Ternary Mononuclear and Ferromagnetically Coupled Dinuclear Copper(II) Complexes of 1,10-Phenanthroline and *N*-Salicylidene-2-methoxyaniline that Show Supramolecular Self-Organization

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The ternary copper(II) complex [Cu(phen)(L)](ClO_4) (**1**) and dinuclear copper(II) complex [Cu_2(phen)$_3$(L)(O_2CMe)](ClO_4)$_2$ (**2**) have been prepared and characterized structurally by X-ray crystallography (HL: *N*-salicylidene-2-methoxyaniline; phen: 1,10-phenanthroline). The crystal structure of **1** displays a square-pyramidal [4+1] coordination geometry in which the basal plane has three nitrogen donor atoms and the phenolate oxygen atom of the Schiff base. The methoxy oxygen atom exhibits axial coordination in the CuN_3O_2 chromophore. Complex **2** has a dinuclear copper(II) core in which the Cu(phen)$_2^{2+}$ and Cu(phen)(L)$^+$ units are linked by an acetate ion showing equatorial/axial modes of bonding. In the bis(phen) unit, the basal plane has three nitrogen atoms and the acetate oxygen atom with one phen nitrogen atom occupying the axial site. In the mono(phen) unit, the basal plane has three nitrogen atoms and one phenolate oxygen atom. The acetate oxygen atom occupies the axial site. The equatorial/axial bridging mode of the acetate ion makes the dicopper(II) unit weakly ferromagnetic ($2J$ = +22 cm^{-1}) and the complex in CH_2Cl_2 glass at 77 K shows an axial EPR spectrum [$g_{\|}$ = 2.23 ($A_{\|}$ = 150 × 10^{-4} cm^{-1}); $g_{\perp}$ = 2.03] corresponding to a ΔM_s = ±1 transition and a half-field signal due to a ΔM_s = ±2 transition. Complex **1** displays an axial EPR spectrum with $g_{\|} > g_{\perp}$ indicating a $\{d_{x^2-y^2}\}^1$ ground state. The complexes show a d–d band near 650 nm and a charge-transfer band at ca. 415 nm in methanol. The complexes are redox-active and exhibit a Cu^{II}/Cu^{I} couple near 0.0 V versus SCE in DMF and CH_2Cl_2/0.1 M TBAP. Complex **1** is catalytically active in the oxidation of ascorbic acid by dioxygen in aqueous methanol. Complex **2** also shows similar catalytic activity, but the core is susceptible to cleavage under the reaction conditions. The complexes show π–π stacking interactions. Complex **1** forms a one-dimensional chain through intermolecular π–π stacking interactions involving phen and the phenolate ring of the Schiff base. Complex **2** displays intramolecular and intermolecular π–π stacking interactions involving phen ligands leading to the formation of a supramolecular tetrameric structure.

Introduction

Ternary copper(II) complexes of the type [CuL^1L^2]$^{n+}$, where L^1 and L^2 together form a square-pyramidal [4+1] coordination geometry with labile binding sites, are of biological relevance.[1−6] Ternary complexes have been used to model the active site structures and catalytic properties of several type-2 copper proteins.[7−17] It has been observed that the biological activities of such copper proteins often are dependent on the noncovalent interactions between aromatic moieties.[1] The complexes are related to the formation of the tyrosine phenoxyl Tyr272 radical in a stacking interaction with Trp290 in galactose oxidase and the involvement of trihydroxyphenylalanine (topa) quinone in amine oxidase.[18,19] Such weak interactions play a crucial role in bioinorganic chemistry toward stabilizing the tertiary structure of proteins, reactivity of the metalloenzymes, in the molecular recognition process and in nucleic acids chemistry.[20,21]

Sigel et al. have studied the stacking interactions of the aromatic rings in ternary complexes.[22] Such weak interactions have profound influence on the structure and function of the complexes.[1,21,22] The present work stems from our interest to prepare ternary copper(II) complexes using an *N*,*N*-donor, 1,10-phenanthroline (phen), and an *O*,*N*,*O*-donor Schiff base, *N*-salicylidene-2-methoxyaniline (HL), to study such noncovalent interactions. We have been able to prepare a mononuclear ternary copper(II) complex [Cu(phen)(L)](ClO_4) (**1**) that forms a 1D chain by intermolecular π−π interactions involving the phen and Schiff-base ligands. We have also prepared a ferromagnetically coupled acetato-bridged dicopper(II) complex [Cu_2(phen)$_3$(L)(O_2CMe)](ClO_4)$_2$ (**2**) that is stabilized by novel intramolecular π−π interactions involving two phen ligands belonging to two copper centers. Interestingly, complex **2** undergoes self-organization through intermolecular π−π interactions of two phen ligands belonging to two dimeric species to form an unusual discrete supramolecular tetrameric species. Her-

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Table 1. Spectral, magnetic and electrochemical data for complexes **1** and **2**

