Novel neutral octanuclear copper(I) complexes stabilized by pyridine linked bis(pyrazolate) ligands†‡§

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Two novel, neutral, octanuclear copper(I) complexes displaying twisted-boat Cu_8 conformations and short Cu–Cu interactions have been synthesized from hydrothermal reactions; the complexes show unusual multiple band emissions.

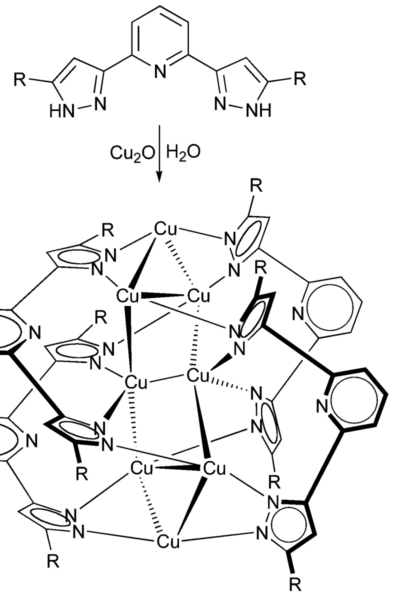
The attractive interaction that exists between closed-shell late transition metals has received extensive attention.[1] Multinuclear complexes or coordination polymers having such direct metal–metal interactions are of great interest since the conductivity, magnetic properties and electrochemical behavior of these metal aggregates have proved to be potential applications in the field of nano-scale or molecular scale electronics.[2]

Pyrazolate ligands can form various complexes with coinage metal ions with diverse structural motifs.[3] They are able to bind two or more closed-shell d^{10} metal centers together in distances close to the sum of the covalent radii of two metals, thus pyrazolate ligands are suitable linkages for the construction of metal aggregates having metal–metal interactions. Several monovalent Group 11 metal–pyrazolate clusters involving trinuclear,[2d,3a–c] tetranuclear,[3d,e] and dimers of trinuclear[3f,g] centers have been reported. However, the higher nuclearity pyrazolate clusters are not known, and the coinage metal complexes of bis(pyrazolate) ligands have been scarcely reported.[4]

As a continuation of our research on the metallophilic interactions between closed-shell metals,[5] herein we report the synthesis, solid-state structures, ESI-MS spectra and photophysical properties of two fascinating octanuclear complexes $[Cu_8(L)_4]$ (**1**, $H_2L^1 = $ 2,6-bis(5-methyl-1*H*-pyrazol-3-yl)pyridine; **2**, $H_2L^2 = $ 2,6-bis(5-phenyl-1*H*-pyrazol-3-yl)pyridine) stabilized by the pyridine linked bis(pyrazolate) ligands (see ESI§).

The bis(pyrazolyl) ligands were prepared from the condensation reactions of the corresponding 1,3-diketones with hydrazine hydrate. The Cu_8 complexes were obtained by the hydrothermal reaction of H_2L with cuprous oxide at 220 °C (Scheme 1). **1** and **2** were isolated as stable yellow crystalline solids.¶ The absence of downfield resonance signals in their ^1H NMR spectra at about 13 ppm due to NH and the disappearance of N–H strectching bands at *ca.* 3200 cm^{-1} in the IR spectra of **1** and **2** show that the ligands are deprotonated.

X-Ray diffraction analysis shows that the octanuclear complexes are neutral and eight copper(I) ions are held together by four dianionic ligands. The structure is shown in Fig. 1. Each of the four deprotonated 2,6-bis(5-methyl-1*H*-pyrazol-3-yl)pyridine ligands links four different copper ions in an *exo*-tetradentate mode. The two pyrazolyl groups in each L^1 are different in their coordination mode, one pyrazolyl ring is bound to two



Scheme 1

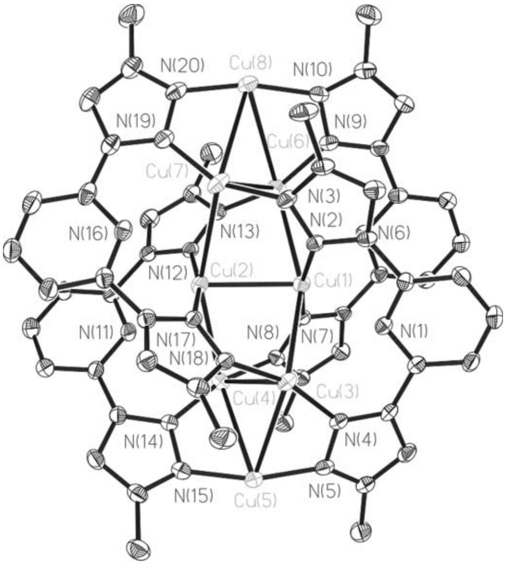


Fig. 1 Molecular structure of $Cu_8L_4^1$ (**1**) with H atoms omitted.

