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Synthesis and Structural Characterization of a Novel Mixed-Valent $Cu^{II}Cu^{I}Cu^{II}$ Triangular Metallomacrocycle Using an Imine-Based Rigid Ligand

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A novel neutral mixed-valent $Cu^{I}Cu^{II}_2$ triangular metallomacrocycle $[Cu_3L_2(HL)]\cdot3CH_3OH\cdot2H_2O$ (**1**) was assembled by reaction of the tetradentate ligand bis(*N*-salicylidene-4,4′-diphenylamine), H_2L, with a copper(II) salt. ESI-MS show peaks only corresponding to the triangular structural species, indicating the high stability of the trimer structure in solution. Magnetic study confirms that there are two Cu^{II} ions and one Cu^{I} ion in a discrete triangular molecule. The crystal structure of **1** reveals that the triangle is formed by three deprotonated ligands and three copper ions with a Cu···Cu separation of ca. 11.8 Å. Each copper atom is coordinated by two oxygen atoms and two nitrogen atoms from two different bis-bidentate ligands in a heavily distorted tetrahedral geometry, while each ligand is bound to two metal ions in a bis-bidentate coordination mode and links the metal centers overlapping in an unprogressive manner. Strong intramolecular π···π interactions between the ligands are found to stabilize the constraint conformation of the triangle. Electrochemical study reveals that the mixed-valent $Cu^{I}Cu^{II}_2$ complex is the most stable state in solution condition, and the electrochemical communication between the copper ions might be explained on the basis of the through-bond interaction. UV−vis−NIR spectral measurement demonstrates the Robin−Day class II behavior of the mixed-valence compound with a weak copper−copper interaction.

Introduction

It is well established that self-assembly processes may generate well-defined architectures in a spontaneous and directed manner,[1] which are dependent upon numerous factors, such as the nature of the coordination site, the structure of the bridging ligand, the geometric preferences of the metal ions, and weaker noncovalent interactions. The application of metal−ligand interactions has proved particularly fruitful, and a considerable variety of frequently pre-designed molecular architectures have all been assembled.[2−4]

Among them, macrocyclic compounds formed by self-assembly of transition metals introduce many special functional properties such as luminescence,[3,5] redox activity,[3] and magnetism[4h] into the structure apart from their particular structural features.

In regard to the triangle, it should be formed by combining three 60° angular fragments and three linear ones.[4f,6] However, in sharp contrast to the numerous examples of other molecular architectures reported, triangular complexes are much less common,[2,7] mainly due to the rarity of suitable building blocks with proper turning angles because of the

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impossibility of generating such an angle in a metal fragment of common coordination number. This is especially true for complexes with rigid heterocyclic ligands, a class of compounds that was very successfully employed for the construction of other polynuclear assemblies. This problem can be circumvented by using rigid ligands having appropriate coordinate vectors or by using flexible ligands that can accommodate the steric requirements.[7a,8,9]

Of all the commonly studied transition metals, copper attracts particular interest because of the different stereo-electronic preferences of its two common oxidation states.[9,10] The Cu^{I}/Cu^{II} interconversion is often accompanied by a pronounced geometric change, and if the conversion is reversible, this geometric change may be the basis of an allosteric effect in which the geometric change at the metal varies the properties of a more remote site in the complex.[11] On the contrary, control of the geometric environment around copper centers allows control of the redox potential of the Cu^{I}–Cu^{II} couple. This is partially the basis of the redox properties of type 1 copper proteins[12] and many synthetic analogues,[13] where the rigidity of a carefully designed ligand environment can impose a geometry on the metal which is anywhere between the extremes preferred by Cu^{I} and Cu^{II} and thereby control the redox potential. Herein we report the synthesis and structural characterization of a mixed-valent Cu^{I}Cu$^{II}_2$ triangular metallomacrocycle with the rigid N,O-bis-bidentate Schiff's-base ligand bis(*N*-salicylidene-4,4′-

Chart 1

H$_2$L
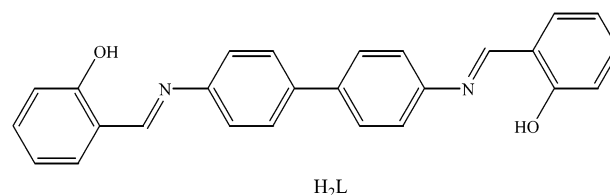
diphenylamine) (H$_2$L) (Chart 1), in which the intramolecular (interstrand) face-to-face $\pi\cdots\pi$ stacking interactions between the aromatic rings of these ligands give rise to the triangle formation and the resulted solid-state structures. The steric constraint geometries around the copper centers might influence the redox potentials of the Cu^{I}–Cu^{II} couples and lead to the existence of the most stable present mixed-valent state.

