substituted with a secondary amino group at the methylene carbon do not show any inequivalence of the β-protons over the whole temperature range. Thus, only the key-in-the-lock possesses the sufficiently large activation energy necessary for the observation of coalescence under the existing conditions.

Experimental Procedure

The receptor **A** is well known [5]. Phenol **1** was synthesized by addition of adenine to 3,5-di-*tert*-butylquinonemethide [11]. Phenols **2** and **3** were obtained by condensation of 4-bromomethyl-2,6-di-*tert*-butylphenol with adenine and with 2-aminobenzimidazole [10], respectively. All compounds were characterized by current methods. The ^{1}H NMR spectra were obtained on a Bruker AC 250 (250 MHz) spectrometer in CDCl3.

The radicals **1***, **2***, and **3*** were generated in CH_2Cl_2 by oxidation of the corresponding phenols with PbO_2; **A** can be added before or after radical generation. Deoxygenation was done by bubbling argon through the samples. The spectra were recorded with a Bruker ESP 300E spectrometer equipped with an ENDOR unit (Bruker ER 810). Typical instrumental parameters for ENDOR investigations: MW power 30 mW; RF power 7 dB, 500 W; modulation 70 kHz.

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Bis(bipyridine) Ligands in Manganese Carboxylate Cluster Chemistry: Self-Assembly of a Cluster Complex with Two Butterfly-Like $[Mn_4(\mu_3\text{-}O)_2]^{8+}$ Cores**

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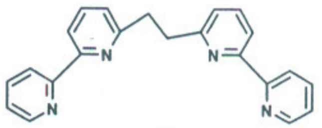
Polypyridyl, oligo-2,2′-bipyridine, and related ligands L have received considerable attention over the last several years.[1–11] The use of such ligands as "programmed" components in self-assembly reactions with metal ions has been a central theme in supramolecular chemistry, and has led to the formation of a variety of metal/ligand supramolecular ensembles. The latter have fascinating structures such as double or triple helices, and "capped", "cylindrical" and "circular" architectures. The resulting redox and photophysical properties have also been of interest. In all the work to date the ligands L have been bound to mononuclear centers and they have also been the only (or in some cases, the majority) ligands to the metals.

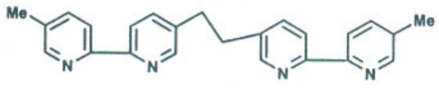
Metal cluster chemistry is another area in which self-assembly of multiple components occurs to produce a "supermolecular" product. We have been interested in carboxylatomanganese clusters for a number of reasons, including the fact that they exhibit highly unusual magnetic properties and, in some cases, are single-molecule magnets.[12, 13]

We report herein the amalgamation of the above two areas, namely the use of bis-2,2′-bipyridine ligands L in carboxylatomanganese cluster formation, in order to explore the influence of the ligand "programming" on both the cluster formed and the nature of the multicomponent assembly; the overall objective is the development of supramolecular chemistry involving metal clusters as components of the supramolecular ensemble.

