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Supramolecular Interactions as Determining Factors of the Geometry of Metallic Building Blocks: Tetracarboxylate Dimanganese Species**

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Notwithstanding the richness of manganese carboxylate chemistry,[1] dimanganese tetracarboxylate species with a copper acetate-like core have been characterized only

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recently.[2] At the time of our report on $[Mn(tda)(bipy)]_n$ (**1**) (tda = thiodiacetate = $S(CH_2COO)_2^{2-}$; bipy = 2,2′-bipyridine),[2] the only other known examples either lacked detailed structural information ($[Mn_2(C_3F_7CO_2)_4(bipy)_2]$[3]) or had not been deposited in the Cambridge Structural Database[4] ($[Mn_2(Ph_2XCCO_2)_4(quinoline)_2]$;[5] X = H, Me). Another example, $[Mn_2(\mu\text{-}OOC\mathit{t}Bu)_4\{OC(\mathit{t}Bu)OHNEt_3\}_2]$, has appeared recently.[6] In **1**, the bimetallic $\{Mn_2(\mu\text{-carboxylate})_4\}$ units, completed by two terminal bipy ligands and interconnected by pairs of CH_2SCH_2 spacers, form linear chains which further organize into a supramolecular structure through noncovalent interactions.[7,8] Copper acetate itself and other metal carboxylate synthons often generate metal-organic frameworks (MOF) through coordinative bonds,[7] whereas the overall architecture of **1** stems from the interactions between the 1D polymeric chains. In fact, the bipy ligands of adjacent chains, which are all parallel to each other, are π-stacked in a gearlike arrangement with the formation of compacted 2D sheets. In order to understand better the correlations between the geometry of the building blocks and the given supramolecular structure, we have tried to combine the Mn–tda unit with other N-donor chelating ligands.

X-ray studies of complexes obtained with 1,10-phenanthroline[9] and 4,4′-dimethoxy-2,2′-bipyridine showed that they are not isostructural with **1**, possibly because of the steric requirements of the different ligands (see the Supporting Information). To minimize these, we selected the ligands 4,4′-dimethyl-2,2′-bipyridine (4,4′-Me_2bipy) and 5,5′-dimethyl-2,2′-bipyridine (5,5′-Me_2bipy), which contain a pair of the smallest alkyl substituents, CH_3 groups, that are not adjacent to the N donors. The synthetic procedure was maintained as close as possible to that of **1**: we treated each of the above ligands with $[Mn(tda)(H_2O)]_n$ (**2**), which is obtainable in good yields by the reaction of aerobic aqueous solutions of $MnCl_2$ with a 1:1 mixture of Na_2CO_3 and thiodiacetic acid.[2] Two new compounds were crystallized that, like **1**, exhibit a 1:1:1 ratio of Mn, tda, and the N-chelate. From X-ray analyses, both products were shown to be one-dimensional polymers of formula $[\{Mn(N\text{-}N)\}_2(\mu\text{-}tda)_2(\mu\text{-}H_2O)]_n$ (N-N = 4,4′-Me_2bipy, **3**; 5,5′-Me_2bipy, **4**), formed by binuclear units with a core different from that of copper acetate. Both compounds exhibit antiferromagnetic behavior (see the Supporting Information for details). The estimated value of J (5.5 ± 0.1 cm^{-1}) matches those of other binuclear Mn^{II} species with structures similar to **3** and **4** (i.e., similar local coordination, Mn–Mn separation, and a unique Mn–O–Mn bridge).[10–12] The larger J value found for **1** (8.2 cm^{-1})[2] indicates that the exchange interaction is more efficient with four rather than two *syn-syn* carboxylato and one μ-H_2O bridges.[13]