Experimental Section

Materials and Methods. All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded on a VECTOR 22 Bruker spectrophotometer with KBr pellets in the 4000–400-cm^{-1} regions, and ^{1}H NMR spectra, on a DRX500 Bruker spectrometer at 298 K with TMS as an internal reference. Electrospray mass spectrometry was carried out on a LCQ system (Finnigan MAT) with methanol as the mobile phase. The UV–vis–NIR spectrum was obtained at room temperature on a Shimmadzu 3100 spectrophotometer in chloroform solution. The magnetic measurement on polycrystalline samples was carried out using a CAHN-2000 Faraday magnetometer in the 75–300 K temperature range. Differential pulse voltammetry was done with an EG&G PAR model 273 instrument in a three-electrode cell with a pure Ar gas inlet and outlet, which has a 50 ms pulse width with current sample 40 ms after the pulse was applied. A sweep rate of 20 mV s^{-1} was used in the pulse experiment. The cell comprises a platinum wire working electrode, a platinum auxiliary electrode, and a Ag/AgCl wire reference electrode. The voltammogram of the complex was obtained in chloroform with *n*-Bu$_4$NClO$_4$ (0.1 mol·dm^{-3}) as supporting electrolyte. Ferrocene (1.0 × 10^{-3} mol·dm^{-3}) was used as external standard with $E_{1/2}$ = 0.46 V vs the Ag/AgCl electrode.

Caution! Although no problems were encountered in this work, perchlorates are potentially explosive and should be handled with care.

Synthesis of Bis(*N*-salicylidene-4,4′-diphenylamine), H$_2$L. The ligand H$_2$L was synthesized according to the literature methods.[14] Benzidine (0.55 g, 3.0 mmol) and salicylaldehyde (0.73 g, 6.0 mmol) were mixed in methanol (30 mL) and refluxed for 1 h. The solution was then evaporated to 5 mL, and the yellow product (1.1 g, 2.7 mmol, yield 90%) was filtered out and dried under vacuum. Anal. Calcd for C$_{26}$H$_{20}$N$_2$O$_2$: C, 79.6; H, 5.1; N, 7.1. Found: C, 79.8; H, 4.8; N, 7.3. ^{1}H NMR (500 MHz, CDCl$_3$): δ 11.04 (bs, 2H, OH), 8.00 (d, 2H, imine), 7.60 (m, 4H), 7.28 (m, 8H), 7.07 (d, 2H), 7.02 (t, 2H). IR (KBr, cm^{-1}): 3448.5 w, 3051.5 w, 1619.9 vs, 1600.2 m, 1572.7 s, 1498.9 m, 1487.2 s, 1455.9 m, 1411.1 m, 1365.3 m, 1283.4 s, 1190.4 s, 1176.6 m, 1150.7 m, 910.9 m, 847.5 m, 826.8 s, 749.3 s, 527.7 m.

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Table 1. Crystallographic Data for Complex **1**

formula	$C_{78}H_{55}N_6Cu_3O_6 \cdot 3CH_3OH \cdot 2H_2O$
fw	1495.06
cryst system	monoclinic
space group	$P2_1/c$
a/Å	18.687(10)
b/Å	24.161(13)
c/Å	18.484(10)
β/deg	112.92(1)
V/Å^3	7687(7)
Z	4
T/K	293(2)
μ/mm^{-1}	0.884
no. reflcs measd	30 319
no. of unique reflcns	10 026
$R_1{}^a$	0.076
$wR_2{}^a$	0.127

