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Chemical design of high spin polynuclear manganese(II) and iron(II) carboxylates

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Abstract. Methods for synthesis and the structures of high spin polynuclear carboxylate complexes of divalent manganese and iron are considered. The bibliography includes 153 references.

I. Introduction

Currently, polynuclear coordination compounds containing high spin atoms of transition elements have become the focus of keen attention of specialists of various profiles. Due to the presence of open-shell metal sites, these compounds are, as a rule, extremely reactive with respect to different donating organic and inorganic molecules, inducing their unusual chemical transformations in the coordination sphere of the metal core.[1] In addition, the presence of unpaired electrons on the metal atoms of polynuclear coordination compounds determines their unique magnetic and electrophysical properties. It is these particular properties that suggest that in the future this kind of compounds can be used as building blocks of electronic molecular devices.[2–5]

Carboxylate complexes of high spin 3d-metals are special among a wide variety of polynuclear molecular systems. Their distinguishing feature is high solubility in organic solvents (particularly, the derivatives with alkanoate anions). This is quite important, because performing the reactions in organic solvents excludes hydrolysis, which, as a rule, results in decomposition of polynuclear molecules. Moreover, this provides an opportunity of chemical assembly of the molecules in relatively inert media (including non-polar ones), which significantly simplifies the methods of targeted synthesis of magneto-active polynuclear molecules.

Carboxylate complexes are not only the subject of fundamental investigations, but are also compounds of potential industrial importance. For instance, it has recently been shown that pivalate complexes with three and six Fe(III) atoms are promising components of a homogeneous catalytic Gif-system for hydrocarbon oxidation.[6] High solubility of polynuclear complexes in hydrocarbon solvents facilitates the transfer of the metal ions into nonaqueous media. This is of great importance for manufacturing diverse metal-containing films on surfaces of different supports. It is known that thermolysis of pivalate complexes results in elimination of the carboxylate ligands thus building up the metal core and yielding ultimately oxide materials.[7] Currently, the methods of synthesis of molecular ferromagnets based on polynuclear carboxylate systems are being intensively developed. These compounds can potentially be used as materials for molecular electronics.[8–15]

The present review describes the methods of synthesis of high spin polynuclear manganese(II) and iron(II) carboxylates. In spite of the obvious interest in these compounds, their synthetic chemistry is not well developed due to problems in the preparation and, especially, isolation of the complexes related to their extreme sensitivity to atmospheric oxygen. Manganese(II) and iron(II) carboxylate derivatives undergo much easier oxidation than similar cobalt(II), nickel(II) and copper(II) compounds, yielding various stable polynuclear Mn(III) and Fe(III) oxocarboxylate systems.[16, 17] This feature largely determines specific demands as regards synthetic methods and physicochemical studies, which seriously impedes the development of this promising branch of inorganic chemistry.

II. Binuclear carboxylate complexes

Binuclear carboxylate complexes represent the most numerous class of Mn(II) and Fe(II) polynuclear structures. Their potential use as models with bridging carboxylate groups for mimicking active sites of enzymes is a reason for the increased attention to this class of compounds.[18–27] Usually, these complexes contain high spin metal sites and therefore, magnetic methods can successfully be employed to reveal the structure – property relationships. This is extremely important for the development of advanced methods for calculations of the magnetic properties and for more efficient search for new 'magnetic' molecules.[28–30] Such studies are undoubtedly valuable as a significant contribution to the development of approaches to control the magnetic properties of complexes by chemical methods.

Preparation of binuclear complexes requires special conditions such as to enable a carboxylate group to bind only two metal sites. Therefore, geometrical and electronic parameters of the carboxylate ligand [or rather the substituent R in the RC(O)O group] as well as other donating ligands in the complex should be adjustable. The number of donating 'non-carboxylate' ligands should not be too large to prevent the formation of mononuclear

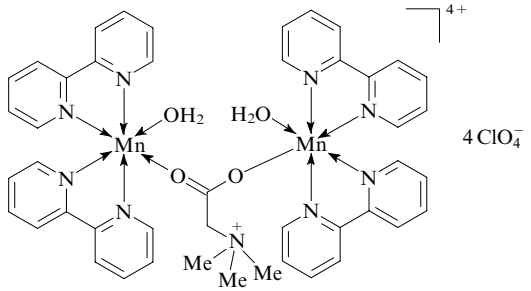
M A Kiskin, I L Eremenko N S Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky prosp. 31, 119991 Moscow, Russian Federation. Fax (7-495) 954 12 79, tel. (7-495) 955 48 35, e-mail: mkiskin@igic.ras.ru (M A Kiskin), ilerem@igic.ras.ru (I L Eremenko)

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complexes. Therefore, it is necessary to measure out the number of donating ligands per metal atom when carrying out the synthesis.

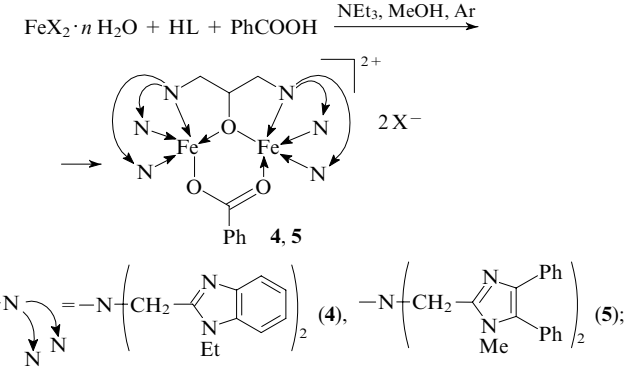
The Mn(II) and Fe(II) binuclear complexes may be subdivided into complexes with one, two, three and four carboxylate bridges. The molecules of the first two groups usually contain a bridging ligand of another type (*e.g.*, a water molecule, a hydroxyl group, *etc.*).

'Singly bridged' manganese binuclear carboxylate complexes are formed in the reaction of manganese(II) inorganic salts with salts of the corresponding carboxylic acids in the presence of strong chelating ligands such as 2,2′-bipyridyl (2,2′-bipy), 1,10-phenanthroline (1,10-phen), *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,2-ethylenediamine (tpen) and others. The complexes $[Mn_2(\mu\text{-}OOCCH_2NMe_3)(2,2'\text{-bipy})_4(H_2O)_2](ClO_4)_4$ (**1**), $[Mn_2.\{(OOC)_2CH_2\}(1,10\text{-phen})_3(H_2O)_2(Cl)]Cl$ (**2**) and $[Mn_2(\mu\text{-}OAc).(tpen)_2](ClO_4)_3$ (**3**) belong to this class.[31–33]



1

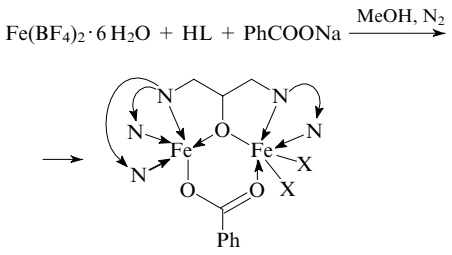
The binuclear iron complexes $[Fe_2(\mu\text{-}OOCPh)(\mu\text{-}L)]X_2$ [HL is *N*,*N*,*N*′,*N*′-tetrakis(1-ethylbenzoimidazol-2-ylmethyl)-2-hydroxy-1,3-diaminopropane, X = BF_4 (**4**); HL is *N*,*N*,*N*′,*N*′-tetrakis(1-methyl-4,5-diphenylimidazol-2-ylmethyl)-2-hydroxy-1,3-diaminopropane, X = ClO_4 (**5**)], in which iron ions are linked together by a bridging carboxylate group and by a bridging oxygen atom of polydentate ligand HL, are known. These complexes were obtained by the reaction of iron(II) salts with benzoic acid and the corresponding ligand in the presence of triethylamine.[22,23]



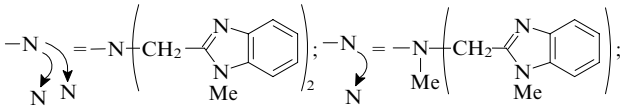
4, **5**

X = BF_4^- (**4**), ClO_4^- (**5**).

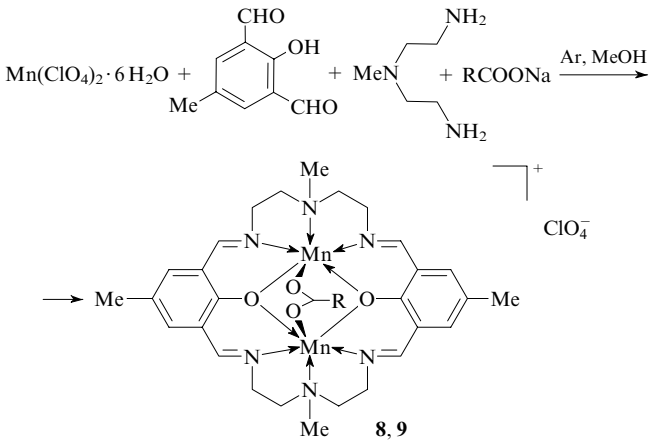
Similar reactions with less sterically hindered polydentate ligands, for example, *N*,*N*,*N*′-tris(1-methylbenzoimidazol-2-ylmethyl)-*N*′-methyl-2-hydroxy-1,3-diaminopropane (HL), in which the number of donating nitrogen atoms is insufficient to fill the metal coordination sphere, result in the formation of complexes with coordinated solvent molecules or anions of salts. Thus the binuclear ionic complex $[Fe_2(\mu\text{-}OOCPh).(\mu\text{-}L)(MeOH)_{1.5}(H_2O)_{0.5}](BF_4)_2$ (**6**) was obtained by the reaction of $Fe(BF_4)_2 \cdot 6H_2O$ with benzoic acid and HL. Treatment of this complex with a solution of NaSCN results in substitution of thiocyanate anions for the coordinated water and alcohol molecules and in the formation of a neutral complex $[Fe_2(\mu\text{-}OOCPh)(\mu\text{-}L)(SCN)_2]$ (**7**).[34]



6 (X = MeOH, H_2O)
7 (X = SCN)



Macrocyclic ligands normally produce mononuclear complexes due to their geometrical features. However, complexes containing two carboxylate-bridged metal atoms in the cavity of macrocycle are known. For instance, high spin manganese binuclear complexes **8** and **9** with one bridging carboxylate group and [2 + 2]-macrocyclic ligands were obtained by the condensation of 2,6-diformyl-4-methylphenol with *N*,*N*-bis(2-aminoethyl)methylamine in the presence of manganese(II) ions.[18,19]

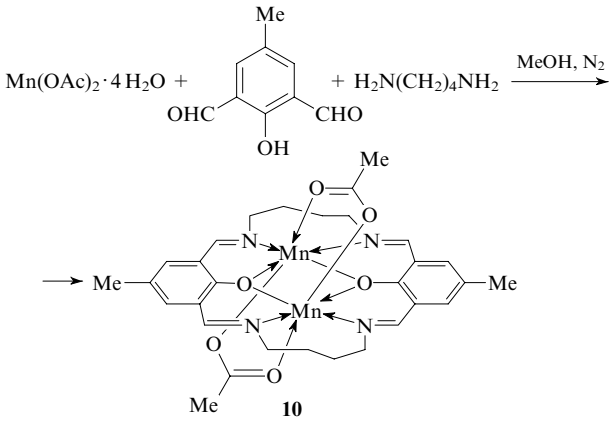


8, **9**

R = Me (**8**), 2-$O_2NC_6H_4$ (**9**).

Two manganese atoms in molecules of complexes **8** and **9** linked by one bridging carboxylate group occur inside a distorted macrocycle and coordinate the donating atoms of the macrocyclic ligand.

