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Design, synthesis and crystal structure of a copper dimetallocyclophane complex exhibiting unique rotational isomerism

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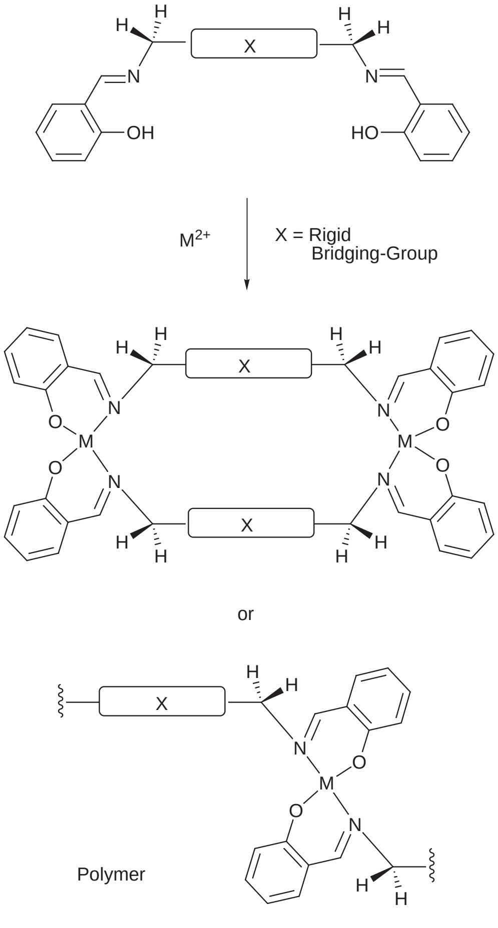
Reaction of *N*,*N′*-bis(salicylidene)-1,4-phenylenedimethanamine with copper(II) acetate under high-dilution conditions at room temperature in methanol yielded a dimetallocyclophane in 85% yield. In the crystal structure of the dimeric complex, two rotational isomers of the phenylene bridging groups were observed. For one isomer, the nearly parallel arrangement of these groups provided a cavity with dimensions 7.31 × 5.23 Å. The rings were exactly perpendicular in the second rotational isomer. The distance between ring centers in this perpendicular arrangement is identical to the optimized value for the edge-to-face CH–π interaction determined by molecular dynamics calculations for liquid benzene, suggesting a strong edge-to-face interaction in this rotational isomer.

Assembly of elaborate structures using metal co-ordination is an area of great current interest.[1] Many interesting topologies have been prepared such as boxes, grids, rotaxanes, and helicates.[2] The requisite structural elements of these systems are metal binding moieties and a bridging group(s) linking these moieties. The structure of the bridging group, the metal binding moiety, the metal co-ordination geometry and weak non-covalent interactions all dictate the architecture obtained after reaction with metal cations.

As part of a study of unique bis-salicylidene ligands and their complexation chemistry, we became interested in designing a system that would form a macrocyclic bimetallic complex with a well defined cavity for possible host–guest investigations. Maverick[3] and Steel[4] and co-workers have prepared macrocyclic metal dimer complexes using a rigid arene-based linker to join the two metal binding moieties. Recently, Mirkin *et al.*[5] have developed a macrocyclic complex that binds a guest by expanding the cavity of the complex. Others have prepared metallomacrocycles using a variety of metal binding moieties, however the salicylidene ligand has not been employed.[2] In the only similar report concerning a bis-salicylidene ligand, Yoshida and Ichikawa[6] utilized a 4,4′-diaminodiphenyl sulfone linker which yields a tetrameric helical structure presumably induced by π–π and CH–π interactions. Our focus was to produce a [2+2] copper:ligand bis-salicylidene complex as opposed to the helical tetramer reported by Yoshida. Therefore, the ideal bridging unit linking the two salicylidene moieties to produce a discrete macrocyclic structure was envisioned to be a rigid group, X, with two flanking methylene groups (Scheme 1). The methylene groups were thought to provide the crucial flexibility required to allow the two X groups to be aligned parallel, thereby forming a macrocyclic dimeric complex. Attractive forces between these two groups, such as intramolecular aromatic π–π interactions, would also favor dimer formation and deter the formation of polymeric materials. If successful, this general design could be used to develop macrocyclic systems of various dimensions by increasing the size of the X group employed.