			1	**2**
(a)	IR[a]	ν(C=N)/cm^{-1}	1588	1614
		ν(ClO_4)/cm^{-1}	1096	1087
(b)	UV/Vis	λ_{max}/nm [ε/dm^3 mol^{-1} cm^{-1}][b]	641 [125],[c] 413 [2865],[d] 380 [2775],[d] 321 [2820][d]	650 [132],[c] 414 [2900],[d] 380 [2775],[d] 321 [2820][d]
(c)	EPR[e]	$g_{\parallel}$ ($10^4 \times A_{\parallel}$/cm^{-1})	2.28 [163]	2.23 [150]
		$g_{\perp}$	2.02	2.03
(d)		μ_{eff} (per Cu)[f]/μ_B	1.82	1.97[g]
(e)	CV	$E_{1/2}$/V [ΔE_P/mV][h] for Cu^{II}/Cu^{I} couple		
		in CH_2Cl_2/0.1 M TBAP	0.063 [546][i]	0.030 [640][j]
		in DMF/0.1 M TBAP	−0.070 [390][k]	

[a] KBr phase. [b] MeOH solvent. [c] d−d band. [d] Charge-transfer band. [e] In a DMF glass at 77 K for **1** and in a CH_2Cl_2 glass at 77 K for **2**. [f] In μ_B unit at 298 K. [g] $2J$ value of +22 cm^{-1}. [h] At 50 mV s^{-1}; $\Delta E_P = E_{pc} - E_{pa}$, where E_{pc} and E_{pa} are cathodic and anodic peak potentials; $E_{1/2} = (E_{pc} + E_{pa})/2$. [i] The i_{pc}/i_{pa} ratio of 3.5 (i_{pc} and i_{pa} are cathodic and anodic peak currents, respectively). [j] The i_{pc}/i_{pa} ratio of 14. [k] The i_{pc}/i_{pa} ratio of 4.1.

ein, we present the synthesis, crystal structure and properties of complexes **1** and **2**.

Results and Discussion

Synthesis and General Properties

The ternary monomeric complex **1** was prepared in high yield by a reaction of copper(II) perchlorate with 1,10-phenanthroline and the Schiff base (HL) in methanol. When the reaction of phen and HL is carried out with dimeric copper(II) acetate hydrate in methanol, followed by addition of sodium perchlorate, the major product is a dicopper(II) species of formulation $[Cu_2(phen)_3(L)(O_2CMe)](ClO_4)_2$ (**2**) along with **1** as a minor product. The complexes were characterized by analytical, spectral and single-crystal X-ray diffraction methods. The spectroscopic and magnetic data are given in Table 1.

The mononuclear complex **1** is one-electron paramagnetic. Magnetic susceptibility measurements in the range 30−302 K for the polycrystalline sample of **2** show weak ferromagnetic behavior of the complex. A theoretical fitting of the $\chi_M T$ vs. T plot gives a J value of +11 cm^{-1} with g = 2.17, $g1$ = 2.11 and ρ = 0.001 (Figure 1). Complexes **1** and **2** display axial X-band EPR spectra giving $g_{\parallel} > g_{\perp}$ indicating a $\{d_{x^2-y^2}\}^1$ ground state and a tetragonally distorted square-pyramidal geometry at the copper centers. Complex **2** in a CH_2Cl_2 glass at 77 K shows an additional signal at half-field corresponding to a $\Delta M_S = \pm 2$ transition indicating that it has dimeric nature and the triplet ground state (Figure 1).[23] This signal is, however, absent in a DMF glass at 77 K, possibly because of cleavage of the dimeric core. The complexes display a d−d band near 650 nm in methanol along with a charge-transfer band at ca. 415 nm.

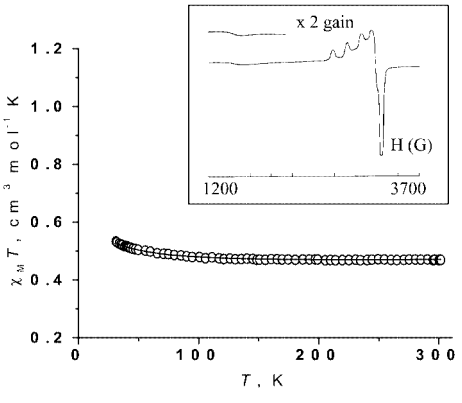

Figure 1. Plot of $\chi_M T$ vs. T for a polycrystalline sample of $[Cu_2(phen)_3(L)(O_2CMe)](ClO_4)_2$ (**2**) (circles); the solid line represents the best theoretical fit to the experimental data; an X-band EPR spectrum of **2** in a CH_2Cl_2 glass at 77 K is shown in the inset

