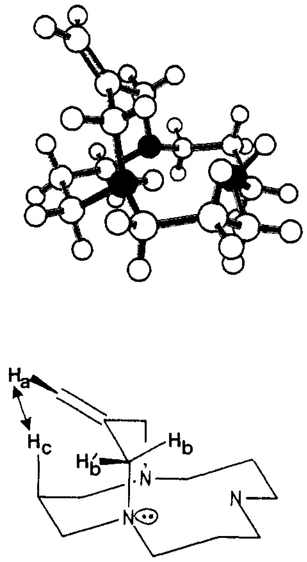

Figure 2. Crystal conformation (top) and ^1H NMR features of **3**·HI (bottom). Two-dimensional NOE correlation indicated by arrow.

We estimate that the acid dissociation constants for **3** and **4** correspond to $pK_{a_3} > 13.5$, since they cannot be measured by aqueous titration.[14] Moreover, **3**·H^+ and **4**·H^+ strongly resist protonation, as indicated by the low values of their second acid dissociation constants: $pK_{a_2} = 4.4$ and 4.9 for **3** and **4**, respectively. Thus, $pK_{a_3} - pK_{a_2}$ is at least 8.6 pK_a units, whereas this value is only 5.0[5b] or 5.8[4] pK_a units for macrocycle **1**. This phenomenon has been observed for bridgehead diamines in which protonation relieves strain and indicates that **3**·H^+ and **4**·H^+ are stabilized species.[2] The exceptional stability of **3**·H^+ suggests that bicyclization could be a proton-templated process, as has been observed in cryptand synthesis.[15] Unlike many bridgehead bicyclic diamines,[7,16] **3** and **4** immediately form internally protonated salts when trifluoroacetic acid is added to the $CDCl_3$ solutions. Alder et al. have reported that 1,5-diazabicyclo[6.3.3]tetradecane must be heated overnight in trifluoroacetic acid to obtain the inside protonated species [δ(NH) = 17.25].[7]

In summary, we have found that bicyclization of a macrocyclic triamine can enhance the conformational organization of three basic sites. In contrast to bicyclic diamines that protonate slowly, bicyclic triamines in which a third site is positioned on a flexible bridge are protonated very rapidly. This "proton relay" concept should prove to be of considerable utility in the design of rapid-acting "proton sponges"[17] and receptors for other ions.

Acknowledgment. We gratefully thank Professor Joseph Lauher for his assistance with X-ray crystallographic and computer graphic techniques and Dr. Lisa Deuring for her aid with two-dimensional NMR experiments. Support by the New York Science and Technology foundation through the Center for Biotechnology is gratefully acknowledged.

Supplementary Material Available: Lists of atomic coordinates, thermal parameters, bond distances, and bond angles for **3**·HI (4 pages). Ordering information is given on any current masthead page.

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(14) The pH of 0.1 M solutions of these bases are approximately 13. ^1H NMR experiments have established that in Me_2SO-d_6 **3** is slightly more basic than 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), which has an aqueous pK_a of approximately 13.5: Barton, D. H.; Eliot, J. D.; Gero, S. D. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2085-2090.

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Ferromagnetic Transition in a Bimetallic Molecular System

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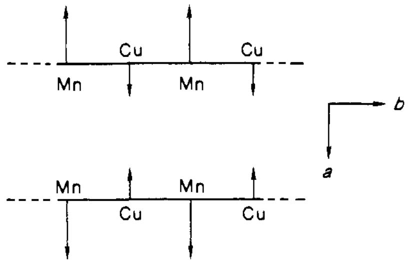
For a few years, we have participated to the efforts to design molecular compounds ordering ferromagnetically.[1,5] Our first strategy has been to impose ferromagnetic interactions between nearest-neighbor metal centers owing to the orthogonality, strict (symmetry imposed) or accidental, of the magnetic orbitals. This approach allowed us to design ferromagnetically coupled dinuclear complexes[6] but we have not been able yet to extend it to three-dimensional lattices. Recently, we have proposed an alternative strategy[3] consisting to polarize local spins $^5/_2$ (Mn^{2+} or Fe^{3+}) along the same direction through antiferromagnetic interactions with local spins $^1/_2$ (Cu^{2+}). That approach already led us to a $Mn^{2+}Cu^{2+}Mn^{2+}$ trinuclear species with a spin $^9/_2$ ground state[7] and to $Mn^{2+}Cu^{2+}$ ordered bimetallic chains exhibiting one-dimensional ferromagnetic-like behaviors in the low-temperature range.[3,8] However, all those compounds display a three-dimensional antiferromagnetic ordering at very low temperature. $MnCu(pba)(H_2O)_3{\cdot}2H_2O$ (**1**) where pba denotes 1,3-propylenebis(oxamato) is a recently described chain compound of this kind.[3,9] The variation vs. the temperature T of the product $\chi_M T$, χ_M being the molar magnetic susceptibility per MnCu unit, increases upon cooling down below 115 K in a ferromagnetic-like fashion but exhibits a sharp maximum at 2.3 K due to the antiferromagnetic ordering of the ferrimagnetic chains.[9] In **1**, the chains run along the *b* axis of the orthorhombic system and are linked together through hydrogen bonding, which provides an interchain interaction pathway. The relative positions of two adjacent chains in the *a* direction are as shown in I with Cu···Cu = 6.545 Å and Mn···Mn = 6.997 Å as shortest interchain metal-metal separations in this direction. In the *c* direction, the shortest interchain separations are also Cu···Cu = Mn···Mn = 5.2105 Å. This



