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The use of di-2-pyridyl ketone in manganese(II) benzoate chemistry: Two novel Mn_3^{II} linkage isomers containing the ketone form of the ligand and a neutral Mn_4^{II} cubane containing the ligand in its *gem*-diolate(-1) form

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Dedicated to the memory of Xavier Solans, a great structural chemist and a great friend.

Abstract

The use of di-2-pyridyl ketone, $(py)_2CO$, in manganese(II) benzoate chemistry has yielded two Mn_3^{II} linkage isomers containing the ketone form of the ligand and a neutral Mn_4^{II} cubane cluster containing the *gem*-diolate(-1) form of the ligand. The 3:2 $Mn(O_2CPh)_2 \cdot 2H_2O/(py)_2CO$ reaction system in MeCN gives a mixture of the orange complex $[Mn_3(O_2CPh)_6\{(py)_2CO\text{-}\kappa^2N,N'\}_2]$ (**1**) and the yellow compound $[Mn_3(O_2CPh)_6\{(py)_2CO\text{-}\kappa^2N,O\}_2] \cdot 2MeCN$ (**2** · 2MeCN). The known compound $[Mn_6O_2(O_2CPh)_{10}(MeCN)_4]$ (**3**) appears as a by-product when the initial reaction solution, that leads to **1** and **2** · 2MeCN, is allowed to slowly evaporate in the air. The trinuclear molecules adopt a linear structure in both complexes, with one monoatomically bridging $\eta^1:\eta^1:\mu_2$ and two *syn*,*syn*-$\eta^1:\eta^1:\mu_2$ carboxylate groups spanning each pair of Mn^{II} ions. The terminal Mn^{II} ions are each capped by one chelating-*N*,*N′* $(py)_2CO$ ligand in **1** and by one chelating-*N*,*O* $(py)_2CO$ molecule in **2**. The 1:1 reaction of $Mn(O_2CPh)_2 \cdot 2H_2O$ and $(py)_2CO$ in CH_2Cl_2 results in the isolation of $[Mn_4(O_2CPh)_4\{(py)_2C(OH)O\}_4]$ (**4**). The tetranuclear molecule has a cubane topology with the Mn^{II} ions and the deprotonated oxygen atoms from the $(py)_2C(OH)O^-$ ligands occupying alternate vertices. The IR data are discussed in terms of the nature of the bonding. The magnetic properties of **4** in the 300–5 K range have been modeled with two *J* values and reveal weak intramolecular antiferromagnetic interactions. The low temperature X-band EPR spectra of **1**, **2** and **4** are also discussed.

Keywords: Di-2-pyridyl ketone complexes; EPR spectra; Magnetic properties; Manganese(II) benzoate clusters; Manganese(II) cubanes

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Polynuclear manganese carboxylate chemistry is an area of research that has attracted scientists from multi-disciplinary fields including biology [1], material science [2], magnetochemistry [3], physics [4] and synthetic inorganic chemistry [5]. For example, in material science a great number of polynuclear manganese carboxylate complexes have been found to possess large spin ground states [6] and some have also been shown to display the phenomenon of single-molecule magnetism [7]. The latter property is the ability of

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discrete molecules to exhibit the superparamagnetic-like behaviour of slow magnetization relaxation and thus to behave as magnets below their blocking temperature.

Discovering new preparative routes towards the synthesis of manganese carboxylate clusters is thus of intense interest not only for the discovery of completely new compounds but also as a means of building up families of related species so that structure–property relations can be developed. With this in mind, our group [8] and others [9] have been exploring 'ligand blend' reactions involving the monoanion, $(py)_2C(OH)O^-$, or the dianion, $(py)_2CO_2^{2-}$, of the *gem*-diol form (derivative) of di-2-pyridyl ketone, $(py)_2CO$ (the formulae of these ligands are shown in Fig. 1) and carboxylates in Mn chemistry, with the belief that they can foster the formation of discrete clusters. The reactions of $(py)_2CO$ with 3d-metal ions have been well studied over the years [10]. Water and alcohols (ROH) have been shown to add to the carbonyl group *upon coordination of the carbonyl oxygen and/or the pyridyl rings* forming the ligands $(py)_2C(OH)_2$ [the *gem*-diol form of $(py)_2CO$] and $(py)_2C(OR)(OH)$ [the hemiacetal form of $(py)_2CO$], respectively (Fig. 1). The immense structural diversity displayed by the 3d-metal complexes reported stems in part from the ability of $(py)_2C(OH)O^-$, $(py)_2C(OH)O^-$ and $(py)_2CO_2^{2-}$ to exhibit not less than 10 distinct bridging (μ_2–μ_5) coordination modes [10]. Employment of carboxylates as ancillary ligands in the reaction mixtures gives an extraordinary structural flexibility in the mixed-ligand systems, allowing the synthesis of a variety of 3d-metal clusters with nuclearities ranging from 3 to 14 [8–12], and with interesting physical properties including single-molecule magnetism [13].