Scheme 1

Results and discussion

To test this approach, compound **I** (X = phenyl) was prepared in high yield from commercially available *p*-phenylenedimethanamine and salicylaldehyde using trimethyl orthoformate as the solvent and dehydrating agent. Surprisingly, a literature search on **I** yielded only one previous preparation and no complexation chemistry of **I** was reported.[7] Interestingly, we found crystalline **I** to be photochromic, changing from yellow to orange with exposure to ambient light. Many such salicylidene compounds are photochromic[8] and we are currently investigating the properties of **I** and will report those findings elsewhere. Copper(II) was chosen for the initial complexation studies due to its flexible co-ordination geometry (square planar to tetrahedral). Treatment of **I** under the standard conditions for form-

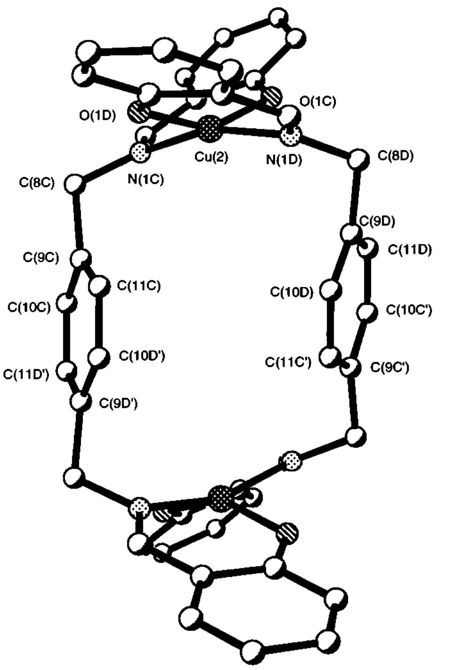
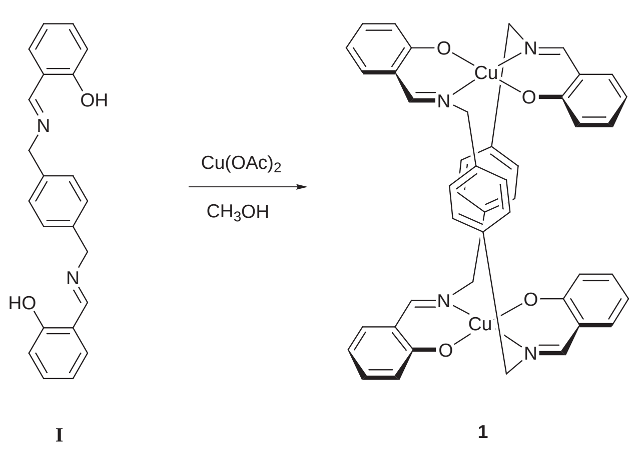


Fig. 1 Conformation **1a** in the crystal of **1**·CH_3NO_2.

ing salicylidene complexes [$Cu(OAc)_2$, EtOH at reflux] yielded polymeric material that was insoluble in common solvents. The attractive forces between the phenylene rings, presumed to be π-stacking interactions, are weak (at most 1–2 kcal mol^{-1})[9] providing little energetic preference for macrocycle formation. Three adjustments were made to provide optimum conditions for macrocycle formation: (1) a more polar solvent, methanol, was used to increase the hydrophobic interactions of the X groups, (2) the reaction was run at lower temperature (room temperature instead of the 78 °C of refluxing ethanol) and (3) the reaction was conducted at higher dilution to diminish intermolecular complexation leading to polymer formation. In fact, slow addition (over 3 h) of a copper acetate solution (6 mM, MeOH) to a 0.8 mM solution of **I** in methanol at room temperature yielded an olive green solid that was freely soluble in CH_2Cl_2 and $CHCl_3$, and sparingly soluble in THF and acetone. Mass spectral analysis of the product was consistent with dimer formation (MH^+, *m*/*z* 811) and demonstrated that no oligomeric or polymeric materials were formed in the synthesis. X-Ray quality crystals were obtained from a saturated solution of nitromethane and the structure was determined to be complex **1**·CH_3NO_2 (Scheme 2).