Crystal Structures

Complexes **1** and **2** were characterized by single-crystal X-ray crystallography. Selected bond lengths and angles are given in Table 2. Perspective views of the molecules are shown in Figures 2 and 3. Complex **1** has a ternary structure consisting of a bidentate *N*,*N*-donor phen and tridentate *O*,*N*,*O*-donor Schiff base (L) bonded to the metal center in the cationic complex with a perchlorate counterion. While the basal plane is occupied by three nitrogen atoms and the phenolate oxygen atom, the methoxyl oxygen atom of the Schiff base shows axial bonding in the 4+1 coordination geometry with a CuN_3O_2 chromophore. The axial Cu−O bond length is 2.627(2) Å, which is similar to the metal-to-axial-tyrosinate-oxygen-atom distance of 2.69 Å in galactose oxidase.[18,24] The structure of **1** is distorted square-pyramidal, giving a trigonal distortion parameter (τ) value of 0.13.[25] In **1**, the torsion angle at the C=N (imine) moiety of the Schiff's base is 45.8°, which is similar to those angles observed in analogous complexes having axial sulfur ligation.[26] Complex **1** displays an intermolecular $\pi-\pi$ stacking interaction involving the phen and phenolate ring moieties with an interplanar distance of ca. 3.6 Å between the centroids of the rings that have essentially a parallel orientation (Figure 4).

The crystal structure of **2** displays a dicationic dicopper(II) complex crystallized with two perchlorate anions. The structure consists of two copper(II) centers, viz. $\{Cu(phen)_2^{2+}\}$ and $\{Cu(phen)(L)^{+}\}$, that are covalently

Table 2. Selected bond lengths [Å] and angles [°] for [Cu(phen)(L)]ClO_4 (**1**) and [Cu_2(phen)$_3$(L)(O_2CMe)](ClO_4)$_2$ (**2**) with estimated standard deviations in parentheses

	1	**2**
Cu(1)···Cu(2)		4.342(2)
Cu(1)−O(1)	1.867(3)	1.857(5)
Cu(1)−O(2)	2.627(2)	
Cu(1)−O(3)		2.230(6)
Cu(1)−N(1)	1.930(3)	2.005(6)
Cu(1)−N(2)	2.039(3)	2.011(6)
Cu(1)−N(3)	1.999(3)	2.029(6)
Cu(2)−O(4)		1.966(5)
Cu(2)−N(4)		2.185(7)
Cu(2)−N(5)		1.983(6)
Cu(2)−N(6)		1.991(6)
Cu(2)−N(7)		2.069(6)
O(1)−Cu(1)−O(2)	134.06(11)	
O(1)−Cu(1)−O(3)		93.1(2)
O(1)−Cu(1)−N(1)	96.19(12)	93.0(2)
O(1)−Cu(1)−N(2)	146.32(13)	166.2(2)
O(1)−Cu(1)−N(3)	93.19(12)	89.2(2)
O(2)−Cu(1)−N(1)	68.98(11)	
O(2)−Cu(1)−N(2)	79.25(12)	
O(2)−Cu(1)−N(3)	87.10(12)	
O(3)−Cu(1)−N(1)		96.1(2)
O(3)−Cu(1)−N(2)		84.6(2)
O(3)−Cu(1)−N(3)		124.7(2)
N(1)−Cu(1)−N(2)	102.46(12)	100.7(2)
N(1)−Cu(1)−N(3)	153.94(13)	139.0(2)
N(2)−Cu(1)−N(3)	82.19(13)	81.0(2)
O(4)−Cu(2)−N(4)		112.2(2)
O(4)−Cu(2)−N(5)		93.5(2)
O(4)−Cu(2)−N(6)		92.8(2)
O(4)−Cu(2)−N(7)		148.2(2)
N(4)−Cu(2)−N(5)		79.6(3)
N(4)−Cu(2)−N(6)		94.6(2)
N(4)−Cu(2)−N(7)		99.4(2)
N(5)−Cu(2)−N(6)		172.7(3)
N(5)−Cu(2)−N(7)		95.5(3)
N(6)−Cu(2)−N(7)		81.0(2)

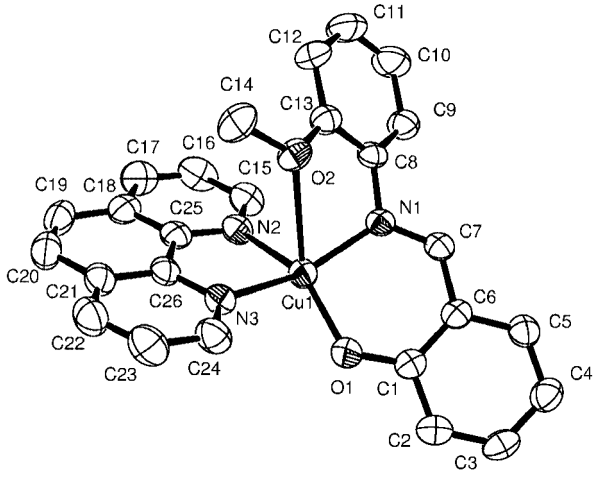

Figure 2. An ORTEP view of [Cu(phen)(L)](ClO_4) (**1**) showing thermal ellipsoids of 50% probability along with the atom numbering scheme.