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

Synthesis of Complex 1. A methanolic solution (10 mL) of Cu-$(BF_4)_2$ (0.36 g, 1.5 mmol) was added with stirring to a methanol solution (20 mL) of H_2L (0.59 g, 1.5 mmol) and NaOH (1.2 g, 3.0 mmol). A brown precipitate developed immediately and was filtered out. Then the solid was extracted by chloroform and the resulting solution was allowed to evaporate slowly in air. Dark brown crystals of **1** (0.52 g, 0.35 mmol, yield 70%) suitable for single crystal X-ray diffraction were isolated directly from solution after 1 week. As the crystals slowly deteriorated on standing, presumably due to loss of solvent, samples for microanalysis were first dried in vacuo. Anal. Calcd for $C_{78}H_{55}N_6Cu_3O_6 \cdot 3CH_3OH \cdot 2H_2O$: C, 65.1; H, 4.8; N, 5.6. Found: C, 65.7; H, 4.6; N, 6.2. IR (KBr, cm^{-1}): 3423.5 w, 3027.2 w, 1610.6 vs, 1583.2 s, 1531.4 s, 1490.8 m, 1463.2 s, 1441.9 s, 1378.2 m, 1254.1 w, 1326.4 m, 1181.7 s, 1148.8 s, 1003.3 w, 863.2 w, 828.7 w, 756.7 m, 537.2 m. UV/vis [CHCl$_3$; λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})]: 318 (29 100), 420 (23 600), 660 (640), 1500 (340).

Crystallography. Parameters for data collection and refinement of the complex are summarized in Table 1. Intensities of complex **1** were collected on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710$ 73 Å) using the SMART and SAINT programs.[15] The structure was solved by direct methods and refined on F^2 using full-matrix least-squares methods with SHELXTL version 5.1.[16] Anisotropic thermal parameters were refined for non-hydrogen atoms for complex **1**. Hydrogen atoms of the triangle were located geometrically, whereas those of solvent molecules were found on Fourier difference maps, and all the hydrogen atoms were refined in riding model. Since the quality of the single crystal was not satisfactory, the observed/unique reflection ratio was only 22% and there were also 643 restraints employed.

Results and Discussion

Synthesis and Characterization. Schiff's-base ligands are excellent chelate ligands and employed for their ease of synthesis and high yield in a single-step reaction from commercial, inexpensive reagents allowing us to systematically probe the effect of modifications to the ligand backbone through which we are attempting to control the precise topography, or microarchitecture, of the arrays.[17,18] The bis-bidentate ligand H_2L appears to be able to take a constraint

torsion about the central C−C bond between two aromatic rings, which provides an opportunity for constructing metal triangular complexes. On the other hand, in the presence of a ligand which can serve both as a ligand and as a reducing agent, for example,[19] benzimidazole or polypyridyl ligands, copper(II) salts may be partially reduced to give mixed-valent copper compounds and the courses of the redox reactions often occur highly dependent upon the specific conditions used: reagent and acid/base concentrations; medium; reaction temperatures; duration of reaction; crystallization temperatures.

Elemental analyses reveal the formation of the title complex of the form $[M_nL_n]$. ESI-MS[20] of complex **1** in dichloromethane−methanol solution (Figure 1) shows one cation peak corresponding to $[Cu^ICu^{II}L(HL)_2 \cdot CH_3OH]^+$ ($m/z = 1397$) and one anion peak ($m/z = 1362$) related to $[Cu^ICu^{II}_2(L)_3]^-$, which are both consistent with the formation of the triangular structure and indicate that the triangular species have great stability in solution. The IR spectrum of H_2L displays a sharp peak characteristic of the C=N bond at 1620 cm^{-1}, which upon complexation of metal shifts to lower frequency (ca. 1583 cm^{-1}) and is consistent with coordination to the imino nitrogen.[21] The electronic spectrum of complex **1** exhibits an intense band at 318 nm, which is assigned to the $\pi-\pi^*$ transition associated with the azo-methine linkage,[22] and a peak at 420 nm, which is attributed to Cu(I)-to-ligand MLCT.[11a,12,23] A broad transition at 660 nm (640 dm^3 mol^{-1} cm^{-1}) is considered to associate with the metal-centered d−d transition of tetrahedral coordinated Cu^{II} center at the N(imine)$_2$O$_2$ site in the complex.[22] It seems that this complex contains both Cu^I and Cu^{II} ions.