Scheme 2

Table 1 Selected bond lengths (Å) and angles (°) for molecules **1a** and **1b**

Dimer **1a**			
Cu(2)–N(1C)	1.966(3)	Cu(2)–N(1D)	1.965(3)
Cu(2)–O(1C)	1.912(2)	Cu(2)–O(1D)	1.905(2)
N(1C)–C(8C)	1.469(4)	N(1D)–C(8D)	1.485(4)
C(8C)–C(9C)	1.505(5)	C(8D)–C(9D)	1.509(4)
N(1C)–Cu(2)–O(1C)	93.43(11)	N(1D)–Cu(2)–O(1D)	93.37(11)
N(1C)–Cu(2)–O(1D)	89.34(11)	N(1D)–Cu(2)–O(1C)	92.47(11)
O(1C)–Cu(2)–O(1D)	151.34(12)	N(1C)–Cu(2)–N(1D)	162.47(11)
N(1C)–C(8C)–C(9C)	111.0(3)	N(1D)–C(8D)–C(9D)	113.6(3)
Dimer **1b**			
Cu(1)–N(1A)	1.972(3)	Cu(1)–N(1B)	1.970(3)
Cu(1)–O(1A)	1.903(2)	Cu(1)–O(1B)	1.900(2)
N(1A)–C(8A)	1.488(4)	N(1B)–C(8B)	1.469(5)
C(8A)–C(9A)	1.516(5)	C(8B)–C(9B)	1.514(5)
N(1A)–Cu(1)–O(1A)	94.12(11)	N(1B)–Cu(1)–O(1B)	93.85(11)
N(1A)–Cu(1)–O(1B)	92.14(11)	N(1B)–Cu(1)–O(1A)	91.52(11)
O(1A)–Cu(1)–O(1B)	155.18(11)	N(1A)–Cu(1)–N(1B)	152.72(11)
N(1A)–C(8A)–C(9A)	110.2(3)	N(1B)–C(8B)–C(9B)	113.6(3)

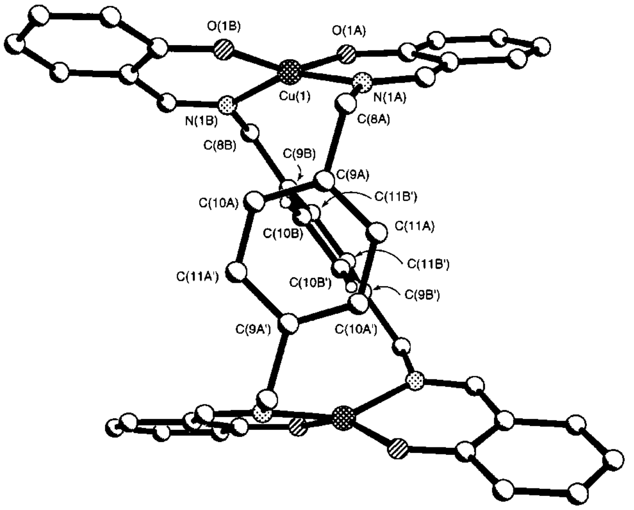


Fig. 2 Conformation **1b** in the crystal of **1**·CH_3NO_2.