As shown in Figure 1,[14] the structure of **3** (that of **4** is similar, see the Supporting Information) consists of extended ribbons formed by binuclear Mn_2 units linked through pairs of CH_2SCH_2 spacers. In contrast to **1**, two of the four carboxylate groups coordinated to the Mn_2 unit adopt monodentate coordination to each metal atom, thereby affording an unprecedented bridging mode (μ_3-κ^1(O),κ^1(O′)-κ^1(O″)) for the tda ligand. In the binuclear core, a bridging water molecule (O9) forms two strong hydrogen bonds with the uncoordinated oxygen atoms of the two monodentate carboxylate groups (the contacts O2···O9 and O6′···O9 are 2.547 and 2.561 Å, respectively). Finally, two terminal Me_2bipy ligands, which are now almost orthogonal to each other (dihedral angle 72°) rather than parallel, complete a pseudo-octahedral geometry at each metal. With respect to **1**, the loss of the trigonal-prismatic coordination (TP) does not affect the Mn···Mn separation, which remains nonbonding (3.581(1) Å and 3.502(1) Å, in **3** and **1**, respectively). The arrangement $[\{M(\kappa^1\text{-}OOCR)L_2\}_2(\mu\text{-}OOCR)_2(\mu\text{-}H_2O)]$ (L_2 = two monodentate N-donor ligands or a bidentate one) is common for divalent metal ions,[15] and includes four manganese examples.[10,11,16] One of these, which contains the ligand 4,4′-Me_2bipy,[11] has been proposed as a model for the active site of dimanganese enzymes.[17]

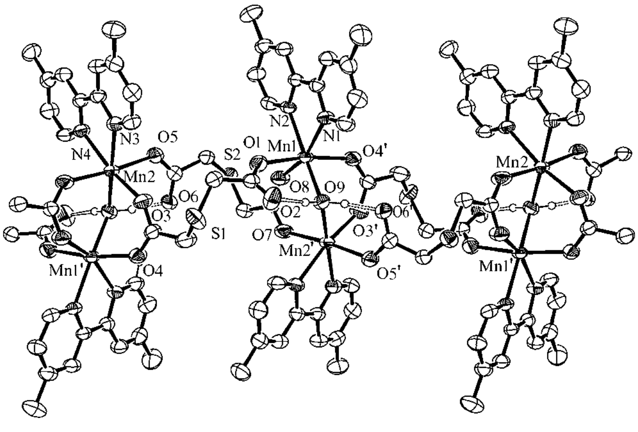

Figure 1. ORTEP drawing of polymer **3** propagated along the y axis. The H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Mn1–O1 2.203(4), Mn1–O8 2.113(4), Mn1–O4′ 2.166(3), Mn1–O9 2.218(3), Mn2–O3 2.140(3), Mn2–O5 2.182(4), Mn2′–O7 2.136(4), Mn2′–O9 2.234(4), Mn1···Mn2′ 3.581(1); Mn1-O9-Mn2′ 107.1(2). The symbol ′ corresponds to the transformation $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

The fact that the structure of **1** differs from those of **3** and **4** seems attributable to the methyl substituents on the bipyridine ligand in **3** and **4**. As highlighted before,[2] the threading of the ribbons in **1** stems from a head-to-tail interpenetration of the parallel bipy ligands and the formation of extended 2D sheets. The degree of π-stacking is definitely more compact here than that described for similar systems.[18] In this respect, the interaction mode between the bipy ligands in **3** and **4** is evidently different from that in **1** (see the Supporting Information). First, the nonparallel disposition of the two bipy ligands in each binuclear unit determines the presence of an extended 3D packing rather than 2D sheets. Moreover, the presence of methyl substituents does not allow the same degree of interpenetration between the parallel bipy ligands of adjacent chains. The loss of compactness with respect to **1** is confirmed by the lower crystal densities of **3** and **4**, in spite of their 10% larger molecular weights (1.520, 1.540, and 1.705 g cm^{-3} for **3**, **4**, and **1**, respectively). The different situation can be qualitatively appreciated by looking at the projections of two facing bipy ligands down their normal vectors (Figure 2).