To determine the coexistences of Cu^I and Cu^{II} ions as well as their molar ratio, the temperature dependence of the molar magnetic susceptibility χ_M and the effective magnetic mo-

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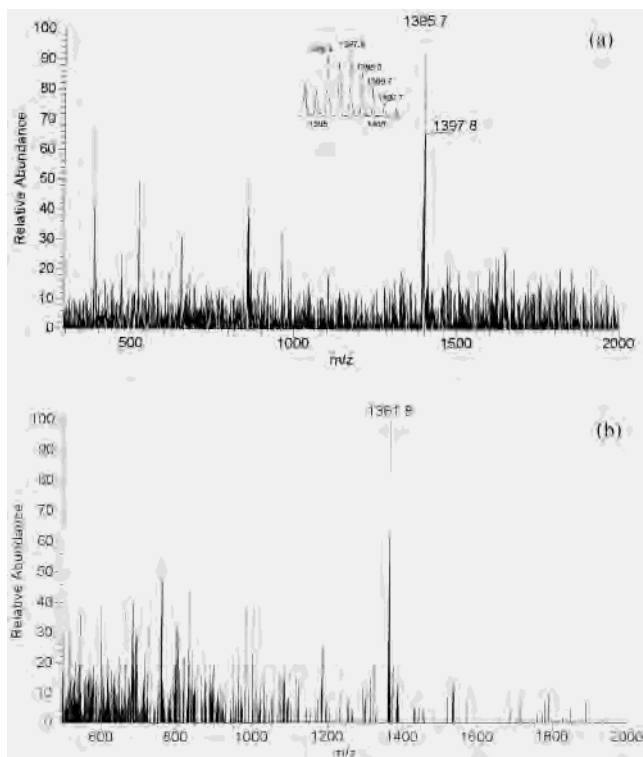
Figure 1. Cation (a) and anion (b) electrospray mass spectra of complex **1** in dichloromethane−methanol.
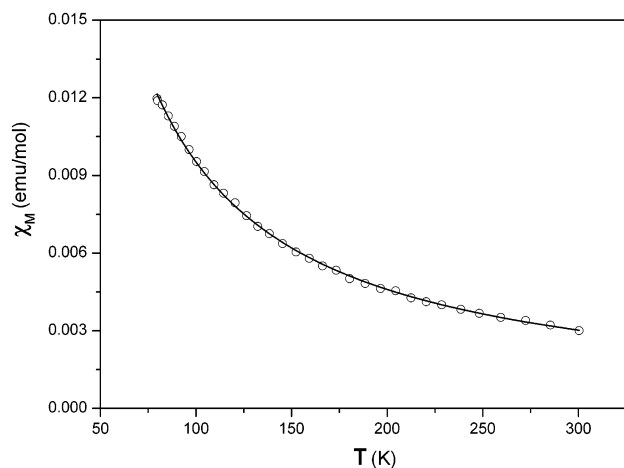

Figure 2. Thermal dependence of the magnetic susceptibility χ_M for the triangular copper complex. The solid line represents the theoretical results (see text).
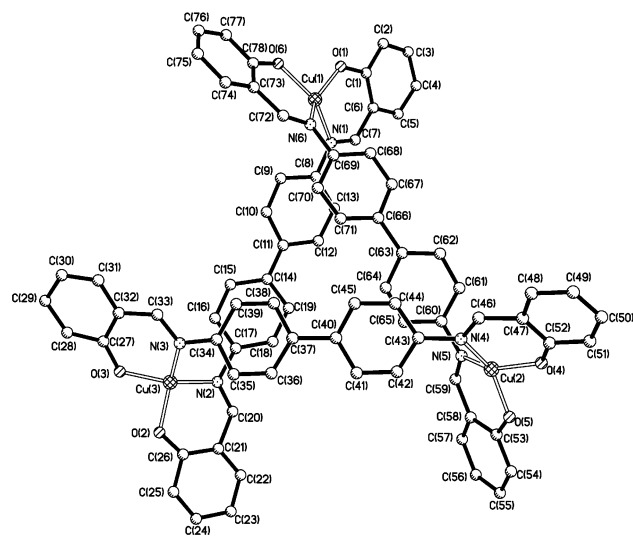

