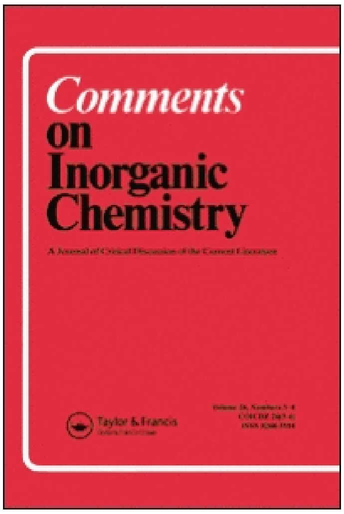

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PERSPECTIVES OF STUDY ON LOW NUCLEARITY CARBOXYLATE COMPLEXES

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PERSPECTIVES OF STUDY ON LOW NUCLEARITY CARBOXYLATE COMPLEXES

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Due to resurgence of applications of carboxylate complexes, there is a necessity to revisit the structural and synthetic aspects along with supramolecular aspects of carboxylate complexes of lower nuclearity and this article elaborates such aspects with a few selected examples limiting mononuclear to tetranuclear carboxylate complexes.

INTRODUCTION

Due to diversity in coordination modes of carboxylate group, complicacy arises in designing a synthesis of polynuclear metal carboxylates.[1] Various carboxylate ligands containing metal-organic frameworks have utilities such as in gas storage,[2] molecular recognition,[3] molecular magnet,[4] catalyst,[5] and non-linear optical materials.[6] A prior structural understanding on smaller building blocks would help to achieve the synthetic goal of such supermolecules with carboxylate functionality. The metal organic frameworks that are classified according to their dimensionality[7] and by the type of carboxylate ligands[8] have been reviewed recently. There are large numbers of structures possible in carboxylate complexes that have multiple numbers of metal ions. Dinuclear carboxylate complexes of divalent metal ions itself has various types of structural backbones, some of which are shown in Scheme 1. Such permutations and combinations in structures may be brought about by

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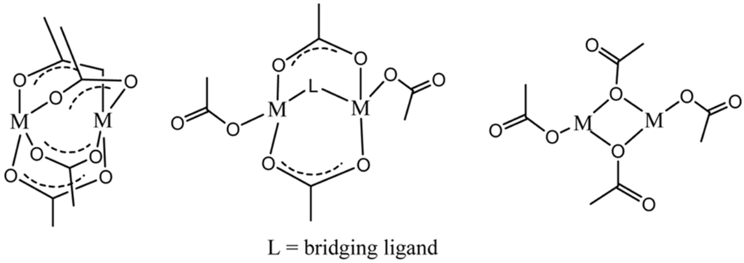


Scheme 1. Structural backbone of some dinuclear metal complexes of metal (M) in divalent state.

change of coordination numbers, coordination modes, oxidation states of the metal ions, and type of the metal ions, etc. Some of these factors may be decided by solvents and reaction conditions. We describe here a critical evaluation of some of the commonly observed lower nuclearity carboxylate complexes limiting the description to mono to tetra nuclear metal carboxylates with a view that they can provide guidelines to build higher nuclearity carboxylate complexes.

MONONUCLEAR CARBOXYLATES

The supramolecular interactions and steric effect are driving forces in the stabilization of unusual coordination numbers in mononuclear carboxylate complexes. For example, [Cu(N-benzoylanthranilato)$_2$(1,10-phenanthroline)] has four-coordinated distorted tetragonal geometry[9] around the copper ion (Figure 1A). In this complex the hydrophobic effects of the ligand prevent further coordination of a ligand. The penta coordinated mononuclear [Zn(8-aminoquinoline)$_2$(benzoato)] benzoate complex has a five co-ordination geometry due to complementary hydrogen bonding of the benzoate anion with the 8-aminoquinoline, which blocks the approach of another ligand (Figure 1B). The complex has a square pyramidal geometry with a benzoate anion outside the co-ordination sphere.[10]

The geometry around mononuclear bis-3,5-dimethylpyrazole (abbreviated as DMP) copper(II) benzoate complexes are controlled by steric factors.[11] Structure of four such complexes derived from 4-methylbenzoate, 3-methylbenzoate, 2-nitrobenzoate, and 4-nitrobenzoate are shown in Figure 2. Each of them has a distorted square planar geometry with difference in bond geometries. The two complexes derived

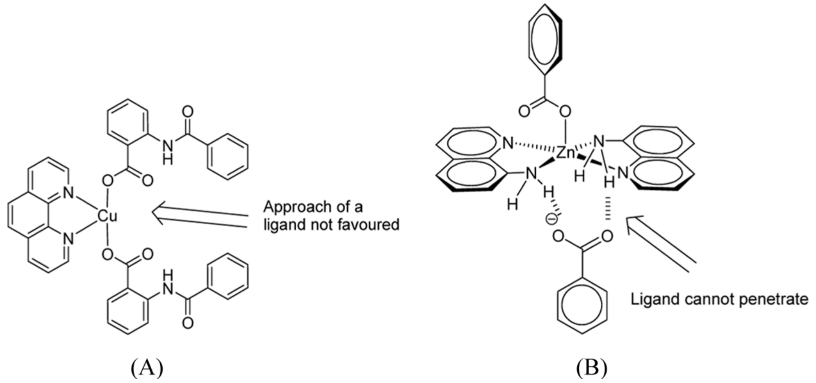


Figure 1. (A) Four coordinated copper(II) complex; (B) five coordinated zinc(II) complex.