Complexes with two carboxylate bridges can be obtained using simpler N-donating ligands (with fewer number of functional groups or less sterically hindered). Thus the complex $[Mn_2(\mu\text{-}OAc)_2L]$ (**10**) was obtained by the condensation of 2,6-diformyl-4-methylphenol with 1,4-diaminobutane in the presence



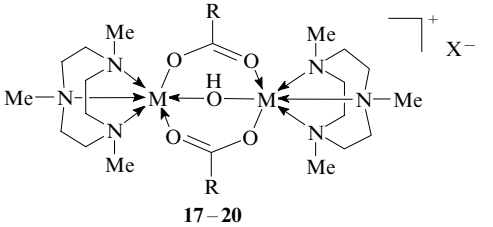
10

of magnesium acetate. In this complex, two metal atoms are located inside the macrocycle formed and are additionally linked by two bridging acetate groups.[21]

The binuclear complexes $[Mn_2(\mu\text{-}OAc)_2(L)](ClO_4)$ (**11**, **12**), $[Mn_2(\mu\text{-}OAc)_2(L)(SCN)]$ (**13**), $[Mn_2(\mu\text{-}OOCPh)_2(L)(SCN).(MeOH)]$ (**14**), $[Mn_2(\mu\text{-}OAc)_2(L)(MeOH)](ClO_4)$ (**15**), $[Mn_2(\mu\text{-}OPh)_2(L)](BPh_4)$ (**16**), HL is 2,6-bis{bis[2-(2-pyridyl)-ethyl]aminomethyl}phenol (**11**), 4-methyl-2,6-bis[bis(2-pyridylmethyl)aminomethyl]phenol (**12**), 2,6-bis[2-(dialkylamino)ethyliminomethyl]-4-methylphenol (Alk = Me, Et) (**13**), 2,6-bis{[*N*-(2-dimethylaminoethyl)-*N*-methyl]aminomethyl}-4-methylphenol (**14**), 4-methyl-2-[bis(2-pyridylmethyl)aminomethyl]-6-[(2-pyridylmethyl)benzylaminomethyl]phenol (**15**) and 4-methyl-2,6-bis-[bis(2-methoxyethyl)aminomethyl)]phenol (**16**), with two carboxylate bridges [35–40] were obtained by direct reaction of manganese carboxylates (or of a solution of an inorganic manganese salt and a carboxylic acid salt) with the ligand HL in the presence of a base (for example, triethylamine). NaSCN can be used to precipitate the reaction products, as has been done for complexes **13** and **14**.

Aza-crown ethers containing three tertiary amino groups [for example, *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane (Me_3tacn)] form binuclear complexes in reactions with manganese, iron, cobalt and nickel salts. The metal atoms in these complexes are linked by bridging oxygen atom of the hydroxyl anion and by two bridging carboxylate anions.[41–47] The complexes containing the labile bridging OH-fragment constitute active sites of a number of enzymes and therefore can be of interest for bioinorganic chemistry as potential catalysts.

Binuclear manganese(II) and iron(II) complex cations $[M_2(\mu\text{-}OOCR)_2(\mu\text{-}OH)(Me_3tacn)_2]^+X^-$ (**17**–**20**)

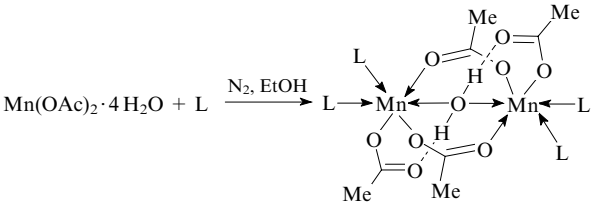


17–**20**

M = Fe (**17**, **20**), Mn (**18**, **19**); R = Me (**17**, **18**), Bu^t (**19**), CPh_3 (**20**); X = ClO_4 (**17**, **19**), PF_6 (**18**), BPh_4 (**20**)

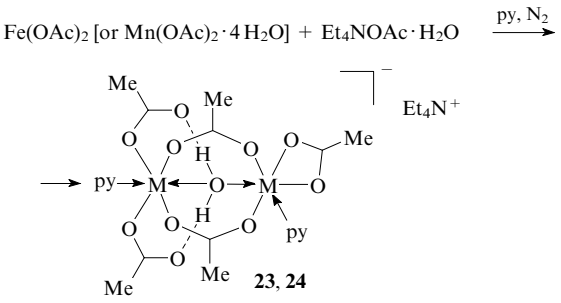
can be obtained both by direct reaction of inorganic metal salts with RCOONa (or RCOOH) and Me_3tacn (syntheses of compounds **17**–**19**) and by reaction of mononuclear complex $[Fe(Me_3tacn)(MeCN)_3](CF_3SO_3)_2$ with triphenylacetic acid and triethylamine in acetonitrile (synthesis of complex **20**). Since three out of six coordination sites of each metal atom are blocked by tridentate aza-crown, all dimers of this type are cations. The metal atom and three donating nitrogen atoms of *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane in dimers **17**–**20** form a triangular pyramid with nitrogen atoms at the base. The mean values of the N–M–N bond angles are equal to 76.8° (M = Mn) and 79.5° (M = Fe) (in an ideal octahedral environment, these angles are equal to 90°). Thus, the tridentate aza-crown ligand proves to be relatively compact and leaves enough space for dimerisation of metal fragments through various bridges.

Binuclear complexes with a bridging water molecule can be formed even if trace amounts of water are present in solvents or in the starting materials. Thus the complexes $[Mn_2(\mu\text{-}OH_2)(\mu\text{-}OAc)_2(L)_4(OAc)_2]$ [L is imidazole (**21**) and benzoimidazole (**22**)] are obtained by reactions of manganese acetate with imidazole or benzoimidazole in dry ethanol,[24] the bridging water molecule in complexes **21** and **22** originates from the starting acetate.



21 (L is imidazole),
22 (L is benzoimidazole).

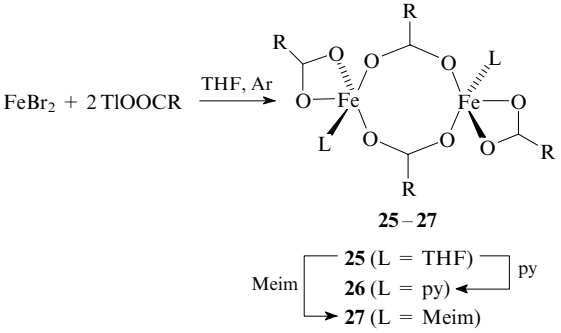
Complex anions $[M_2(\mu\text{-}OH_2)(\mu\text{-}OAc)_2(py)_4(OAc)_3]^-$ (**23**, **24**) are formed in the reaction of the corresponding acetates with $Et_4NOAc\cdot H_2O$ in pyridine.[25]



23, **24**

M = Mn (**23**), Fe (**24**).

The complexes containing two metal atoms linked by two carboxylate groups are the functional precursors of triply bridged hydroxo-carboxylate (oxo- or aqua-carboxylate) binuclear complexes of the type **17**–**24**. In contrast to the previously discussed compounds, the carboxylate groups in these complexes can be both bridging and chelating. Such complexes are usually formed when the reaction is carried out in anhydrous solvents. For example, the reaction of iron(II) bromide with thallium 2,6-di(*p*-tolyl)benzoate in THF yields the complex $[Fe_2(\mu\text{-}OOCR)_2.(\eta^2\text{-}OOCR)_2(THF)_2]$ (**25**).

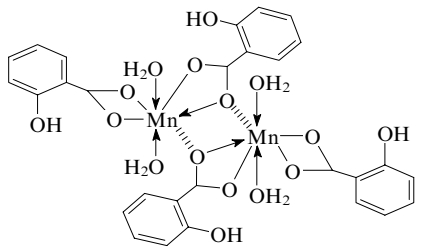


25–**27**

R = 2,6-(4-$MeC_6H_4)_2C_6H_3$.

It was shown that the reaction of complex **25** with N-donating ligands, such as pyridine and 1-methylimidazole (Meim), results in the substitution of these ligands for THF molecules to give the corresponding complexes **26** and **27** of similar structures.[26,27] Doubly bridged manganese complex $[Mn_2(\mu\text{-}OOCC_6H_4Cl\text{-}4)_2.(bipy)_4](ClO_4)_2$ was obtained in the reaction of $Mn(OOCC_6H_4Cl\text{-}4)_2\cdot H_2O$ with 2,2′-bipyridyl in dry ethanol in the presence of $NaClO_4$.[48]

Polynuclear carboxylate systems can also be prepared in aqueous solutions. Thus the reaction of an aqueous solution of sodium salicylate (NaHsal) with manganese chloride yields binuclear complex $[Mn_2(Hsal)_4(H_2O)_4]$ (**28**) in which the carboxylate groups are chelating–bridging.[49]



28

Complexes containing two carboxylate bridges together with other labile donating ligands are convenient starting compounds for the synthesis of triply bridged dimers. For instance, the reaction of complex **25** with 2-diphenylphosphinopyridine or 2-phenylthiopyridine results in the substitution of two THF molecules and transformation of one chelating carboxylate group into a bridging one (Scheme 1).

However, in the reaction of complex **25** with 3-diphenylphosphinopyridine only the replacement of THF molecules occurs with retention of the original metallo-carboxylate core. The reaction of **25** with 4-phenylphosphinopyridine results in rearrangement of two chelating carboxylate groups into the bridging ones and in formation of a quadruply bridged binuclear complex in which the metal atoms have a pseudo-octahedral coordination formed by four oxygen atoms of four symmetrical bridging carboxylate groups and one donating atom of the axial ligand $NC_5H_4PPh_2$-4. The second metal atom formally occupies the sixth position in the coordination sphere of each Fe atom. This rearrangement is accompanied by shortening of the Fe···Fe distance upon the transition from doubly bridged complexes **25** and **31** [4.283 Å (in **25**) and 4.035 Å (in **31**)] to triply bridged complexes **29** and **30** [3.310 Å (in **29**) and 3.272 Å (in **30**)] and to quadruply bridged complex **32** (2.813 Å).[50] It was suggested that the type of the resulting binuclear system is mostly determined by the geometrical parameters of the pyridine ligand, particularly by the position of a bulky PPh_2-substituent in the ring.

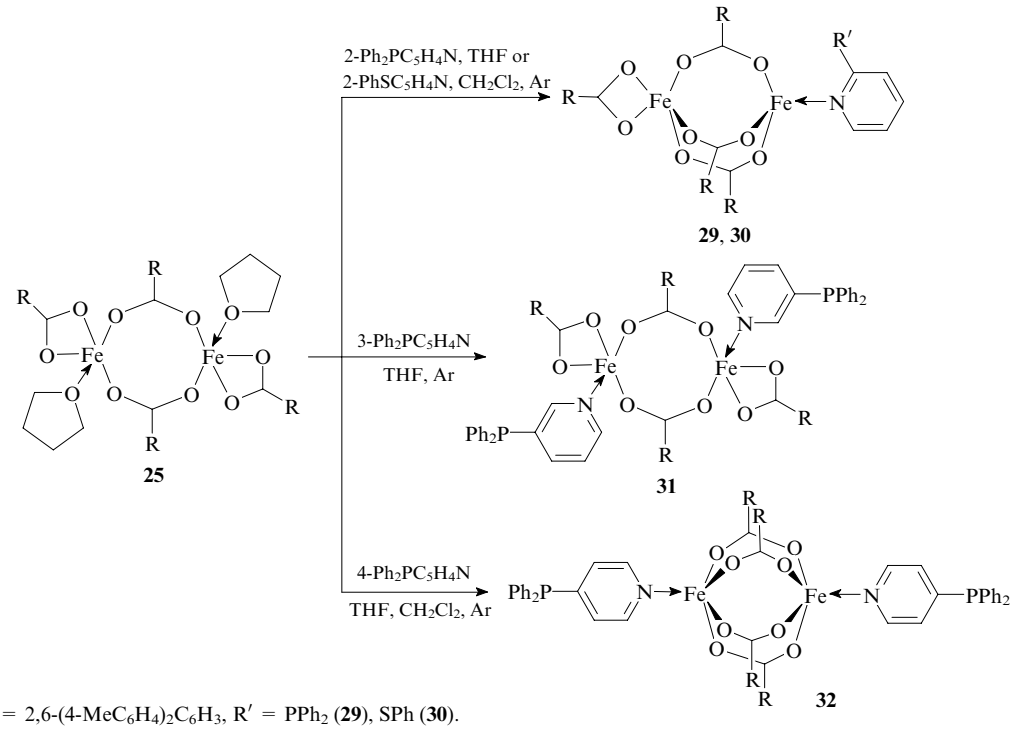
Binuclear manganese(II) and iron(II) tetracarboxylates $[LM(\mu\text{-}OOCR)_4ML]$ are known to a lesser extent than similar cobalt, nickel and copper derivatives. In spite of relatively short distances M···M [~ 3.1 Å (M = Mn) and ~ 2.8 Å (M = Fe)], such dimers are paramagnetic, which suggests the presence of high spin metal atoms in these complexes.