Figure 3. Molecular structure of the helical triangular macrocycle with hydrogen atoms and solvent molecules of crystallization omitted for clarity.

ment μ_{eff} for a polycrystalline sample of the trinuclear complex in the range of 75−300 K are carried out. The effective magnetic moment at room temperature of 2.72 μ_B, which is consistent with that expected for two independent Cu^{II} ions, increases slightly with decreasing temperature and reaches 2.78 μ_B. This magnetic behavior is characteristic of a very weak ferromagnetic coupling among the two Cu(II) ions. The temperature dependence of the magnetic susceptibilities for complex **1** is displayed in Figure 2 in the form of a χ_M vs T plot, χ_M being the corrected magnetic susceptibility per two Cu(II) atoms. Upon cooling of the sample from room temperature, the χ_M value increases continuously. The susceptibility data were analyzed by the Bleaney−Bowers expression for isotropic dimers of $S = 1/2$

ions on the basis of the Heisenberg Hamiltonian $H = -JS_A \cdot S_B$.[24] An excellent fit, shown as a solid line in Figure 2, is obtained with $g = 2.17$ and $J = 11.9$ cm^{-1}.

Structural Characterization of Complex 1. An X-ray crystallographic study has unequivocally confirmed the existence of a molecular triangle. The atomic numbering scheme and atom connectivity for the molecular triangle were shown in Figure 3. Three ligands link the three metal centers overlapping to show a triangular fashion: in one of these three ligands, one imine binding unit lies above the averaged plane of the molecule, while the other imine binding unit lies below the averaged plane; of the other two ligands, both imine binding units of each ligand all lie on the same side. Each metal center has a distorted four-coordinated geometry arising from coordination by two bi-dentate chromophores from two different ligands to permit the triangular arrangement with the metal···metal distances about 12.2 for Cu(1)···Cu(2), 11.6 for Cu(1)···Cu(3), and 11.5 Å for Cu(2)···Cu(3), respectively. The hydroxybenzene rings point outward giving the molecule an outer diameter of 22.4 Å and a height of 9.3 Å. The shortest distance between center of the triangle and atoms of the ligands is ca. 2.4 Å, indicating that the cavity at the center of the triangle too small to include any guests.

In regard to four-coordinated geometry of copper ions, the geometric change is in part parametrized by the angle θ, the dihedral angle between the two CuNO planes, which is 90° for a pseudotetrahedral (D_{2d}) structure and 0° for a planar structure (D_{2h}). The θ angles of 43.2, 45.2, and 47.8° at Cu(1), Cu(2), and Cu(3), respectively, indicate intermediate structures between the pseudotetrahedral and the planar geometries, even though, in practice, the solid-state θ values tend to be around 70−80° for Cu^I complexes,[23] which decreases to 40−50° for Cu^{II} complexes depending on the steric properties of the ligands.[25] It seems that the sites of

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Table 2. Selected Bond Distances (Å) and Angles (deg) of Complex **1**

Cu(1)–O(1)	1.905(6)	Cu(1)–O(6)	1.899(5)
Cu(2)–O(4)	1.888(5)	Cu(2)–O(5)	1.849(6)
Cu(3)–O(2)	1.849(7)	Cu(3)–O(3)	1.854(6)
Cu(1)–N(1)	1.995(5)	Cu(1)–N(6)	1.938(5)
Cu(2)–N(4)	1.989(5)	Cu(2)–N(5)	1.962(4)
Cu(3)–N(2)	1.931(5)	Cu(3)–N(3)	1.892(5)
O(1)–C(1)	1.323(8)	O(2)–C(26)	1.235(8)
O(3)–C(27)	1.286(9)	O(4)–C(52)	1.268(8)
O(5)–C(53)	1.353(9)	O(6)–C(78)	1.355(8)
O(6)–Cu(1)–O(1)	90.5(2)	O(6)–Cu(1)–N(1)	148.4(2)
O(1)–Cu(1)–N(1)	94.0(2)	O(6)–Cu(1)–N(6)	96.2(2)
O(1)–Cu(1)–N(6)	148.1(2)	N(1)–Cu(1)–N(6)	96.2(2)
O(5)–Cu(2)–O(4)	88.6(3)	O(5)–Cu(2)–N(5)	96.1(2)
O(4)–Cu(2)–N(5)	145.3(2)	O(5)–Cu(2)–N(4)	147.8(3)
O(4)–Cu(2)–N(4)	93.2(2)	N(5)–Cu(2)–N(2)	100.5(2)
O(2)–Cu(3)–O(3)	89.3(3)	O(2)–Cu(3)–N(3)	145.5(2)
O(3)–Cu(3)–N(3)	96.1(2)	O(2)–Cu(3)–N(2)	97.1(2)
O(3)–Cu(3)–N(2)	143.3(2)	N(3)–Cu(3)–N(2)	98.5(2)