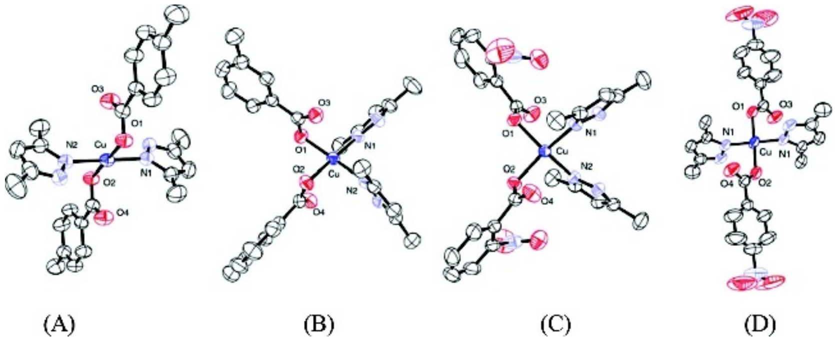


Figure 2. The ORTEP (50% thermal ellipsoid, H-atoms are omitted for clarity) of (A) $Cu(DMP)_2(4\text{-}MeC_6H_4CO_2)_2$; (B) $Cu(DMP)_2(3\text{-}MeC_6H_4CO_2)_2$; (C) $Cu(DMP)_2(2\text{-}NO_2C_6H_4CO_2)_2$; (D) $Cu(DMP)_2(4\text{-}NO_2C_6H_4CO_2)_2$.

Table 1. Selected bond distances and angles in few copper benzoate complexes

Complex	Cu-O3 bond distance (Å)	N1-Cu-N2 bond angle (°)
$Cu(DMP)_2(4\text{-}MeC_6H_4COO)_2$	2.64	180.0
$Cu(DMP)_2(3\text{-}MeC_6H_4COO)_2$	2.56	92.3
$Cu(DMP)_2(2\text{-}NO_2C_6H_4COO)_2$	2.69	92.0
$Cu(DMP)_2(4\text{-}NO_2C_6H_4COO)_2$	2.91	180.0

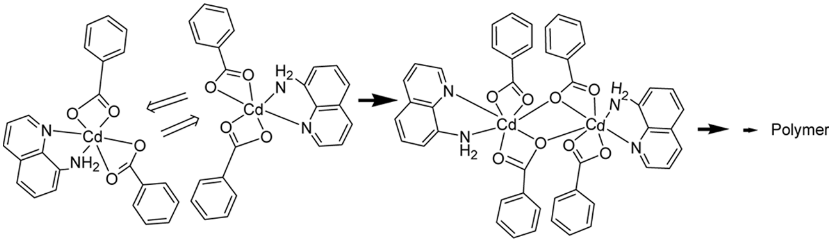


Figure 3. Self assembling of mononuclear complexes to form coordination polymer.

from *para* carboxylate isomers have the 3,5-dimethylpyrazole in trans disposition whereas in the case of the complex derived from meta and ortho substituted benzoate have 3,5-dimethylpyrazole in *cis* positions. The differences in the structural pattern in four differently substituted copper complexes are reflected in the Cu-O3 bond distances and the N1-Cu-N2 bond angles; these are listed in Table 1.

The mono-(8-aminoquinoline)cadmium benzoate has a polymeric structure with eight co-ordination in solid state, but it is a hexa-coordinated mononuclear complex in solution.[12] This happens due to self assembling of the mono-nuclear hexa coordinated species to form self-assembled coordination polymer having coordination number eight, as illustrated in Figure 3.

The supramolecular interaction leads to formation of molecular complexes of hydrated metal complexes with appropriate substrates.[13] One such example is $[Zn(H_2O)_4(OH)_2] \cdot 4\text{-}NO_2C_6H_5CO_2H \cdot C_6H_5NO$, which is illustrated in Figure 4. The complementing hydrogen bond interactions are a driving force for formation and stability of these molecular complexes.

Other intriguing features in the case of mononuclear carboxylate complexes are some of their associations as supramolecular assemblies. For

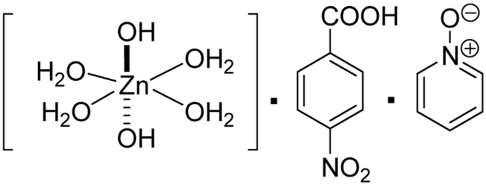


Figure 4. Three components of the molecular complex of zinc(II).

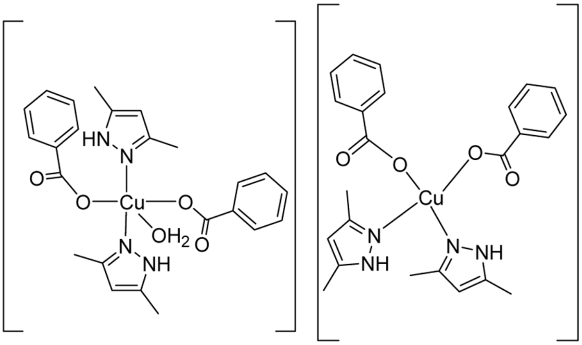


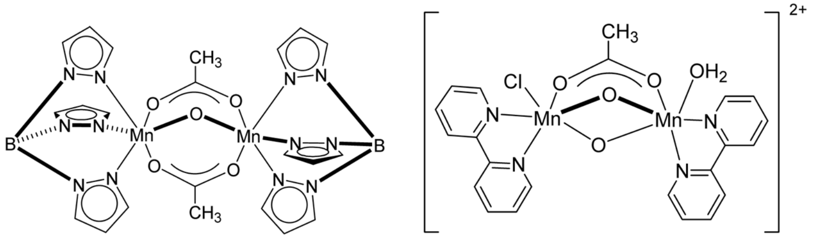
Figure 5. An example of cocrystals of neutral benzoate complexes.

