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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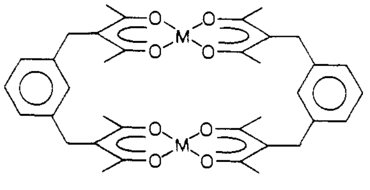
The study of the interactions between "host" and "guest" molecules is an area of continuing activity. Previous investigations of this type have dealt with organic hosts, including crown ethers,[1] cyclophanes,[2] and calixarenes,[3] as well as with cyclic nitrogen donors that can accommodate both transition-metal 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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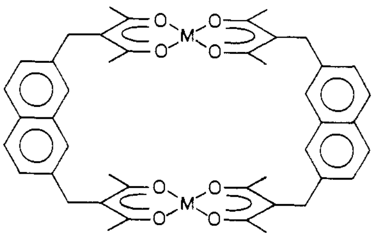

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The new ligand $NBAH_2$[6] is readily converted to $Cu_2(NBA)_2$ by treatment with aqueous $Cu(NH_3)_4^{2+}$. The structure of $Cu_2(NBA)_2 \cdot 2CHCl_3$ (see ORTEP[7] drawing in Figure 1)[8a] contains centrosymmetric binuclear units (Cu---Cu 7.349 (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.

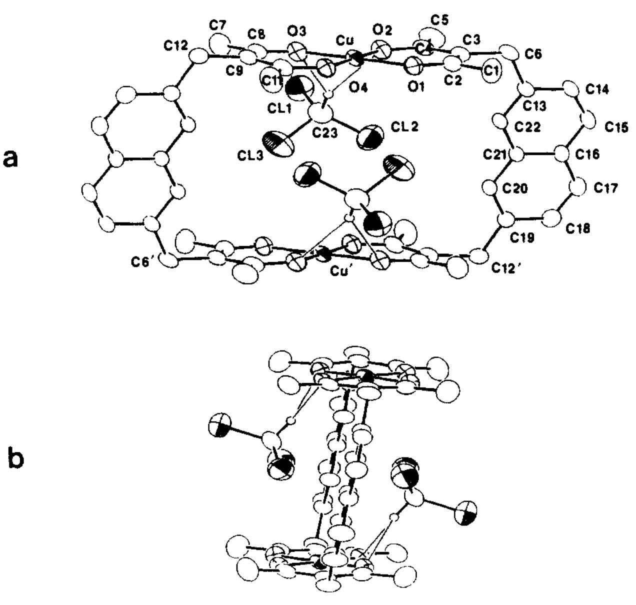
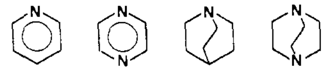


Figure 1. ORTEP[7] drawings for $Cu_2(NBA)_2 \cdot 2CHCl_3$, with thermal ellipsoids at the 33% probability level. Hydrogen bonds (Cl_3CH---O) shown in single lines; other hydrogen atoms omitted for clarity. (a) Side view, including atom labeling scheme. Primed and unprimed atoms are related by the crystallographic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



3 4 5 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.

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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(8) Nicolet P3 diffractometer, Mo Kα radiation, ω scan, variable scan rate; VAXSDP program system; solution via Patterson map and subsequent difference Fourier syntheses; full-matrix least-squares refinement. Satisfactory microanalyses for the complexes could not be obtained because of solvent loss. (a) $Cu_2(NBA)_2 \cdot 2CHCl_3$, crystallized from chloroform by layering with acetonitrile. Space group $C2/c$; a = 19.942 (5) Å, b = 10.371 (2) Å, c = 26.656 (9) Å; β = 116.85 (2)°; V = 4919 (2) Å^3; Z = 4; 3050 reflections ($I > 3\sigma(I)$); 372 parameters; R = 0.038; R_w = 0.056. (b) $Cu_2(NBA)_2(\mu\text{-Dabco}) \cdot 2CH_2Cl_2 \cdot 2H_2O$, crystallized from dichloromethane by layering with hexane. Space group $Pnma$; a = 22.771 (6) Å, b = 22.326 (5) Å, c = 11.621 (3) Å; V = 5908 (2) Å^3; Z = 4; 1490 reflections ($I > 2\sigma(I)$); 281 parameters; R = 0.105; R_w = 0.135.