Binuclear antiferromagnetic dimanganese tetracarboxylates $[M_2(\mu\text{-}OOCR)_4L_2]$ containing quinoline as a labile N-donating ligand are formed in the reaction of quinoline with the reaction product of diphenylacetic acid with manganese acetate.[51] The pivalate binuclear complex $[Mn_2(\mu\text{-}OOCBu^t)_4(Bu^tCOO\cdot\cdot HNEt_3)_2]$ (**33**) has been obtained by reaction of manganese acetate with pivalic acid and triethylamine in hexane at room temperature. The structure of compound **33** is similar to that of complex **32**, but the axial positions of both metal atoms are occupied by oxygen atoms of the salt $Bu^tCOO\cdot HNEt_3$.[52]

Binuclear quadruply bridged iron(II) carboxylates **34** – **36** were obtained by reactions of complex **25** with 4-(*tert*-butyl)pyridine, benzylamine or 4-methoxybenzylamine, respectively, under the conditions similar to those shown in Scheme 1 for complex **32**.[53, 54] The change in the nature of the axial ligand results in distortion of the dimer structure. The fragment N – Fe···Fe – N in complex **34** is almost linear (the Fe – Fe – N bond angles are equal to 177.5 and 179.5°), these angles in complexes **35** and **36** are significantly smaller [157.1 and 160.7° (in **35**) and 161.1 and 176.2° (in **36**)]. The Fe···Fe distances in complexes **35** and **36** are ~0.03 – 0.06 Å shorter than that in compound **34**. It should be noted that in contrast to other paramagnetic quadruply bridged dimers of 3d-elements where antiferromagnetic exchange interactions occur, structural distortions in complexes **35** and **36** bring about ferromagnetic intramolecular exchange interactions. Presumably, this effect is due to the difference in electronic and geometrical characteristics of the apical ligands.

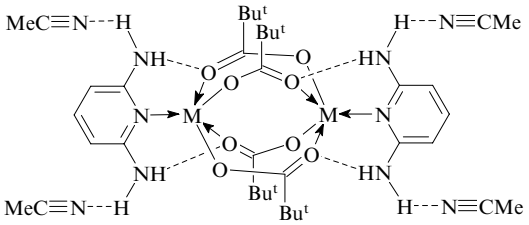
Earlier studies aimed at the synthesis of manganese, iron, cobalt and nickel quadruply bridged pivalate complexes have revealed that α-substituted pyridines as apical ligands favour the formation of such complexes,[55 – 57] while with unsubstituted pyridine or γ-picoline monomeric or polymeric complexes $[L_2M(OOCBu^t)_2]$ are formed. Undoubtedly, the chemical properties of α-substituents in the pyridine rings are extremely important in subsequent transformations of the complex. However, it has recently been shown that the reaction of polymers $[Fe(\mu\text{-}OOCBu^t)_2]_n$ and $[(EtOH)M(\mu\text{-}OOCBu^t)_2]_n$ (M = Fe, Mn) or the tetranuclear complex $[Fe_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCBu^t)_4(\eta^2\text{-}OOC.Bu^t)_2(EtOH)_6]$ with 2,3-lutidine or 2,6-diaminopyridine results

Scheme 1



R = 2,6-(4-$MeC_6H_4)_2C_6H_3$, R′ = PPh_2 (**29**), SPh (**30**).

in the formation of dimers $[(Me_2C_5H_3N)_2Fe_2(\mu\text{-}OOCBu^t)_4]$ (**37**) and $[(\eta^1\text{-}(NH_2)_2C_5H_3N)_2M_2(\mu\text{-}OOCBu^t)_4]$ [M = Mn (**38**), Fe (**39**)], respectively,[58–60] with virtually the same structures regardless of the chemical properties of the α-substituent in the pyridine ring. The only difference is that α-amino groups of pyridine ligands in complexes **38** and **39** form strong hydrogen bonds with the solvent molecules (MeCN) yielding the solvates $[\{2\,MeCN\cdot(NH_2)_2C_5H_3N\}_2M_2(\mu\text{-}OOCBu^t)_4]$ (compounds **40**, **41**).



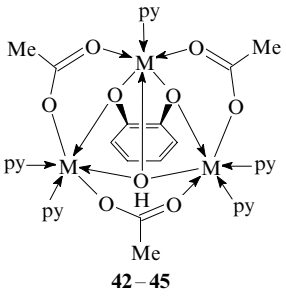
40, **41**

M = Mn (**40**), Fe (**41**).

Strong antiferromagnetic† exchange interactions have been observed in binuclear compounds **40** and **41**. The structural phase transitions that occur in complexes **40** and **41** at 173 and 184 K, respectively,[59,64] do not affect the character of these spin–spin interactions. Presumably, such indifference of the magnetic behaviour of the dimers with respect to the change in molecular packing due to phase transition suggests a predominantly intramolecular nature of spin exchange in these compounds.

III. Mn(II) and Fe(II) carboxylate complexes with three and more metal sites

Trinuclear manganese(II) and iron(II) high spin complexes are represented by a small group of compounds with triangular or linear arrangement of metal sites. Isostructural complexes $[M_3(\mu_3\text{-}OH)(\mu\text{-}OAc)_3L(py)_5]$ [M = Mn (**42**), Fe (**43**), Co (**44**), Ni (**45**), $L = C_6H_4O_2^{2-}$] are trinuclear complexes of divalent metals with a triangular metal core of the $M^{II}_3(\mu_3\text{-}OH)$ type.[65]



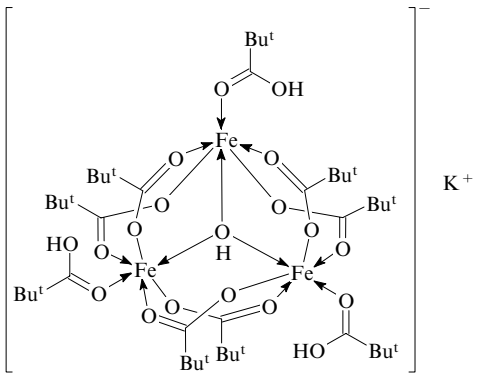
42–**45**

M = Mn (**42**), Fe (**43**), Co (**44**), Ni (**45**).

This is a rare example of a series of structurally studied, similar polynuclear carboxylate complexes of divalent metals. All these complexes were obtained by reactions of stoichiometric amounts of $M(OAc)_2\cdot 4H_2O$ with catechol in pyridine in the presence of 0.2 M ethanolic triethylammonium hydroxide.

A triangular iron(II) complex containing only the molecules of a carboxylic acid and carboxylate anions as the organic ligands, *viz*., a hydroxo-pivalate ionic antiferromagnetic complex $K[Fe_3(\mu_3\text{-}OH)(\mu\text{-}OOCBu^t)_6(HOOCBu^t)_3]$ (**46**), is known.[66]

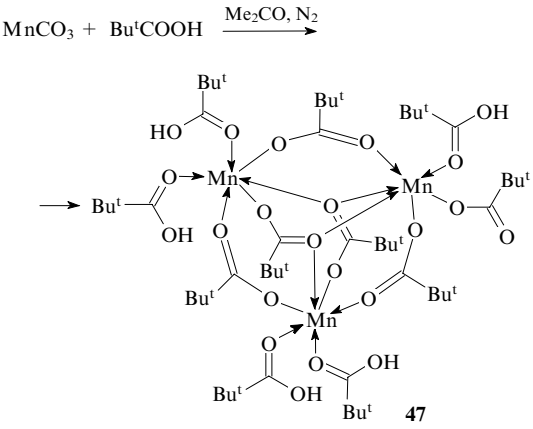
† Such interactions are also typical of binuclear nickel and cobalt carboxylates.[57,61–63]



46

Complex **46** is formed in the reaction of $FeSO_4\cdot 7H_2O$ with $KOOCBu^t$ and $HOOCBu^t$ in acetonitrile under argon.

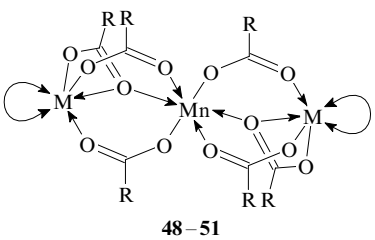
Yet another triangular antiferromagnetic manganese(II) complex $[Mn_3(OOCBu^t)_6(HOOCBu^t)_5]\cdot 2\,HOOCBu^t$ (**47**) was obtained in the reaction of manganese carbonate with pivalic acid.[16]



47

This compound is unique, because the triangular fragment is composed only of bridging carboxylate ligands, while in the majority of known trinuclear systems the metal atoms are linked by μ_3-bridging oxygen atoms of oxo or hydroxo groups.

Linear trinuclear manganese(II) and iron(II) complexes of $[M_3(OOCCR_3)_6L_2]$ are formed in the reactions of the corresponding metal carboxylates with N,O- and N,N-donating chelating ligands. Thus the complexes $[Mn_3(\mu,\eta^2\text{-}OOCR)_2(\mu\text{-}OOCR)_4(2,2'\text{-bipy})_2]$ [R = Me (**48**), CH_2Cl (**49**)] were isolated from the reaction of manganese acetate or chloroacetate with the stoichiometric amount of 2,2′-bipyridyl. The Mn(II) atoms in these complexes form a linear structure and are linked by bridging and chelating-bridging carboxylate groups, the peripheral metal sites are additionally chelated by 2,2′-bipyridyl molecules.[67–69]

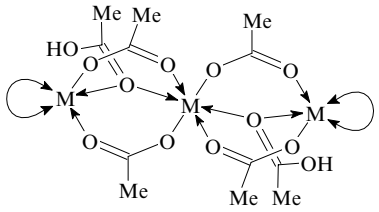


48–**51**

= 2,2′-bipy (**48**, **49**), 1,10-phen (**50**), 2-bepy (**51**);
R = Me (**48**, **50**), CH_2Cl (**49**), Ph (**51**).

It was shown[70–73] that the chelating properties of a carboxylate group depend upon sterical features of the terminal ligand that can hinder the chelating process. For instance, the reaction with 2-benzoylpyridine (2-bepy) or 1,10-phenanthroline instead of

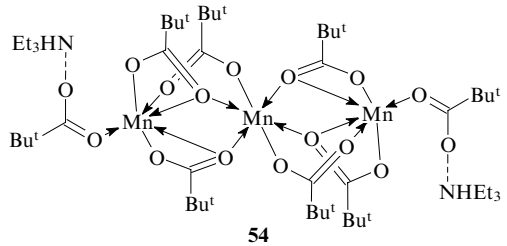
2,2′-bipyridyl results in the formation of complexes **50** and **51** similar to **48** and **49**. At the same time, bis(1-methylimidazol-2-yl)(methoxy)phenylmethane (biphme) blocks chelation of the carboxylate group due to increase in the N–Mn–N(O) bond angle from ~72.3° in complexes **48**–**51** [72.2° (in **48**), 73.2° (in **49**), 73.4° (in **50**), 70.5° (in **51**)] up to 81.9° in complex **52**.



52, **53**

M = Mn (**52**), Fe (**53**);  = biphme.

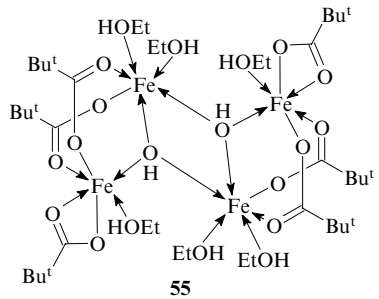
The change in the conditions of synthesis affects the structures of the final products. Thus the above-described binuclear complex **33** with four bridging carboxylate groups was obtained in hexane at room temperature. However, heating of the starting reaction mixture in heptane to the solvent boiling point affords the trinuclear complex $[Mn_3(\mu,\eta^2\text{-}OOCBu^t)_4(\mu\text{-}OOCBu^t)_2(Bu^tCOO\cdot\cdot HNEt_3)_2]$ (**54**). In this complex, two carboxylate groups are bridging and four others are chelating-bidging groups.[52]



54

The change in the conditions of synthesis of complex **46**, namely, the use of EtOH instead of acetonitrile and the removal of pivalic acid from the reaction mixture results in the tetranuclear hydroxopivalate complex $[Fe_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCBu^t)_4(\eta^2\text{-}OOC..Bu^t)_2(EtOH)_6]$ (**55**).[60]

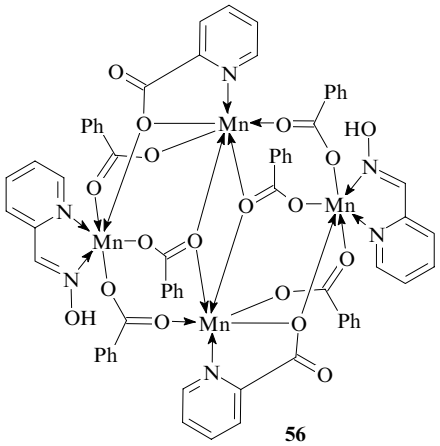
The metal core of this complex consists of two $\{Fe_2(\mu\text{-}OOCBu^t)_2(\eta^2\text{-}OOCBu^t)(EtOH)_3\}$ fragments linked by two μ_3-OH-groups. All metal atoms of complex **55** lie in the same plane. Cobalt and nickel isostructural analogues of complex **55** are also known.[74, 75]



55

The magnetic properties of these isostructural complexes are different. Thus the antiferromagnetic exchange interactions exist between paramagnetic sites in iron and cobalt complexes, while in the nickel derivative, these interactions are ferromagnetic.

