Current interests in the chemistry of high-nuclearity transition-metal complexes draw from their utility in the emerging science of nanomaterials,[1] as models for the multimetal active sites of metal-storage proteins,[2] and as single molecule magnets (SMMs).[3,4] In addition, such super-sized molecules often show a variety of supramolecular interactions.[5] The “self-assembly” process of generating a high-nuclearity cluster from a mono- or dimeric precursor generally involves low-dentate organic ligands.

Using a pentadentate Schiff base, \( \text{N,N'}-(2\text{-hydroxypropane-1,3-diyl)bis(acetylacetoneimine)} \) (H\(_3\)L), we have been successful in isolating a discrete tetranuclear copper(II) cubane cluster \([\text{Cu}^{\text{II}}(\text{HL})]_4 \)(I) which, unlike other clusters, has four pendant arms with eight donor sites (four imine nitrogen atoms and four hydroxy groups) available for binding to additional metal ions. Complex I, as a “molecular octopus”, is a new precursor for high nuclearity copper clusters. This complex on reaction with copper(II) perchlorate in presence of KOH forms an octanuclear copper(II) species.
[CuL₄(OH)₃][ClO₄] that has already been prepared by us from a different reaction using a binuclear precursor.[6] The same metal-driven self-assembly process under different reaction conditions leads to the formation of a new discrete tetradecanuclear mixed-valent complex [Cu₄L₄][ClO₄]₂, (2). Herein, we present the synthesis, crystal structures and magnetic properties of 1 and 2. Complex 2 is a rare discrete molecular tetradecanuclear transition-metal complex with multidentate ligand system.[7] In addition two copper(ii) atoms are encapsulated in a core containing twelve copper(II) atoms giving a prismatic propeller structure.

Complex [Cu(HL)]₄ (1), prepared from a reaction of [Cu(H₂O)₆][ClO₄]₂ with H₂L in presence of triethylamine in CH₂Cl₂/MeOH, crystallizes in the cubic space group P43n with one copper center and one ligand along with one lattice water in the crystallographic asymmetric unit.[8] The structure consists of a tetranuclear core with the metal centers linked by μ₂-oxyo oxygen atom, to form a cubic arrangement of the metal and the oxygen atoms (Figure 1). The copper centers are in an essentially square-pyramidal (4+1) geometry with one bridging Cu–O bond being the axial group (2.437(5) Å). The Cu–Cu distances are 3.438(1) and 3.124(1) Å. The potentially pentadentate ligand (H₂L) binds in a dianionic tridentate form through one imine nitrogen, one enolized oxygen as the terminal, and the anionic alkoxo-oxygen atom as the bridging site. This leaves the remaining hydroxy group and the imine nitrogen atom as pendant, noncoordinating sites suitable for cluster expansion through metal-driven self-assembly process (Figure 2). The nonbonded shortest Cu–O and Cu–N separations involving the pendant donor sites are 3.6 and 3.2 Å, respectively.

![Figure 1](image1.png)

**Figure 1.** A perspective view of the complex in (1-H₂O) the thermal ellipsoids are set at 50% probability, the carbon atoms are shown as spheres with a reduced size for clarity. Selected interatomic distances [Å] and angles [°]: Cu1-O1 1.905 (6), Cu1-O2 1.974(5), Cu1-O2A 1.971(5), Cu1-O2B 2.437(5), Cu1-N1 1.927(7); Cu1-O2-Cu1B 101.9(2), Cu1-O2-Cu1C 104.7(2), Cu1-O2-Cu1D 89.61(19). Symmetry operations: A: -x+3/2,y-1/2,-z+1/2; B: x,-y,-z+1; C: -x+3/2,-z+1/2, y+1/2.