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† The HTML version of this article has been enhanced with colour images.

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§ Electronic supplementary information (ESI) available: Full experimental and characterization details for **1** and **2**. See DOI: 10.1039/b712411b neighboring Cu atoms, while the other links two discrete Cu atoms. Because of deprotonation and complexation, one pyrazole ring in each L^1 is twisted severely from the pyridine ring with dihedral angles ranging from 21.1 to 32.7°, which are distinctly reflected by its ^{1}H NMR spectrum, where two sets of resonance signals for the pyrazole protons are observed. The central pyridine rings are not coordinated as indicated by the rather long $Cu–N_{pyridine}$ distances ranging from 2.547(6) to 2.808(6) Å. Each copper atom is coordinated by two pyrazolate nitrogen atoms from different L^1 moieties in bent geometries with N–Cu–N angles in the range 155.6(3)–167.1(2)°. The $Cu–N_{pyrazolate}$ bond distances are observed to be 1.850(6)–1.883(6) Å, which are consistent with the known values of other Cu(I)–pyrazolate complexes.[3b,d]

Interestingly, the eight copper ions form an eight-membered ring with a twisted boat conformation because of the cuprophilic interaction. The copper ring is stabilized by eleven Cu–Cu bonds, which can be divided into three classes: four pyrazolate-bridged, four ligand-bridged, and three "unbridged" Cu–Cu bonds are within the ranges 2.901(1)–3.054(1) Å, 2.824(1)–2.897(1) Å, and 2.616(1)–3.037(1) Å, respectively. The shortest Cu–Cu separation is observed for the "ligand-unsupported" Cu(1)–Cu(2) (2.616(1) Å), whereas the longest one is Cu(6)–Cu(8) (3.054(1) Å). These Cu–Cu separations are approximately similar to the sum of the van der Waals radii of 2.80 Å.[6]

Although **1** and **2** crystallize in quite different space groups, the two complexes have similar Cu_8 cores (see ESI§). The central Cu_8 core is surrounded by four L^2 ligands. The eleven Cu–Cu contacts fall in the range 2.588(4)–3.019(4) Å. Again the shortest one is found to be the "ligand-unbridged" Cu–Cu distance, contrary to what one might suppose, and is comparable to the Cu–Cu distance of 2.556 Å found in the metal.

There has been much discussion of cuprophilicity, and relatively short Cu–Cu contacts in bi-, oligo-, and polynuclear copper(I) complexes, which may or may not involve some kind of bonding, in recent years.[2c,3b,7] Although cuprophilic interaction is much weaker than those between other coinage metals, it often determines the self-assembly of copper(I) aggregates and plays an important role in the luminescent properties of the multinuclear copper(I) complexes containing *N*- or *P*-donating ligands.[8] The copper–copper distances are found to cover a wide range from 2.5 Å to 2.9 Å, and even longer distances of 3.3 Å have been attributed to cuprophilicity to some extent. Although there is some dispute over the existence of the cuprophilic interaction, more and more theoretical and experimental evidence has been accumulated over the past decade to support Cu–Cu interaction rather than a simple approach of two metals because of the steric constraints of the bridging ligands.

Also interestingly, the complexes contain several neutral metallacycles such as Cu_2N_2, Cu_3N_2, $Cu_2N_3C_4$, *etc*., which are linked together by eight copper, twenty nitrogen and sixteen carbon atoms (Fig. 2). Most of the reported pyrazolate metallacycles are of nine membered M_3N_6 metallacycles,[2d,3a–c] the neutral Cu_4N_{12} and Ag_4N_{12} metallacycles are also known.[3d] Coordination compounds having geometrically shaped metallacycles show promise in various applications such as selective sensors, gas storage, sorters, catalysis, and luminescent materials.