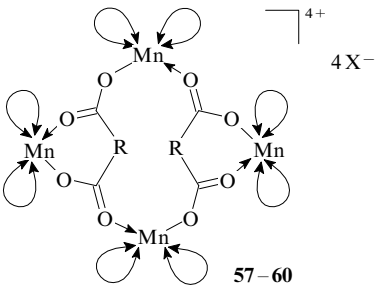
The tetranuclear manganese complex $[Mn_4(O_2CPh)_6..(2\text{-}OOCC_5H_4N)_2\{2\text{-}(HON{=}C)C_5H_4N\}_2\cdot 0.6\,CHCl_3]$ (**56**) was obtained by reaction of manganese benzoate with 2-pyridinaldoxime in MeCN.[76]



56

The metal core of complex **56** is planar and the metal atoms form a rhomb. Manganese atoms are linked by six μ_3-bridging benzoate groups and two chelating-bridging (2-pyridyl)carboxylate groups resulting from hydrolysis of the oxime and oxidation.

Tetranuclear manganese carboxylate complexes with a planar metal core are also formed in reactions of manganese salts with dicarboxylic acids [maleic (H_2male) or phthalic (H_2phth)] and N-donating ligands (2,2′-bipyridyl or 1,10-phenanthroline). The manganese complexes $\{Mn_4[(OOC)_2R]_2L_8\}X_4$ (**57**–**60**) were obtained in this way.[77, 78]

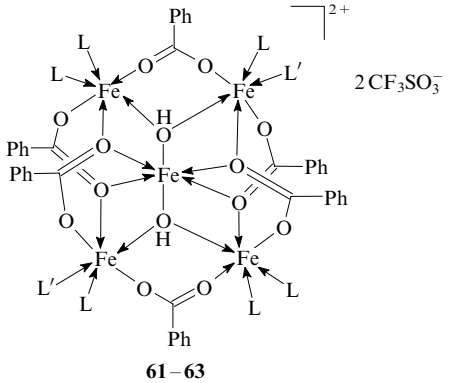


57–**60**

R = CH=CH (**57**, **58**), C_6H_4-*o* (**59**, **60**);
 = 2,2′-bipy (**57**, **60**), 1,10-phen (**58**, **59**);
X = ClO_4 (**57**, **58**, **60**), PF_6 (**59**).

The manganese atoms in these complexes form a parallelogram and are linked by four bridging carboxylate groups of two molecules of doubly deprotonated acids.

Unusual antiferromagnetic pentanuclear systems $[Fe_5(\mu_3\text{-}OH)_2(OOCPh)_6L_6L'_2](CF_3SO_3)_2$ (**61**–**63**) were obtained in the reactions of $Fe(CF_3SO_3)_2\cdot 2\,MeCN$, N-donors [pyridine, butyronitrile or ethylenediamine (en)], benzoic acid and triethylamine in acetonitrile in the presence of small amount of water. The metal cores of these complexes are formed of two triangular fragments sharing a vertex.[79]



61–**63**

L = L′ = py (**61**); L = py, L′ = PrCN (**62**); L–L′ = en (**63**).

Unfortunately, the chemistry of manganese(II) and iron(II) carboxylates is still insufficiently explored. Only hypothetically, the existence of hexa-, hepta- and octa-nuclear molecules, similar to the known cobalt and nickel derivatives, can be imagined. So far, the range of synthesised polynuclear molecular structures of iron derivatives is limited to the nonanuclear (II) complex‡ $[Fe_9(\mu_4\text{-}N_3)_2(\mu\text{-}OAc)_8(\mu_5\text{-}L)_4]$ $[H_2L = (2\text{-}C_5H_4N)_2C(OH)_2]$ (**64**) (Fig. 1 *a*).[80] At present, this is the only known representative of polynuclear iron(II) carboxylate complexes with molecular magnets properties (the ground spin state is $S = 14$ at 2 K). It was obtained by the reaction of iron(II) acetate with bis(2-pyridyl) ketone in acetonitrile and treatment of the reaction product with sodium azide. In this process, bis(2-pyridyl) ketone is converted into a *gem*-diol, which binds five metal atoms simultaneously (Fig. 1 *b*).

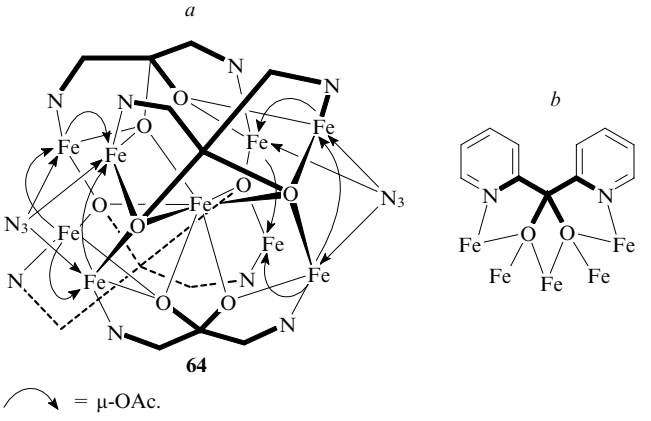


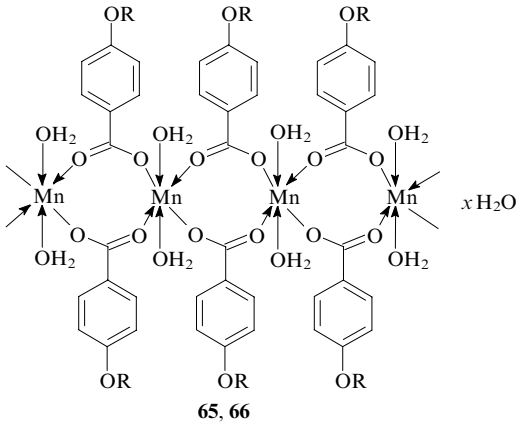
Figure 1. The schematic representation of the structure of complex **64** (*a*) [the non-coordinated atoms of $(2\text{-}C_5H_4N)_2COO^{2-}$ moiety are not shown] and coordination of the *gem*-diol form of bis(2-pyridyl) ketone in complex **64** (*b*).

IV. Polymeric carboxylate complexes

Most of the so-called 'dicarboxylates' of divalent transition metals with the composition $M(OOCR)_2 \cdot x\,H_2O$ [M = Mn(II), Fe(II) and others, $x = 3-8$] are mononuclear aqua-complexes,[83–88] however some of them are polymeric. Usually, the latter are stable only in a solid state and are easily converted to monomers when dissolved in water. Complexes $[M(dmba)_2(H_2O)_3]_n$ (M = Mn, Co, Ni, Zn), containing 2,6-dimethoxybenzoic acid (Hdmba) anions, represent this type of polymers. Upon action of a hot aqueous solution of 2,6-dimethoxybenzoic acid on aqueous solutions of metal acetates or sulfates (pH 4–5) followed by cooling, crystalline polymeric complexes are formed.[89] The polymeric chains in these complexes consist of square-planar *trans*-$\{M(dmba)_2(H_2O)_2\}$ units linked by axial bridging water molecules.

In addition to the metallopolymers linked in chains by bridging water molecules, metallopolymers with bridging carboxylate anions are known. Thus polymeric products $[Mn(OOC.C_6H_4OR\text{-}p)_2(H_2O)_2 \cdot x\,H_2O]_n$ (**65**, **66**) were obtained in the reaction of sodium *para*-hydroxy- or *para*-methoxybenzoate with a Mn(II) salt. In these compounds, octahedral coordination of metal atoms is formed by four oxygen atoms of bridging carboxylate anions and two oxygen atoms of terminal water molecules in *trans*-configuration.[90, 91]

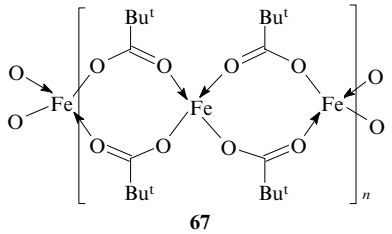
‡ Analogous cobalt and nickel complexes have been prepared.[81, 82]



65: R = H, $x = 0$; **66**: R = Me, $x = 1$.

In aqueous medium, it is possible to obtainpolynuclear structures devoid of water molecules in the coordination sphere of the metal atoms. For instance, the ionic polymer $[Mn(\mu\text{-}OOCCH_2NMe_3)_3]_n \cdot n\,MnCl_4$ has been synthesised by the reaction of manganese chloride with betaine $Me_3N^+CH_2COO^-$ in water.[92] The metal atoms in this compound are linked by three carboxylate groups. The complex $\{[Mn_3(\mu\text{-}OOC(CH_2)_2NH_3)_8] \cdot 6\,ClO_4 \cdot 2\,H_2O\}_n$ is formed upon action of manganese perchlorate on β-alanine. This crystallises as a linear polymer the repeating unit of which consists of three manganese atoms linked by two bridging and one chelating-bridging carboxylate groups.[93]

Pivalate complexes crystallise most easily as linear polymers since the *tert*-butyl groups provide a high solubility of these compounds. Thus the polymer $[Fe(\mu\text{-}OOCBu^t)_2]_n$ (**67**) devoid of neutral ligands was obtained by refluxing the tetranuclear complex $[Fe_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCBu^t)_4(\eta^2\text{-}OOCBu^t)_2(EtOH)_6]$ (**55**) in acetonitrile.[60]



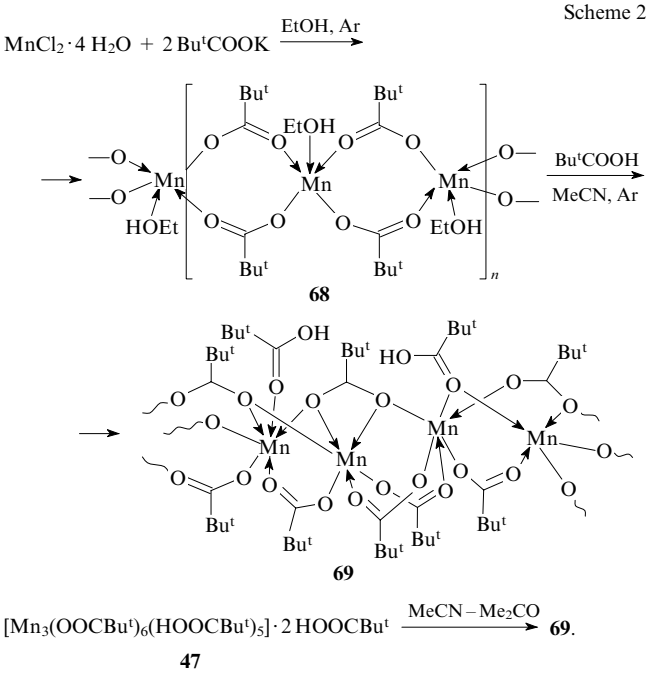
Ferromagnetic exchange interactions are observed in this compound. Polymer **67** undergoes phase transition into magnetic-ordered state at $T_c = 3.8$ K and becomes a 'soft magnet'. It should be noted that dissolution of polymer **67** in oxygen-free (but not anhydrous) ethanol results in the formation of the original tetranuclear complex **55**.

Antiferromagnetic manganese(II) pivalate polymer $[(\eta^1\text{-}HOEt)Mn(\mu\text{-}OOCBu^t)_2]_n$ (**68**) can be obtained by reaction of $MnCl_2 \cdot 4\,H_2O$ with potassium pivalate in ethanol under argon (Scheme 2).