The monoclinic unit cell consists of eight molecules of nitromethane solvent and four pairs of copper dimers (*i.e.* 16 copper centers in all). The dimers in each pair exhibit different orientations of the phenylene rings, as shown in Figs. 1 and 2. Each dimer sits on different twofold axes (1/2, *y*, 3/4 and 0, *y*′, 1/4, respectively). The axes lie approximately perpendicular to the page in both figures. The CuN_2O_2 co-ordination geometry about each copper can be described as distorted *trans* planar based on (1) the O–Cu–O and N–Cu–N angles of 151 to 162°, (2) O–Cu–N angles of 89 to 94°, and (3) the dihedral angles of 33 and 36° for the Cu(2)–O(1C)–N(1C) *vs.* Cu(2)–O(1D)–N(1D) and Cu(1)–O(1A)–N(1A) *vs.* Cu(1)–O(1B)–N(1B) planes, respectively (see Tables 1 and 2).

Data from Tables 2, 3 and 4 indicate that the phenylene rings "C" and "D" of dimer **1a** are relatively parallel [with dihedral angle 39.7(1)°]. The distance between ring centers is 5.226(1) Å. There is some distortion within the rings (rms deviation of the six ring carbons is 0.013 Å in both cases), and the C(8)–C(9)–C(10)–C(11′) torsion angles of 175° indicate modest distortion of the phenylene framework. In contrast, the phenylene rings "A" and "B" of dimer **1b** lie exactly perpendicular to one another [90.00(1)°]. The distance between the ring centers is 4.991(1) Å and the distance between the center of ring "A" and the H(10B)–H(10B′) centroid is 3.050(1) Å. There is little distortion in the rings themselves (rms deviation of the six ring carbons is 0.004 Å for ring "A" and 0.006 Å for ring "B"), and the C(8)–C(9)–C(10)–C(10′ or 11′) torsion angles are close to 180° as expected. No systematic differences were observed in the N(1)–C(8) and C(8)–C(9) bond lengths or in the N(1)–C(8)–

Table 2 Selected dihedral angles for complex **1**

Dimer	Plane	Dihedral angle/°
1a	Cu(2)–O(1C)–N(1C) *vs.* Cu(2)–O(1D)–N(1D)	32.8(1)
1b	Cu(1)–O(1A)–N(1A) *vs.* Cu(1)–O(1B)–N(1B)	35.9(1)
1a	C(9C)–C(10C)–C(11C)–C(9D′)–C(10D′)–C(11D′) (ring "C") *vs.* C(9D)–C(10D)–C(11D)–C(9C′)–C(10C′)–C(11C′) (ring "D")	39.7(1)
1b	C(9A)–C(10A)–C(11A)–C(9A′)–C(10A′)–C(11A′) (ring "A") *vs.* C(9B)–C(10B)–C(11B)–C(9B′)–C(10B′)–C(11B′) (ring "B")	90.00(1)

Table 3 Selected torsion angles for complex **1**

Dimer	Atoms defining angle	Torsion angle/°
1a	C(8C)–C(9C)–C(10C)–C(11D′) (ring "C")	−174.8(4)
1	C(8D)–C(9D)–C(10D)–C(11C′) (ring "D")	−174.9(3)
1b	C(8A)–C(9A)–C(10A)–C(11A′) (ring "A")	179.9(3)
1	C(8B)–C(9B)–C(10B)–C(10B′) (ring "B")	−178.0(5)

Table 4 Deviations from selected least-squares planes for complex **1**

Dimer	Plane	Deviation/Å	Plane	Deviation/Å
1a	ring "C"		ring "D"	
	C(9C)	0.018(2)	C(9D)	−0.019(2)
	C(10C)	−0.005(3)	C(10D)	0.006(3)
	C(11C)	−0.012(2)	C(11D)	0.013(3)
	C(9D′)	0.019(2)	C(9C′)	−0.018(2)
	C(10D′)	−0.006(3)	C(10C′)	0.005(3)
	C(11D′)	−0.013(3)	C(11C′)	0.012(2)
1b	ring "A"		ring "B"	
	C(9A)	0.001(3)	C(9B)	0.005(2)
	C(10A)	0.004(3)	C(10B)	−0.009(4)
	C(11A)	−0.005(3)	C(11B)	−0.001(4)
	C(9A′)	0.001(3)	C(9B′)	−0.005(2)
	C(10A′)	0.004(3)	C(10B′)	0.009(4)
	C(11A′)	−0.005(3)	C(11B′)	0.001(4)

C(9) angle for **1a** and **1b**. The Cu···Cu distance is 7.306(1) Å in **1a** and 7.275(1) Å in **1b**. The methyl group of nitromethane is disordered.