I

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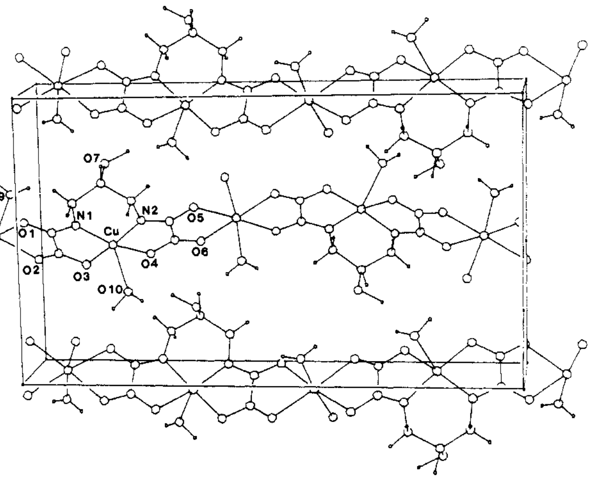
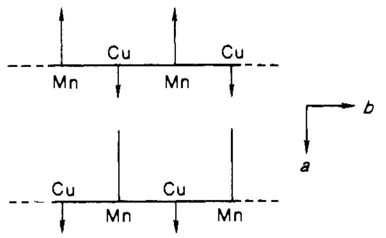


Figure 1. Perspective view of three neighboring chains in **2**. The origin of the unit cell is in the upper left hand corner; the *a* axis runs top to bottom and the *b* axis left to right.

situation leads to a cancellation of the spin if, as is most likely, the $Mn^{2+}Mn^{2+}$ and $Cu^{2+}Cu^{2+}$ interchain interactions are antiferromagnetic. If we are able to displace every other chain by half a repeat unit along *b* as shown in II, a ferromagnetic order may be expected, provided that the $Mn^{2+}Cu^{2+}$ interchain interaction is antiferromagnetic.



II

We have succeeded in synthesizing the chain compound $MnCu(pbaOH)(H_2O)_3$ (**2**), in which the relative orientations of the chains are close to II. Chemically, **2** differs from **1** only in the replacement of the central methylene group of the propylene chain by CHOH.[10] **2** crystallizes in the orthorhombic system, space group $P2_12_12_1$ with a = 12.351 (7) Å, b = 21, 156 (11) Å, c = 5.073 (10) Å, and Z = 4 MnCu units. The structure of the chains in **2** is very close to that found in **1**, with the same surroundings for the Mn^{2+} and Cu^{2+} ions. The arrangement of neighboring chains in the *a* direction is illustrated in Figure 1. The shortest interchain metal–metal separation in this direction is Mn···Cu = 5.751 Å. In **2**, as well as in **1**, the chains closest to one another are those related by a unit cell translation along *c*, Cu···Cu = Mn···Mn being 5.073 Å in **2**.

The χ_MT vs. T plot for **2** between 300 and 4.2 K is shown in Figure 2. Down to about 60 K, the magnetic behavior of **2** is, within the experimental uncertainties, identical with that of **1**, with a minimum of χ_MT about 115 K. The minimum is the signature of the antiferromagnetically coupled bimetallic chains.[8,11,12] Below 60 K, on the other hand, the increase of χ_MT upon cooling down is much more abrupt in **2** than in **1**. At 4.2 K, χ_MT for **2** reaches the extraordinary high value of about 100 cm^3 mol^{-1} K, which strongly suggests that a ferromagnetic order occurs in the liquid-helium temperature range. To confirm this, we have studied the variation vs. T of the magnetization M in fields between 3 × 10^{-2} and 10 G with a SQUID magnetometer.[13] The field-cooled magnetization (FCM) at 3 × 10^{-2} G shows the usual feature of a ferromagnetic transition, i.e., a rapid increase of M below 4.8 K and a break in the curve around $T_c \simeq$ 4.6 K (see Figure 3). The ferromagnetic transition is distroyed when the field reaches a few Gauss. We have also measured M by cooling the sample down to 3.5 K in zero field, then applying the field of 3 × 10^{-2} G and heating up (zero field cooled magnetization, ZFCM). The ZFCM below T_c is much smaller than the FCM, owing to the fact that the applied field is too weak to move the domain walls. The ZFCM exhibits a maximum around T_c, as is usual in polycrystalline ferromagnets.[14]