Although the use of $(py)_2CO$-based ligands has been investigated widely in Fe, Co, Ni, Cu and Zn carboxylate chemistry [8–13], its use in Mn *carboxylate* chemistry is confined to two examples: the cationic acetate complex $[Mn^{II}_4(O_2CMe)_3\{(py)_2C(OH)O\}_4(H_2O)](ClO_4)$ [9] with a cubane topology and a mixed-valent acetate cluster $[Mn^{II}_{10}Mn^{III}_4O_4(O_2CMe)_{20}\{(py)_2C(OH)O\}_4]$ comprising two $[Mn^{II}_4Mn^{III}_2(\mu_4-O)_2]^{10+}$ subcores each of which is attached to a seventh Mn^{II} ion [8]. In the present work, we describe the first use of $(py)_2CO$ in Mn *benzoate* chemistry that resulted in the isolation of two novel Mn^{II}_3 linkage isomers containing the ketone form of the ligand [$(py)_2CO$, see Fig. 1] and a Mn^{II}_4 cubane containing the ligand in its *gem*-diolate(-1) form [$(py)_2C(OH)O^-$, see Fig. 1].

The 3:2 reaction between $Mn(O_2CPh)_2 \cdot 2H_2O$ and $(py)_2CO$ in freshly distilled MeCN at room temperature gave a pale yellow solution which upon storage in a closed flask for one week turned to pale orange and yielded crystals that were obviously a mixture of two products. Microscopic examination showed both orange and yellow prisms to be present in a visual ratio of 4:1. The total yield (based on the total available Mn) is ~55%. The difference in colour was fortuitous and allowed easy manual separation of the two materials. The orange crystals are stable in the normal laboratory atmosphere for at least 3 days, whereas the yellow ones collapse rapidly giving a yellow powder. The IR spectra of the orange and yellow samples show a strong band at 1710 and 1640 cm^{-1}, respectively, suggesting that the ligand is present in its ketone form [14]. Somewhat to our surprise both dried samples gave identical analytical results, consistent with the empirical formula $Mn(O_2CPh)_2\{(py)_2CO\}_{0.7}$ [15]. Full single crystal X-ray data sets were collected for both compounds and the structures solved [16,17]. The orange crystals proved to be $[Mn_3(O_2CPh)_6\{(py)_2CO\}_2]$ (**1**), while the yellow ones were shown to be $[Mn_3(O_2CPh)_6\{(py)_2CO\}_2] \cdot 2MeCN$ (**2** · 2MeCN). If the initial reaction solution – that leads to **1** and **2** · 2MeCN – is left to slowly evaporate in the air, its colour turns to red brown and few reddish brown crystals of the known $(py)_2CO$-free cluster $[Mn^{II}_4Mn^{III}_2O_2(O_2CPh)_{10}(MeCN)_4]$ (**3**) [18] appear as a by-product [19].

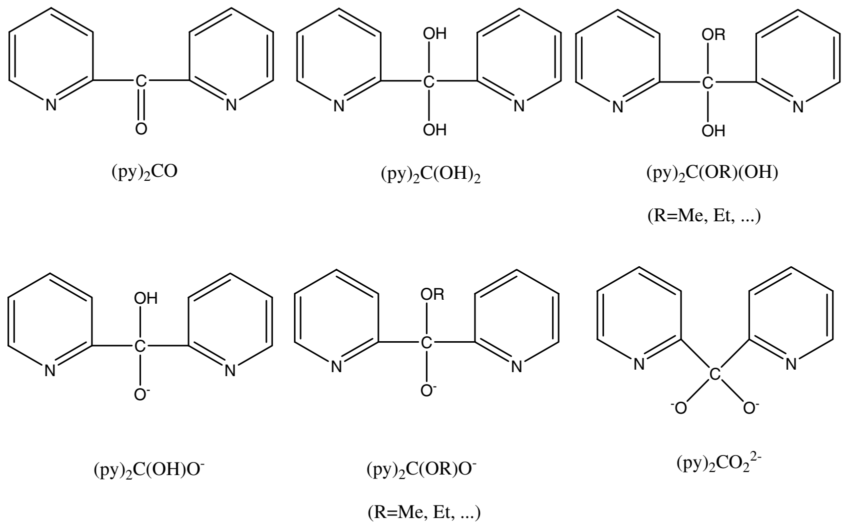


Fig. 1. The structural formulae of the ligands discussed in the text; note that $(py)_2C(OH)_2$, $(py)_2C(OR)(OH)$ and all four anions do not exist as free species but exist only in their respective metal complexes.