Cu^I and Cu^{II} centers in triangle could not be recognized from each other only by the θ values. Since the C–O bonds from phenolic moiety are not significantly different from others (Table 2), it is difficult to determine which phenolate oxygen atom is protonated.[26] However, it is noticed that the Cu–O bonds (ca. 1.90 Å) for Cu(1) are a little longer than those for Cu(2) and Cu(3) (ca. 1.86 Å on average), which suggests the predominant +1 charge on Cu(1) and prevalent +2 charge for both Cu(2) and Cu(3), since the presence of monovalent copper ion results in the weaker static attraction to the phenolate oxygen atoms of the ligand than that of divalent Cu ions.

The dihedral angles between two hydroxybenzene rings in one ligand are ca. 14.8 for ligand I, 22.8 for ligand II, and 62.7° for ligand III, respectively (where ligands I, II, and III are appointed to the ligands containing O(1), O(3), and O(5), respectively). Coordination to the metal center also causes the internuclear twisting among the benzene rings with the dihedral angles between the benzene rings of 23.4 in ligand I, 20.5 in ligand II, and 38.7° in ligand III, respectively, which indicates the ligand III is distorted strongly much more than ligands I and II. The ligand torsion probably derives from the steric constraints imposed by the tetrahedrally disposed copper centers. However, when the rigid benzidine spacer is replaced by flexible ones, helical complexes can be created.[17a,21,27] It is suggested that thus enhanced flexibility of N,O-bis-bidentate Schiff's-base ligands, bis(*N*-salicylidene-4,4′-diaminodiphenyl)methane and bis(*N*-salicylidene-4,4′-diaminodiphenyl) ether, permits the ligands to support helical ligand arrays, which indicates that the flexibility of the spacer groups is the important factor controlling the outcome architectures.

It is worthy to note that each of the six benzene rings stack with the adjacent one of the other ligand by strong intramolecular (interstrand) face-to-face $\pi\cdots\pi$ interactions, although they are not strictly coplanar. The shortest interplanar
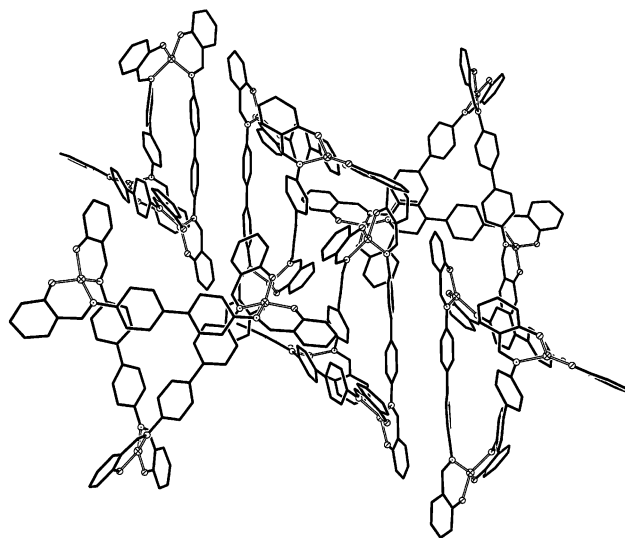
Figure 4. Stereo illustration showing intermolecular interactions in **1**.

