(EtOH)(H_2O)][O_2CPr^n]: The complex [Mn_2(salen)$_2$ (O_2CPr^n) (EtOH)(H_2O)] [O_2CPr^n] crystallized as the dinuclear form (Figure 7). The manganese(III) atoms are situated in the equatorial plane of two phenolic oxygen atoms and two imine nitrogen atoms of the salen ligand and are bridged by a single butyrate group [23]. Octahedral coordination is completed by an ethanol molecule for Mn(1) and a water molecule for Mn(2). The cationic charge of the dinuclear unit [Mn_2(salen)$_2$(O_2CPr^n)(EtOH)(H_2O)]$^+$ is balanced by an uncoordinated butyrate anion. This represents the first example of noncharged donors, such as water and ethanol, coordinating to manganese in preference to the strongly coordinating carboxylate group. IR studies show two stretching frequencies [$\upsilon_{asym}(CO_2)$ 1558, 1542 and $\upsilon_{sym}(CO_2)$ 1403, 1388] for both the stretches for the carboxylate groups, an observation we attribute to the two different environments of the carboxylate groups [23, 27].

[Mn(msalen)(O_2CMe)(H_2O)]. $2H_2O$: The structure is found to consist of a monomeric manganese (III) centre (Figure 8) which is ligated in the *xy* plane by the tetradentate Schiff base ligand. The axial co-ordination sites of manganese are filled by a water molecule and a unidentate acetate ligand. It is important to note that, with the exception of ^{i}Pr and ^{t}Bu (later shown with msaltn ligand), the carboxylate is always coordinated in the unidentate mode when a methoxy group is *ortho* to the phenolic oxygen donor.

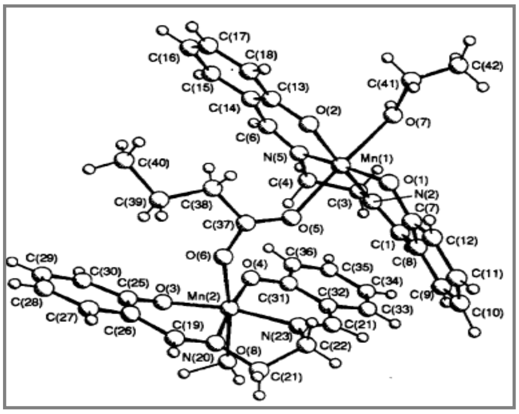


Figure 7. Crystal structure of $[Mn_2(salen)_2(O_2CPr^n)(EtOH)(H_2O)][O_2CPr^n]$.

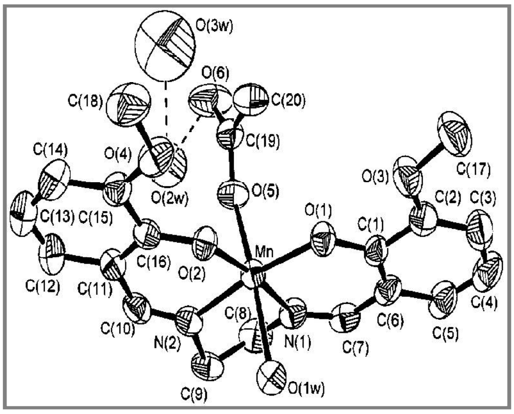


Figure 8. Molecular structure of $[Mn(msalen)(O_2CMe)(H_2O)].2H_2O$.

$[\{Mn(msalen)(O_2CEt)\}_2].EtOH$: The structure of $[\{Mn(msalen)(O_2CEt)\}_2].EtOH$, found to be a dimer in which the manganese(III) centers are linked by phenoxy bridges between one phenolic oxygen atom of each ligand (Figure 9). The planar nature of the ligand, msalen in conjunction with the phenoxy bridges, leaves only one site of each manganese(III) centre available for coordination, resulting in the propionate binding in the relatively rare unidentate mode. Each manganese(III) center adopts a distorted octahedral geometry.