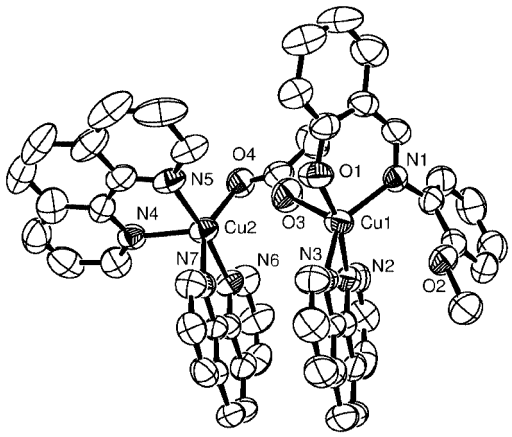

Figure 3. An ORTEP view of the cationic complex in [Cu_2(phen)$_3$(L)(O_2CMe)](ClO_4)$_2$ (**2**) showing thermal ellipsoids of 50% probability and the atom numbering scheme for the metal atom and the heteroatoms; for clarity, carbon atoms are not labeled

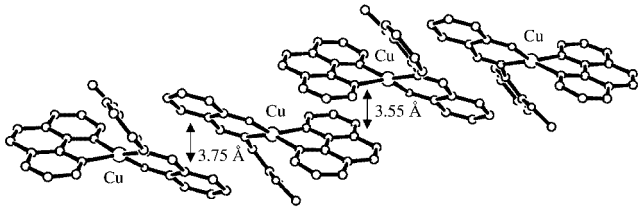

Figure 4. The intermolecular π−π stacking interaction in [Cu(phen)(L)](ClO_4) (**1**) involving phen ligands and phenolate rings to form a 1D chain

linked by an acetate ion showing a *syn*,*anti*-binding mode. The dimeric structure is stabilized by an intramolecular noncovalent π-stacking interaction involving two phen ligands belonging to two copper centers. An angle of 4.6° between the two phen planes indicates their near parallel orientation. A distance of 3.728 Å between the two centroids of the phen ligands suggests the significant stabilizing effect of the π−π interaction. Besides this interaction, two phen ligands belonging to two dimeric units are involved in an intermolecular π−π stacking interaction. This interaction leads to an association of two dimeric complexes into a discrete supramolecular tetrameric species (Figure 5). The Cu(1) center in **2** is bonded to one phen unit, the Schiff base and the bridging acetate ion. The Schiff base shows a bidentate chelating mode of bonding through the phenolate oxygen atom and the imine nitrogen atom. The methoxy oxygen atom essentially is nonbonded to the metal atom [Cu(1)···O(2), 2.966(6) Å]. The basal plane of Cu(1) comprises the phen unit and the Schiff-base ligand. The axial site is occupied by the acetate oxygen atom at a distance of 2.240(6) Å. The Cu(1) atom has a significantly distorted square-pyramidal [4+1] coordination geometry that gives a τ value of 0.45. The Cu(2) atom is bonded to one acetate and two phen ligands. The basal plane is occupied by three nitrogen atoms of the phen ligands and one oxygen atom of the acetate bridge. One nitrogen atom of a phen ligand occupies the axial site. The coordination geometry is axially

elongated distorted square-pyramidal (4+1) with a CuN_4O chromophore ($\tau = 0.4$).

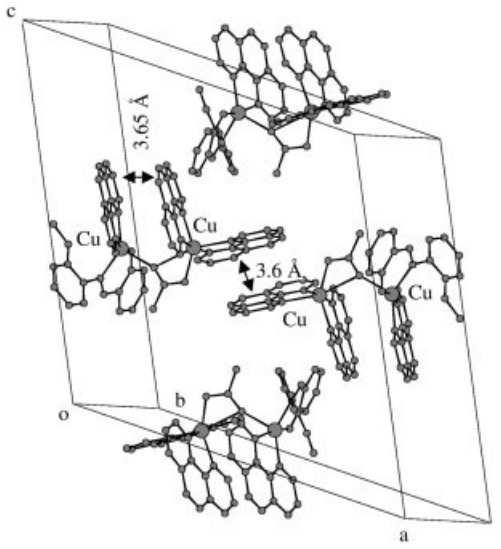

Figure 5. A unit-cell packing diagram showing the intra- and intermolecular π−π stacking interactions in $[Cu_2(phen)_3(L)(O_2CMe)](ClO_4)_2$ (**2**) to form the discrete supramolecular tetranuclear species; for clarity, the perchlorate anions are not shown

The Cu(1)−Cu(2) distance in **2** is 4.342(2) Å. The metal centers are linked by the acetate ion that shows an equatorial/axial mode of bonding. Such a binding mode involving the $d_{x^2-y^2}$ orbital of Cu(2) and the d_z^2 orbital of Cu(1) makes the metal centers essentially uncoupled because of the orthogonality of the orbitals. As a consequence, the magnetic exchange interaction in **2** becomes weakly ferromagnetic as is evidenced in the variable-temperature magnetic susceptibility studies and in the EPR spectrum in a CH_2Cl_2 glass at 77 K.[23,27] Complex **2** with two copper centers having different ligand environments and a weakly coupled dicopper(II) core has structural similarity to the dimeric sites of type-2 proteins, viz. dopamine β-hydroxylase and peptidylglycine α-hydroxylating monooxygenase.[3,28]