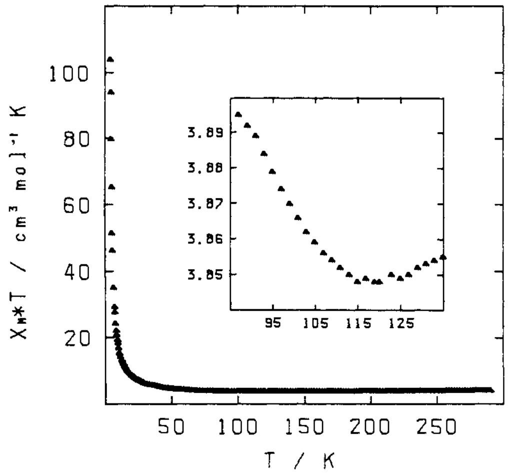


Figure 2. Temperature dependence of χ_MT for $MnCu(pbaOH)(H_2O)_3$ (**2**) in the 300–4.2 temperature range. In the inserted frame, we expanded the χ_MT axis in the 50–200 K temperature range to give evidence of the minimum of χ_MT.

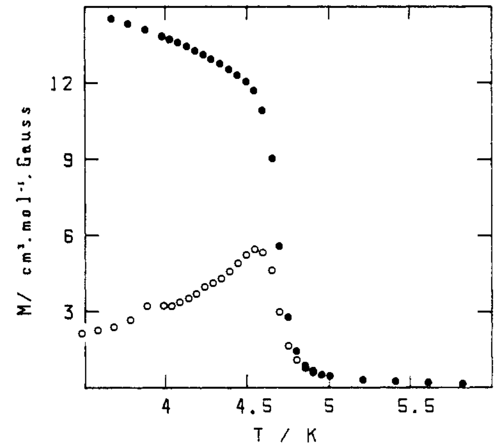


Figure 3. Temperature dependence of the magnetization M for $MnCu(pbaOH)(H_2O)_3$ (**2**) in the 6–3.5 K temperature range and a field of 3 × 10^{-2} G: (●) sample cooled in the field (FCM); (○) sample cooled in zero field and then heated in the field applied at 3.5 K (ZFCM).

$MnCu(pbaOH)(H_2O)_3$ (**2**) may be considered as one of the first genuine molecular ferromagnets. When examining carefully the arrangement of the chains in Figure 1, one notices that the displacement of every other chain in the *b* direction is slightly less than half a repeat unit, so that the ideal structural situation is not yet reached. It follows that in the frame of our strategy, one may expect to shift the ferromagnetic transition toward the higher temperatures.

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(10) **2** was synthesized as follows: the action of 1 mol of 2-hydroxy-1,3-propylenediamine on 2 mol of ethyl oxamate affords the 2-hydroxy-1,3-propylenebis(oxamide). This compound reacts with 1 mol of $Cu(NO_3)_2{\cdot}3H_2O$ in the presence of 4 mol of OH^- to give after hydrolysis of the primary amine groups $Na_2[Cu(pbaOH)]$. Blue single crystals of **2** were obtained by slow diffusion of aqueous solutions of $Mn(ClO_4)_2{\cdot}6H_2O$ and $Na_2[Cu(pbaOH)]$. Anal. Calcd for $C_7H_{12}N_2O_{10}CuMn$: C, 20.88; H, 3.00; N, 6.96; Cu, 15.7; Mn, 13.64. Found: C, 20.95; H, 3.18; N, 6.97; Cu, 16.01; Mn, 13.79.

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J. Am. Chem. Soc. 1986, 108, 7430-7431

Supplementary Material Available: Table of atomic parameters for **2** (1 page); listing of structure factor amplitudes for MnCu(pbaOH)$(H_2O)_3$ (**2**) (4 pages). Ordering information is given on any current masthead page.

