# A mixed-metal $\mathrm{Cu^{II}_2Ni^{II}_2}$ complex derived from a phenol-based heterotetranucleating macrocyclic ligand

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**A new phenol-based tetranucleating macrocycle, having two $\mathrm{N(amine)_2O_2}$ and two $\mathrm{N(imine)_2O_2}$ metal-binding sites in the macrocyclic framework, forms a $\mathrm{Cu^{II}_2Ni^{II}_2}$ complex of a defective double-cubane structure.**

Heteronuclear metal complexes are of current interest for their physicochemical properties and functions arising from an interplay of dissimilar metal ions in close proximity. In order to provide discrete heterodinuclear metal complexes, phenol-based dinucleating macrocyclic ligands containing two different metal-binding sites have been developed.[1] In contrast, less attention has been paid to multinucleating ligands that can provide mixed-metal complexes with higher nuclearities, though phenol-based macrocyclic ligands having four $\mathrm{N(amine)_2O_2}$ or four $\mathrm{N(imine)_2O_2}$ metal-binding sites have been reported.[2] We report here, a mixed-metal $\mathrm{Cu^{II}_2Ni^{II}_2}$ complex derived from a phenol-based heteronucleating macrocycle $\mathrm{R^{4-}}$ that has two $\mathrm{N(amine)_2O_2}$ and two $\mathrm{N(imine)_2O_2}$ metal-binding sites (Fig. 1).

The macrocycle was obtained as a by-product in the cyclization of *N*,*N*′-dimethyl-*N*,*N*′-ethylenebis(2-aminomethyl-4-bromo-6-formylphenolato)copper(II)[3] ([Cu(L′)]) with ethylenediamine (Scheme 1). A solution of ethylenediamine (0.06 g, 1 mmol) in methanol (5 $\mathrm{cm^3}$) was added dropwise to a hot solution of [Cu(L′)] (0.58 g, 1 mmol) in *N*,*N*-dimethylformamide (40 $\mathrm{cm^3}$), and the mixture was stirred under reflux for 1 h to give a brown precipitate. This was shown to be a mixture of [Cu(L)] and $\mathrm{[Cu_2(R)]}$ using FAB mass spectrometry; multiple signals centered at *m/z* 600 and 1200 are assigned to $\mathrm{\{Cu(L)\}^+}$ and $\mathrm{\{Cu_2(R)\}^+}$, respectively. The separation of the two products by fractional crystallization was difficult owing to the very low solubility of the two complexes in common solvents. The mixture of the complexes (0.20 g) was treated with $\mathrm{NiCl_2{\cdot}6H_2O}$ (0.08 g) in methanol to form a $\mathrm{Cu^{II}Ni^{II}}$ complex, $\mathrm{[CuNi(L)Cl_2]{\cdot}0.5H_2O}$,[4] as dark green microcrystals (0.06 g). The solution remaining after removal of the CuNi complex was diffused with diethyl ether to obtain brown crystals, which were shown to be a mixed-metal tetranuclear $\mathrm{Cu^{II}_2Ni^{II}_2}$ complex, $\mathrm{[Cu_2Ni_2(R)(Cl)_2]Cl_2{\cdot}H_2O}$ (0.12 g).[5] FAB mass spectrometry showed signals centered at *m/z* 1422 and 1387 which are assigned to $\mathrm{\{Cu_2Ni_2(R)Cl_3\}^+}$ and $\mathrm{\{Cu_2Ni_2(R)Cl_2\}^{2+}}$, respectively.

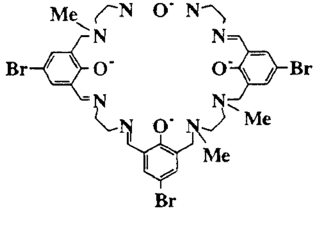
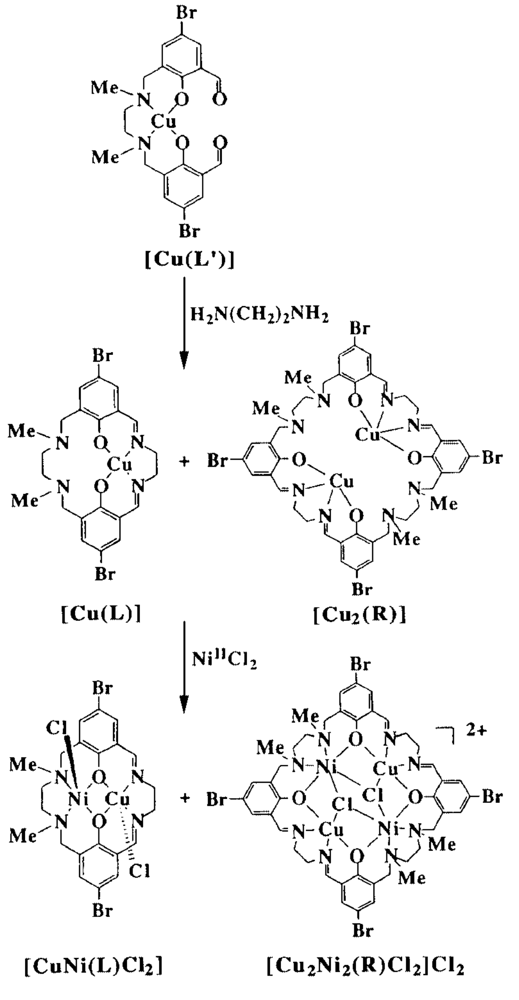