Redox and Catalytic Properties

The electron-transfer behavior of the complexes **1** and **2** was studied by cyclic voltammetry using a glassy-carbon working electrode. Selected data are given in Table 1 and voltammograms are shown in Figure 6. Complex **1** in CH_2Cl_2/0.1 M TBAP or DMF/0.1 M TBAP shows a cathodic peak near −0.25 V with an anodic counterpart at 0.34 V in CH_2Cl_2 and 0.13 V in DMF. The peaks are assignable to the Cu^{II}/Cu^{I} couple. The reduced ternary species [Cu(phen)(L)] is unstable as is evidenced from the i_{pc}/i_{pa} ratio of ca. 4.0.[29] The dimeric complex **2** displays a cathodic peak at −0.29 V with an anodic response at 0.35 V in CH_2Cl_2/0.1 M TBAP. Again, the i_{pc}/i_{pa} ratio of 14.0 indicates poor stability of the reduced species. The $E_{1/2}$ value of 0.03 V for the $Cu_2^{II}/Cu^{II}Cu^{I}$ couple compares well with that of **1**. The dimeric core was unstable in DMF/0.1 M TBAP solution. The DMF solution of **2** shows two cathodic peaks at −0.07 and −0.29 V with a broad anodic peak at 0.15 V. The cathodic peaks are assignable to the Cu^{II}/Cu^{I} couple of the $[Cu(phen)_2]^{2+}$ and $[Cu(phen)(L)]^{+}$ species.[30] It is likely that the weak axial bond of the acetate ion in **2** undergoes cleavage in a polar solvent such as DMF. Such a cleavage has been evidenced from the EPR spectrum of **2** showing no half-field signal in a DMF glass. Complex **2** also displays an irreversible cathodic peak at −0.89 V resulting from reduction of the Schiff's base.

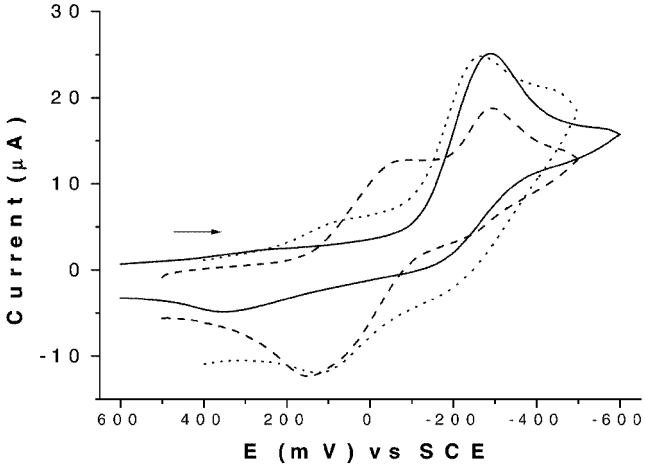

Figure 6. Cyclic voltammograms of $[Cu(phen)(L)](ClO_4)$ (**1**) in DMF/0.1 M TBAP (···), $[Cu_2(phen)_3(L)(O_2CMe)](ClO_4)_2$ (**2**) in DMF/0.1 M TBAP (---) and CH_2Cl_2/0.1 M TBAP (—) at 50 mV s^{-1}

Complex **1** reacts with ascorbic acid (H_2A) in aqueous methanol to form an unstable, brown copper(I) species, which on exposure to air converts to the parent complex. The catalytic cycle is effective at an H_2A/**1** molar ratio of 60:1. At higher concentrations of H_2A, a catalytically inactive oxalato species is formed. The formation of oxalic acid takes place from the oxidation of a dehydroascorbate species.[31] Complex **2** is also active in the oxidation of H_2A by dioxygen, but the complex is susceptible to cleavage in a polar reaction medium. The observed catalytic activity of **2** could be due to the formation of two catalytically active monomeric copper(II) species.

Conclusion

A ternary monomeric copper(II) complex having a tridentate *O*,*N*,*O*-donor Schiff base and bidentate *N*,*N*-donor phen unit was prepared and characterized structurally. The complex has a CuN_3O_2 square-pyramidal [4+1] coordination geometry with a methoxy oxygen atom as a weak axial ligand. A dicopper(II) complex was prepared and structurally characterized that has $Cu(phen)_2^{2+}$ and $Cu(phen)(L)^{+}$ units linked by an acetate ion showing equatorial/axial modes of bonding. Complex **2** has a ferromagnetically coupled dicopper(II) core. Crystal structures of the complexes **1** and **2** show intermolecular π−π stacking interactions. In addition, the dimeric complex **2** shows the presence of an intramolecular π−π stacking interaction involv-

ing the phen ligands of two different metal centers having CuN_4O and CuN_3O_2 coordination environments. While complex **1** forms a 1D chain, the intermolecular interaction in **2** results in the aggregation of two dimeric units to form an unusual discrete supramolecular tetranuclear structure.