(9) Kitaigorodskii, A. N.; Nekipelov, V. M.; Zamaraev, K. I. *J. Struct. Chem.* (*Engl. Transl.*) **1978**, *19*, 686–693.

(10) An ORTEP[7] diagram illustrating these interactions (Cu---C and C---O distances 3.20–3.25 Å) is available as supplementary material. For a discussion of aggregation in mononuclear copper(II) complexes, see: Chikira, M.; Yokoi, H. *J. Chem. Soc., Dalton Trans.* **1977**, 2344–2348.

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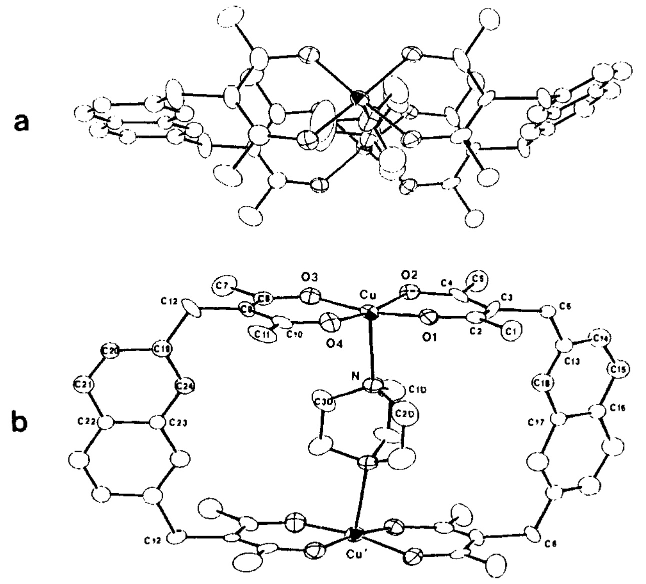

Figure 2. ORTEP[7] drawings for $Cu_2(NBA)_2(\mu\text{-Dabco})$, with thermal ellipsoids at the 33% probability level. (a) Top view, showing tilting of one naphthalene plane. (b) Side view, including atom labeling scheme. Primed and unprimed atoms are related by the crystallographic mirror plane, which passes through C16, C17, C22, and C23.

Solutions of $Cu_2(NBA)_2$ change from olive green to turquoise on addition of Lewis bases B, as expected for the reaction $Cu_2(NBA)_2 + B \rightleftharpoons Cu_2(NBA)_2B$. (The electronic spectra of $Cu_2(NBA)_2$ and $Cu_2(NBA)_2B$ are similar to those previously reported[5] for $Cu_2(m\text{-}XBA)_2$ and $Cu_2(m\text{-}XBA)_2(py)_2$.) Equilibrium constants (Table I) for binding of pyridine (**3**) and quinuclidine (**5**) to $Cu_2(NBA)_2$ are comparable to those in the literature for binding to $Cu(acac)_2$:[11] these bases cannot assume an internal bridging position in **2**. On the other hand, the larger binding constants for pyrazine (**4**) and Dabco (**6**), respectively, are consistent with internal coordination. We have conclusively demonstrated this coordination mode in the case of Dabco by performing a crystal-structure analysis of $Cu_2(NBA)_2(\mu\text{-Dabco})$ (see Figure 2).[8b]

In the $Cu_2(NBA)_2(\mu\text{-Dabco})$ structure (Cu- - -Cu 7.403 (4) Å), the coordination environment about Cu is square pyramidal, with the copper atoms displaced ca. 0.14 Å out of the β-diketone plane toward the Dabco N atoms (see Figure 2). This geometry is similar to those in complexes such as $(quinoline)Cu(acac)_2$[12] and $[(hfac)_2Cu]_2(\mu\text{-L})$ (L = pyrazine and Dabco).[13]