Polymer **68** consists of Mn(HOEt) fragments linked by two carboxylate groups.[59] Surprisingly, an isostructural analogue of compound **68**, *viz.*, the polymer $[(HOEt)Fe(\mu\text{-}OOCBu^t)_2]_n$ is formed from tetranuclear complex **55** in the presence of *o*-phenylenediamine.[60]

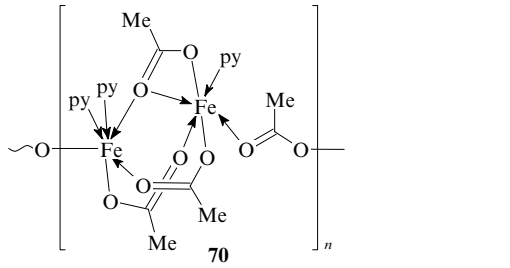
The structure of polymeric chain can be made more complicated by changing the number of metal atoms in the repeating unit. For instance, the polymeric product $[Mn_4(OOC.Bu^t)_8(HOOCBu^t)_2]_n$ (**69**) is obtained in the reaction of complex **68** with an excess of pivalic acid in acetonitrile.[94] It can also be obtained by recrystallisation of the trinuclear complex $[Mn_3(OOCBu^t)_6(HOOCBu^t)_5] \cdot 2\,HOOCBu^t$ (**47**) from an acetonitrile–acetone mixture.[16] Thus, the substitution of a carboxylic

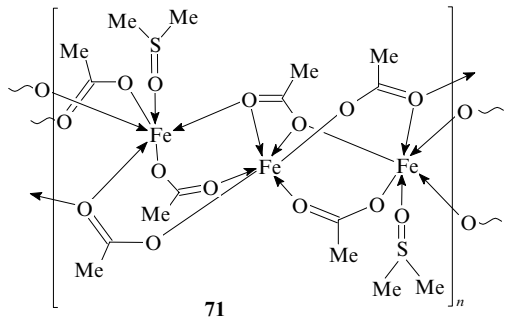
Scheme 2



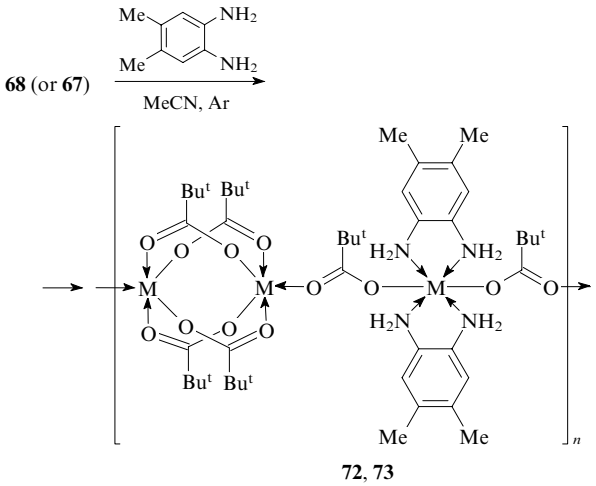
acid in polymeric complex **68** for ethanol resulted in the structural changes of the polymeric chain due to the ability of pivalate anions to coordinate metal in different modes. The pivalate groups easily pass from O,O-bridging to O-bridging ones (see Scheme 2).

The number of metal atoms in a repeating unit can be controlled by selecting conditions of synthesis. For example, the polymeric structures $[Fe_2(OAc)_4(py)_3]_n$ (**70**) and $[Fe_3(OAc)_6.(DMSO)_2]_n$ (**71**), containing bi- and trinuclear fragments, were obtained from the same starting mononuclear complex $[Fe(OAc)_2(py)_4]$ (**72**), but under different conditions. Compound **70** is obtained upon dissolution of complex **72** in diethyl ether, while compound **71**, upon dissolution of complex **72** in DMSO.[17,95]





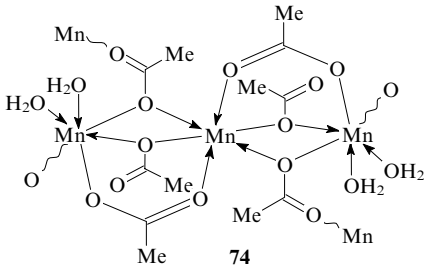
Further complication of repeating units of a polymeric chain is also possible by combining bi- and mononuclear fragments, which was demonstrated on an example of manganese and iron pivalate derivatives. *o*-Phenylenediamine ligands have been chosen as the components that control the polymer chain formation. Isostructural polymeric compounds $\{[(\eta^2\text{-}(NH_2)_2C_6H_2Me_2)_2M(\mu\text{-}OOC.(Bu^t)_2][M_2(\mu\text{-}OOCBu^t)_4]\}_n$ [M = Mn (**72**), Fe (**73**)] were obtained by reactions of polymers **68** and **67** with 4,5-dimethyl-1,2-phenylenediamine in acetonitrile.[60]



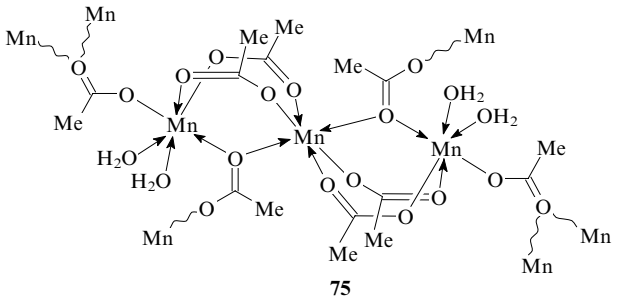
M = Mn (**68**, **72**), Fe (**67**, **73**).

Complexes **72** and **73** are magnetically different: intra- and intermolecular exchange interactions in complex **72** are antiferromagnetic, while in the iron complex **73**, ferromagnetic interactions were observed at low temperature.

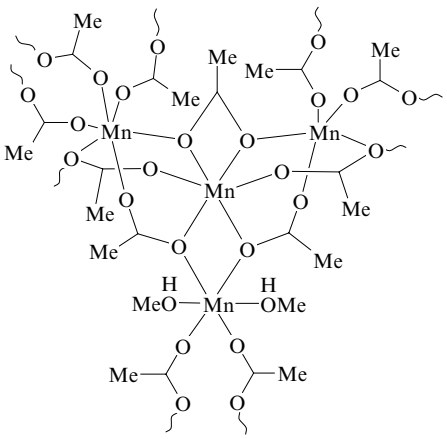
A carboxylate group can bind three or even four metal atoms; therefore, the existence of two- or three-dimensional polymers is possible. Thus high-temperature (230 °C) treatment of Mn_3O_4 with acetic acid yields the polymeric complex $\{[Mn_3(\mu\text{-}OAc)_6(H_2O)_4]\cdot 2\,H_2O\}_n$ (**74**) of a layered structure.[96] The crystallisation water molecules in crystals of this compound form the interlayer hydrogen bonds.



The commercially available $Mn(OAc)_2\cdot 4\,H_2O$ widely used in carboxylate synthesis is in fact a layered polymer $\{[Mn_3(OAc)_6.(H_2O)_4]\cdot 8\,H_2O\}_n$ (**75**) in which the crystallisation water molecules take part in linking the layers by hydrogen bonds.[97]



Dissolution of $Mn(OAc)_2\cdot 4\,H_2O$ in anhydrous methanol leads to the formation of the polymer $[Mn_4(OAc)_8(MeOH)_2]_n$ (**76**). The repeating unit of this polymer consists of four Mn atoms linked by acetate bridges.[98]



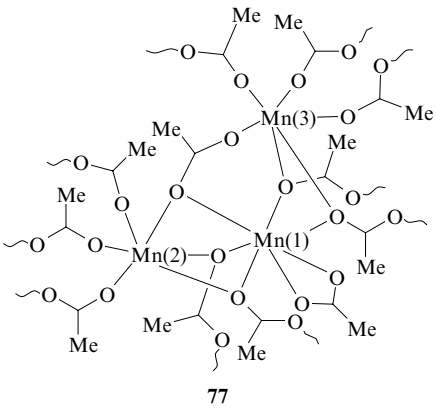
76

The increase in the number of metal atoms in a repeating unit up to four results in their distorted non-planar Y-shaped arrangement. Non-planarity of the metal core together with the decrease in the number of neutral molecules in the repeating unit results in the formation of three-dimensional structure (in contrast to layered structures of complexes **74** and **75**). Antiferromagnetic exchange interactions between high spin manganese(II) atoms exist in this compound.

Three-dimensional manganese acetate $[Mn(OAc)_2]_n$ (**77**) devoid of neutral molecules was obtained by dehydration of $Mn(OAc)_2 \cdot 4H_2O$ in acetonitrile under elevated pressure at 150 °C.[99] A 3D-system of polymer **77** is built of trinuclear fragments in which the coordination number of one of the manganese atoms is as high as 7 (Fig. 2 *a*).

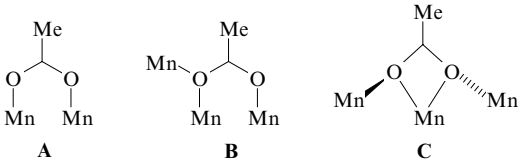
A variety of the carboxylate group coordination modes can be exemplified in complex **77** (Fig. 2 *b*). Besides, the dependence of the Mn···Mn distances on the bridging group type is observed in this structure. Thus, while the distance between Mn(1) and Mn(2) atoms linked by three monoatomic carboxylate bridges is 3.202 Å, the distance between Mn(1) and Mn(3) linked by two monoatomic and one triatomic carboxylate bridges increases to 3.373 Å. The Mn···Mn distances between the atoms linked by two triatomic and one monoatomic carboxylate bridges increase to 3.816 and 3.887 Å. At temperatures below 15 K, compound **77** exists in an ordered antiferromagnetic state.

a



77

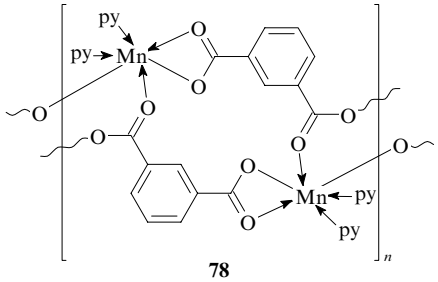
b



A **B** **C**

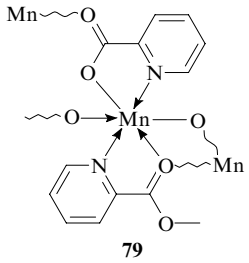
Figure 2. The structure of a fragment of polymer **77** (*a*) and the coordination types of bridging carboxylate groups in it (*b*).

The use of polycarboxylic acids favours the formation of polymeric carboxylate complexes, the arrangement of the carboxy groups in the acid molecule being very important. For instance, the reaction of manganese chloride with isophthalic acid [*m*-$(HOOC)_2C_6H_4$] in the presence of pyridine in aqueous methanol yields the linear polymer $[Mn\{m\text{-}(OOC)_2C_6H_4\}(py)_2]_n$ (**78**) with the binuclear fragment as a repeating unit.[100]



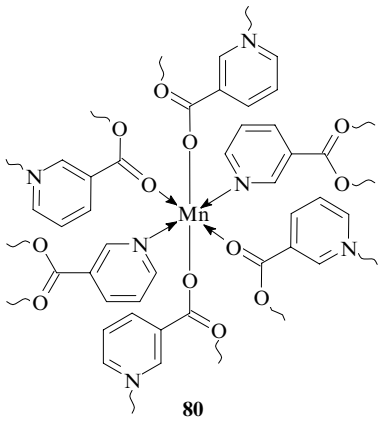
78

The presence of other functional groups in the carboxylic acid molecule also induces the formation of polymeric structures that depend on the geometrical parameters of the ligand. Thus the structure of isomers of pyridinecarboxylic acid determines the type of a carboxylate complex formed. For example, the layered polymeric complex $[Mn(2\text{-}OOCC_5H_4N)_2]_n$ (**79**) containing no water molecules is formed in the reaction of $MnCl_2 \cdot 4H_2O$ with α-picolinic acid in aqueous methanol at 145 °C (Ref. 102).§



79

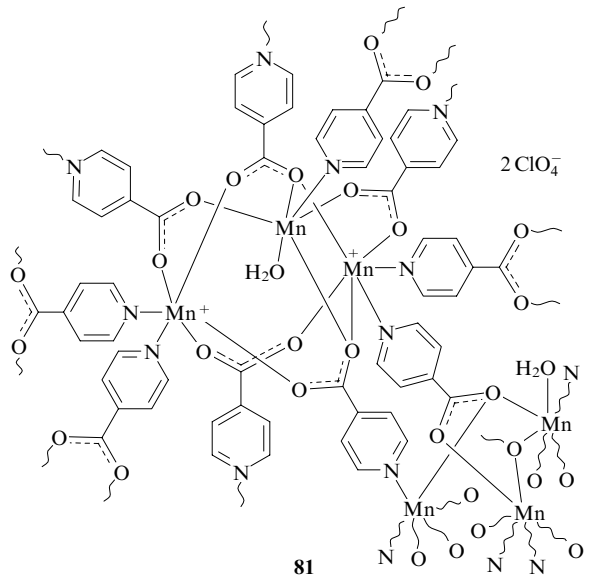
In the case of β-picolinic acid, the three-dimensional polymeric complex $[Mn(3\text{-}OOCC_5H_4N)_2]_n$ (**80**) is formed.[100, 103]



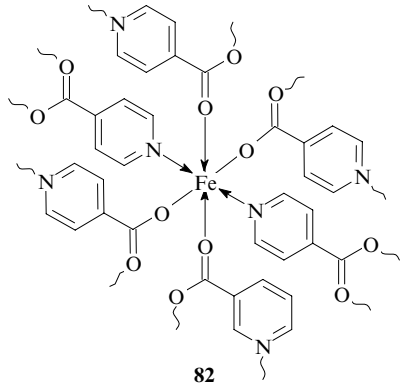
80

Manganese(II) perchlorate reacts with γ-picolinic acid in aqueous ethanol yielding the three-dimensional ionic polymer $[Mn_6(4\text{-}OOCC_5H_4N)_{10}(H_2O)_2](ClO_4)_2$ (**81**),[104] while the reaction of iron(II) perchlorate with γ-picolinic acid results in the formation of 3D-polymer with a different structure [Fe(4-$C_5H_4NCOO_2)_2]_n$ (**82**).[105]

§ At room temperature, the mononuclear complex $[Mn(\eta^2\text{-}2\text{-}OOCC_5H_4N)_2(H_2O)_2]$ is formed.[101]



81

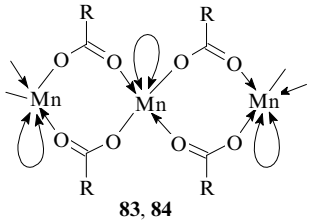


82

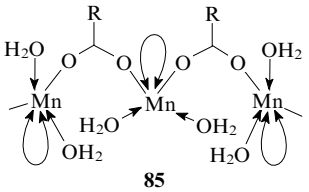
Polyfunctional ligands of various denticity and geometry (for example, linear or angular bidentate, planar or pyramidal tridentate, planar or tetrahedral tetradentate ligands) are used for the targeted synthesis of polymeric carboxylate complexes of different dimensionality.¶ The maintainance of a correct balance between such ligands and metal sites is very important in this case, because an excess of the ligand brings about smooth formation of mono- and binuclear compounds.