atom···atom separations and the dihedral angles are 3.11 Å (16.6°), 3.08 Å (13.1°), and 3.14 Å (7.8°) for the stacked pairs IC and IIB, IB and IIIC, and IIC and IIIB, respectively.[28] The distances are similar to the standard distance for a strong π–stacking interaction between two aryl rings (3.35 Å for graphite[29] and 3.10 Å for 4,5-diazafluorene rings[30]). Although these stacking interactions are weak compared to the metal–nitrogen and metal–oxygen coordinating bonds, it could be suggested that this kind of interaction was important in the molecular assembly of the trinuclear metal macrocycle. Furthermore, the triangular molecules pack together through a combination of face-to-face $\pi\cdots\pi$ (3.4–3.8 Å) interactions and edge-to-face $\pi\cdots\pi$ (3.5–3.8 Å) interactions (Figure 4). These interactions combine to form an entangled three-dimensional network. This arrangement creates cavities within the lattice in which the disordered solvent molecules are located.

Mixed-Valence Properties. The differential pulse voltammetry (DPV) technique is employed to obtain well-resolved potential information, while the individual redox processes for the multinuclear complexes are poorly resolved in the CV experiment, in which individual $E_{1/2}$ potentials cannot be easily or accurately extracted from the data.[31] DPV of **1** (Figure 5) shows three peaks with the half-wave potentials ($E_{1/2}$) at 0.02, 0.17, and 0.51 V (vs Ag/AgCl), corresponding to the one-electron metal-based oxidation $Cu^I_2Cu^{II}/Cu^I_3$, Cu^{II}_2-$Cu^I/Cu^{II}Cu^I_2$, and $Cu^{II}_3/Cu^{II}_2Cu^I$, respectively. Such an electrochemical communication behavior might be explained

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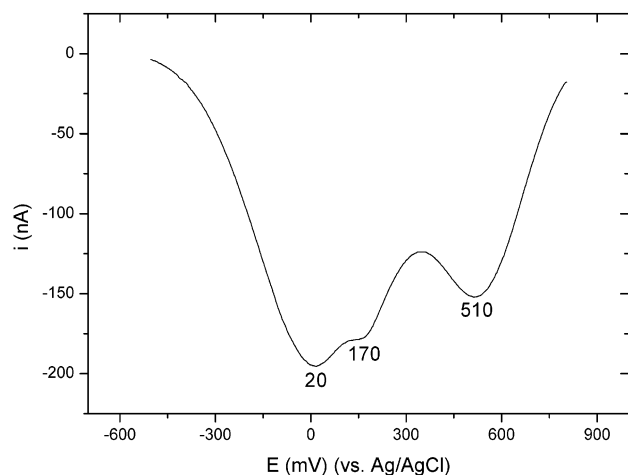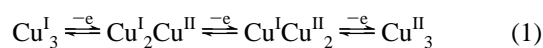(27) Yoshida, N.; Oshio, H.; Ito, T. *J. Chem. Soc., Perkin Trans. 2* **1999**, 975.

(28) Plane IA is defined by atoms C(1)–C(6); plane IB is defined by atoms C(8)–C(13); plane IC is defined by atoms C(14)–C(19); plane ID is defined by atoms C(21)–C(26); plane IIA is defined by atoms C(27)–C(32); plane IIB is defined by atoms C(34)–C(39); plane IIC is defined by atoms C(40)–C(45); plane IID is defined by atoms C(47)–C(52); plane IIIA is defined by atoms C(53)–C(58); plane IIIB is defined by atoms C(60)–C(65); plane IIIC is defined by atoms C(66)–C(69); plane IIID is defined by atoms C(73)–C(78).

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Figure 5. Differential pulse voltammetry for compound **1** (1.0×10^{-3} M) in CHCl$_3$ containing *n*-Bu$_4$NClO$_4$ (0.1 M).

semiquantitatively on basis of through-bond interactions, since the bridging moiety is a molecule containing conjugated unsaturation. As expected, the mixed-valence triangular complex undergoes three sequential one-electron oxidations (eq 1).

$$Cu^{I}_3 \underset{}{\overset{-e}{\rightleftharpoons}} Cu^{I}_2Cu^{II} \underset{}{\overset{-e}{\rightleftharpoons}} Cu^{I}Cu^{II}_2 \underset{}{\overset{-e}{\rightleftharpoons}} Cu^{II}_3 \qquad (1)$$