The crystal structure of **1** [17] reveals the formation of trinuclear molecules (Fig. 2). The central metal ions, Mn(2), which is located on a crystallographic inversion center, is coordinated by six oxygen atoms belonging to six different benzoates. Thus, the trinuclear molecule adopts a linear structure, with one monoatomically bridging η^1:η^1:μ_2 and two *syn*,*syn*-η^1:η^1:μ_2 carboxylate groups spanning each pair of Mn^{II}. The termini of the $\{Mn(O_2CPh)_3Mn(O_2CPh)_3Mn\}$ unit are each capped by one bidentate chelating-*N*,*N′* (η^2 or κ*N*,*N′*) $(py)_2CO$ ligand, resulting in six coordination at these sites (Mn(1), Mn(1′)). The $Mn(1)N_2O_4$ octahedron is significantly distorted; the main distortion arises from the acute O(6)–Mn(1)–O(7) angle (56.8(1)°). The $Mn(2)O_6$ octahedron is almost perfect. The Mn(2)–O bond lengths are in the narrow 2.133(2)–2.214(2) Å range, with the Mn(2)–O(6) distance (that involving the bridging oxygen) longer as expected. The C(6)–O(1) distance (1.210(6) Å) is comparable to the reported double bond values [20]. The six-membered chelating ring Mn(1)N(1)C(5)C(6)C(7)N(2) adopts a slight boat conformation with the Mn(1) and C(6) atoms 0.032 and 0.099 Å, respectively, below the plane defined by the remaining four atoms. The Mn–N and Mn–O bond lengths agree well with the values expected for octahedral high-spin Mn(II) complexes [21]. Complex **1** is characterized by moderate Mn(1)–O(7) (2.346(3) Å) and Mn(1)···Mn(2) (3.552(2) Å) distances and can be placed in class II in the "carboxylate shift" classification scheme established by Lippard [22]. The dihedral angle between the two 2-pyridyl rings of the $(py)_2CO$ ligand is 10.0°.

The centrosymmetric $\{Mn(O_2CPh)_3Mn(O_2CPh)_3Mn\}$ unit present in complex **2** · 2MeCN (Fig. 3) is almost identical to that present in **1**; however, the termini of the former are each capped by one bidentate chelating-*N*,*O*(η^2 or κ*N*,*O*) $(py)_2CO$ ligand. The $Mn(1)NO_5$ octahedron of **2** · 2MeCN is more distorted than the corresponding $Mn(1)N_2O_4$ octahedron of **1**; for example, the three *trans* angles around Mn(1) are 145.8(1), 160.2(1) and 156.4(1)° in **2** · 2MeCN (average 154.1(1)°) compared to 147.0(1), 162.6(1) and 174.4(1)° in **1** (average 161.3(1)°). The more severe distortions in the former arise from the five-membered chelating ring with a narrow N(1)–Mn(1)–O(1) bond angle (70.4(1)°) and an acute O(6)–Mn(1)–O(7) angle (57.5(1)°). The Mn(1)–O(7) bond is relatively strong with a distance of 2.209(3) Å and thus **2** · 2MeCN belongs to class III in Lippard's classification scheme [22]. The intraligand pyridyl ring dihedral angle is 49.6°.

Complexes **1** and **2** · 2MeCN are linkage isomers. This is the first case of true linkage isomerism in the coordination chemistry of $(py)_2CO$. Toyama et al. have recently prepared the complexes *trans*(Cl), *cis*(S)-$[RuCl_2\{(py)_2CO\text{-}\kappa^2N,O\}(dmso\text{-}S)_2]$ and *cis*(Cl),*cis*(S)-$[RuCl_2\{(py)_2CO\text{-}\kappa^2N,N'\}(dmso\text{-}S)_2]$ [20] which can be considered as linkage isomers; however, these complexes also exhibit geometrical isomerism.