The complex $[Mn(OOCCH_2Cl)_2(1,10\text{-phen})]_n$ (**83**) is formed in the reaction of $Mn(OOCCH_2Cl)_2$ with 1,10-phenanthroline in the ratio 1 : 1. The manganese atoms in this complex are arranged into infinite chains in which two adjacent metal atoms are linked by two carboxylate groups.[69, 107] Similar linear polymer $[Mn(OOCC_6H_4Cl\text{-}m)_2(2,2'\text{-bipy})]_n$ (**84**) was obtained by reaction of manganese *m*-chlorobenzoate with bipyridyl.[48]

In the reaction of 1,10-phenanthroline with a salt of a dicarboxylic acid, *e.g.*, manganese phthalate, instead of a salt of a monocarboxylic acid, the linear polymer $\{Mn[o\text{-}(OOC)_2.C_6H_4](1,10\text{-phen})(H_2O)_2\}_n$ (**85**) is also formed, but its manganese atoms are linked by only one bridging carboxylate group.[108]



83, **84**



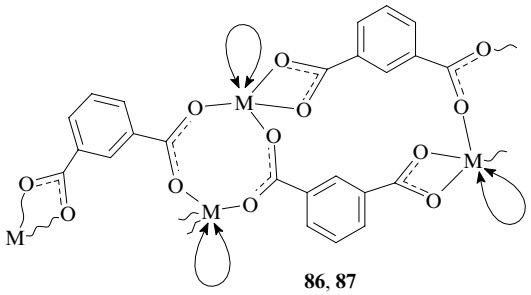
85

= 1,10-phen (**83**, **85**), 2,2′-bipy (**84**);

R = CH_2Cl (**83**), C_6H_4Cl-*m* (**84**), C_6H_4COO-*o* (**85**).

¶ The examples of carboxylate complexes of 3d-metals are given in a review.[106]

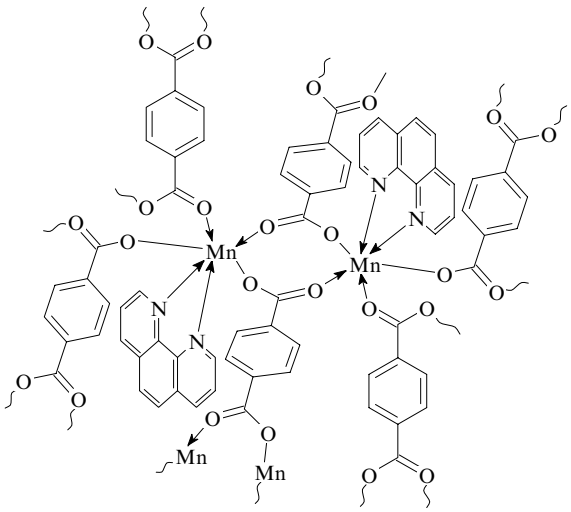
The reactions of complexes $Mn(2,2'\text{-bipy})_2Cl_2$ and $Fe(1,10\text{-phen})_2Cl_2$ with isophthalic acid salts yield the corresponding helical polymeric structures $\{Mn[m\text{-}(OOC)_2C_6H_4](2,2'\text{-bipy})\}_n$ (**86**) and $[Fe(m\text{-}(OOC)_2C_6H_4)(1,10\text{-phen})]_2$ (**87**) due to coordination of the second carboxylate group of the acid anion and stacking interactions of aromatic rings.[109, 110]



86, **87**

M = Mn (**86**), Fe (**87**); = 2,2′-bipy (**86**), 1,10-phen (**87**).

The terephthalic acid dianion obtained upon hydrolysis of 1,4-dicyanobenzene reacts with manganese chloride and 1,10-phenanthroline also to yield the polymer $\{Mn[p\text{-}(OOC)_2C_6H_4](1,10\text{-phen})\}_n$ (**88**) in which this dianion links four manganese atoms at once.[111]



88

Thus, various *n*-dimensional systems can be obtained by modifying the structure (denticity, functionality and geometry) of carboxylate ligands. Usually, the paramagnetic sites in such polymers are in a high spin state and the predominant exchange interactions between them are antiferromagnetic.

V. Mixed-valence complexes containing manganese(II) and iron(II)

Manganese(II) and iron(II) carboxylate complexes are highly liable to oxidation yielding Mn(III) and Fe(III) derivatives. In the case of polynuclear compounds, these processes usually proceed *via* mixed-valence systems, which are often quite stable. Such compounds containing high spin metal sites are definitely of interest, because even if all the metal atoms in the complex are of the same kind, the molecule turns out to be of a hetero-spin type.

Binuclear mixed-valence systems are usually formed as a result of oxidation of M(II) complexes. The controlled oxidation of iron and manganese binuclear complexes, for example, complexes **17** and **19**, results in the oxidation of one out of two metal atoms and affords complexes $[M_2(\mu\text{-}O)(\mu\text{-}OOCR)_2(Me_3tacn)_2]ClO_4$ [M = Fe, R = Me (**89**); M = Mn, R = Bu^t (**90**)].[41, 43] Oxidation of binuclear complex **20** by atmospheric oxygen also yields green mixed-valence complex $[Fe_2(\mu\text{-}O)(\mu\text{-}OOCCPh_3)_2(Me_3tacn)_2]\cdot BPh_4$. Further oxidation of this complex by H_2O_2 results in the

formation of stable orange iron(III) complex $[Fe_2(\mu\text{-}O)(\mu\text{-}OOCCPh_3)_2(Me_3tacn)_2](BPh_4)_2$.[44]

Mixed-valence systems can also be obtained starting from ordinary manganese(II) and iron(II) salts. For example, the reaction of 2,6-bis{bis[(1-methylimidazol-2-yl)methyl]aminomethyl}-4-methylphenol (Hbimp) with sodium acetate and magnesium(II) or iron(II) perchlorate in methanol results in the formation of dimers $[M^{II}M^{III}(bimp)(OOCR)_2](ClO_4)_2$ (M = Mn, Fe).[112, 113]

Mixed-valence cationic complexes with a 'Chinese lantern' structure $[Fe_2(\mu\text{-}OOCR)_4(py)_2]PF_6$ (**93**) and $[Fe_2(\mu\text{-}OOCR)_4.(4\text{-}Bu^tC_5H_4N)_2]CF_3SO_3$ (**94**) were obtained by single-electron oxidation of iron(II) binuclear complexes **26** and **34** with $[FeCp_2]PF_6$ and $AgCF_3SO_3$, respectively (Scheme 3).[114, 115] Oxidation of compounds **26** and **34** by atmospheric oxygen yields complexes $[Fe_2(\mu\text{-}OH)_2(\mu\text{-}OOCR)_2(OOCR)_2L_2]$ [L = py (**95**), 4-$Bu^tC_5H_4N$ (**96**), Scheme 3]. In these complexes, the iron(III) atoms are in a different ligand environment and their coordination number increases up to 6.

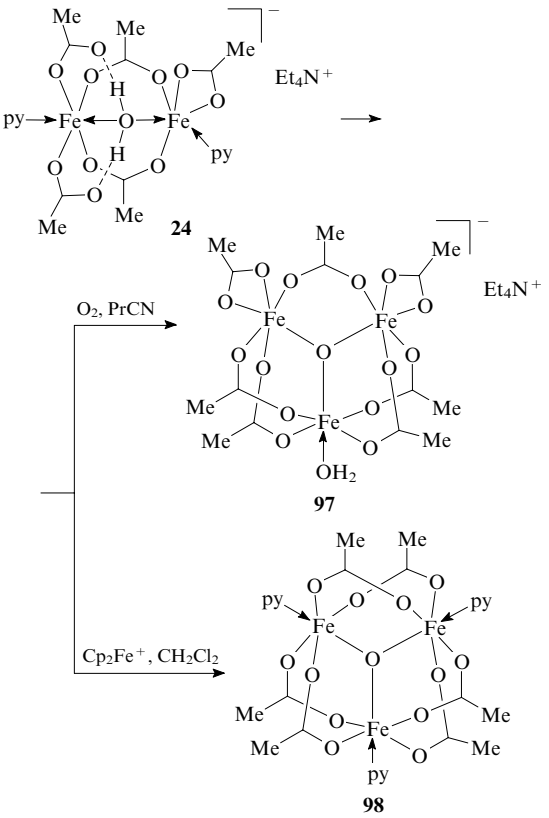
Manganese and iron oxocarboxylate triangular complexes $[M_3(\mu_3\text{-}O)(\mu\text{-}OOCR)_6L_3]^{n+}$ are well studied by magnetic methods.[116–119] These compounds play an important role in bioinorganic systems because they may be regarded as models of active sites of metalloproteins and as structural models of oxygen-containing centres in the photosystem II.[120–122] There are very few neutral ($n = 0$) iron and manganese M(II) and M(III) mixed-valence oxocarboxylate trinuclear complexes. These complexes are interesting as hetero-spin systems with potentially highly variable metal sites.[7, 123]

Iron mixed-valence trinuclear complexes are obtained by either direct reaction of iron powder with an acid {synthesis of $[Fe_3O(OOCBu^t)_6(HOOCBu^t)_3]$} [124] or reactions of inorganic salts with acids {synthesis of $[Fe_3O(OOCCH_2Cl)_6(H_2O)_3]$}.[125] Terminal ligands in such systems can be replaced by various N-donating molecules, *e.g.*, pyridine. The oxocomplex $[Fe_3O(OOCBu^t)_6(py)_3]$ was obtained from $[Fe_3O(OOCBu^t)_6(HOOCBu^t)_3]$ by this method.[124]

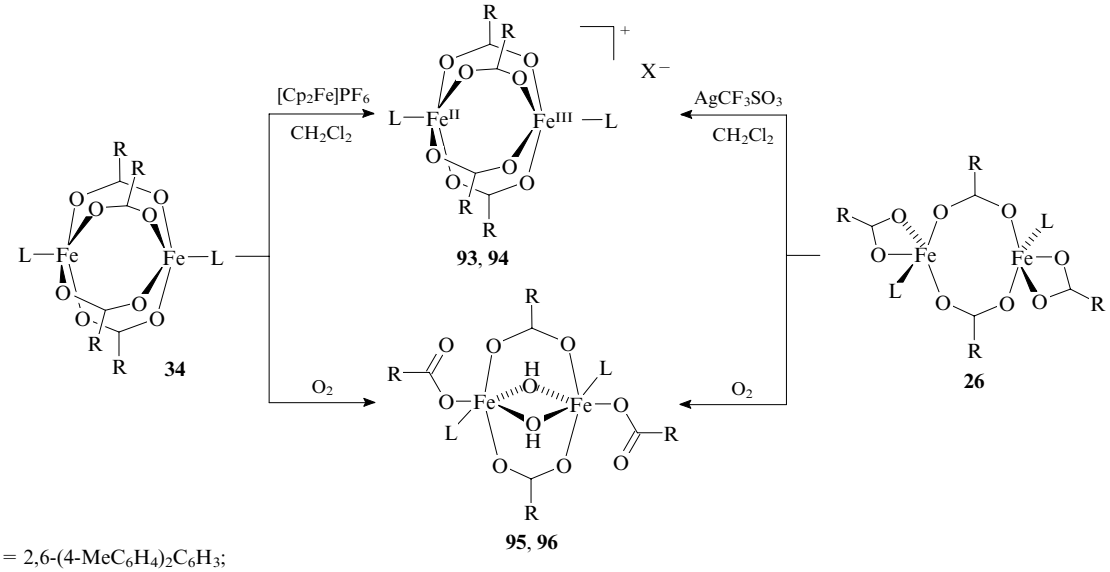
Manganese acetate is typically used as a starting material in the synthesis of neutral manganese mixed-valence trinuclear oxocarboxylates. Oxidation of a solution of $Mn(OAc)_2 \cdot 4H_2O$ by tetrabutylammonium perchlorate in a mixture of glacial acetic acid and pyridine yields the complex $[Mn_3O(OAc)_6(py)_3]$,[119] while the oxidation in the presence of benzoic acid in a mixture of ethanol and pyridine results in the substitution of acetate groups and formation of mixed-valence complex $[Mn_3O(OOCPh)_6.(py)_2(H_2O)]$.[119] Treatment of the latter with a solution of 2,2′-bipyridyl-3,3′-dicarboxylic acid and triethylamine in acetonitrile affords trinuclear complex $[Mn_3O(OOCPh)_6(py)_3]$ with similar structure, but with three terminal pyridine molecules.[126]