When 1 is treated with [Cu(H₂O)₆][ClO₄]₂ in a 1:4 molar ratio in presence of KOH in ethanol, the product is an octanuclear copper(i) complex [Cu₈L₄(OH)₃][ClO₄], that has already been reported by us.[6] The reaction involves an addition of four copper(i) ions. Further addition of metal ions to 1 takes place on treatment of it with [Cu(H₂O)₆][ClO₄]₂ and H₂L in a 1:10:4 mole ratio in presence of piperidine in methanol and CH₂Cl₂ to form the tetradecanuclear mixed-valent complex [Cu₁₅L₄(OH)₂][ClO₄]₂ (2). The cluster expansion process 1→2 involves the addition of ten copper atoms and two ligands to the cubane structure. Single crystals of 2.3H₂O, obtained by slow evaporation of the reaction mixture, belong to the trigonal space group R₃c with six molecules in the unit cell.[9] The structure consists of six [Cu₄L₄]⁺ units, each linked to two μ₂-OH groups attached to two copper(i) centers (Figure 3). The N₃O₃-donor Schiff base displays trionician pentadentate mode of coordination. There are two central encapsulated copper(i) units that are presumably formed by the reduction of cupric ion owing to geometrical constraints within the core (see below). The Cu₃ atom is bonded to three OH groups giving a propeller-shaped structure (see Supporting Information).

![Figure 2](image2.png)

**Figure 2.** Reaction pathways in the self-assembly processes forming tetra-, octa-, and tetradecanuclear copper cores: a) [Cu(H₂O)₆][ClO₄]₂ and KOH in EtOH; b) [Cu(H₂O)₆][ClO₄]₂, H₂L, and piperidine in CH₂Cl₂/MeOH.

[Angew Chem Int Ed 2004, 43, 87–90]

[Cu(H₂O)₆][ClO₄]₂ as a model for cuprous ions. The in situ disproportionation of cuprous ions into cuprous and cupric ions is a well-known reaction, but it is not clear how the Cu²⁺ ions are involved in the reaction. The cuprous ions can be reduced to Cu₀ by H₂, CO or H₂S, or oxidized to Cu⁺ by oxidants such as NO₂⁻, NO₃⁻ or Cl₂⁻. The Cu²⁺ ions can also be reduced to Cu⁺ by reducing agents such as Na₂S, Na₂SO₃ or Na₂SO₄. The Cu²⁺ ions can be oxidized to Cu³⁺ by oxidants such as NO₂⁻, NO₃⁻ or Cl₂⁻. The Cu²⁺ ions can also be oxidized to Cu⁴⁺ by oxidants such as NO₃⁻ or Cl₂⁻.

The disproportionation of cuprous ions into cuprous and cupric ions can be represented as follows:

\[ Cu^{2+} + Cu^{2+} + 2e^- \rightarrow 2Cu^{+} \]

or

\[ Cu^{2+} + Cu^{2+} + 2e^- \rightarrow Cu^{+} + Cu^{+} \]

The reaction can be carried out in the presence of a reducing agent such as Na₂S or Na₂SO₃. The reaction can also be carried out in the presence of a oxidant such as NO₂⁻ or NO₃⁻. The reaction can also be carried out in the presence of a oxidant such as NO₃⁻ or Cl₂⁻.

The in situ disproportionation of cuprous ions into cuprous and cupric ions can be represented as follows:

\[ Cu^{2+} + Cu^{2+} + 2e^- \rightarrow 2Cu^{+} \]

or

\[ Cu^{2+} + Cu^{2+} + 2e^- \rightarrow Cu^{+} + Cu^{+} \]

The reaction can be carried out in the presence of a reducing agent such as Na₂S or Na₂SO₃. The reaction can also be carried out in the presence of a oxidant such as NO₂⁻ or NO₃⁻. The reaction can also be carried out in the presence of a oxidant such as NO₃⁻ or Cl₂⁻.
Fig. 3. A perspective view of the complex in 2.3 H2O with the thermal ellipsoids set at 50% probability the carbon atoms are shown as spheres with a reduced size for clarity. Selected bond lengths [Å] and angles [°]: Cu1-O1 1.899(11), Cu1-O2 1.941(11), Cu2-O3 1.941(11), Cu1-O4 1.957(9), Cu2-O2 1.915(9), Cu2-O3 1.888(9), Cu2-O4 1.966(11), Cu1-N1 1.887(14), Cu2-N2 1.941(13), Cu3-O4 2.282(8); Cu1-O2-Cu2 136.5(6), Cu1C-O4-Cu2 101.8(4), Cu1C-O4-Cu3 100.4(4), Cu2-O4-Cu3 127.5(6).