$[\{Mn(msalen)(O_2CBu^n)\}_2]$: The structure of $[\{Mn(msalen)(O_2CBu^n)\}_2]$ was found to be analogous (Figure 10) to that of $[\{Mn(msalen)(O_2CEt)\}_2].EtOH$.. The complex was found to exist also as a phenoxy bridged dimer, although the linkages were slightly weaker. Again the carboxylate is ligated in the unidentate mode [25], however the bond length Mn(1)–O(10) shorter than the equivalent bond length in $[\{Mn(msalen)(O_2CEt)\}_2]$. EtOH., implying that there is a stronger interaction between the metal centre and the carboxylate in this complex.

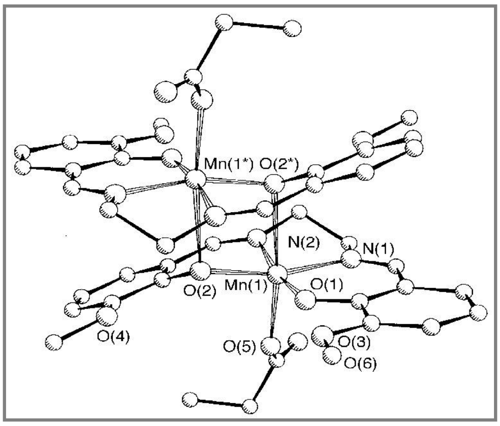


Figure 9. Molecular structure of $[\{Mn(msalen)(O_2CEt)\}_2].EtOH$.

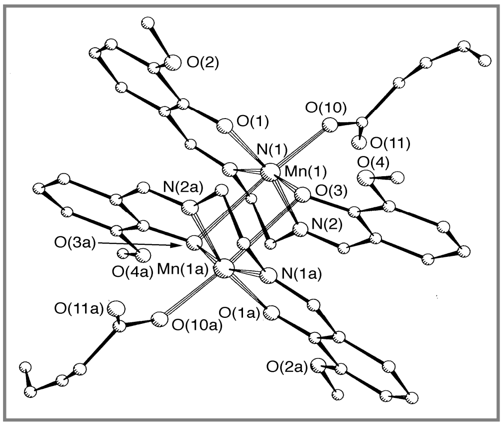


Figure 10. Crystal structure of $[\{Mn(msalen)(O_2CBu^n)\}_2]$.

$[Mn(msalen)(O_2CCH_2Ph)(H_2O)].H_2O$: The coordination sphere of $[Mn(msalen)(O_2CCH_2Ph)(H_2O)].H_2O$ (Figure 11) consists of the tetradentate Schiff base ligand, msalen in the *xy* plane, with the axial sites filled with the unidentate carboxylate O(5) and a water molecule O(1w). A further water molecule of crystallization O(2w) is hydrogen bonded to O(6). It is important to note that, with the exception of ^iPr and ^tBu (later shown with msaltn ligand), the carboxylate is always coordinated in the unidentate mode when a methoxy group is *ortho* to the phenolic oxygen donor.

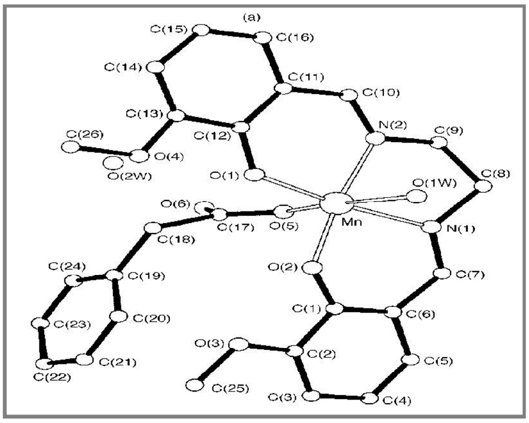


Figure 11. Crystal structure of $[Mn(msalen)(O_2CCH_2Ph)(H_2O)].H_2O$.

$[Mn(msaltn)(O_2CPr^i)]$ and $[Mn(msaltn)(O_2CBu^t)]$: Both complexes were found to exist as monomeric species in which the Schiff base ligand, msaltn affords *cis* sites at the manganese(III) centre for bidentate chelation of the carboxylate ligands. They consist (Figure 12) of extremely distorted octahedral centers, typical in such complexes. The presence of *cis* sites at the metal centre for chelation of the carboxylate results from the flexibility in the trimethylene backbone between the imine nitrogens of the Schiff base ligand.