The two ligands employed were L1[14] and L2.[15] Treatment of $[Mn_3O(O_2CMe)_6(py)_3](ClO_4)$[16] (py = pyridine) with L1 in a 1:1.5 molar ratio in MeCN led to a dark brown solution and subsequent isolation of the tetranuclear complex **1** as a perchlorate salt. Similarly, treatment of $[Mn_3O(O_2CEt)_6(py)_3](ClO_4)$[17] with L2 in a 1:1.5 molar ratio in CH_2Cl_2 led to subsequent isolation of the octanuclear complex **2** as a perchlorate salt. The structure of the cation **1** (Fig. 1)[18] consists of two $[Mn_2O(O_2CMe)_2(L1)]^+$ fragments held together by interfragment linkages Mn1–O3′ and Mn1′–O3. The cation is centrosymmetric and mixed-valent (two Mn^{II}, two Mn^{III}) and, on the basis of the structural parameters, the Mn^{II} and Mn^{III} centers are five-coordinate (Mn2) and six-coordinate (Mn1), respectively. Each resulting $Mn^{II}Mn^{III}$ pair is quadruply bridged by O3, two *syn,syn*-$MeCO_2^-$ groups, and the L1 ligand, which is attached to both metals. There are three types of Mn ··· Mn distances, $Mn^{III} \cdots Mn^{III}$ (2.784(4) Å), intrafragment $Mn^{II} \cdots Mn^{III}$ (3.208(4) Å), and interfragment $Mn^{II} \cdots Mn^{III}$ (3.632(4) Å). The central $[Mn_2O_2]$ unit is asymmetrical; the interfragment Mn^{III}–O bonds (1.8787(6) Å) are noticeably longer than the intrafragment Mn^{III}–O bonds (1.8391(6) Å). Interestingly, all bipyridine (bpy) rings are essentially parallel, providing additional interfragment interactions by π stacking. Complex **1** is a new addition to the family of Mn_4 clusters with a "dimer-of-dimers" structure.[19]



L1



L2

$[Mn_4O_2(O_2CMe)_4(L1)_2](ClO_4)_2$ **1**-$(ClO_4)_2$

$[Mn_8O_4(O_2CEt)_{14}(L2)_2](ClO_4)_2$ **2**-$(ClO_4)_2$

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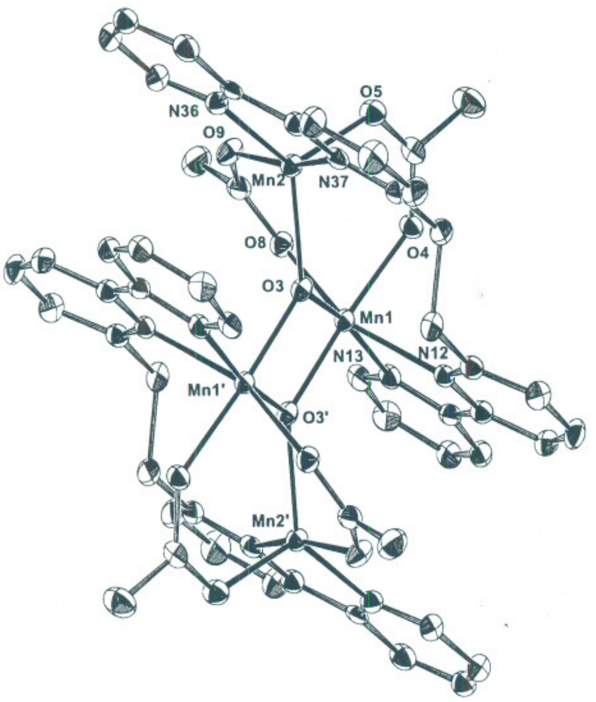

Fig. 1. ORTEP representation of the cation **1**. Selected distances [Å] and angles [ ]: Mn1 ··· Mn1' 2.784(4), Mn1 ··· Mn2 3.208(4), Mn1 ··· Mn2' 3.632(4), Mn1–O3 1.839(1), Mn1–O3' 1.879(1), Mn2–O3 2.030(1), O3-Mn1-O3' 83.01(3), Mn1-O3-Mn1' 96.99(3), Mn1-O3'-Mn2' 136.60(3), Mn1-O3-Mn2 111.93(3).