example, the copper(II) benzoate complexes with 3,5-dimethylpyrazole are a cocrystal of neutral penta co-ordinated and tetra co-ordinated mononuclear copper(II) complexes. They form extensive intermolecular hydrogen bond interactions[14] in the solid state. In the cocrystal, one of the copper site has *cis* geometry with respect to 3,5-dimethylpyrazole ligands whereas the other part has a trans geometry (Figure 5). These types of cocrystals may be considered as a new generation of complexes, and understanding of their nucleation process is not clear.

DINUCLEAR CARBOXYLATES

The dinuclear metal carboxylates having bridging bidentate carboxylate ligands bridged through oxo, aqua or hydroxo ligands are common in manganese, cobalt, and vanadium chemistry. A representative example is $[Mn_2(\mu\text{-O})(\mu\text{-MeCO}_2)_2\{HB(pz)_3\}_2]$, where $HB(pz)_3^-$ is hydrotris(1-pyrazolyl)borate, and has a di-manganese(III) core.[15] In this complex two six-coordinated manganese sites are bridged by an oxo and two acetate groups. The remaining coordination sites are occupied by two tridentate $HB(pz)_3^-$ ligands (Figure 6A).

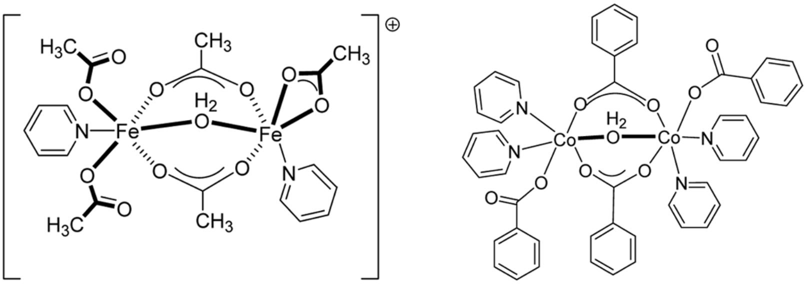
Dinuclear manganese(IV) complex $[Mn_2(\mu\text{-O})_2(\mu\text{-MeCO}_2)Cl(2,2'\text{-bipyridine})_2(H_2O)](NO_3)_2$ has two oxo bridges along with a caboxylate bridge[16] (Figure 6B). Bridging by aqua and carboxylate ligands are very common in iron, nickel, and cobalt carboxylate chemistry. One such example is $Et_4N[Fe_2(\mu\text{-MeCO}_2)_2(MeCO_2)_4(pyridine)_2]$, which has an asymmetric μ-aqua bis(μ-acetato) bimetallic core.[17] The anion of complex has an asymmetric dinuclear core with two bridging



(A) (B)

Figure 6. (A) One oxo and one acetate bridged manganese complex; (B) two oxo and one acetate bridged manganese complex.

bidentate acetate ligands[18] and a bridging water molecule (Figure 7A). Analogous dinuclear aqua bridged complex {$[Co_2(\mu\text{-}H_2O)(\mu\text{-}C_6H_5CO_2)_2(C_6H_5CO_2)_2(\text{pyridine})_4]$ (Figure 7B) forms different cocrystals with benzoic acid, benzene, toluene, etc.[19] The complex contains two bridging benzoate ligands along with a bridging water molecule. Two pyridine molecules and one monodentate benzoate are coordinated to each octahedral cobalt(II) center in the complex. The complex $[Ni_2(\mu\text{-}Cl)(\mu\text{-}H_2O)\{\mu\text{-}(4\text{-}ClC_6H_4CO_2)\}(4\text{-}ClC_6H_4CO_2)_2(C_5H_5N)_4]$ is an example[20] in which chloro as well as aqua bridged (Figure 8) are present. The complex also has two monodentate carboxylate groups attached to the metal centers.



(A) (B)

Figure 7. Examples of binuclear iron and cobalt complexes with aqua and carboxylate bridges.