Experimental Section

Materials and Physical Measurements: Chemicals and reagents were obtained from commercial sources. Solvents were purified by standard procedures.[32] Salicylaldehyde was obtained from Aldrich. 2-Methoxyaniline and 1,10-phenanthroline were purchased from SD Fine Chemicals, Mumbai. Copper(II) acetate hydrate was from BDH (India). The Schiff-base ligand, *N*-salicylidene-2-methoxyaniline (HL) was prepared by a literature method.[33] The infrared, electronic and EPR spectra were recorded with Bruker Equinox 55, Hitachi U3000 and Varian E-109 X-band spectrometers, respectively. The elemental analysis was performed using a Heraeus CHN-O Rapid instrument. Magnetic susceptibility data of the polycrystalline samples were obtained from a George Associates Inc. Lewis-coil-force magnetometer system having Cahn balance and an APD closed-cycle cryostat. Diamagnetic corrections to the susceptibility data were made using Pascal's constants.[34] Variable-temperature magnetic susceptibility data for complex **2** in the 30−302 K range were corrected for temperature-independent paramagnetism ($N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1} per copper atom). The molar magnetic susceptibilities were fitted to the modified Bleaney−Bowers expression[35] based on the isotropic form of the Heisenberg−Dirac−van Vleck (HDvV) model with a spin Hamiltonian $H = -2JS_1S_2$ ($S_1 = S_2 = 1/2$ for d^9-d^9 configuration): $\chi_{Cu} = [Ng^2\beta^2/kT][3 + \exp(-2J/kT)]^{-1}(1 - \rho) + (Ng_1^2\beta^2/4kT)\rho + N\alpha$, where ρ is the fraction of monomeric impurity and $-2J$ is the singlet−triplet energy separation. The magnetic moments at various temperatures were calculated in μ_B units ($\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}). Electrochemical measurements were made at 25 °C with an EG&G PAR Model 253 Versastat Potentiostat/Galvanostat with electrochemical analysis software 270 for voltammetric work with a three-electrode setup comprising a glassy-carbon working electrode, a platinum-wire auxiliary electrode and a saturated calomel reference (SCE) electrode. The electrochemical data are uncorrected for junction potentials. Tetrabutylammonium perchlorate (TBAP) was used as a supporting electrolyte. Ferrocene was used as standard to monitor the reference electrode.

Syntheses

Preparation of [Cu(phen)(L)](ClO$_4$) (1) and [Cu$_2$(phen)$_3$(L)(O$_2$CMe)](ClO$_4$)$_2$ (2): The complexes were prepared as a mixture from a reaction of $Cu_2(O_2CMe)_4(H_2O)_2$ (0.2 g, 0.5 mmol) in methanol (5 mL) with phen (0.19 g, 1.0 mmol) whilst stirring for 0.5 h at 25 °C, followed by addition of the Schiff base (HL, 0.23 g, 1.0 mmol) in methanol (10 mL) and a methanolic solution of $NaClO_4$. On slow concentration, the reaction mixture gave large rhombohedral-shaped crystals of complex **2** (yield: ca. 60%) and thin plate-type

Table 3. Crystallographic data for $[Cu(phen)(L)]ClO_4$ (**1**) and $[Cu_2(phen)_3(L)(O_2CMe)](ClO_4)_2$ (**2**)

	1	**2**
Empirical formula	$C_{26}H_{20}ClCuN_3O_6$	$C_{52}H_{39}Cl_2Cu_2N_7O_{12}$
M_r	569.44	1151.88
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 1014)
a [Å]	9.065(3)	20.845(8)
b [Å]	10.429(3)	12.727(5)
c [Å]	13.607(6)	21.520(8)
α [°]	99.86(3)	90.00
β [°]	103.42(3)	116.303(6)
γ [°]	100.14(3)	90.00
V [Å^3]	1201.0(8)	5118(3)
Z	2	4
T [K]	293(2)	293(2)
λ (Mo-K_α) [Å]	0.71073	0.71073
D_c [g cm^{-3}]	1.575	1.495
μ (Mo-K_α) [cm^{-1}]	10.70	10.06
F(000)	582	2352
Crystal colour and habit	dark green rectangular	dark green rhombohedral
Crystal size [mm]	0.55 × 0.40 × 0.09	0.36 × 0.28 × 0.12
$2\theta_{max}$ [°]	50	52
Reflns. collected	3918	10040
Independent reflns. [$I > 2\sigma(I)$]	3183	4353
Parameters refined	414	673
Goodness-of-fit on F^2	1.018	0.979
R_{int}	0.0379	0.0986
R (obsd. data)	0.0472	0.0826
wR (obsd. data)	0.1210	0.2080
R (all data)	0.0628	0.1844
wR (all data)	0.1314	0.2536
Maximum shift/e.s.d.	0.000	0.001
Largest diff. peak [e·Å^{-3}]	0.591	0.994