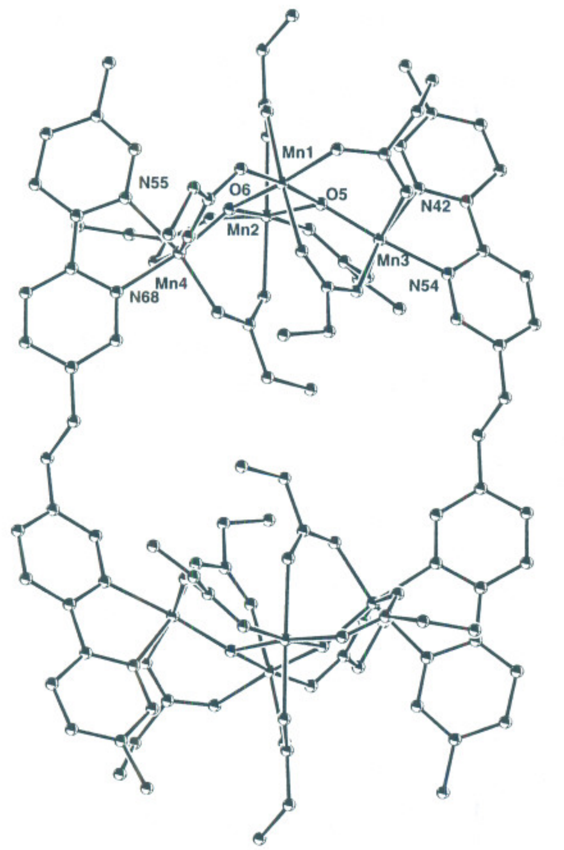

Fig. 2. ORTEP representation of the cation **2**. Selected distances [Å] and angles [ ]: Mn1 ··· Mn2 2.843(4), Mn1–O5 1.889(13), Mn1–O6 1.890(12), Mn2–O6 1.893(13), Mn2–O5 1.899(13), Mn3–O5 1.831(13), Mn4–O6 1.845(13), O5-Mn1-O6 81.6(6), O5-Mn2-O6 81.2(6).

The structure of the centrosymmetric cation **2** (Fig. 2)[18] likewise consists of two fragments, but interfragment linkages are now provided by the two L2 ligands. The fragments have $[Mn_4(\mu_3\text{-}O)_2]^{8+}$ (i.e. four Mn^{III}) butterfly-like cores, arranged face-to-face. If the -CH_2-CH_2- linker groups of the L2 ligands were removed, two previously reported $[Mn_4O_2(O_2CEt)_7(bpy)_2]^+$ units result; this shows that **2** can be viewed as a dimer of clusters with butterfly-like cores in which the fragments are only slightly distorted compared with discrete $[Mn_4O_2(O_2CR)_7(bpy)_2]^+$ species.[17] Inspection of a space-filling model shows no cavity in the center of the cluster.

Variable-temperature magnetic susceptibility data were collected on complexes **1** and **2** (SQUID magnetometer, 10.0 kG field) to investigate the degree of interfragment interaction. Complex **1** exhibits an effective magnetic moment (μ_{eff}) per molecule that smoothly decreases from 8.05 μ_B at 320 K to 1.05 μ_B at 2.0 K (Fig. 3). The data were fit to a model in which the exchange interaction between the interfragment $Mn^{II} \cdots Mn^{III}$ pairs was considered to be negligible because of the relatively long separation. The fit (Fig. 3) employed $-2J\hat{S}_i \cdot \hat{S}_j$ terms for exchange interactions and gives $J(Mn^{III} \cdots Mn^{III}) = -3.2\ cm^{-1}$, J(intrafragment $Mn^{II} \cdots Mn^{III}) = -2.3\ cm^{-1}$, $g = 1.86$ and a small contamination (4%) by paramagnetic Mn^{II} ions. The value of $J(Mn^{III} \cdots Mn^{III})$ shows that interfragment interactions exist in **1**. The variable-field and variable-temperature data indicate that **1** has an $S = 0$ ground state.