The two conformations of complex **1** in the unit cell demonstrate that the two phenylene rings can rotate freely and suggest that either π-stacking or CH–π interactions could be operative in preorganizing the ligands for dimer formation. The distance between the two phenylene rings in **1a** (5.23 Å) is larger than the standard distance for a strong π-stacking interaction between two aryl rings (3.35 Å for graphite[10]). The perpendicular or T-shaped arrangement of the phenylene rings in conformation **1b** is consistent with the preferred orientation in crystalline benzene.[11] This same interaction has also been shown to be important to both protein structure and protein–ligand binding.[12] Molecular dynamics calculations for liquid benzene[9] suggest that the optimum distance between the two ring centers in the T-shaped orientation is 4.99 Å and the energy of that interaction is -2.3 kcal mol^{-1}. In **1b** the distance between the ring centers is 4.99 Å, suggesting a strong edge-to-face interaction.

As expected based on the long Cu···Cu distances of 7.3 Å, the room temperature effective magnetic moment of 2.25μ_B (per copper atom) indicates no interaction between the copper atoms of the dimer. The magnetic moment is more in the range of a tetrahedral copper(II) species,[13] but this may simply reflect the distortion around the copper centers (see above). The position of the broad d–d electronic absorption band, centered at 610 nm (16 400 cm^{-1}) with a molar absorption coefficient of 130 M^{-1} cm^{-1}, is typical of the CuN$_2$O$_2$ chromophore. However spectral–structural correlations for a series of bis(*N*-alkylsalicylaldiminato)copper(II) complexes are not characteristic of the stereochemistry about the copper.[14]

Complexation studies of compound **I** with Zn^{II} and Ni^{II} have yielded insoluble, presumably polymeric or oligomeric materials. These results are not surprising considering the less flexible co-ordination geometries of these two metals. We are continuing to explore the complexation chemistry of **I** with various metals and will report those findings in due course. We envision a number of related studies developing from these results: (1) varying the rigid group, X, to produce macrocycles with different cavity dimensions, (2) investigating the host–guest chemistry of the dimer complex and (3) exploring the conformational preferences of the phenylene groups as shown by the crystal structure which may serve as a model system for studying edge-to-face aryl ring interactions.

Experimental

General

All reactions were carried out under an atmosphere of dry N$_2$ or Ar unless otherwise noted. Solvents and reagents were purchased from Aldrich and used without further purification. The IR spectra were recorded on a Perkin-Elmer Paragon 500 FTIR spectrometer, UV-Vis spectra on a Hewlett-Packard 8453 in CHCl$_3$ and NMR spectra on a Varian INOVA 400 MHz spectrometer in CDCl$_3$. Elemental analyses were performed by the Microanalytical Lab, University of California, Berkeley, CA. Mass spectral analyses were performed by the Mass Spectrometry Facility, University of California, Berkeley, CA. The effective magnetic moment of complex **I** was determined by the Gouy method at room temperature using a Johnson Matthey magnetic susceptibility balance. Diamagnetic corrections (*via* Pascal's constants) and the accepted temperature independent paramagnetic correction of 60×10^{-6} cgsu per copper atom were applied;[13] HgCo(SCN)$_4$ was used as the calibrant.