**Fig. 1** Chemical structure of $\mathrm{R^{4-}}$.

The structure of the $\mathrm{Cu^{II}_2Ni^{II}_2}$ complex was determined by single-crystal X-ray crystallography[6] and an ORTEP view is shown in Fig. 2(a). The asymmetric unit consists of one half of the macrocycle $\mathrm{(R)^{4-}}$, one $\mathrm{Cu^{II}}$ ion, one $\mathrm{Ni^{II}}$ ion and two chloride ions; the remaining two chloride ions and one water molecule are captured in the crystal lattice. Each $\mathrm{Cu^{II}}$ resides in an $\mathrm{N(imine)_2O_2}$ site and each $\mathrm{Ni^{II}}$ resides in an $\mathrm{N(amine)_2O_2}$ site. Thus, the Cu migrates from an aminic site to an iminic site in the cyclization process as previously observed in the conversion of [Cu(L′)] into [Cu(L)] and analogues.[7,8] The Cu adopts a square-pyramidal geometry with a chloride ion at the axial site. The Cu–Cl bond distance [2.563(4) Å] is elongated relative to the in-plane bond distances (1.93–1.98 Å) owing to the Jahn–Teller effect. The Ni in the $\mathrm{N(amine)_2O_2}$ site has a near



**Scheme 1** Synthetic scheme for hetero-dinucleating and -tetranucleating macrocyclic complexes.

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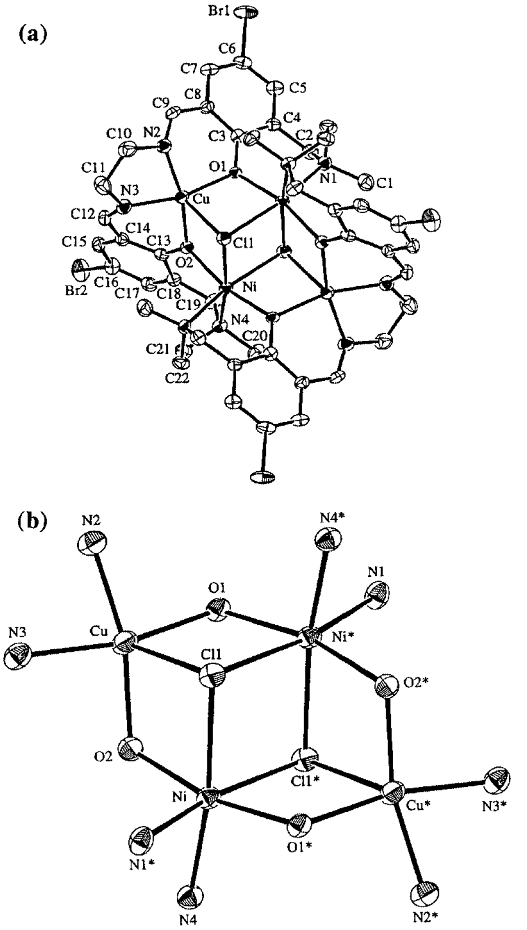

**Fig. 2** (a) An ORTEP view of $[Cu_2Ni_2(R)Cl_2]Cl_2\cdot H_2O$ and (b) its core structure. Selected bond distances (Å) and angles (°): Cu–O(1) 1.972, Cu–O(2) 1.978(9), Cu–(2) 1.93(1), Cu–N(3) 1.93(1), Cu–Cl(1) 2.563(4), Ni(1)–O(1)* 2.068(9), Ni–O(2) 2.078(9), Ni–N(1)* 2.09(1), Ni–N(4) 2.08(1), Ni–Cl(1) 2.451(4), Ni–Cl(1)* 2.471(4), Cu··Ni 3.375(3), Cu··Ni* 3.366(3), Ni··Ni* 3.543(4); Cu–O(1)–Ni* 112.8(4), Cu–O(2)–Ni 112.6(5), Ni–Cl(1)–Ni* 92.0(1), Cl(1)–Cu–O(1) 81.1(3), Cl(1)–Cu–O(2) 80.6(3), Cl(1)–Ni–O(2) 81.5(3), Cl(1)–Ni–Cl(1)* 88.0(1), Cl(1)–Ni*–O(1) 81.6(3).