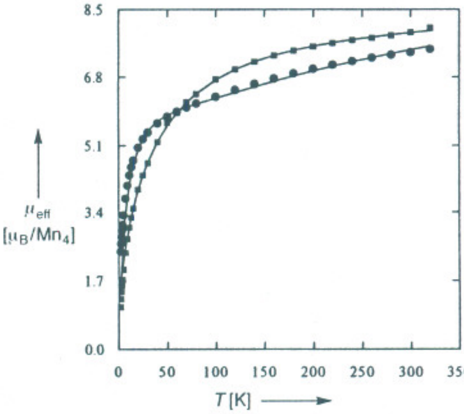

Fig. 3. Plot of the effective magnetic moment, μ_{eff}/Mn_4, vs. temperature for $[Mn_4O_2(OAc)_4(L1)_2](ClO_4)_2$ (**1**, ■) and $[Mn_8O_4(O_2CEt)_{14}(L2)_2](ClO_4)_2$ (**2**, ●) in an applied magnetic field of 10.00 kG. The solid line represents the best fit to the theoretical equation. See text for fitting parameters.

The data for **2** indicate there is negligible exchange interaction between the two butterfly-like $Mn^{III}_4O_2$ fragments. In Figure 3, μ_{eff} per butterfly unit is plotted as a function of temperature. The decrease from 7.51 μ_B (per Mn_4O_2 fragment) at 320 K to 5.82 μ_B at 50.0 K, followed by a rapid decrease to 2.42 μ_B at 2.0 K, parallels what has been seen[17, 20] for other butterfly-like $Mn^{III}_4O_2$ complexes. In fact, the data could be fit assuming the two butterfly-like fragments do not interact to give $J_{wb} = -10.5\ cm^{-1}$, $J_{bb} = -27.4\ cm^{-1}$, and $g = 2.00$, where J_{wb} characterizes the wing-tip-body $Mn^{III} \cdots Mn^{III}$ interaction and J_{bb} the body–body interaction. The rapid decrease in μ_{eff} at low temperatures was accommodated by assuming the $S = 3$ ground state in each butterfly-like core has an axial zero-field splitting with $|D| = 3.0\ cm^{-1}$.

L1 and L2 possess two important properties: 1) the 2,2'-bpy character of each half of the ligands and 2) their overall "linkedbpy" nature. Given that bpy itself will react with $[Mn_3O(O_2CR)_6(py)_3](ClO_4)$ to afford butterfly-like clusters of the type $[Mn_4O_2(O_2CR)_7(bpy)_2](ClO_4)$,[17] it can be seen that in L2 the 5,5″ linkage results in the above-mentioned properties being independent: property 1) triggers self-assembly of a butterfly-like $[Mn_4O_2]^{8+}$ cluster (as does free bpy), and property 2) yields a resulting "dimer-of-clusters" supramolecular assembly. In contrast, properties 1) and 2) are coupled (not independent) in L1, and the 6,6″ linkage therefore yields the new cluster type in complex **1**.

It is clear that there is great potential for suitably "programmed" polypyridyl and related ligands in this area of supramolecular chemistry involving metal clusters, complementing the current use of mononuclear metal centers. Such an approach might be one potential means of amalgamating, for example, the often unusual magnetic properties of metal clusters and the multidimensional controlled ordering of supramolecular chemistry.

Experimental Procedure

$[Mn_4O_2(O_2CMe)_4(L1)_2](ClO_4)_2$ (**1**). Solid L1 (0.30 g, 0.90 mmol) was added to a stirred red-brown solution of $[Mn_3O(O_2CMe)_6(py)_3](ClO_4)$ (0.52 g, 0.60 mmol) in MeCN (60 mL), which caused a rapid color change to dark red-brown. The solution was stirred for 12 h, filtered, and the filtrate layered with an equal volume of THF. After several days, dark red-brown block-shaped crystals of **1**·2THF had formed; this formulation was indicated crystallographically, but dried solid analyzed as **1**·THF·$2H_2O$. Yield 46%. Anal. calcd (found) for $C_{56}H_{60}N_8O_{21}Cl_2Mn_4$: C 45.70 (45.87), H 4.11 (3.96), N 7.61 (7.67), Mn 14.93 (14.99)%.