The most interesting feature of structure **2** · 2MeCN is the κ^2*N*,*O* coordination mode of $(py)_2CO$ (**II** in Fig. 4). In the majority [10,20] of the metal complexes containing bidentate chelating $(py)_2CO$ molecules, the ligands are in the κ^2 *N*,*N′* mode (**I** in Fig. 4). Complex **2** · 2MeCN is

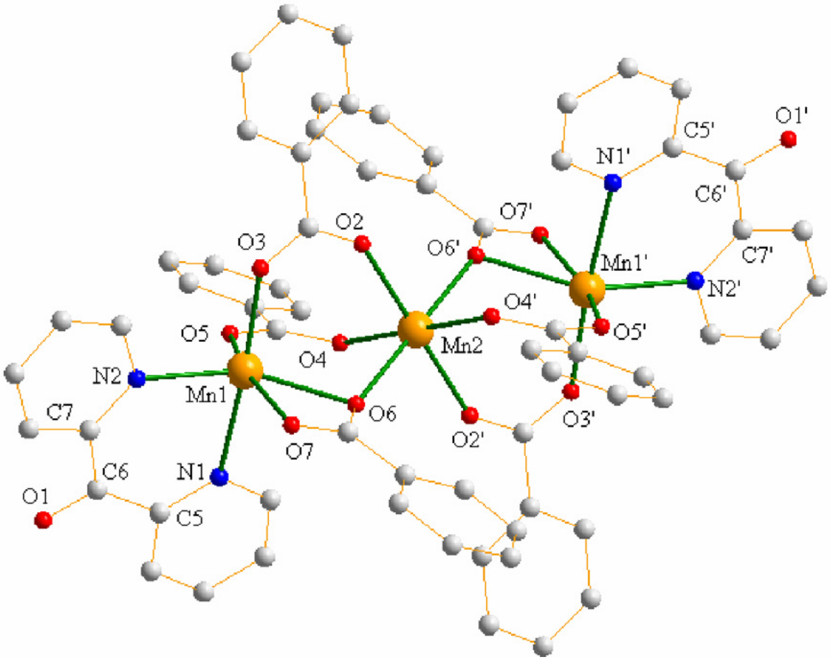


Fig. 2. Partially labeled plot of the linear trinuclear molecule present in complex **1**. Primes are used for symmetry related $(-x, -y, -z + 1)$ atoms. Selected interatomic distances (Å) and angles (°): Mn(1)···Mn(2) 3.552(2), Mn(1)–N(2) 2.240(3), Mn(1)–O(6) 2.238(2), Mn(2)–O(6) 2.214(2), C(6)–O(1) 1.210(6), N(1)–Mn(1)–N(2) 83.7(1), Mn(1)–O(6)–Mn(2) 105.9(1).

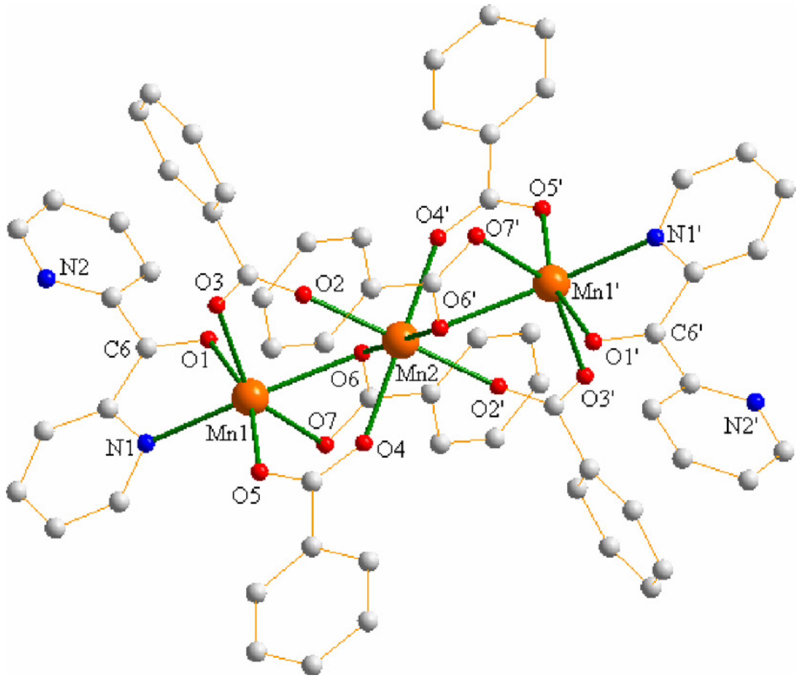
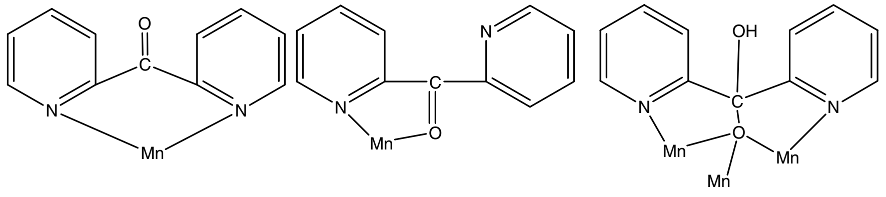


Fig. 3. Partially labeled plot of the linear trinuclear molecule present in complex **2** · 2MeCN. Primes are used for symmetry related ($-x, -y, -z$) atoms. Selected interatomic distances (Å) and angles (°): Mn(1)···Mn(2) 3.573(2), Mn(1)–N(1) 2.260(3), Mn(1)–O(1) 2.311(3), Mn(1)–O(6) 2.322(3) Mn(2)–O(6) 2.272(3), C(6)–O(1) 1.220(4), O(1)–Mn(1)–N(1) 70.4(1), Mn(1)–O(6)–Mn(2) 102.2(1).