The prismatic structure involving the CuI centers can be seen. Symmetry operations: C−x+y+2/3, −z+1/6, −x+4/3.

Fig. 4. Plots of χmT (per molecule) versus T for complexes 1 (Δ) and 2 (○) in the temperature range 305–18 K.

Experimental Section

Complex 1 was prepared from a reaction of [Cu(H2O)6](ClO4)2 (2.96 g, 8.0 mmol) with H2L9 (3.79 g, 14.9 mmol) in CH2Cl2/MeOH mixture (1:1 v/v, 40 mL) in presence of triethylamine (28.03 mmol) under reflux for 30 min. Dark blue crystalline product in ∼87% yield was obtained on slow evaporation of the solvent at 25°C. Single crystals were obtained by slow diffusion of hexane to a CH2Cl2 solution of 1. Complex 2 was prepared in ∼66% yield from a reaction of 1 (0.2 g, 0.16 mmol) in CH2Cl2 (10 mL) with [Cu(H2O)6](ClO4)2 (0.6 g, 1.6 mmol) in presence of H2L (0.19 g, 0.64 mmol) and piperidine (0.15 mL, 1.5 mmol) in MeOH (10 mL). The octanuclear complex [Cu8L8(H2O)4](ClO4)2 was prepared from a reaction of 1 (0.21 g, 0.16 mmol) with [Cu(H2O)6](ClO4)2 (0.24 g, 0.64 mmol) and KOH (0.53 g, 0.94 mmol) in ethanol (15 mL) in 55% yield (0.14 g). The crystals of the octanuclear complex gave cell parameters similar to those reported earlier. Elemental analysis (% calee for 1: C 40.44, H 6.38, N 8.87; found: C 40.21, H 6.54, N 9.02, (%) calee for 2: C 34.72, H 4.48, N 6.23; found: C 34.88, H 6.54, N 6.33. UV/Vis in MeOH: λmax (ε, M−1 cm−1): 233 (22.500), 310 (43000), 630 nm (280) for 1 and 281 (60000), 315 (91000), 620 nm (1000) for 2. χmT (per molecule) cm3 M−1 K−1: 2.675 at 18.54 K and 1.551 at 305.31 K for 1; 0.048 at 18.41 K and 1.954 at 304.73 K for 2 (Supporting Information).
Crystal data for 1·4HCl·CuCl2·3H2O: C38H30N8O16Cu4, Mw = 1335.46, blue prisms (0.265 × 0.18 × 0.145 mm), cubic, P43n, a = b = c = 22.421(4) Å, V = 11272(3) Å³, Z = 6, P = a/2c = 1.077, N/N0 = 2960/180. Crystal data for 2·3H2O: \( \text{C}_78\text{H}_{126}\text{N}_{12}\text{O}_{35}\text{Cl}_2\text{Cu}_{14} \), Mw = 2752.37, green prisms (0.325 × 0.185 × 0.09 mm), trigonal, R3c, a = b = c = 16.318(2), V = 16193(6) Å³, Z = 6, P = a/2c = 1.048, N/N0 = 3077/205. X-ray diffraction data were measured in frames with increasing \( \omega \) (width of 0.3 deg./frame) and with a scan speed at 6 s/frame for 1 and at 12 s/frame for 2 on a Bruker SMART APEX CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube X-ray source. Empirical absorption corrections were carried out using MULTISCAN (for 1) and SADABAS (for 2) program: R. Blessing, Acta Crystallogr. Sect. A 1999, 55, 33. The structures were solved by the heavy atom method and refined by full matrix least-squares using SHELX system of programs: G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany), 1997. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon atoms in the complex were generated and assigned isotropic thermal parameters, riding on their parent carbon atoms, and used for structure factor calculation only. CCDC 214522 and 214523 contain the supplementary crystallographic data for 1 and 2, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk). ORTEP and packing diagrams in color for 1 and 2 are given as Supporting Information.