More complex starting reagents can also be used for the synthesis of trinuclear complexes. Thus the decomposition of the dodecanuclear complex $[Mn_8^{III}Mn_4^{IV}O_{12}(OAc)_{16}(H_2O)_4] \cdot 2\,HOAc \cdot 4\,H_2O$ in trichloroacetic or trifluoroacetic acid is accompanied by partial reduction of manganese atoms and the formation of the mixed-valence complex $[Mn^{II}Mn_2^{III}O(OOCR)_6(H_2O)_3]$ (R = CCl_3 or CF_3).[127, 128]

Yet another type of trinuclear systems, *viz.*, asymmetric triangular oxocarboxylate $(Et_4N)[Fe_3O(OAc)_7(OH_2)]$ (**97**), was obtained by reaction of atmospheric oxygen with the complex $(Et_4N)[Fe_2(\mu\text{-}OH_2)(\mu\text{-}OAc)_2(py)_4(OAc)_3]$ (**24**).[129] It was noted



Scheme 3

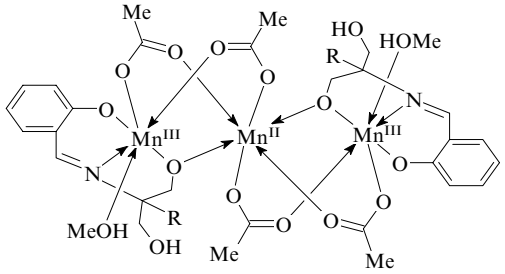


R = 2,6-(4-$MeC_6H_4)_2C_6H_3$;

L = py (**26**, **93**, **95**), 4-$Bu^tC_5H_4N$ (**34**, **94**, **96**).

that the oxidation of compound **24** with ferrocenyl cation affords the symmetrical mixed-valence complex $[Fe_3O(OAc)_6(py)_3]$ (**98**).

Trinuclear linear complexes of general formula $[Mn^{II}Mn^{III}_2L_2(\mu\text{-}OAc)_4(MeOH)_2]$ [**99**: H_2L is 1,3-dihydroxy-2-methyl-2-(salicylidenamino)propane, **100**: H_2L is tris(hydroxymethyl)(salicylidenamino)methane] were obtained by reaction of salicylaldehyde with 2-amino-2-methylpropane-1,3-diol [or tris(hydroxymethyl)aminomethane] and manganese acetate in methanol.[130] Manganese(II) atom in the obtained complexes occupies the central position and the Mn(III)–Mn(II)–Mn(III) bond angle is equal precisely to 180°. Coordinated methanol molecules in complexes **99** and **100** are labile and can be replaced by other donating ligands, *e.g.*, H_2O or 2-pyridone.

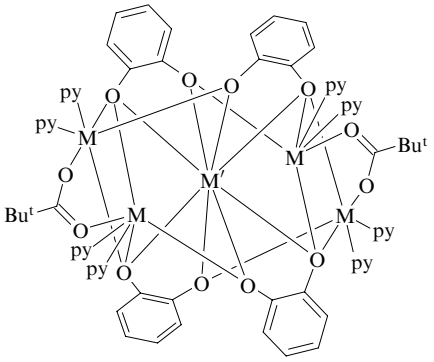


99, **100**

R = Me (**99**), CH_2OH (**100**).

Mixed-valence tetranuclear complexes of the 'butterfly' geometry are known only for manganese. The ratio of two- and three-valence metals in such complexes may be equal to 1 : 1 as in the complex $[Mn^{II}_2Mn^{III}_2(\mu_3\text{-}O)_2(\mu\text{-}OAc)_6.(2,2'\text{-bipy})_2]$ (**101**), or 1 : 3 as in compounds $[Mn^{II}Mn^{III}_3(\mu_3\text{-}O)_2(\mu\text{-}OOCC_6H_4X\text{-}2)_7(2,2'\text{-bipy})_2]$ [X = Cl (**102**), Br (**103**)].[131, 132] Complex **101** is formed in the reaction of the trinuclear complex $[Mn^{II}Mn^{III}_2O(OAc)_6(py)_3]$ with 2,2′-bipyridyl in acetonitrile and compounds **102**, **103** are formed in the reaction of the complexes $[Mn^{II,III}_3O(\mu\text{-}OOCC_6H_4.X\text{-}2)_6(py)_3]$ (X = Cl, Br) with 2,2′-bipyridyl in CH_2Cl_2. The metal atoms in complexes **101**–**103** are 'butterfly'-shaped, the Mn(II) atoms in compound **101** being located in the 'wings' of the 'butterfly', while in complexes **102** and **103** the 'wings' are formed by one Mn(II) and one Mn(III) atom.

Pentanuclear mixed-valence complexes $[M_5(OOCBu^t)_2.(C_6H_4O_2\text{-}o)_4(py)_8]^+$ [M = Mn (**104**), Fe (**105**)] are obtained in reactions of metal pivalates and chlorides with tetrabutylammonium catecholate $(Bu_4N)_2(C_6H_4O_2\text{-}o)$ in pyridine.[133] They were isolated as salts with outer-sphere anions Cl^-, Br^-, PF_6^-. The only three-valence metal atom is located in the central position and can be replaced by another metal. Thus the partial replacement of $MnCl_2$ by $FeCl_3$ in the starting reagents (Mn : Fe = 4 : 1) results in the formation of the heterometallic complex $[Mn_4Fe(OOC.Bu^t)_2(C_6H_4O_2\text{-}o)_4(py)_8]Cl$ (**106**). The heterometallic complex



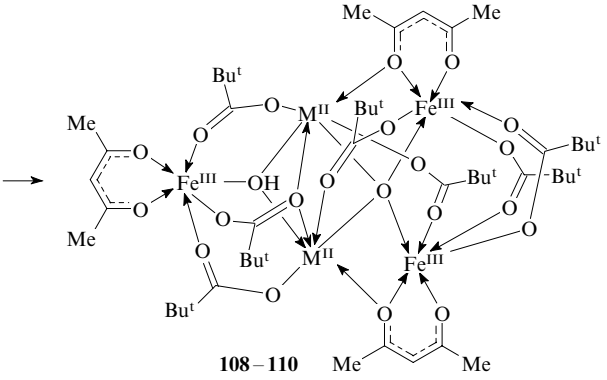
104–**107**

104: M = M′ = Mn; **105**: M = M′ = Fe;
106: M = Mn, M′ = Fe; **107**: M = Mn, M′ = Tb.

$[Mn_4Tb(OOCBu^t)_2(C_6H_4O_2\text{-}o)_4(py)_8]NO_3$ (**107**) was obtained by the same method.[134]

Refluxing of $[Fe^{III}_3O(OOCBu^t)_6](OOCBu^t)$ and $M(acac)_2$ in pentadecane yields pentanuclear complexes $[Fe_3M_2(\mu_4\text{-}O)(\mu_3\text{-}OH)(\mu_3\text{-}OOCBu^t)(\mu_2\text{-}OOCBu^t)_6(\mu,\eta^2\text{-}acac)_2(\eta^2\text{-}acac)]$ [M = Mn (**108**), Co (**109**), Ni (**110**)].[135]

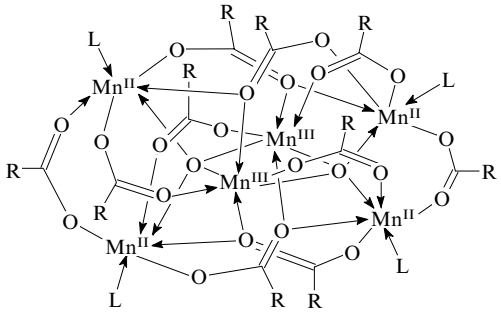
$$[Fe_3O(OOCBu^t)_6](OOCBu^t) + M(acac)_2 \xrightarrow{C_{14}H_{30},\ \Delta}$$



108–**110**

M = Mn (**108**), Co (**109**), Ni (**110**).

Unlike iron(II) carboxylates, which are easily oxidised by atmospheric oxygen producing iron(III) derivatives, the oxidation of manganese(II) carboxylates affords stable mixed-valence hexanuclear complexes $[Mn_6(\mu_4\text{-}O)_2(OOCR)_{10}L_4]$ (**111**–**117**). The metal core of these complexes $Mn^{II}_4Mn^{III}_2O_2$ is surrounded by six μ_2-bridging, four μ_3-bridging carboxylate groups and four N- or O-donating terminal monodentate ligands.[16, 136–141] Four manganese(II) atoms in these complexes occupy peripheral positions.



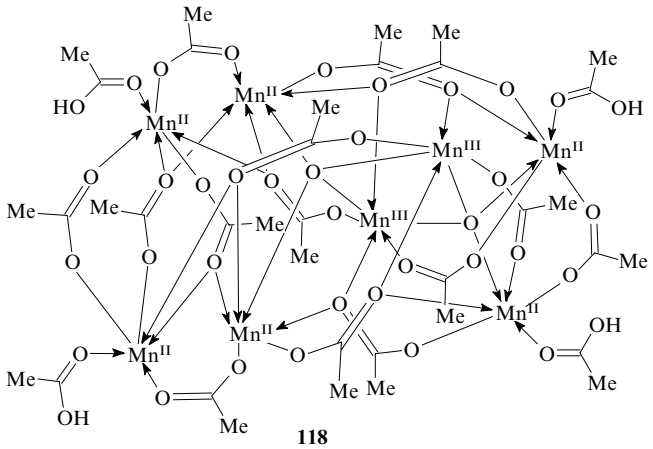
111–**117**

111: R = Me, L = py; **112**: R = Ph, L = py; **113**: R = Ph; L = 1/2 py, 1/2 MeCN; **114**: R = Bu^t, L = HO_2CBu^t; **115**: R = Bu^t, L = py; **116**: R = Bu^t, L = THF; **117**: R = Bu^t, L = .

The methods of synthesis of such complexes are quite diverse. For example, complex **114** is obtained by refluxing $Mn(NO_3)_2\cdot x\,H_2O$ (x = 4–6) with an excess of pivalic acid in dioxane, while complex **115**, by reaction of complex **114** with pyridine in chloroform, whereupon the terminal pivalic acid molecules are replaced by pyridine molecules. Complex **116** can be obtained either by oxidation of a mixture of $MnCl_2\cdot 4\,H_2O$ and $NaOOCBu^t$ in methanol and recrystallisation of the reaction product from THF or by oxidation of the complex $[Mn_3(OOC.Bu^t)_6(HOOCBu^t)_5]$ (**47**) in THF.

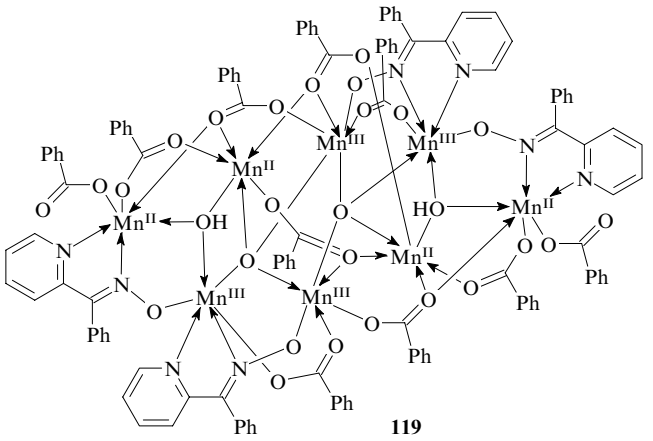
Among octanuclear complexes, compounds $[Mn^{II}_6Mn^{III}_2(\mu_4\text{-}O)_2(\mu\text{-}OOCCH_2Bu^t)_{14}(HO_2CCH_2Bu^t)_4]$ (**118**) and $[Mn^{II}_4Mn^{III}_4.O_2(OH)_2(OOCPh)_{10}(L)_4]$ (**119**, L is phenyl 2-pyridyl ketone oxime) have to be noted.[142, 143] Complex **118** was obtained by reduction of the dodecanuclear cluster $[Mn^{III}_8Mn^{IV}_4O_{12}(OOCCH_2.Bu^t)_{16}(H_2O)_4]$ (**120**) with pyridine-2,6-dimethanol. The metallofragment $[Mn^{III}_2Mn^{II}_4(\mu_4\text{-}O)_2]^{10+}$ in this complex is identical to

those in compounds **111**–**117**. The build-up of the metal core $Mn_2^{III}Mn_4^{II}(\mu_4\text{-}O)_2$ occurs upon linking of two adjacent bridging carboxylate ligands with two Mn(II) atoms.