I **II** **III**

Fig. 4. The crystallographically established coordination modes of $(py)_2CO$ and $(py)_2C(OH)O^-$ in complexes **1**, **2** · 2MeCN and **4**.

the third structurally characterized example of a compound that contains $(py)_2CO$ in its κ^2N,O ligation mode; the previous two examples are the above mentioned Ru(II) complex [20] and the organometallic compound $[(\eta^5\text{-}C_5H_5)Rh\{(py)_2CO\}]$ [23]. Based on their excellent synthetic and NMR studies in $Ru^{II}/Cl^-/dmso/(py)_2CO$ chemistry [20], Toyama et al. have reached the conclusion that the κ^2N,O coordination mode of $(py)_2CO$ is kinetically favourable due to the small O donor atom of the carbonyl group, but the κ^2N,N' mode is more thermodynamically stable. In accordance with this, the $Mn(O_2CPh)_2/(py)_2CO$ reaction solution was yellow (i.e. the colour of **2** · 2MeCN) in the initial stage, which suggested that the species with κ^2N,O-$(py)_2CO$ formed. The solution turned orange (i.e. the colour of **1**) upon storage and the amount of crystalline **1** precipitated and was significantly larger than that of **2** · 2MeCN. It should be mentioned at this point that when reflux was applied to the reaction only orange crystals of **1** were isolated [24]. Furthermore, once formed and isolated, the orange isomer **1** does not transform into **2** in MeCN even though the reaction mixture is refluxed overnight.

With hindsight: (i) the instability of the yellow crystals is attributed to the lattice MeCN molecules, and (ii) the low wavenumber (1640 cm^{-1}) for the ν(CO) vibration in the IR spectrum of **2** · 2MeCN is due to the carbonyl coordination in the yellow isomer; this vibration appears at 1684 cm^{-1} in the spectrum of free $(py)_2CO$ [14].

Complexes **1** and **2** · 2MeCN join a small family of trinulear Mn(II) carboxylate complexes containing the $\{Mn_3(\eta^1{:}\eta^1{:}\mu_2\text{-}O_2CR)_6\}$ unit [21,22,25].

The X-band powder EPR spectra of **1** and **2** at 4 K are similar and quite complicated with resonances at $g = {\sim}6.3$, ~3.4 and ~2.0 denoting [26] that the populated spin state exhibits zero-field splitting (ZFS). If the ZFS effects are negligible only a narrow signal may arise around $g = 2$. However, if the ZFS is considerable, this signal should be split into several features and thus signals at low field may be observed [26], as found here.

Complexes **1** and **2** are not the only products from the general $Mn(O_2CPh)_2 \cdot 2H_2O/(py)_2CO$ reaction system. The 1:1 reaction of $Mn(O_2CPh)_2 \cdot 2H_2O$ and $(py)_2CO$ in CH_2Cl_2 (used as received) gives a colourless solution which upon layering with *n*-hexane yields polyhedral, colourless crystals of $[Mn_4(O_2CPh)_4\{(py)_2C(OH)O\}_4]$ (**4**) according to Eq. (1); the yield is ~55%.The metal ion-mediated nucleophilic attack of H_2O (from the solvent and/or the starting material) on the carbonyl group is responsible for the formation of the *gem*-diolate(-1) ligand $(py)_2C(OH)O^-$ (Fig. 1) [10]. The eletrophilic character of the carbonyl carbon atom of $(py)_2CO$ is increased by coordination of the carbonyl oxygen to Mn^{II} (direct polarization) and/or coordination of the more remote 2-pyridyl sites (induced polarization) [10]

$$4Mn(O_2CPh)_2\cdot 2H_2O + 4(py)_2CO \xrightarrow{CH_2Cl_2} \underset{\mathbf{4}}{[Mn_4(O_2CPh)_4\{(py)_2C(OH)O\}_4]} + 4PhCO_2H + 4H_2O \qquad (1)$$