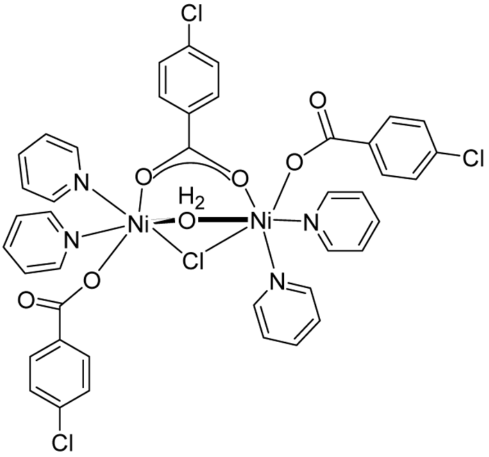
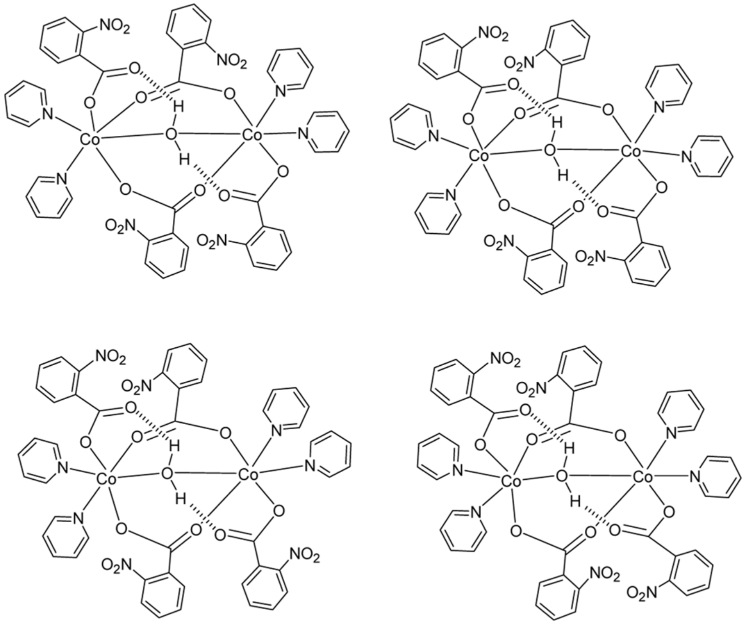


Figure 8. A chloro and aqua bridged dinuclear nickel complex.

The binuclear aqua bridged cobalt (II) ortho-nitrobenzoate complexes having pyridine as ancillary ligands show conformers[21] due to orientations of the nitro-groups across the dinuclear core. If one imagines the binuclear core of the two cobalt centers as a rigid spacer, then the orientation of the nitro groups across this spacer can be in different ways, as illustrated in Scheme 2. The nitro groups may be oriented in an orderly manner as described by (in, out: in, out) or they may be less ordered leading to (in, in; in, out); (in, in: out, out) or (in, in; in, in) orientations. All these arrangements are replicas of conformers. Three of these conformers are obtained on crystallization under different conditions and are characterized by X-ray crystallography. Their structures are shown in Figure 9.

Dinuclear metal carboxylates of aromatic dicarboxylic acids may adopt linear or cyclic structures depending on the orientations of carboxylate ligands. Generally, cyclic structures are obtained from *ortho* or *meta*-benzene dicarboxylates[22], whereas the *para*-benzene dicarboxylates lead to a linear bridged structure. The presence of chelating ancillary ligands in such complexes prevents them from forming coordination polymers.

A dinuclear copper(II) complex having the composition $[Cu_2(phen)_4(L)]L \cdot LH_2$ (phen = 1,10-phenanthroline, L = 2,5-dicarbomethoxy benzene-1,4-dicarboxylate dianion) has copper(II) ions bridged by 2,5-dicarbomethoxy benzene-1,4-dicarboxylato dianion in a bridging monodentate fashion. The charges on the metal ions are neutralized by



Scheme 2. Some conformational isomers of an aqua-bridged binuclear cobalt(II) complex.

a dianion of an uncoordinated dicarboxylic acid.[22] The compound has five coordinated square-pyramidal geometry around the copper(II) center (Figure 10).

The bis(unidentate) coordination mode of carboxylate anion are observed in coordination polymers or in multinuclear complexes; however, a solitary coordination mode to bridge two metal centers in dinuclear carboxylate complexes is not common. An example of such a

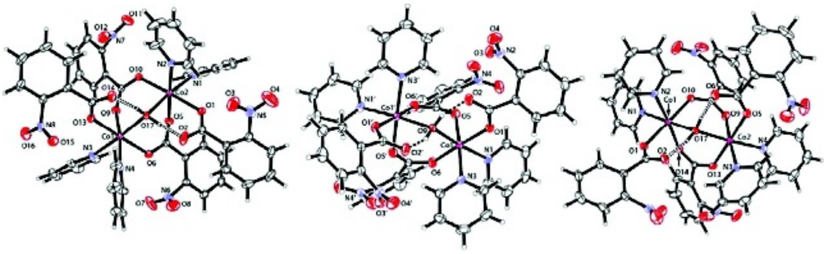
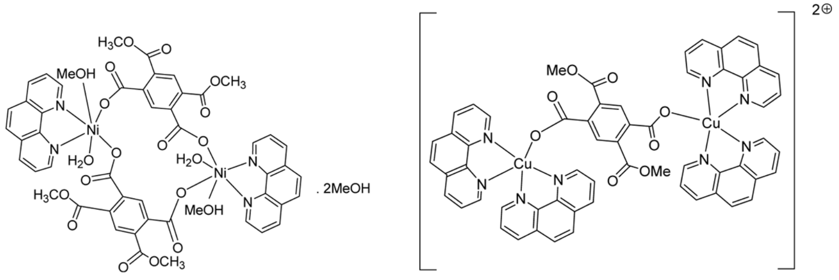


Figure 9. Three different conformers of an aqua-bridged binuclear cobalt(II) complex.



(a) (b)

Figure 10. (A) Cyclic nickel(II) dicarboxylate complex; (B) Linear copper (II) dicarboxylate complex.