It is noted that octanuclear copper(I) clusters are relatively rare and are often stabilized by functional ligands incorporating heteroatoms such as S, P, Se and halides *etc*.,[9] and most of them are ionic compounds. So far, no neutral octanuclear copper(I) clusters supported by N donating ligands have been reported. In addition, most of the reported octanuclear copper(I) clusters are of cubic arrangement, compounds **1** and **2** represent the first examples displaying a twisted-boat conformation of Cu_8 clusters.

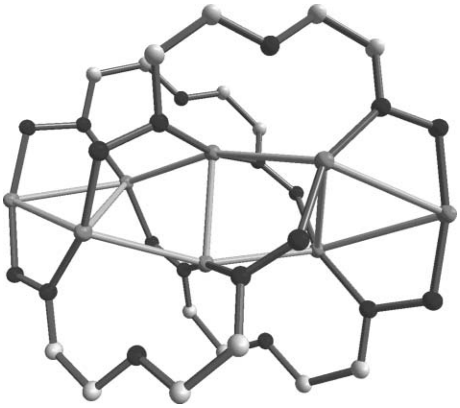

Fig. 2 Metallacycles connected by $Cu_8N_{20}C_{16}$ showing the twisted boat conformation of the copper(I) atoms of **1**.

One surprise is the scarcity of reports of the ESI-MS studies on pyrazolate closed-shell d^{10} coinage metal complexes.[3g] In the ESI-MS spectra of **1** in acetonitrile, the molecular peak at 1457.90 amu was observed corresponding to $[Cu_8(L^1)_4]^+$ (calcd 1455.84 amu), whereas the most intense peak was seen at 665.04 amu assignable to $[Cu_3(L^1)_2]^+$ (calcd 665.16 amu). Interestingly, the peaks at 806.74, 947.22, and 1394.93 amu were also observed ascribed to $[Cu_5(L^1)_2(H_2O)]^+$ (calcd 806.86), $[Cu_3(L^1)_3(CH_3CN)]^+$ (calcd 946.49 amu), and $[Cu_7L^1{}_4]^+$ (calcd 1393.86 amu), respectively. Peaks larger than the molecular weight, at 1522.07 and 1839.71 amu, can also be observed and are assigned to $[Cu_9(L^1)_4]^+$ (calcd 1520.77 amu) and $[Cu_{10}(L^1)_5]^+$ (calcd 1839.77 amu), respectively. The ESI-MS spectra of **2** in DMF displays a molecular peak at 1954.72 amu corresponding to $[Cu_8(L^2)_4]^+$ (calcd 1954.96 amu). Under the ESI-MS conditions, compound **2** also undergoes extensive fragmentation through loss of ligand or copper atoms. The peaks corresponding to $[Cu_7(L^2)_4]$, $[Cu_6(L^2)_4]$, $[Cu_6(L^2)_3]$, $[Cu_4(L^2)_2]$, $[Cu_3(L^2)_2]$, and $[Cu_2(L^2)]$ are all found. The observation of the molecular peaks for both **1** and **2** suggests that the octanuclear copper frameworks are maintained in solution.

The electronic absorption spectrum of **1** in acetonitrile shows notable absorption bands centered at 224, 246, 273, and 306 nm. The high-energy wavelength bands below 300 nm are quite similar to the π–π band absorptions for H_2L^1, whereas the intense absorption band at 306 nm which is not observed for the ligand may be assigned to the metal–metal 3d–4p transition. The absorption band greater than 300 nm for **2** is concealed by the tail of the strong absorption at 269 nm. A similar absorption at 310 nm has also been seen in $[Cu_2(dcpm)_2]^{2+}$ (dcpm = bis(dicyclohexylphosphino)methane) complexes due to 3d–4p transitions.[8]

The solid-state emissive spectra for the crystals of the copper complexes are shown in Fig. 3. The ligand precursors and the copper clusters are intensely emissive in their solid states. The solid state emission spectra of H_2L^1 and H_2L^2 show similar single sharp bands at 366 nm upon excitation at 338 nm. The emission