The tetranuclear molecule of **4** (Fig. 5) lies on an inverse four-fold axis (S_4 symmetry) and the asymmetric unit contains a quarter of the cluster molecule. The molecule has a cubane $[Mn_4(\mu_3\text{-}OR)_4]^{4+}$ core with Mn^{II} and oxygen atoms occupying alternate vertices of the cube. Thus, the molecule consists of two interpenetrating tetrahedra: one of the four Mn^{II} atoms and one of the four μ_3-oxygen atoms originating from the $(py)_2C(OH)O^-$ ligands. In addition to three μ_3-oxygen atoms, each Mn^{II} is coordinated to two N atoms belonging to two different $(py)_2C(OH)O^-$ ligands and to one oxygen atom belonging to a monodentate benzoate group to complete a distorted octahedral N_2O_4 coordination environment. One oxygen atom (O(2)) of each $(py)_2C(OH)O^-$ ligand remains protonated and unbound to the metal ions. The resultant monoanion functions as an $\eta^1:\eta^1:\eta^1:\mu_3$ ligand (**III** in Fig. 4) forming two five-membered MnNCCO chelating rings with two different metal ions (these rings share a common C–O edge) and an alkoxide-type bond to a third Mn^{II} atom.

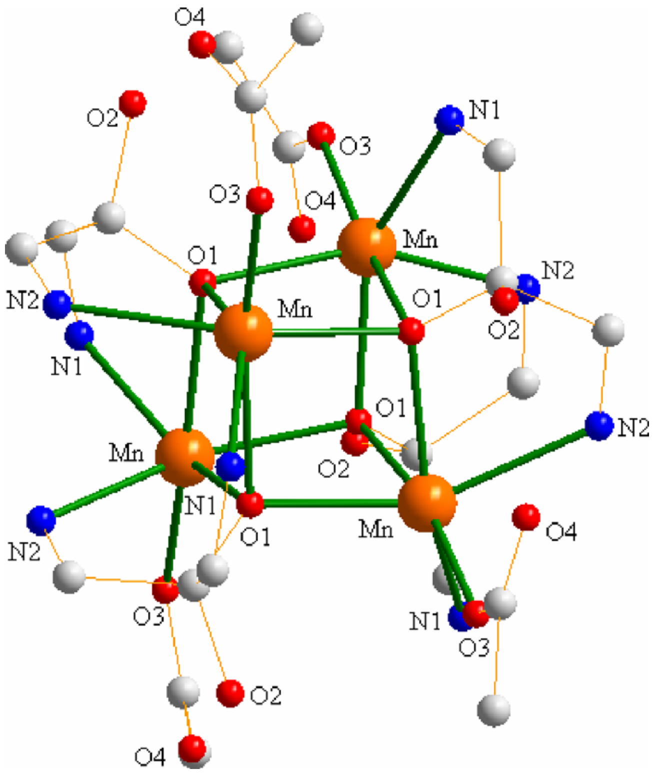


Fig. 5. Partially labeled plot of the linear tetranuclear molecule present in complex **4**. Identical numbers are used for symmetry related atoms. Most carbon atoms of the 2-pyridyl rings have been omitted for clarity. Only the *ipso* atoms of the $PhCO_2^-$ ligands have been drawn. O(1) and O(2) are the oxygen atoms of the $(py)_2C(OH)O^-$ ligands, while O(3) and O(4) belong to the benzoate group. Selected interatomic distances (Å) and angles (°): Mn···Mn 3.353(2) and 3.445(2), Mn–N(1) 2.250(6), Mn–N(2) 2.273(5), Mn–O(1) 2.170(4), 2.178(4) and 2.327(5), Mn–O(3) 2.086(5), O(1)–Mn–O(3) 165.4(2), N(1)–Mn–O(1) $(-x+2, -y, z)$ 146.0(2), Mn–O(1)–Mn 96.4(1), 99.7(1) and 100.9(1).

The Mn_4 tetrahedron is distorted by compression along a S_4 axis and this gives four shorter Mn···Mn distances (3.353 Å) and two longer (3.445 Å). There are two types of Mn–O (alkoxide-type) bonds for each metal ion: one bond is long (2.327(5) Å), whereas the other two distances are shorter (average 2.174(4) Å). The cube deviates from the ideal geometry. The internal cube angles at the metal vertices (RO–Mn–OR) average 80.2°, whereas the corresponding angles at the alkoxide corners (Mn–OR–Mn) are larger averaging 99.0°. Each $(py)_2C(OH)O^-$ hydroxyl group is strongly intramolecularly hydrogen bonded to the uncoordinated oxygen atom of a benzoate ligand; the dimensions of the intracubane hydrogen bonds are O(2)···O(4) 2.693 Å, HO(2)···O(4) 1.884 Å and O(2)–HO(2)···O(4) 168.4°. A few more cubane clusters containing the $[Mn_4(\mu_3\text{-}OR)_4]^{4+}$ cores have been reported previously [9,11f,27].