octahedral geometry together with two chloride ions [Cl(1) and Cl(1)*] in *cis* positions. The Cl(1) [Cl(1)*] is involved in a $\mu_3$-bridge to Cu, Ni and Ni* (Cu*, Ni and Ni*), forming a defective double-cubane structure [Fig. 2(b)]. The Cu··Ni, Cu··Ni* and Ni··Ni* separations are 3.375(3), 3.366(3) and 3.543(3) Å, respectively. The asymmetric nitrogens N(1) and N(4) [N(1)* and N(4)*] have *R* and *S* configurations, respectively.

The electronic spectrum of the $Cu^{II}_2Ni^{II}_2$ complex in dmso shows an intense band at 354 nm ($\varepsilon$ = 14000 $M^{-1}$ $cm^{-1}$ per molecule), a discernible shoulder near 440 nm and a weak band at 747 nm ($\varepsilon$ = 380 $M^{-1}$ $cm^{-1}$). The former intense band is assigned to the $\pi$–$\pi^*$ transition associated with the azomethine linkage[9] and the latter weak band to a d–d band due to $Cu^{II}$. A shoulder near 440 nm can be assigned to a charge-transfer band from $Cl^-$ to $Cu^{II}$.[8] The d–d transition bands arising from $Ni^{II}$ are not resolved.

The $Cu^{II}_2Ni^{II}_2$ complex has a magnetic moment of 4.94 $\mu_B$ (per $Cu_2Ni_2$) at room temperature, and the moment decreased with decreasing temperature to a plateau value of 3.3 $\mu_B$ around 30 K before sharply decreasing below 10 K. Evidently antiferromagnetic spin-exchange interaction operates within the tetanuclear core. Detailed magnetic analyses are under way.

A related macrocycle having four $N(amine)_2O_2$ metal-binding sites forms homotetranuclear $Ni^{II}$ complexes of a rectangular or a non-symmetric core structure.[2] Mixed-metal trinuclear $Cu^{II}_2M^{II}$ (M = Zn or Mg) complexes have also been obtained which consist of a dinuclear $Cu^{II}M^{II}$ core and an isolated $Cu^{II}$ center. The present macrocycle possessing alternating dissimilar $N(amine)_2O_2$ and $N(imine)_2O_2$ sites is a promising ligand for providing mixed-metal complexes of the $M^a_2M^b_2$ type; detailed studies for $Cu^{II}_2M^{II}_2$ complexes (M = Mn, Co, *etc.*) will be shortly reported.

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4 Anal. Found: C, 35.63; H, 3.32; N, 7.48; Cu, 9.12; Ni, 7.64. Calc. for $C_{22}H_{25}Br_2Cl_2CuN_4NiO_{2.5}$: C, 35.79; H, 3.41; N, 7.59; Cu, 8.61; Ni, 7.95%. FAB mass: *m/z* 694 for $\{NiCu(L)Cl\}^+$.

5 Anal. Found: C, 35.84; H, 3.39; N, 7.53; Cu, 8.72; Ni, 6.54%. Calc. for $C_{44}H_{50}Br_4Cl_4Cu_2N_8Ni_2O_5$: C, 35.79; H, 3.41; N, 7.59; Cu, 8.64; Ni, 7.95%.

6 *Crystal data*: $C_{44}H_{50}Br_4Cl_4Cu_2N_8Ni_2O_5$; *M* = 738.42, triclinic, space group $P\bar{1}$, $a$ = 11.592(4), $b$ = 12.132(3), $c$ = 11.024(3) Å, $\alpha$ = 114.66(2), $\beta$ = 101.92(3), $\gamma$ = 85.74(2)°, $V$ = 11378.3(7) $Å^3$, $Z$ = 1, $D_c$ = 1.779 g $cm^{-3}$, $\mu$(Mo-K$\alpha$) = 45.85 $cm^{-1}$ and $T$ = 296 K.

CCDC 182/1592. See http://www.rsc.org/suppdata/cc/b0/b000516i/ for crystallographic files in .cif format.

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