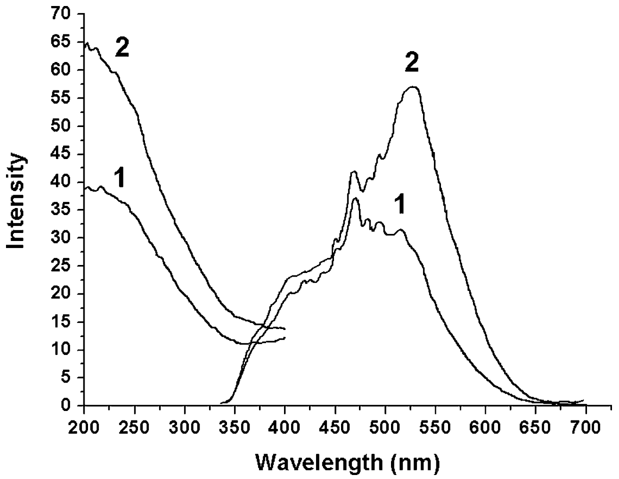

Fig. 3 The solid-state emission (right) and excitation (left) spectra of **1** and **2**.

spectra of **1** and **2** display unusual multiple bands (407 sh, 440, 454, 470, 484, 497 and 511 nm for **1** and 409 sh, 443, 455, 473, 486, 498 and 517 nm for **2**) with λ_{max} = 470 nm and 517 nm upon excitation at 220 nm, respectively. Vibronically structured bands with a spacing between the local maxima of the emission bands of about 1446 cm^{-1} for **1** and about 1432 cm^{-1} for **2**, characteristic of the ν(C=N) or ν(N=N) stretch,[3e] were also observed. The appearance of this structure is suggestive of involvement of the pyrazolate ligands in the emission process.

The photophysical properties of trinuclear Cu(I) clusters[2d,3b] have been fully investigated. However, little attention has so far been focused on the photophysical properties of copper(I) complexes with a larger cluster core structure. Because emission bands greater than 400 nm were not observed for the ligands, the low-energy emission bands centered at *ca.* 470 nm for the complexes may tentatively be assigned to Cu–Cu bonded excited states. The Cu$_8$ complexes exhibit emission bands at almost the same positions, suggest that these emissions probably originate from the same electronic states assignable to ligand-to-ligand charge transfer and MLCT (d–π) transitions. The low-energy bands around 511 nm for **1** and 517 for **2** may be attributed to metal-centered charge transfer processes. In CH_2Cl_2, complexes **1** and **2** are also luminescent. The spectra show broad bands centered at *ca.* 465 nm with not well-resolved vibronic features upon excitation at 227 nm. The large Stokes shifts and the spectral features again demonstrate that the low-energy emissions of the complexes originate from the metal-centered excitation states.

In summary, we have demonstrated the synthesis, structures, and emission properties of two Cu$_8$ clusters featuring eleven Cu–Cu bonds and twisted-boat Cu$_8$ cores representing the first octanuclear copper(I) complexes supported by N-donating ligands. They are stable in the solid state as well as in solution. The emission spectra of these compounds are interesting and worthy of further investigation. Variation of the pyrazolyl ring substituents and bridges between the two pyrazolyl rings may lead to novel aggregates with different nuclearities. The ligand effect on the solid-state structures and luminescence of the Cu(I) aggregates will be studied further.

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Notes and references

¶ Crsytal data for **1**: $C_{55}H_{50}Cu_8N_{20}O$, triclinic, $P\bar{1}$, a = 11.901(2) Å, b = 14.426(2) Å, c = 18.410(2) Å, α = 80.163(2), β = 73.035(2), γ = 70.652(2)°, V = 2842.8(7) Å^3, Z = 2, D_{calc} = 1.770 Mg m^{-3}, 14775 reflections collected, 9836 reflections independent [R_{int} = 0.0285], goodness-of-fit on F^2 1.021, R [$I > 2\sigma I$]: 0.0484, 0.1055. For **2**: $C_{92}H_{60}Cu_8N_{20}$, orthorhombic, *Fdd*2, a = 23.916(15) Å, b = 39.80(3) Å, c = 16.666(10) Å, V = 15864(18) Å^3, Z = 8, D_{calc} = 1.636 Mg m^{-3}, 18203 reflections collected, 3664 reflections independent [R_{int} = 0.1065], goodness-of-fit on F^2 0.906, R [$I > 2\sigma I$]: 0.0769, 0.1827.

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