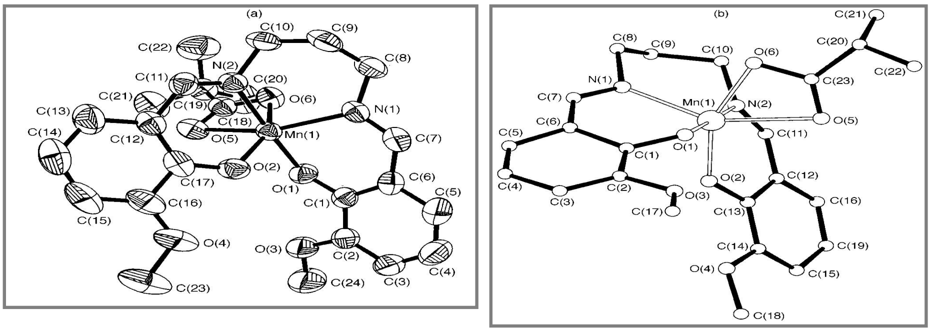


Figure 12. Crystal structures of (a) $[Mn(msaltn)(O_2CBu^t)]$ and (b) $[Mn(msaltn)(O_2CPr^i)]$.

$[\{Mn(bsaltn)(O_2CCH_2Ph)\}_n]$ and $[Mn(msaltn)(O_2CCH_2Ph)(H_2O)]$: $[\{Mn(bsaltn)(O_2CCH_2Ph)\}_n]$ found to consist of a polymeric complex, (Figure 13a) Unlike the other polymeric complexes of this type the $[Mn(bsaltn)]^+$ units are linked by the carboxylate binding in the relatively rare *syn-anti* rather than *anti-anti* mode [25]. The bsaltn ligands are orientated at 180° with respect to each other which results in the polymer having a dimeric repeat unit as was observed in $[\{Mn(saltn)\ (O_2CMe)\}_{2n}].3nH_2O$. The reason for the *syn-anti* mode of binding in the carboxylate anion and the twist in the polymer may lie in the increased steric bulk of the carboxylate (caused by the methylene linkage between the carboxylate donor and phenyl ring). Despite the fact that this binding mode brings the manganese centres closer together it does serve to minimise steric interactions, as can be clearly seen in figure 13b.

Unlike the polymeric complexes $[\{Mn(bsaltn)(O_2CCH_2Ph)\}_n]$ with *syn-anti* carboxylate bridges, changing the substituent of the Schiff base from bromine (bsaltn) to methoxy (msaltn) results a mononuclear complex of the type $[Mn(msaltn)(O_2CCH_2Ph)(H_2O)]$ (Figure 14). Here the carboxylate behaving as a unidentate ligand. The isolation of such monomeric species indicates that the governing factor may be the steric nature of the *ortho*-methoxy group in the Schiff base.