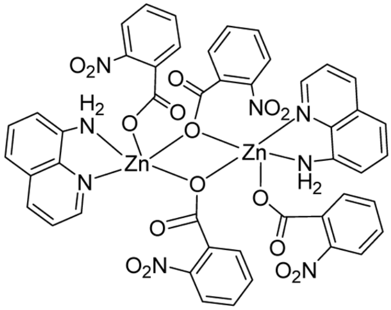
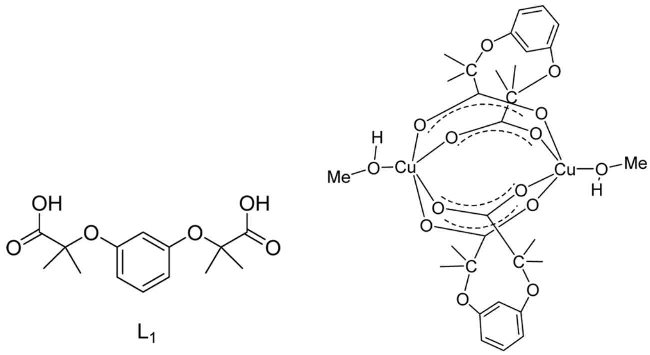


Figure 11. Dinuclear zinc(II) *ortho*-nitro benzoate complex.



(A) (B)

Figure 12. (A) The ligand L_1; (B) Dinuclear copper complex of L_1.

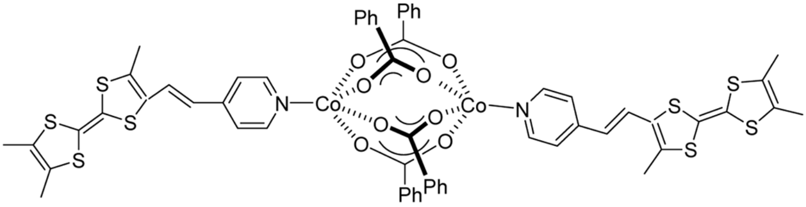


Figure 13. Paddle-wheel dinuclear cobalt(II) complex.

complex is $[Zn_2(\mu\text{-}2\text{-}NO_2C_6H_4CO_2)_4(AQ)_2]$, where AQ is 8-aminoquinoline (Figure 11); besides bridging carboxylate the zinc ions have monodentate carboxylate, chelating 8-aminoquinoline. The distance between two zinc ions in the dinuclear complex is 3.31 Å, which is higher than 3.03 Å observed for complexes of zinc having a paddle-wheel structure.[23]

Paddle-wheel geometry is most common in dinuclear copper and zinc carboxylate complexes. The simplest example of such a complex is copper(II) acetate monohydrate. Such structures may be formed by flexible dicarboxylate ligands; as in the case of copper(II) complex of 2-[3-(1-carboxy-1-methylethoxy)-phenoxy]-2-methyl-propionate (L_1). In this case the dicarboxylate acts as a bis-chelate to form a complex $[Cu_2(L_1)_2(MeOH)_2]$ having a paddle-wheel structure [24] as shown in Figure 12B.

Binuclear cobalt(II) complexes with paddle-wheel type of structures are uncommon. One such example of a complex is shown in Figure 13. These types of structures are formed under anhydrous conditions.[25]

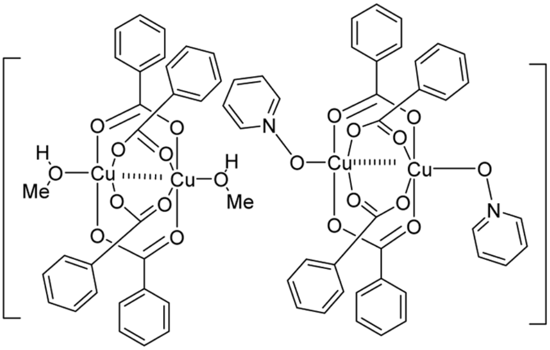


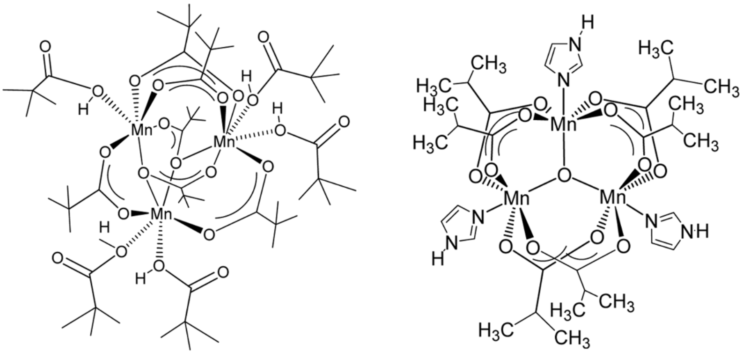
Figure 14. Cocrystals of two dinuclear complexes.

There are examples of cocrystals of two complexes, both having paddle-wheel structures.[26] They are formed due to interaction between two neutral carboxylate complexes through hydrogen bond interactions to form assembled structure. One such example is the cocrystal between two copper complexes with paddle-wheel structures, one of which has pyridine N-oxide as ancillary ligand and the other has methanol (Figure 14).

TRINUCLEAR CARBOXYLATES

Two types of trinuclear metal carboxylates are generally encountered. They are three metal centers forming a triangle or a linear chain-like structure. The manganese(II) pivalate $[Mn_3(\mu\text{-}Me_3CCO_2)_6(Me_3CCO_2H)_5]\cdot 2(Me_3CCO_2H)$ has triangular geometry among manganese. The structure consists of a triangle of hexa-coordinate manganese(II) ions bridged by two pivalates. The edges of the triangle are bridged by three other pivalates. The remaining positions of Mn(II) site are occupied by two molecules of pivalic acid [27] (Figure 15A).