Experimental and theoretical treatments of $Cu_2(NBA)_2(\mu\text{-Dabco})$ indicate that rotation of bound Dabco is rapid at room temperature. Molecular-mechanics calculations,[14] for example, yield a rotation barrier of ca. 20 kJ mol^{-1}. Also, thermodynamic data for binding of Dabco to $Cu_2(NBA)_2$ ($\Delta H = -30$ kJ mol^{-1} and $\Delta S = -50$ J mol^{-1} K^{-1}; 0–30 °C., in $CHCl_3$) are similar to those expected if the guest molecule retains one rotational degree of freedom.[15]

These experiments constitute the first investigation of selective intramolecular coordination of bifunctional Lewis bases to a relatively rigid transition-metal host. We are currently studying the dynamics of these complexation reactions by NMR in analogous diamagnetic species and examining the effects of insertion of guest molecules on the electronic, magnetic, and redox properties of these complexes.

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Supplementary Material Available: Illustration of close intermolecular contacts in $Cu_2(NBA)_2{\cdot}2CHCl_3$, packing diagrams, and tables of bond distances and angles, fractional coordinates, and thermal parameters for $Cu_2(NBA)_2{\cdot}2CHCl_3$ and $Cu_2(NBA)_2(\mu\text{-Dabco}){\cdot}2CH_2Cl_2{\cdot}2H_2O$ (16 pages); tables of observed and calculated structure factors for $Cu_2(NBA)_2{\cdot}2CHCl_3$ and $Cu_2(NBA)_2(\mu\text{-Dabco}){\cdot}2CH_2Cl_2{\cdot}2H_2O$ (37 pages). Ordering information is given on any current masthead page.

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[11] Graddon, D. P. *Coord. Chem. Rev.* **1969**, *4*, 1–28.

[12] Ooi, S.; Fernando, Q. *Chem. Commun.* **1967**, 532–533. These pyramidal environments compare with the "$Cu(acac)_2$" moieties in $Cu_2(NBA)_2{\cdot}2CHCl_3$, which are planar within ca. 0.02 Å.

[13] HfacH = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione. Durley, R. C. E.; Hughes, D. L.; Truter, M. R. *Acta Crystallogr., Sect. B* **1980**, *36*, 2991–2997. Belford, R. C. E.; Fenton, D. E.; Truter, M. R. *J. Chem. Soc., Dalton Trans.* **1974**, 17–24.

[14] The barrier to rotation was estimated by using van der Waals interactions calculated with the SYBYL program set: Naruto, S.; Motoc, I.; Marshall, G. R.; Daniels, S. B.; Sofia, M. J.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 5262–5270.

[15] The theoretical value of ΔS (−73 J mol^{-1} K^{-1}) was calculated according to: Fowler, R.; Guggenheim, E. A. *Statistical Thermodynamics*; Cambridge University Press: Cambridge, 1949; pp 106–111. Geometric data for Dabco are from: Nimmo, J. K.; Lucas, B. W. *Acta Crystallogr., Sect. B* **1976**, *32*, 348–353.

Photoinitiated Quadricyclane–Quadricyclane Rearrangements

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The norbornadiene–quadricyclane couple has emerged as the most intensively studied valence isomerization[2] because of its latent promise for solar energy storage.[3] The strain energy of quadricyclane (96 kcal mol^{-1})[4] exceeds by 13 kcal mol^{-1} the sum of the strain of its constituent rings. As a consequence, this highly energetic molecule enters readily into thermal[5] and photochemical cycloadditions,[6] is especially prone to metalation,[7a] transition-metal-promoted isomerization,[7b] and attack by electrophiles,[8] and engages in photosensitized cycloreversion.[9] Our recent devel-

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[1] Postdoctoral fellowship awardee of the Deutsche Forschungsgemeinschaft, 1985–1986.

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