$[Mn_8O_4(O_2CEt)_{14}(L2)_2](ClO_4)_2$ (**2**). Solid L2 (0.10 g, 0.30 mmol) was added to a stirred red-brown solution of $[Mn_3O(O_2CEt)_6(py)_3](ClO_4)$ (0.19 g, 0.20 mmol) in CH_2Cl_2 (50 mL). The solution was stirred for 2 h, filtered, and the filtrate layered with an equal volume of hexanes. After several days, dark red crystals of **2**·$4CH_2Cl_2$·xC_6H_{14} were collected; this formulation was indicated crystallographically, but dried solid analyzed as solvent free. Yield 65%. Anal. calcd (found) for $C_{90}H_{114}N_8O_{40}Cl_2Mn_8$: C 43.97 (44.04), H 4.67 (4.53), N 4.56 (4.66), Mn 17.88 (17.92)%.

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[18] Crystal data for **1**·2THF: $C_{52}H_{48}N_8O_{18}Cl_2Mn_4 \cdot 2C_4H_8O$, triclinic, $P\bar{1}$, $T = -169\,^{\circ}C$, $a = 12.017(2)$, $b = 12.197(2)$, $c = 12.343(2)$ Å, $\alpha = 73.29(1)$, $\beta = 78.02(1)$, $\gamma = 68.36(1)^{\circ}$, $V = 1600.1$ Å^3, $Z = 1$, $6^{\circ} \leq 2\theta \leq 45^{\circ}$, 4176 unique reflections, 3757 unique reflections with $F > 2.33\sigma(F)$; $R(F) = 0.0448$, $R_w(F) = 0.0419$. Crystal data for **2**·$4CH_2Cl_2 \cdot xC_6H_{14}$: $C_{90}H_{114}N_8O_{40}Cl_2Mn_8 \cdot 4CH_2Cl_2 \cdot xC_6H_{14}$, monoclinic, $C2/c$, $T = -164\,^{\circ}C$, $a = 22.189(4)$, $b = 32.402(6)$, $c = 22.521(4)$ Å, $\beta = 115.60(1)^{\circ}$, $V = 14602$ Å^3, $Z = 4$, $6^{\circ} \leq 2\theta \leq 45^{\circ}$, 9508 unique reflections, 5341 unique reflections with $F > 4\sigma(F)$; $R(F) = 0.0914$, $R_w(F^2$; all data$) = 0.1777$. Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-52. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code +(1223) 336-033; e-mail: teched@chemcrys.cam.ac.uk).

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Carbaporphyrins**

Kurt Berlin*

In recent years numerous structural variants of porphyrins have been synthesized[1, 2b] which are not only interesting as 18π arenes, but also because of their diverse applications in medicine,[2] and as catalysts and chromophores.[1, 2b] In most of these porphyrinoids, including porphyrin isomers,[3–5] porphyrin analogs, and expanded porphyrins,[1b, 2b, 4] either a pyrrole ring has been formally replaced by a unit containing a nitrogen or a different heteroatom, or the arrangement of pyrroles and CH groups has been changed. But few porphyrinoids with less than four heteroatoms in the inner cycle have been reported that can bridge the gap to the formally related C-annulenes, which are prepared by completely different synthetic strategies and display strongly contrasting spectroscopic and physical properties.[6]

Novel porphyrin isomers, in particular one with an inverted pyrrole ring and an inner CH unit,[5] were inspiration to proceed further and replace one pyrrole ring of porphine by a five-membered unsaturated all-carbon ring. In these compounds only one nitrogen atom of the porphyrin system is replaced by carbon; thus they are referred to as carbaporphyrins.

Since the replacement of one pyrrole ring of the porphyrin core by 6π arenes was successful,[7] the reaction of a tripyrrane like **2b** (see Scheme 1) with a cyclopentadiene-1,3-dialdehyde appeared to be promising. Unfortunately the latter compound is not known, and it would probably be unstable under the

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