The $[Mn_3(\mu\text{-}\eta^3\text{-}O)(\mu\text{-}Pr^iCO_2)_6(\text{imidazole})_3]\cdot 3Pr^iCO_2H$ is such a type of mixed valence complex.[28] This complex has manganese in slightly distorted octahedron geometry. Four oxygen atoms from bridging isobutyrate groups, one bridging oxo group and a terminal imidazole nitrogen



(A) (B)

Figure 15. (A) Trinuclear manganese(II) pivalate complex; (B) oxo centered trinuclear manganese complex.

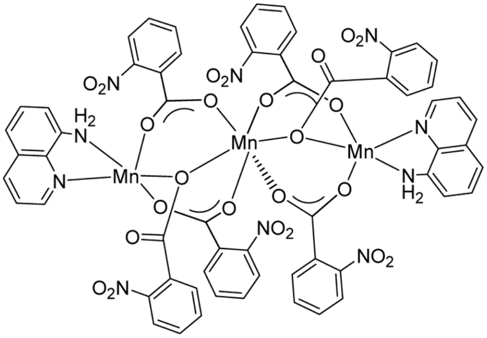


Figure 16. Trinuclear 2-nitrobenzoate manganese(II) complex.

atom makes the hexa coordination environment around each metal center (Figure 15B).

The $[Mn_3(\mu\text{-}2\text{-}NO_2C_6H_4CO_2)_6(AQ)_2]$ where AQ is 8-aminoquinoline has a linear chain type trinuclear manganese complex.[13] In this complex all the manganese centers are in distorted octahedral geometry. The central manganese(II) is coordinated to six oxygen atoms from the carboxylate ligands. The carboxylate ligands attached to the central metal atom are connected through two different types of bridges. One is the conventional bridging bridge and the other is through a bis(unidentate) carboxylate bridge with Mn-O-Mn type of interactions. The 8-aminoquinoline coordinates to manganese at the terminus of the linear structure as chelating ligand (Figure 16).

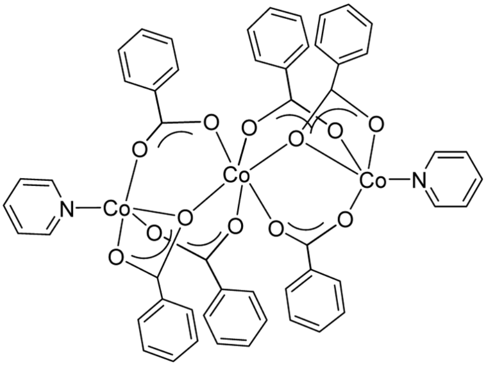


Figure 17. A trinuclear cobalt(II) benzoate complex.

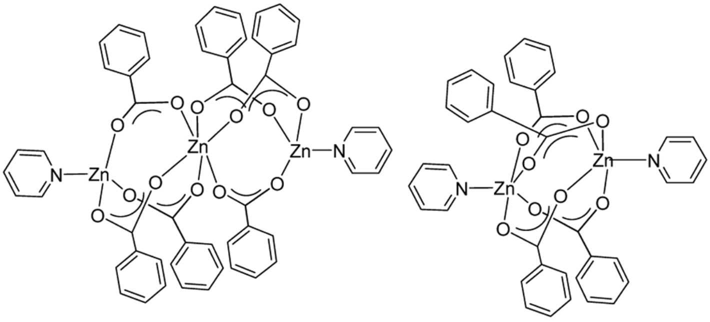


Figure 18. A cocrystal of trinuclear and dinuclear zinc complex.

Another example of the linear trinuclear complex[29] is [$Co_3(\mu\text{-}C_6H_5CO_2)_6(pyridine)_2$]. The structure of this complex consists of a central cobalt ion in an octahedral coordination sphere, and is coordinated by six oxygens from six benzoate ions. All benzoates in the complex act as bridging ligands (Figure 17).

Cocrystals among dinuclear and trinuclear benzoate complexes are the outcome of the packing effect through intermolecular hydrogen bonds.[30] The zinc(II) benzoate has a paddle-wheel structure with two pyridine as ancillary lignads; however, depending on the method of preparation it can be crystallized. A cocrystal between a trinuclear and dinuclear zinc complex having a composition [$Zn_3(\mu\text{-}C_6H_5CO_2)_6(py)_2$][$Zn_2(\mu\text{-}C_6H_5CO_2)_4(py)_2$] (where py is pyridine) is shown in Figure 18.

TETRANUCLEAR CARBOXYLATES

Tetranuclear manganese complexes with mixed-valent states are well known. For example, [$Mn_4(\mu\text{-}O)_2(\mu\text{-}2\text{-}Cl\text{-}C_6H_4CO_2)_7(2,2'\text{-bipyridine})_2$] contains one manganese (II) and three manganese(III) metal centers in its core. In this complex manganese ion has distorted octahedral geometry[31] as shown in Figure 19.

Tetranuclear zinc carboxylate complexes having one central oxy-ligand are formed in the reactions of zinc salts with corresponding carboxylates. In an illustrative example shown in Figure 20A, the oxy anion acts as a central point in a tetrahedral geometry formed by four zinc ions. In this complex, three equivalent zinc centers having tetrahedral geometry are observed. These three zinc centers are anchored by three carboxylate bridges and also are coordinated to the central oxygen.