Preparations

***N*,*N*′-Bis(salicylidene)-1,4-phenylenedimethanamine I.** To a solution of *p*-phenylenedimethanamine (1.40 g, 10.3 mmol) in trimethyl orthoformate (35 mL) was added salicylaldehyde (2.20 mL, 20.6 mmol) over a 15 min period. The reaction was then warmed to 60 °C and allowed to stir for 24 h. Evaporation of the solvent and recrystallization of the residue from ethyl acetate provided 3.0 g (85%) of **I** as a orange-yellow solid, mp 139–140 °C (Found: C, 76.44; H, 5.59; N, 8.10. C$_{11}$H$_{10}$NO requires C, 76.71; H, 5.86; N, 8.14%). IR (neat): $\tilde{\nu}$/cm^{-1} 3051w, 3006w, 2875w, 2821w, 2700vw (v br), 1611m and 1578s. ^{1}H NMR (CDCl$_3$): δ 13.3 (2 H, s, OH), 8.4 (2 H, s, CH=N), 7.2–7.3 (m, 8 H, Ar), 6.9 (m, 2 H, Ar), 6.8 (m, 2 H, Ar) and 4.7 (s, 4 H, CH$_2$N). ^{13}C NMR (CDCl$_3$): δ 165.6, 161.0, 137.2, 132.3, 131.4, 128.0, 118.7, 118.6, 117.0 and 62.8. UV/Vis (CHCl$_3$): λ/nm (ε/M^{-1} cm^{-1}) 258 (24 000), 318 (9000).

The copper complex 1. To a solution of compound **I** (0.20 g, 0.58 mmol) in methanol (700 mL) was added *via* cannula a solution of Cu(OAc)$_2$·4H$_2$O (0.116 g, 0.58 mmol) in methanol (100 mL) over a period of 3 h. The solution was concentrated *in vacuo* to one-third the volume and an olive green powder was collected (0.2 g, 85% yield) by filtration: mp 312–313 °C [Found: C, 64.90; H, 4.22; N, 6.74%; MH$^+$ (mass spectrum) *m*/*z* 811. $C_{22}H_{18}CuN_2O_2$ requires C, 65.09; H, 4.47; N, 6.90%; MH$^+$ 811]. IR (neat): $\tilde{\nu}$/cm^{-1} 3028vw, 2916vw, 1611s and 1537m. UV/Vis ($CHCl_3$): λ/nm (ε/M^{-1} cm^{-1}) 247 (36 000), 272 (23 000), 305 (9500), 370 (7600) and 610 (130).

Crystal structure determination of compound 1

The structure of complex **1** was determined using a Siemens/Bruker AXS P4 four-circle diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) on a single crystal grown from nitromethane. Systematic absences *hkl*, $h + k \neq 2n$ and 00*l*, $l \neq 2n$ indicated space group *C*2/*c* or *Cc*. The former was chosen based on E-statistics favoring the centrosymmetric group, unreasonable thermal parameters generated in *Cc*, and successful solution in *C*2/*c*. The structure was solved by direct methods using SHELXS 86[15] and Fourier difference methods. Refinement was done by full-matrix least squares on F^2 using SHELXL 93.[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the dimers were found *via* Fourier difference maps and refined; those of nitromethane were added ideally and treated as a disordered methyl group.

Crystal data. $C_{45}H_{39}Cu_2N_5O_6$, $M = 872.89$, dark green block, $0.26 \times 0.38 \times 0.46$ mm, monoclinic; space group *C*2/*c*, $a = 29.647(3)$, $b = 14.834(3)$, $c = 19.991(2)$ Å, $\beta = 115.257(5)°$, $U = 7951(2)$ Å^3, $Z = 8$, $D_c = 1.458$ g cm^{-3}, μ(Mo-Kα) = 1.126 mm^{-1}, $T = 183$ K, 7009 independent reflections ($R_{int} = 0.033$), 668 parameters, $R1 = 0.0453$, $wR2(F^2) = 0.1069$, $S = 1.020$.

CCDC reference number 186/1423.

See http://www.rsc.org/suppdata/dt/1999/1831/ for crystallographic files in .cif format.

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