The separations (ΔE) 0.15 and 0.34 V between the potentials for the metal-based couples [Cu$^{I}_2$Cu^{II}]/[Cu$^{I}_3$] and [Cu$^{II}_2$Cu^{I}]/[Cu^{II}Cu$^{I}_2$], [Cu$^{II}_2$Cu^{I}]/[Cu^{II}Cu$^{I}_2$], and [Cu$^{II}_3$]/[Cu$^{II}_2$Cu^{I}], respectively, clearly show that the complex Cu^{I}-Cu$^{II}_2$ species is the most stable one of the four redox species in common condition.[11a]

The properties of multinuclear mixed-valence (MV) compounds have been extensively investigated,[32−35] because of their potential application to electrochromic devices, solar energy conversion catalysts, photoinduced magnetic memory devices, chemical sensors, nanoscale switches with ultrafast write times, and molecular-scale rectifiers.[36] Intervalence metal−metal interactions of complex **1**, verified by the information of intervalence transition (IT) band[37] in the UV−vis−NIR spectrum, shows one broad band at ca. 1500 nm ($\epsilon = 340$ dm^3 mol^{-1} cm^{-1}). Intervalence charge-transfer bands in mixed-valence Cu(I)/Cu(II) complexes generally occur in the near-IR region of the electronic spectra and have extinction coefficients of several hundred or a few thousand

dm^3 mol^{-1} cm^{-1},[38] so both the position and the intensity of the 1500 nm peak are consistent with it being an IT band.

Assuming that the MV compounds behave as Robin−Day class II compounds, the IT absorption band of MV compounds can be modeled by classical Marcus−Hush theory to obtain kinetic information about the electron transfer thermodynamic data:[39]

$$H_{ab} = 0.0205 \left\{ \frac{\epsilon_{max}\Delta\nu_{1/2}}{\nu_{max}g} \right\}^{1/2} \frac{\nu_{max}}{r} \qquad (2)$$

$$\alpha = [H_{ab}^2/\nu_{max}^2]^{1/2} \qquad (3)$$

In eqs 2 and 3, H_{ab} (cm^{-1}) is a measure of the electronic coupling between the donor and acceptor, ϵ_{max} is the molar absorptivity of the IT band at its maximum value, $\Delta\nu_{1/2}$ is the IT absorption bandwidth at half its maximum height (cm^{-1}), ν_{max} is the energy of the IT absorption maximum in wavenumber units, g is the degeneracy, r is the distance (Å) between the donor and acceptor (which in this case is estimated from the copper−copper distances in the X-ray crystal structure), and α is the delocalization parameter. When these equations for mixed-valence complexes are applied to the Cu$^{II}_2$Cu^{I} species ($\nu_{max} = 6700$ cm^{-1} and $\Delta\nu_{1/2} = 1100$ cm^{-1}) with the copper−copper distance (11.8 Å), they lead to a degree of electronic delocalization (α^2) of 0.0002 and the interaction energy (H_{ab}) is ca. 90 cm^{-1}. The calculated delocalization parameter (α) is less than the 0.25 upper limit for class II MV compounds, indicating that the valences on the metal centers can be considered as essentially trapped.[37]

Summary

The structural study of the new neutral mixed-valence Cu^{I}Cu$^{II}_2$ triangular metallomacrocycle gives insight into the factors favoring the self-assembly of supramolecular architectures. It is suggested that steric effects do not appear to play a major role in determining the assembled product, while the intra- and intermolecule $\pi\cdots\pi$ interactions are considered to be important in stabilizing this complex. Since the bridging moiety is a conjugated unsaturation molecule, the electrochemical communication behavior might be explained semiquantitatively on the basis of through-bond interaction. The UV−vis−NIR spectral measurement demonstrates the Robin−Day class II behavior of the mixed-valence compound with weak copper−copper interaction. Mixed-valence compounds

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have played a crucial role not only in the exploration of electron transfer theory but also for addressing contemporary issues in electron-transfer research,[40] especially, when the emphasis in this field has shifted away from simple dinuclear MV species and focused instead on multinuclear supramolecular species.[41]

Supporting Information Available: An X-ray crystallographic file for compound **1** (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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