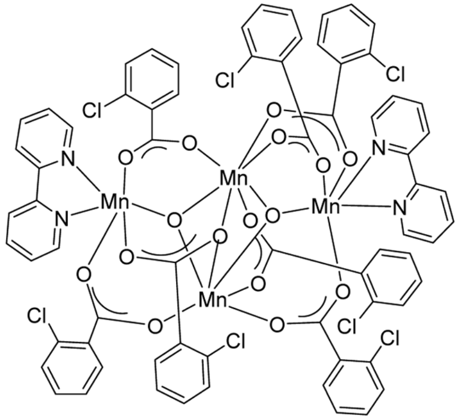


Figure 19. A mixed-valent tetranuclear manganese complex.

The remaining zinc center fulfills the octahedral geometry by three bridging carboxylates, one oxy ligand, and two dimethylsulfoxide ligands.[32]

A linear chain type tetranuclear complex having composition $[Zn_4(\mu\text{-}C_6H_5CO_2)_6(C_6H_5CO_2)_2(\mu\text{-}pyO)_3(H_2O)_2]\cdot H_2O$ is prepared by the reaction of zinc(II)acetate with benzoic acid and pyridine N-oxide (pyO). In this complex the zinc centers have distorted octahedral geometry (Figure 20B) and are part of a linear chain-like structure. The terminal zinc centers have two monodentate carboxylates and a coordinated water molecule.[26]

The tetranuclear complex having composition $[Fe_4(\mu\text{-}OHO)(\mu\text{-}OH)_2(\mu\text{-}MeCO_2)_4(1,10\text{-phenanthroline})_4](ClO_4)_3$ represents a mixed

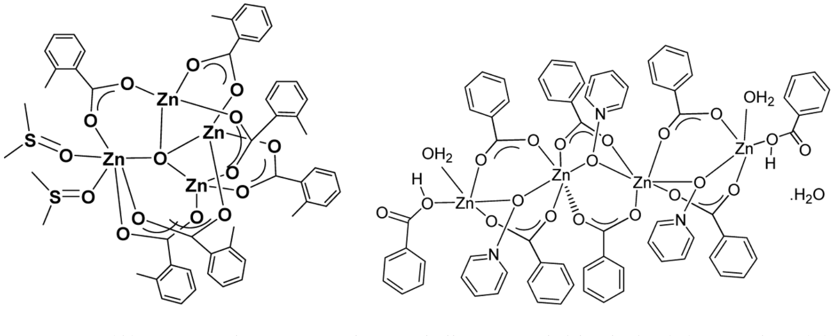


Figure 20. (A) Tetranuclear oxo and o-methylbenzoato bridged zinc(II) complex; (B) tetranuclear linear benzoate bridged zinc(II) complex.

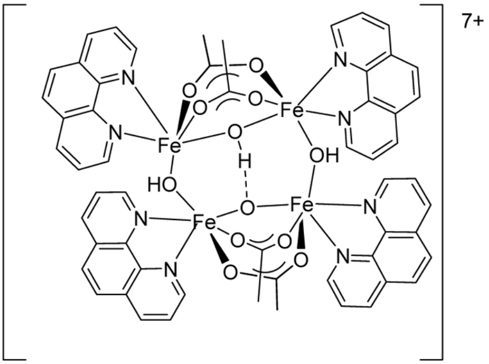


Figure 21. A tetranuclear iron(III) carboxylate complex.

hydroxyl and oxy bridged carboxylate complex[33] (Figure 21). The complex may be considered as dimeric assembly of two oxo and carboxylato bridged dinuclear complexes by two hydroxy groups and a proton.

Tetranuclear copper(I) carboxylate cluster, $[Cu_4(\textit{meta}\text{-}F\text{-}C_6H_4CO_2)_4]$ has a planar Cu_4-core, which is anchored by carboxylate bridges[34] (Figure 22). This complex is formed as a cyclic tetramer to form a neutral complex, which has caroxylate bridges among all the copper(I).

A cyclic tetranuclear zinc complex $[Zn_4(L_3)_4(pyrazole)_4(H_2O)_8]\cdot DMF$ can be prepared by reaction of zinc salts with pyrazole and ligand L_3. In the cyclic units, two of the zinc centers have octahedral geometry and the other two zinc centers have trigonal-bipyramidal geometry. Zinc atoms having octahedral geometry are co-ordinated to three water molecules, one pyrazole and two carboxylate groups. Other

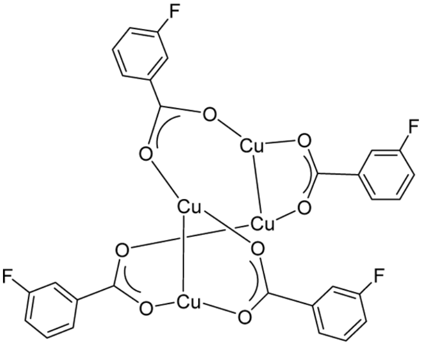
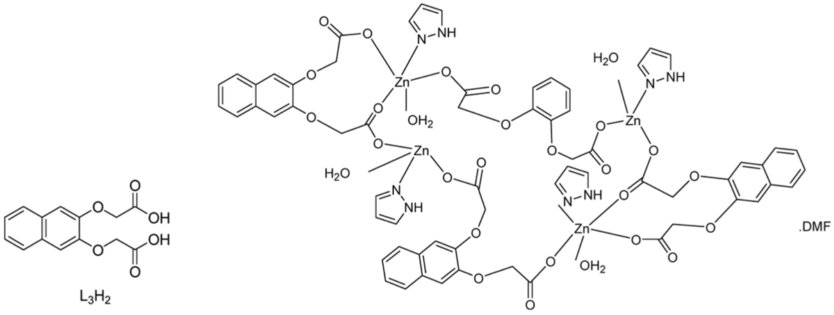


Figure 22. Tetranuclear copper(I) carboxylate cluster.