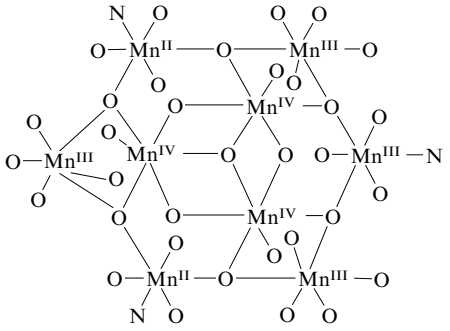
118

Complex **119** obtained by oxidation of $Mn(OOCPh)_2 \cdot 2\,H_2O$ with tetrabutylammonium permanganate in the presence of phenyl 2-pyridyl ketone oxime also contains metallofragment $[Mn_4^{III}Mn_2^{II}(\mu_4\text{-}O)_2]^{12+}$ but with four Mn(III) and two Mn(II) atoms. In this case, the build-up of the metal core proceeds from the opposite sides of the metal moiety.



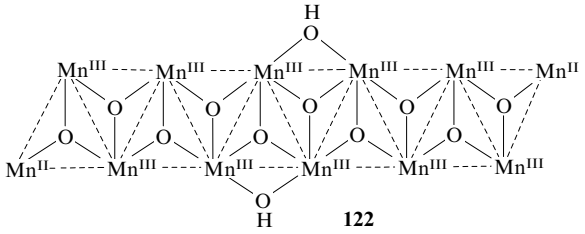
119

In contrast to iron derivatives, mixed-valence manganese complexes are known that contain simultaneously bi-, tri- and tetra-valent manganese ions. For example, the reaction of mixed-valence acetate complex $[Mn_3O(OAc)_6(py)_3]$ with 1,1,1-tris-(hydroxymethyl)ethane (H_3L) results in the formation of nona-nuclear complex $[Mn_2^{II}Mn_4^{III}Mn_3^{IV}O_7(OAc)_{11}L(py)_3(H_2O)_2]$ (**121**).[144]



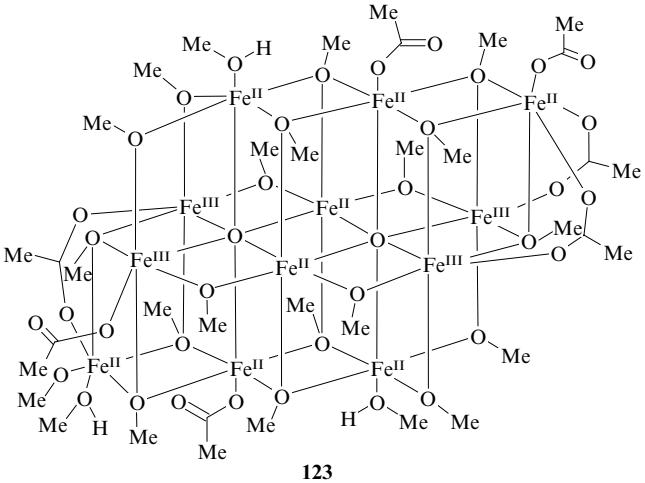
121

However, the reaction of similar triphenylacetate complex $[Mn^{II}Mn_2^{III}(\mu\text{-}O)(OOCCPh_3)_6(py)_2(H_2O)]$ with 1,1,1-tris(hydroxymethyl)ethane yields the dodecanuclear complex $[Mn_2^{II}Mn_{10}^{III}O_4(OH)_2(OOCCPh)_{12}(L)_4(py)_2]$ (**122**). The metal core of this complex consists of ten triangular fragments $\{Mn_3(\mu_3\text{-}O)\}$ with nine common sides.[145] The Mn(II) atoms occupy the peripheral positions in this system.



122

The dodecanuclear complex $[Fe_8^{II}Fe_4^{III}(O)_2(OMe)_{18}(OAc)_6 \cdot (MeOH)_{4.67}]$ (**123**) is obtained by controlled oxidation of a methanolic solution of iron acetate in the presence of lithium methoxide.[146] In this compound, six Fe(II) and four Fe(III) atoms are linked by two μ_6-oxo-bridges.



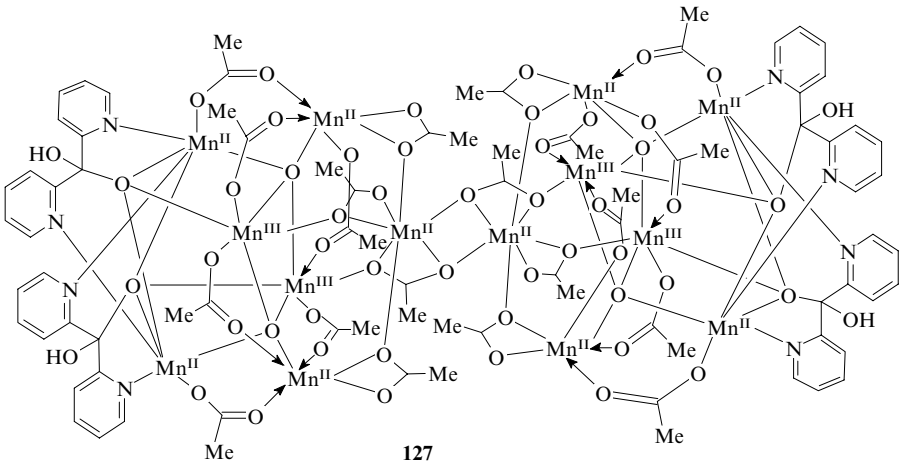
123

If a $FeCl_2$–$ClCH_2COOH$ mixture is used instead of iron acetate, the reaction with LiOMe and atmospheric oxygen results in a similar dodecanuclear complex with a part of carboxylate groups replaced by chlorine atom: $[Fe_8^{II}Fe_4^{III}(O)_2(OMe)_{18} \cdot (OOCCH_2Cl)_{5.3}Cl_{0.7}(MeOH)_4]$ (**124**).[147] More profound oxidation yields the Fe(III) cyclic complex $[Fe(OMe)_2(OOCCH_2Cl)]_{10}$ known as a molecular 'iron ring'.[147]

The reaction of manganese dodecanuclear complexes with reducing agents not always results in their decomposition. For instance, one-electron reduction of the complex $[Mn_8^{III} \cdot Mn_4^{IV}O_{12}(OOCR)_{16}(H_2O)_4]$ (R = Et, C_4H_3S) with tetraphenylphosphonium iodide produces the corresponding ionic molecular magnets $[PPh_4][Mn^{II}Mn_7^{III}Mn_4^{IV}O_{12}(OOCR)_{16}(H_2O)_x]$ [R = Et, x = 4 (**125**), R = C_4H_3S, x = 2 (**126**)], in which just one manganese atom is in the oxidation state +2 (see Refs 9, 148).

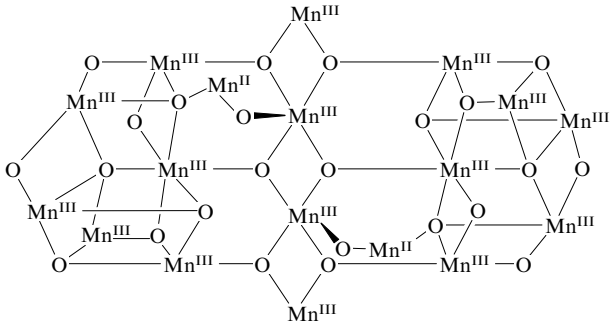
As was mentioned above, the use of polyfunctional ligands in the reactions with metal carboxylate increases the possibility of formation of polynuclear complexes. Thus the tetradecanuclear carboxylate complex $[Mn_{10}^{II}Mn_4^{III}O_4(OAc)_{20}(HL)_4]$ [**127**, H_2L = $(2\text{-}C_5H_4N)_2C(OH)_2$] is the reaction product of manganese acetate with bis(2-pyridyl) ketone, which can exist as a *gem*-diol when coordinated by metal ions, in acetonitrile in air.[143]

The reaction of two triangular complexes $[Mn_3^{III}O(OAc)_6 \cdot (py)_3]ClO_4$ and $[Mn_3O(OAc)_6(py)_3]$ with 2-(2-hydroxyethyl)pyridine (HL) in acetonitrile results in the formation of polynuclear ionic complex $[Mn_2^{II}Mn_{16}^{III}O_{14}(OAc)_{18}L_4(HL)_2(H_2O)_2](ClO_4)_2$



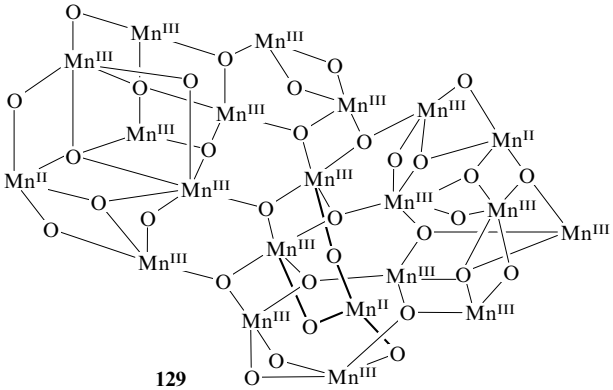
127

(**128**) in which the linear fragment $[Mn_4^{III}O_6]$ is linked to two heptanuclear fragments $[Mn^{II}Mn_6^{III}O_9]$.[149]



128

The complex $[Mn_3^{II}Mn_{18}^{III}O_{14}(OH)_2(OAc)_{16}L_8(pic)_2(py).(H_2O)](ClO_4)_4$ (**129**, Hpic is α-picolinic acid) is formed in the reaction of $[Mn_{10}^{III}O_4(OH)_2(OAc)_8L_8](ClO_4)_4$ [HL is 2-(hydroxymethyl)pyridine] and $[Mn_3^{III}O(OAc)_6(py)_3]ClO_4$ in MeCN.[150] It should be noted, that partial reduction of manganese atoms proceeds due to the oxidation of 2-(hydroxymethyl)pyridine anions to anions of α-picolinic acid. Thus, starting from manganese(III) complex, it is possible to obtain a mixed-valence complex with the $[Mn_{21}(\mu_4\text{-}O)_4(\mu_3\text{-}O)_{12}(\mu\text{-}O)_{16}]$ metal core. In this metal core, the linear fragment $[Mn_4^{III}O_6]$ is surrounded by two octanuclear fragments $[Mn^{II}Mn_7^{III}O_{12}]$ and one mononuclear $[Mn^{II}O_3]$ fragment (marked with bold lines).



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Recrystallisation of the complex $[Mn_8^{III}Mn_4^{IV}O_{12}(OOC.CH_2Bu^t)_{16}(H_2O)_4]$ (**120**), which can be obtained by oxidation of manganese(II) acetate with potassium permanganate in the presence of Bu^tCH_2COOH, from $CH_2Cl_2-MeNO_2$ affords the complex $[Mn_3^{II}Mn_{26}^{III}Mn^{IV}O_{24}(OH)_8(OOCCH_2Bu^t)_{32}(H_2O)_2.(MeNO_2)_4]$.[151,152] This compound has a virtually linear $[Mn_4O_6]$ core, which is fixed between two $[Mn_{13}O_9(OH)_4]$ fragments. The quantum tunnelling of magnetisation (QTM) was reported for this compound as well as for not numerous polynuclear complexes **64**, **121**, **122**, **125**, **126**, **128** and **129**. The QTM is possible in polynuclear systems with several states of different multiplicity and a hysteresis at low temperature, thus these compounds belong to a unique class of molecular magnets (SMMs, Single Molecular Magnets).[8,9,153] It should be noted, that the complexes containing eight and more metal atoms are exceptional for such carboxylate systems, rather unique and do not have analogues among carboxylate complexes of other transition metals.

VI. Conclusion

In conclusion, an exceptional diversity of structures of Mn(II) and Fe(II) carboxylates discussed — from relatively simple binuclear complexes up to highly complicated 30-nuclear hetero-spin compounds — is worth noting. Undoubtedly, these compounds with unique magnetic properties, which should be a subject of another review, are extremely important blocks for the creation of molecular electronic devices in the nearest future. The first synthetic strategies of the targeted production of high spin bi- and trinuclear systems with required structure and magnetic properties, already exist. However, the approaches to the synthesis of structures more complicated and probably more interesting as molecular magnets are obviously yet to be developed.

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