crystals of **1** (yield: ca. 20%). The crystals were separated manually and dried under vacuum over P_4O_{10}. $C_{26}H_{20}ClCuN_3O_6$ (569.5) (**1**): calcd. C 54.72, H 3.51, N 7.37; found C 54.78, H 3.68, N 7.32. $C_{52}H_{39}Cl_2Cu_2N_7O_{12}$ (1151.9) (**2**): calcd. C 54.16, H 3.38, N 8.51; found C 54.01, H 3.52, N 8.40. IR (KBr phase): $\tilde{\nu}$ = 3065 br, 1588 s, 1522 s, 1430 m, 1320 m, 1186 m, 1096 vs, 842 m, 778 m, 721 m, 618 w cm^{-1} for **1**; $\tilde{\nu}$ = 3434 br, 3065 m, 1614 s, 1442 m, 1329 m, 1242 m, 1150 m, 1087 vs, 843 m, 748 m, 620 w cm^{-1} for **2** (vs, very strong; s, strong; m, medium, w, weak; br, broad). Complex **1**, formed as a single product, was prepared from the reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1.0 mmol) in methanol (10 mL) and phen (0.19 g, 1.0 mmol) in methanol (10 mL) followed by the addition of the Schiff base (HL, 0.23 g, 1.0 mmol) in methanol (5 mL). The mixture was stirred for 0.5 h at 25 °C. Removal of the solvent in a rotary evaporator gave **1** as a single product that was washed with water and diethyl ether before drying in vacuo over P_4O_{10} (yield: 70%). ***Caution!*** *Perchlorate salts are potentially explosive and should be handled in small quantities with suitable safety measures.*

X-ray Crystallographic Study: Intensity data for complex **1** in the triclinic crystal system were collected with an Enraf−Nonius CAD4 diffractometer fitted with a graphite-monochromated Mo-K_α radiation. The data were corrected for Lorentz, polarization and absorption effects.[36] The cell parameters and the intensity data for complex **2** were obtained from a Bruker SMART APEX CCD diffractometer, equipped with a fine-focus 1.75-kW sealed-tube Mo-K_α X-ray source, with increasing ω (width, 0.3° per frame) at a scan speed of 8 s/frame. The SMART software was used for data acquisition and the SAINT software for data extraction.[37] Absorption correction was done using SADABS.[38] The structures were solved and refined using SHELX programs.[39] The relations used for residuals are $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o)^2]\}^{1/2}$, $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$ having A and B values of 0.0843 and 0.8796 for **1** and 0.1266 and 0.0000 for **2**. While complex **1** refined well without showing any significant disorder, the crystals of complex **2** diffracted poorly. The atoms belonging to the cationic complex of **2** and one perchlorate anion refined well. The other perchlorate anion in **2** showed positional disorders. This perchlorate anion was refined with two sets of five peaks having site occupancies of 0.7 and 0.3. The hydrogen atoms of **1** were located from the difference Fourier maps and were refined isotropically. The hydrogen atoms of **2** were generated and assigned isotropic thermal parameters, riding on their parent carbon atoms and used only for calculation of the F_o^2 structure factor. Selected crystal data for complexes **1** and **2** are given in Table 3. Perspective views of the complexes were obtained by ORTEP.[40] CCDC-192652 and -192653 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] O. Yamauchi, A. Odani, M. Takani, *J. Chem. Soc., Dalton Trans.* **2002**, 3411−3421.
[2] B. Sarkar, *Chem. Rev.* **1999**, *99*, 2535−2544.
[3] J. P. Klinman, *Chem. Rev.* **1996**, *96*, 2541−2561.
[4] W. Kaim, J. Rall, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 43−60.
[5] B. Abolmaali, H. V. Taylor, U. Weser, *Struct. Bonding* **1998**, *91*, 91−190.
[6] A. G. Blackman, W. B. Tolman, *Struct. Bonding* **2000**, *97*, 179−211.
[7] P. S. Subramanian, E. Suresh, P. Dastidar, S. Waghmode, D. Srinivas, *Inorg. Chem.* **2001**, *40*, 4291−4301.
[8] H. Masuda, T. Sugimori, A. Odani, O. Yamauchi, *Inorg. Chim. Acta* **1991**, *180*, 73−79.
[9] F. Zhang, A. Odani, H. Masuda, O. Yamauchi, *Inorg. Chem.* **1996**, *35*, 7148−7155.
[10] O. Yamauchi, A. Odani, T. Kohzuma, H. Masuda, K. Toriumi, K. Saito, *Inorg. Chem.* **1989**, *28*, 4066−4068.
[11] T. Sugimori, H. Masuda, O. Yamauchi, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 131−137.
[12] K. Aoki, H. Yamazaki, *J. Chem. Soc., Dalton Trans.* **1987**, 2017−2021.
[13] M. A. Halcrow, L. M. LindyChia, X. Liu, E. J. L. McInnes, L. J. Yellowlees, F. E. Mabbs, I. J. Scowen, M. McPartlin, J. E. Davies, *J. Chem. Soc., Dalton Trans.* **1999**, 1753−1762.
[14] P. A. N. Reddy, M. Nethaji, A. R. Chakravarty, *Inorg. Chim. Acta* **2002**, *337*, 450−458.
[15] H. Sigel, R. Tribolet, O. Yamauchi, *Comments Inorg. Chem.* **1990**, *9*, 305−330.
[16] T. Sugimori, H. Masuda, N. Ohata, K. Koiwai, A. Odani, O. Yamauchi, *Inorg. Chem.* **1997**, *36*, 576−583.
[17] T. Yajima, M. Okajima, A. Odani, O. Yamauchi, *Inorg. Chim. Acta* **2002**, *339*, 445−454.
[18] N. Ito, S. E. V. Philips, C. Stevens, Z. B. Ogel, M. J. McPherson, J. N. Keen, K. D. S. Yadav, P. F. Knowles, *Nature* **1991**, *350*, 87−90.
[19] M. R. Parsons, M. A. Convery, C. M. Wilmot, K. D. S. Yadav, V. Blakely, A. S. Corner, S. E. V. Phillips, M. J. McPherson, P. F. Knowles, *Structure* **1995**, *3*, 1171−1184.
[20] [20a] J.-M. Lehn, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304−1319. [20b] G. R. Desiraju, *Acc. Chem. Res.* **1996**, *29*, 441−449. [20c] P. J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502−518.
[21] [21a] C. A. Hunter, J. K. M. Sanders, *J. Am. Chem. Soc.* **1990**, *112*, 5525−5534. [21b] A. M. Pyle, J. K. Barton, *Prog. Inorg. Chem.* **1990**, *38*, 413−475. [21c] D. S. Sigman, T. W. Bruise, A. Mazumdar, C. L. Sutton, *Acc. Chem. Res.* **1993**, *26*, 98−104.
[22] [22a] H. Sigel, *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 394−402. [22b] H. Sigel, B. Song, *Met. Ions Biol. Syst.* **1996**, *32*, 135−205. [22c] H. Sigel, *Pure Appl. Chem.* **1989**, *61*, 923−932. [22d] H. Sigel, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 389−400.
[23] K. Geetha, M. Nethaji, A. R. Chakravarty, N. Y. Vasanthacharya, *Inorg. Chem.* **1996**, *35*, 7666−7670.
[24] N. Ito, S. E. V. Philips, K. D. S. Yadav, P. F. Knowles, *J. Mol. Biol.* **1994**, *238*, 794−814.
[25] A. W. Addison, T. N. Rao, J. Reedijk, J. V. Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.
[26] B. K. Santra, P. A. N. Reddy, M. Nethaji, A. R. Chakravarty, *Inorg. Chem.* **2002**, *41*, 1328−1332,
[27] [27a] S. Meenakumari, S. K. Tiwary, A. R. Chakravarty, *Inorg. Chem.* **1994**, *33*, 2085−2089. [27b] M. Koman, D. Valigura, E. Durcanská, G. Ondrejovic, *J. Chem. Soc., Chem. Commun.* **1984**, 381−383. [27c] S. P. Perlepes, E. Libby, W. E. Streib, K. Folting, G. Christou, *Polyhedron* **1992**, *11*, 923−936. [27d] Y. Kani, M. Tsuchimoto, S. Ohba, H. Matsushima, T. Tokii, *Acta Crystallogr., Sect. C* **2000**, *56*, 923−925. [27e] C. T. Yang, B. Moubaraki, K. S. Murray, J. D. Ranford, J. J. Vittal, *Inorg. Chem.* **2001**, *40*, 5934−5941.
[28] S. T. Prigge, A. S. Kolhekar, B. A. Eipper, R. E. Mains, L. M. Amzel, *Science* **1997**, *278*, 1300−1305.