The IR spectrum of **4** does not exhibit a band in the region for the carbonyl stretching vibration as expected, with the nearest band at 1596 cm^{-1} which can be assigned as a 2-pyridyl stretching mode (this band also has a $\nu_{as}(CO_2)$ character) raised from 1582 cm^{-1} on coordination, as observed earlier [11f] upon complex formation involving hydration of $(py)_2O$. The strong band at 1390 cm^{-1} is assigned to the $\nu_s(CO_2)$ mode. The difference $\Delta(\Delta = \nu_{as}(CO_2) - \nu_s(CO_2) = 1596 - 1390 = 206\ cm^{-1})$ is larger than that for NaO_2CPh (184 cm^{-1}), as expected [28] for the monodentate mode of carboxylate ligation.

Variable-temperature dc magnetic susceptibility data (Fig. 6) were collected at 1000G for powdered **4** over the temperature range $5 \leqslant T \leqslant 300$ K. The room temperature $\chi_M T$ value is 16.5 $cm^3\ mol^{-1}$ K, slightly lower than the expected value of 17.5 $cm^3\ mol^{-1}$ K for four $S = 5/2$ uncoupled spins with $g = 2$. The $\chi_M T$ product remains practically constant down to 150 K and then decreases sharply, reaching a value of 5.57 $cm^3\ mol^{-1}$ K at 5 K. The data suggest that the cluster appears to possess weak intramoleular antiferromagnetic interactions [9,11f,27]. Since the spin carriers are all d^5 Mn^{II} ions, and therefore orbital singlet (S) ions, only the isotropic part of the exchange interaction was considered.

When a symmetrical spin Hamiltonian, $H = \Sigma_{i,j(i=j)}\ 2J\ (S_iS_j)$, with all coupling constants assumed to be equal was applied, the high-temperature $\chi_M T$ could not be

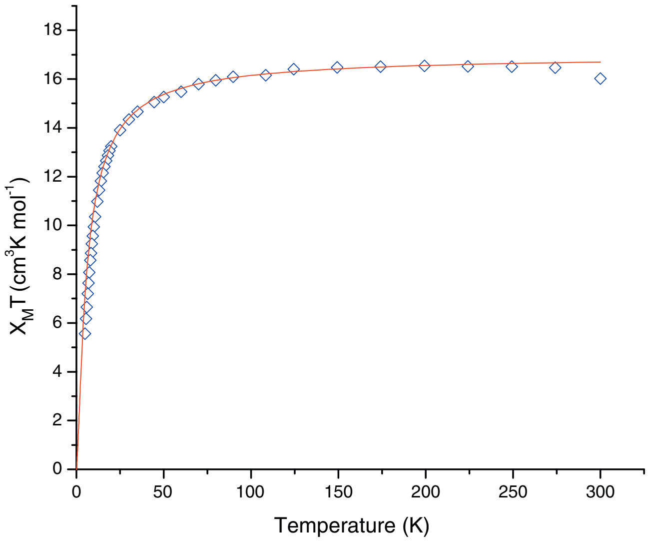


Fig. 6. Plot of $\chi_M T$ as a function of T for a powdered sample of **4**. The solid line represents the simulated data function plot.

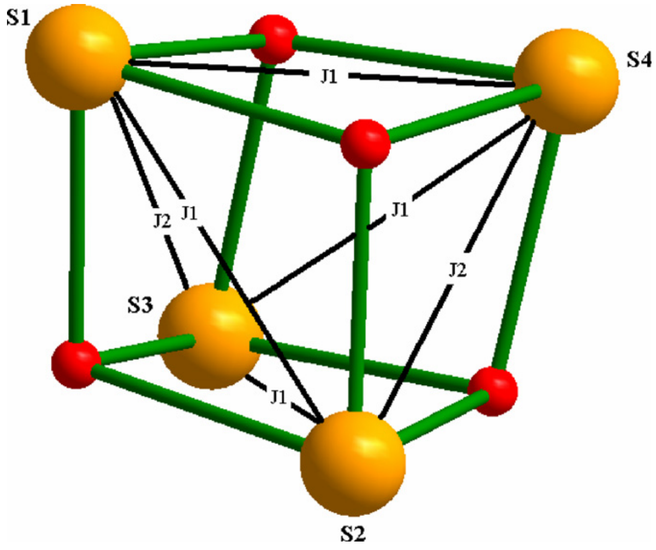


Fig. 7. Assignments of J values to Mn···Mn interactions for the best magnetic model with two coupling constants for **4**.