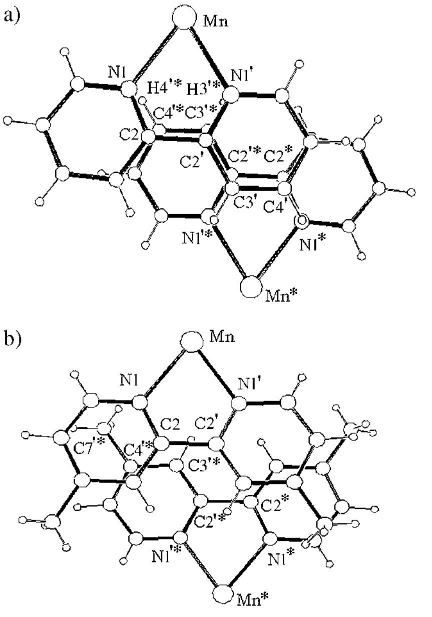

Figure 2. Comparative projections of the facing {Mn(bipy)} and {Mn(4,4'-Me$_2$bipy)} fragments in **1** (a) and **3** (b) down axes perpendicular to the bipy ligands. The atom of the bipy skeleton are indicated by standard labeling (the applied symmetry operations (*) are: $-x$, $1-y$, $1-z$ and $-x+{}^1\!/_2$, $-y+{}^1\!/_2$, $-z$ for compounds **1** and **3**, respectively).

In **1**, five C–C bonds of two stacked bipy ligands are mutually eclipsed, as are seven C–H bonds. Conversely, a slippage of the two projected ligands in **3** elongates the separation between the symmetry-related Mn atoms by about 0.4 Å with respect to **1**. This avoids a shortened contact between one CH$_3$ group and the coordination sphere of the facing metal atom (e.g., the atom Mn and the group at C7'* in **3**). If, in the lattice of **1**, the H4'* atom was replaced by a CH$_3$ group, the latter would clash with the coordination sphere of the facing Mn atom (contacts <2 Å). Another aspect of the bipy geometry in **1** is the 10° twisting of the two six-membered rings around the connecting C2–C2' bond. As a consequence, the contacts between the eclipsing atoms N1/H4'* and N1'/H3'* (and their symmetry equivalents) are significantly shorter (3.15 and 3.45 Å) than the separation of the bipy mean squares planes (4.01 Å). Although not exceptionally short, the latter N···H distances suggest that an important contribution to the overall stacking originates from the four π–σ interactions between the H atoms and the p$_\pi$-orbitals of the N atoms for any pair of bipy ligands.[18] Finally, another possible contribution to the compactness of the interpenetrating ribbons in **1** may be due to a residual interaction between the thioether sulfur atom and a bipy C–H bond (3.32 Å). Conversely, the slippage in **3** minimizes such a hydrogen bonding (if any), since the S···H–C separation increases to 3.71 Å.

Comparative DFT calculations were performed for the discrete binuclear units of **1** and **3**, with no methyl substituents in either case. The optimized geometry of [Mn$_2$(OOCH)$_2$(bipy)$_2$(μ-OOCH)$_2$(μ-H$_2$O)] (**3a**) satisfactorily reproduces that of the building block in **3**, including the two quasi-orthogonal bipy ligands (84°). The [Mn$_2$(μ-OOCH)$_4$(bipy)$_2$] unit was first optimized by imposing D_{2h} symmetry (model **1a**). The computed parameters are sufficiently similar to those of the actual compound **1** (see the Supporting Information), but the number of imaginary frequencies suggested that **1a** is not a minimum. A new optimization without symmetry constraints provided an actual minimum, **1b**, with a different coordination geometry. In particular, the local coordination at the Mn atoms is no longer TP but almost octahedral (one of the O–Mn–O angles opens to 166°), and the terminal bipy ligands are far from being coplanar (dihedral angle of about 66°). Energetically, **1b** is more stable than **1a** by only 1.2 kcal mol^{-1}, a result which is consistent with the zero crystal-field stabilization energy for d^5 high-spin metal systems and their facile and subtle adaptation to alternative coordination environments.[19] In contrast, the comparison of the energies associated with **3a** and **1a** is very significant as the former species is more stable with respect to the system **1a** + H$_2$O by as much as 20.4 kcal mol^{-1}. While the entropic factor should favor separated components, complex **3a** must receive a considerable amount of stabilization from the intramolecular hydrogen bonding between water and free carboxylate oxygen atoms. Since the structure of **3** is not experimentally observed in the presence of the bipy ligand, the formation of complex **1** can only be caused by more-energetic noncovalent interactions between the coordination polymers.

In conclusion, this study provides evidence that the noncovalent interactions between coordination polymers in a supramolecular system can ultimately affect the primary structure of the metallic building blocks. In general, metallic building blocks are used in supramolecular chemistry to generate specific directional patterns, while the present case reverses such a paradigm. In fact, the geometry of the building block adapts to support the most-stabilized supramolecular architecture.