[29] [29a] R. S. Nicholson, I. Shain, *Anal. Chem.* **1965**, *37*, 178−190. [29b] D. T. Sawyer, J. L. Ruberts, *Experimental Electrochemistry for Chemists*, John Wiley & Sons, New York, **1974**.
[30] C. Lee, F. C. Anson, *Inorg. Chem.* **1984**, *23*, 837−844.
[31] S. Lewin, *Vitamin C: Its Molecular Biology and Medical Potential*, Academic Press, London, **1976**.
[32] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, **1980**.
[33] [33a] L. M. Shkol'nikova, A. E. Obodovskaya, E. A. Shugam, *Zh. Struct. Khim.* **1970**, *11*, 54−61. [33b] L. M. Shkol'nikova, A. E. Obodovskaya, E. A. Shugam, *Zh. Struct. Khim.* **1973**, *14*, 286−290.
[34] O. Kahn, *Molecular Magnetism,* VCH, New York, **1993**.
[35] B. Bleany, K. D. Bowers, *Proc. R. Soc., London, Sec. A* **1952**, *214*, 451−465.
[36] *DIFABS*, Program for applying empirical absorption corrections: N. Walker, D. Stuart, *Acta Crystallogr., Sect. A* **1983**, *39*, 158−166.
[37] Bruker *SMART and SAINT*, Versions 6.22a, Bruker AXS Inc., Madison, Wisconsin, USA, **1999**.
[38] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33−38.
[39] G. M. Sheldrick, *SHELXL-97, Program for the Solution of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**.
[40] C. K. Johnson, *ORTEP*, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, **1976**.

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