(A) (B)

Figure 23. (A) Structure of the ligand L_3; (B) a tetranuclear complex of L_3.

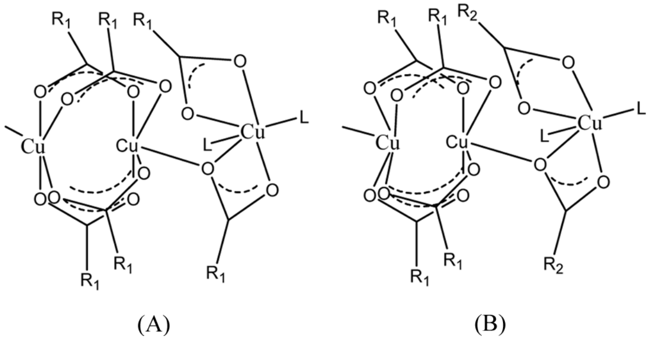
zinc atoms have coordination through a water molecule, one pyrazole, and three oxygen atoms of carboxylate[35](Figure 23).

CONCLUSIONS

There is a challenge to design synthesis of functional materials in carboxylate chemistry. In such synthesis the reaction conditions, solvent polarity, and coordination of solvent molecules become deciding factors and the understanding structure and reactivity of low nuclearity carboxylate complexes can provide insight to them. As an example, the reactions to design a carboxylate coordination polymer with alternate dinuclear and mononuclear complexes can be achieved from such understanding; an example of a copper complex having paddle-wheel structure in which the axial positions are bridged by mononuclear copper(II) complex is demonstrated [11] (Figure 24). The construction of mixed metal carboxylate clusters with interesting magnetic properties is achieved by simple reaction procedures illustrated in Eq. (1). Such reactions are versatile and have been developed from understanding of molecular structures of building blocks derived from tris-oxalato complexes.[37]

$$K_3[Cr(ox)_3 + Mn(NO_3)_2 + (nBu)_4NBr \rightarrow \{(nBu)_4N\}[MnCr(ox)_3]_x + KNO_3 + KBr \qquad (1)$$

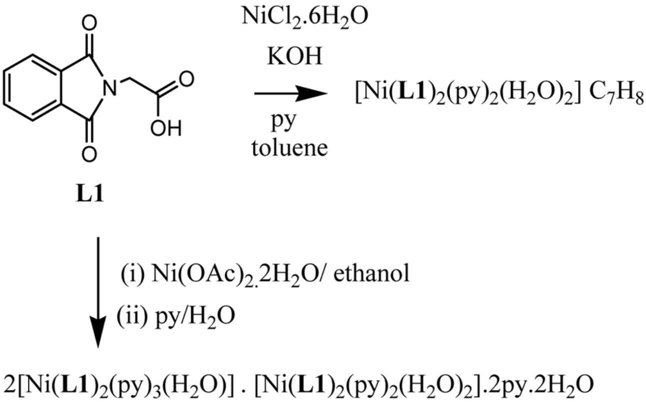
where ox = oxalate dianion.



(A) (B)

Figure 24. Two possible building blocks for coordination polymer of copper(II).

The reason for the formation of molecular complexes between neutral carboxylate complexes is yet to make headway. Such complexes may be considered to be metastable species[38] formed during the crystallization process. For example, in the reactions shown in Scheme 3, the N-phthaloyl glycine can lead to molecular complex of three neutral coordination complexes having pyridine and water as solvent of crystallization. Such molecular complexes are formed due to hydrogen bonded assembly formation and the complex may be considered to be a metastable molecular complex. The same reaction carried out under slightly different conditions leads to a mononuclear copper(II) complex. The change in reaction condition leads to different species in



Scheme 3. Different nickel complexes of N-phthaolylglycine.

solution; for example, dinuclear $[Cu_2(MeCO_2)_4]$ can be converted to $[Cu_2(MeCO_2)_3]^+$ or $[Cu_2(OH)(H_2O)(MeCO_2)]^{2+}$ by varying reaction condition, which is useful in synthesis of varieties of copper complexes.[39] To make larger polymeric structures with novel material properties with well-defined identified smaller building blocks have recently been demonstrated.[40] The structural information on low nuclearity complex helps in designing higher ones, as well as mixed metal carboxylates, as in the case of the formation of hexa-nuclear cobalt(II) benzoate derivative, which can be accounted as a combination of two sets of trinuclear cobalt complexes.[29] The complexes containing supramolecularly bound cations to anionic metal carboxylate counterparts, such as the one derived from dipicolinic acid, are shown to be promising porous materials[41a] and precursor for rare metal oxides[41b] and metal oxides synthesis.[41c] Thus, there is a clear need for a retro analysis of the building blocks of higher nuclearity clusters and coordination polymers to take another look at the structural diversity of low nuclearity coordination complexes with a strong theoretical support.

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