reproduced. To find a more accurate, less symmetrical Hamiltonian, the actual S_4 symmetry of the molecule was taken into account. This suggested the use of the spin Hamiltonian given in Eq. (2).

$$H = -2J_1(S_1S_2 + S_1S_4 + S_2S_3 + S_3S_4) - 2J_2(S_1S_3 + S_2S_4) \tag{2}$$

J_1 was attributed to the four shorter Mn···Mn distances of 3.353 Å (the Mn–O(1)–Mn angles are 96.4 and 100.9°) and J_2 to the two longer ones of 3.445 Å (the corresponding Mn–O(1)–Mn angles are equal to 99.7°), see Fig. 7. The simulation was performed using the program MAGPACK [29]. The best fit parameters are $J_1 = -0.25$ cm^{-1}, $J_2 = -0.10$ cm^{-1} and $g = 1.97$. The corresponding energy levels have the $S_T = 0$ as the ground state with the $S_T = 1$ (0.6 cm^{-1}) and $S_T = 2$ (1.8 cm^{-1}) levels very close in energy. The J values of **4** are within (J_1) or close (J_2) to the narrow antiferromagnetic range (−0.22 to −4.11 cm^{-1}) reported [9,11f,27] for other cubane complexes containing the $[Mn_4(\mu_3\text{-}OR)_4]^{4+}$ core.

The X-band powder EPR spectrum of **4** at 18 K exhibits an almost featureless broad resonance with a $g = \sim 2.0$ value. The broadness of this isotropic EPR absorption is consistent with the presence of magnetically interacting Mn^{II} ions in the solid-state [30].

An important chemical message from this preliminary work is that the $PhCO_2^-/(py)_2CO$ 'blend' looks like a promising candidate ligand system for the generation of interesting Mn complexes. Complexes **1**, **2** and **4** augur well that they are merely the first members of a new family of Mn carboxylate clusters with $(py)_2CO$-based ligands. Attempts to prepare high-nuclearity Mn(III) and/or mixed-valence Mn benzoate clusters involving various forms of $(py)_2CO$ (including the dianionic ligand $(py)_2CO_2^{2-}$) are in progress.

Supplementary material

CCDC 660964, 660965 and 660966 contain the supplementary crystallographic data for **1**, **2** · 2MeCN and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[16] The yellow crystals had been found to lose solvent rapidly, and they were kept in the mother liquor until a suitable crystal was selected for crystallography.

[17] *Crystallographic data*: **1**: $C_{64}H_{46}N_4Mn_3O_{14}$, $M = 1259.9$, triclinic, $P\bar{1}$, $a = 12.086(4)$ Å, $b = 11.481(4)$ Å, $c = 11.771(4)$ Å, $\alpha = 80.92(1)°$, $\beta = 68.34(1)°$, $\gamma = 69.73(1)°$, $V = 1423.2(8)$ Å^3, $Z = 1$, $D_c = 1.470\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo\,K\alpha}) = 0.728\ \mathrm{mm^{-1}}$, $T = 298$ K, 5267 reflections collected, 4992 unique ($R_{int} = 0.0100$), R_1 on $F(wR_2$ on $F^2) = 0.0473\ (0.1122)$ for 3998 observed ($I > 2\sigma(I)$) reflections. **2** · 2MeCN: $C_{68}H_{52}N_6Mn_3O_{14}$, $M = 1342.0$, triclinic, $P\bar{1}$, $a = 14.33(1)$ Å, $b = 10.957(4)$ Å, $c = 11.197(9)$ Å, $\alpha = 99.58(3)°$, $\beta = 109.05(2)°$, $\gamma = 99.47(3)°$, $V = 1593(2)$ Å^3, $Z = 1$, $D_c = 1.399\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo\,K\alpha}) = 0.656\ \mathrm{mm^{-1}}$, $T = 298$ K, 5309 reflections collected, 5008 unique ($R_{int} = 0.0355$), R_1 on $F(wR_2$ on $F^2) = 0.0448\ (0.0974)$ for 3620 observed ($I > 2\sigma(I)$) reflections. **4**: $C_{72}H_{56}N_8Mn_4O_{16}$, $M = 1509.03$, tetragonal, $I\text{-}42d$, $a = 14.56(1)$ Å, $b = 14.56(1)$ Å, $c = 38.27(3)$ Å, $V = 8117(11)$ Å^3, $Z = 4$, $D_c = 1.235\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo\,K\alpha}) = 0.671\ \mathrm{mm^{-1}}$, $T = 298$ K, 3881 reflections collected, 3579 unique,($R_{int} = 0.0189$), R_1 on $F(wR_2$ on $F^2) = 0.0560\ (0.1646)$ for 2819 observed ($I > 2\sigma(I)$) reflections.

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