Experimental Section

3: A solution of **2**[2] (0.113 g, 0.5 mmol) in 20 mL of water was treated with a solution of 4,4'-Me$_2$bipy (0.092 g, 0.5 mmol) in 20 mL of ethanol. The mixture was heated at 90 °C for 2 h and then it was concentrated to a volume of 15 mL. The resultant solution was filtered and yellow crystals of **3** suitable for single-crystal X-ray structure analysis were obtained after slow evaporation of the solvent at ambient temperature for several days. Yield: 0.12 g (60 %). IR (Nujol mull on NaCl plates): $\tilde{\nu} = 3588$–3249 (br), 1970 (br, m), 1619 (s), 1553 (s), 1528 (s), 1486 (m), 1454 (s), 1397 (s), 1306 (m), 1289 (w), 1236 (m), 1209 (s), 1166 (w), 1130 (w), 1096 (w), 1037 (w), 1012 (s), 936 (m), 919 (m), 887 (m), 843 (w), 830 (s), 792 (m), 767 (w), 718 (w), 686 (s), 675 (s), 665 (m) cm^{-1}. Elemental analysis (%) calcd for C$_{16}$H$_{17}$MnN$_2$O$_{4.5}$S: C 48.49, H 4.32, N 7.07; found C 47.90, H 4.26, N 6.80.

Complex **4** was obtained by a similar synthetic procedure as yellow crystals (0.17 g, 82 % yield). IR (Nujol mull on NaCl plates): $\tilde{\nu} = 3029$ (br, s), 1970 (br, m), 1615 (s), 1569 (s), 1526 (s), 1499 (s), 1484 (s), 1446 (s), 1387 (s), 1319 (m), 1245 (m), 1234 (m), 1212 (s), 1181 (m), 1164 (m), 1153 (m), 1089 (m), 1043 (s), 990 (w), 953 (w), 938 (m), 892 (m), 843 (m), 832 (m), 810 (w), 793 (m), 771 (m), 734 (m), 670 (s), 648 (m) cm^{-1}. Elemental analysis (%) calcd for C$_{16}$H$_{17}$MnN$_2$O$_{4.5}$S: C 48.49, H 4.32, N 7.07, S 8.09; found C 48.38, H 4.18, N 7.15, S 8.13.

The geometries of the complexes [Mn$_2$(μ-OOCH)$_4$(bipy)$_2$] (**1a** and **1b**) and [Mn$_2$(OOCH)$_2$(bipy)$_2$(μ-OOCH)$_2$(μ-H$_2$O)] (**3a**) were computed by density functional calculations at the unrestricted BP86[20] level of theory using the 6-31G* basis set. The multiplicity was imposed to $S = 5$, in agreement with the experimental data recorded at room temperature. Vibrational frequency calculations by diagonalization of the analytically computed Hessian were carried out for all models. Structures **1b** and **3a** (both optimized without symmetry constraints) correspond to real minima in the potential-energy surface. Conversely, **1a** (imposed D_{2h} symmetry) is characterized by six imaginary frequencies that involve displacement of some atoms in order to break the imposed symmetry (all of them smaller than $60\,\mathrm{cm}^{-1}$). For the energy differences, single-point calculation on the previously optimized structures were carried out with the 6-311+G** basis set. All calculations were performed with the Gaussian 98 package of programs.[21]

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[1] See, for example: *Comprehensive Coordination Chemistry*, *Vol. 4* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, **1987**, chap. 1.

[2] A. Grirrane, A. Pastor, A. Galindo, A. Ienco, C. Mealli, P. Rosa, *Chem. Commun.* **2003**, 512.

[3] a) S. Menage, PhD Thesis, University of Paris Sud, Orsay, France, **1988**, and private communication; b) an ORTEP diagram is shown in: H. Mimoun, L. Sausine, S. Menage, J.-J. Girerd in *New Developments in Selective Oxidation* (Eds.: G. Centi, F. Trifiro), Elsevier, Amsterdam, **1990**.

[4] Cambridge Structural Database: F. H. Allen, O. Kennard, *Chem. Des. Autom. News* **1993**, *8*, 31.