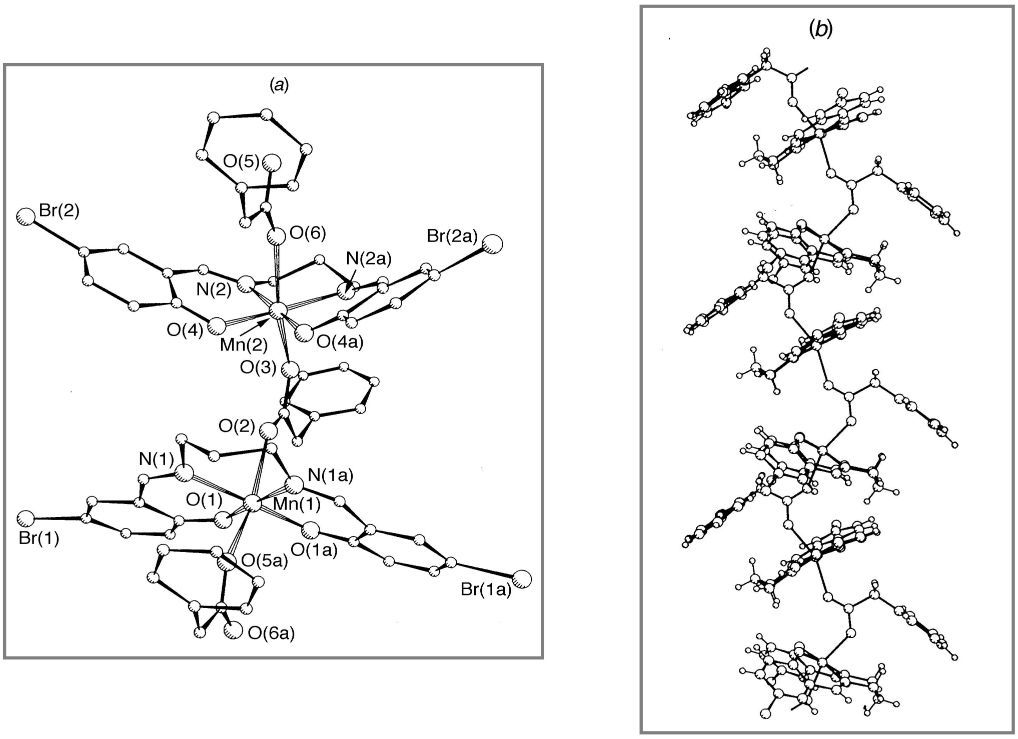


Figure 13. (*a*) Crystal structure of [{Mn(bsaltn)(O_2CCH_2Ph)}$_n$] and (*b*) The polymeric chain in complex [{Mn(bsaltn)(O_2CCH_2Ph)}$_n$].

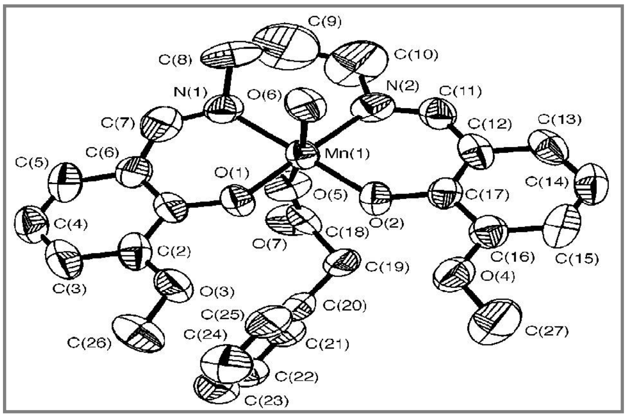


Figure 14. Molecular structure of [Mn(msaltn)(O_2CCH_2Ph)(H_2O)].

APPLICATION

Mono-, di- and polynuclear manganese carboxylate complexes with N,O-donor ligands are primarily useful in two major area of research namely bioinorganic chemistry and molecular magnetism. Along with these two important fields the architectural beauty of aesthetically pleasing structures of such compounds are added advantage of such research. In this concise review mainly the structural diversity of manganese carboxylate complexes have been delineated so that it will be very useful for synthetic inorganic chemist for syntheses of single-molecule magnets (SMMs). Again, this work will also be valuable for preparation of small molecule manganese models that seek to mimic photosynthetic water oxidation chemistry. So this short review will be extremely useful for scientific research fraternity on the discussed field and will be widely applicable in target oriented research.

CONCLUSION

Review of this, found that the structural chemistry associated with manganese(III) carboxylate complexes of different N_2O_2 donor Schiff base ligands appears to be a very diverse and unpredictable area or research. Little obvious correlation can be deduced as yet between the structural chemistry observed in these complexes and the carboxylate anion. It appears that polymeric complexes are obtained with acetate, propionate and phenylacetate. However, since there are only single examples of structurally characterized complexes of this type for propionate and phenylacetate, it is difficult to make this a dedicated rule. When sterically restricting carboxylates O_2CBu^t, O_2CBu^n and O_2CPr^i are employed with saltn based ligands the carboxylate asymmetrically chelates *cis* sites at the metal centre forming monomeric species. In some of the compounds the coordination spheres of the manganese centers were completed by weak m-phenoxy bridges to a second metal centre forming dimmers. When tetradentate Schiff base ligands with methoxy groups *ortho* to the phenolic donor atoms are used (msalen) and sterically very demanding carboxylates are avoided the unique mode of coordination of the carboxylate is unidentate.

ACKNOWLEDGEMENT

Author sincerely thanks Dr. Sumitava Khan, Assistant Professor, Department of Chemistry, Burdwan Raj College, Burdwan-713 104 for his valuable suggestions in preparing the Manuscript.

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