Intramolecular Coordination of Bidentate Lewis Bases to a Cofacial Binuclear Copper(II) Complex

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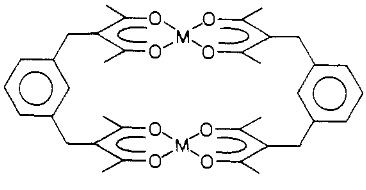
Received May 20, 1986

The study of the interactions between "host" and "guest" molecules is an area of continuing activity. Previous investigations of this type have dealt with organic hosts, including crown ethers,[1] cyclophanes,[2] and calixarenes,[3] as well as with cyclic nitrogen donors that can accommodate both transition-metal ions and small-molecule guests.[4] We have recently studied the formation and properties of cofacial binuclear transition-metal complexes based on bis(β-diketone) ligands. Our first complexes M_2(*m*-XBA)$_2$, with the general structure **1** shown below, utilized the *m*-xylylene bridging group.[5] We have now synthesized a new bis(β-diketone) ligand, which we call $NBAH_2$, based on the larger 2,7-naphthalenediylbis(methylene) bridge. The resulting complexes $M_2(NBA)_2$ (**2**) have significantly larger cavities. We report herein the preparation and structural characterization of $Cu_2(NBA)_2$, its affinity for mono- and difunctional Lewis bases, and its selective intramolecular reaction with the guest molecule 1,4-diazabicyclo[2.2.2]octane (Dabco).



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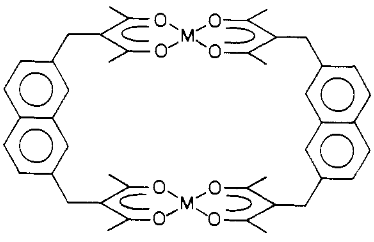

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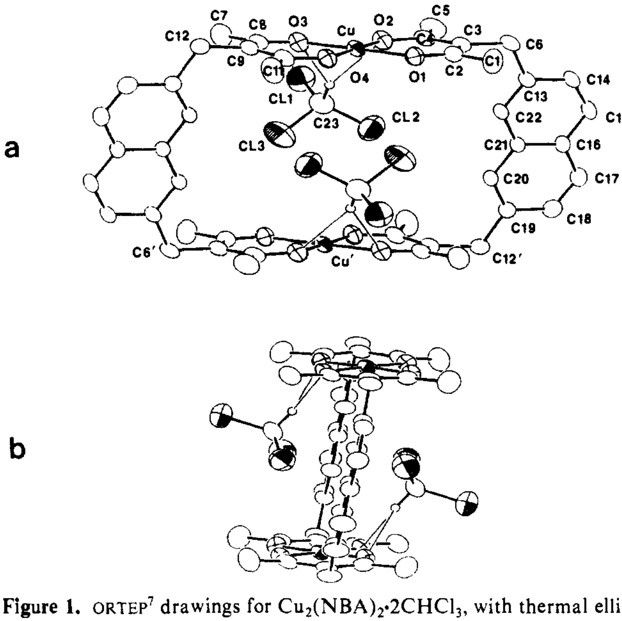
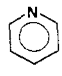


Figure 1. ORTEP[7] drawings for $Cu_2(NBA)_2 \cdot 2CHCl_3$, with thermal ellipsoids at the 33% probability level. Hydrogen bonds (Cl_3CH- - -O) shown in single lines; other hydrogen atoms omitted for clarity. (a) Side view, including atom labeling scheme. Primed and unprimed atoms are related by the crystallographic inversion center. (b) End view, showing orientation of hydrogen-bonded chloroform molecules.

Table I. Binding Constants for $Cu_2(NBA)_2$ with Lewis Bases B[a]



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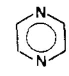

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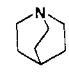

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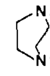

6

B	K/M^{-1}	B	K/M^{-1}
pyridine (**3**)	0.5 ± 0.2	quinuclidine (**5**)	7 ± 2
pyrazine (**4**)	5 ± 1	Dabco (**6**)	220 ± 20

[a] Determined spectrophotometrically in $CHCl_3$ solution, 20 ± 1 °C.

The new ligand $NBAH_2$[6] is readily converted to $Cu_2(NBA)_2$ by treatment with aqueous $Cu(NH_3)_4^{2+}$. The structure of $Cu_2(NBA)_2 \cdot 2CHCl_3$ (see ORTEP[7] drawing in Figure 1)[8a] contains centrosymmetric binuclear units (Cu- - -Cu 7.349 (1) Å). The "$Cu(acac)_2$" (acacH = 2,4-pentanedione) and bridging naphthalene planes make an angle of 82.3°, giving the complex approximate C_{2h} symmetry.

Two weak interactions are evident in the $Cu_2(NBA)_2 \cdot 2CHCl_3$ structure. First, the chloroform molecules lie approximately symmetrically between two β-diketone O atoms, with Cl_3CH- - -O distances (2.32 and 2.40 Å) indicative of weak hydrogen bonding. The resulting bifurcated hydrogen bond, shown in Figure 1, confirms the association between chloroform and β-diketone complexes which was previously proposed on the basis of ^1H NMR line-broadening data.[5,9] The second weak interaction in the $Cu_2(NBA)_2 \cdot 2CHCl_3$ structure is a π-stacking arrangement of adjacent $Cu_2(NBA)_2$ molecules.[10]

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