[5] M. Nakashima, H. Maruo, T. Hata, T. Tokii, *Chem. Lett.* **1999**, 1277.

[6] E. V. Amel'chenkova, T. O. Desinova, S. E. Nefedov, *Mendeleev Commun.* **2004**, *3*, 1.

[7] a) L. Brammer, *Chem. Soc. Rev.* **2004**, *33*, 476; b) C. Janiak, *Dalton Trans.* **2003**, 2781; c) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319; d) L. Brammer, M. D. Burgard, C. S. Rodger, J. K. Swearingen, N. P. Rath, *Chem. Commun.* **2001**, 2468.

[8] Selected examples of the influence of noncovalent interactions on structure include: a) H. Adams, J.-L. Jiménez Blanco, G. Chessari, C. A. Hunter, C. M. R. Low, J. M. Sanderson, J. G. Vinter, *Chem. Eur. J.* **2001**, *7*, 3494; b) J. W. Steed, K. Johnson, C. Legido, P. C. Junk, *Polyhedron* **2003**, *22*, 769.

[9] A Mn–tda complex containing a phen ligand has been characterized recently by X-ray crystallography: J. Marek, Z. Travnicek, P. Kopel, *Acta Crystallogr. Sect. C* **2003**, *59*, m429.

[10] B.-H. Ye, T. Mak, I. D. Williams, X.-Y. Li, *Chem. Commun.* **1997**, 1813.

[11] S.-B. Yu, S. J. Lippard, I. Shweky, A. Bino, *Inorg. Chem.* **1992**, *31*, 3502.

[12] A. Caneschi, F. Ferraro, D. Gatteschi, M. C. Melandri, P. Rey, R. Sessoli, *Angew. Chem.* **1989**, *101*, 1408; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1365.

[13] A dependence of J on the nature of the carboxylate bridge in manganese(II) complexes has been reported recently: S. Durot, C. Policar, G. Pelosi, F. Bisceglie, T. Mallah, J.-P. Mahy, *Inorg. Chem.* **2003**, *42*, 8072.

[14] Diffraction data for **3** and **4** were collected at room temperature on a Philips PW 1100 ($\lambda = 1.54180$ Å) and an Enraf Nonius CAD4 ($\lambda = 0.71073$ Å) automatic diffractometer, respectively. Crystallographic data for **3**: $C_{32}H_{34}Mn_2N_4O_9S_2$, $M_r = 792.63$, monoclinic, $C2/c$, $a = 21.120(4)$, $b = 17.270(5)$, $c = 22.467(4)$ Å, $\beta = 122.29(2)°$, $V = 6927(3)$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.520\,\mathrm{Mg\,m^{-3}}$, $\mu = 7.560\,\mathrm{mm^{-1}}$, reflections collected/unique 4679/4365, $R = 0.0516$ ($I > 2\sigma(I)$), $Rw = 0.1271$. Crystallographic data for **4**: $C_{32}H_{34}Mn_2N_4O_9S_2$, $M_r = 792.63$, monoclinic, $P2_1/n$, $a = 12.4650(14)$, $b = 17.101(6)$, $c = 16.1130(19)$ Å, $\beta = 95.42(1)°$, $V = 3419.4(13)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.540\,\mathrm{Mg\,m^{-3}}$, $\mu = 0.920\,\mathrm{mm^{-1}}$, reflections collected/unique 4936/4746, $R = 0.0369$ ($I > 2\sigma(I)$), $Rw = 0.0848$. CCDC-257325 (**3**) and -257326 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] CCDC search: 38 hits.

[16] B.-H. Ye, I. D. Williams, X.-Y. Li, *J. Inorg. Biochem.* **2002**, *92*, 128.

[17] For a recent review on this subject see, for example: A. J. Wu, J. E. Penner-Hahn, V. L. Pecoraro, *Chem. Rev.* **2004**, *104*, 903.

[18] For a critical account on π–π stacking see, for example: C. Janiak, *J. Chem. Soc. Dalton Trans.* **2000**, 3885.

[19] See, for example: N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Pergamon, Oxford, **1997**.

[20] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; b) J. O. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.

[21] Gaussian 98 (Revision A.7): M. J. Frisch et al., see Supporting Information