Structure and spectroscopic properties of a luminescent inorganic cyclophane from self-assembly of copper(I) and two ligand components

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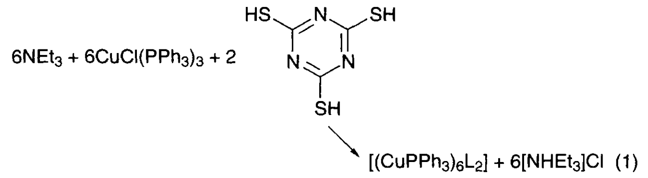
The reaction of trithiocyanuric acid (H_3L) with $CuCl(PPh_3)_3$ gives $[(CuPPh_3)_6L_2]$, the structure of which shows two parallel triazine rings held in a close proximity of 3.07 Å by six Cu–S bridges; the complex $[(CuPPh_3)_6L_2]$ shows visible emission in the solid state and in fluid solution at room temperature.

The self-assembly of Cu^I with ligands containing different binding sites results in the formation of novel supramolecules having intriguing structures and/or electronic properties. Examples include double and triple helicates,[1] cylindrical complexes[2] and also the molecular trefoil knots[3] using polypyridyl strands as the building blocks. Supramolecules with cyclophane like structures would have interesting physiochemical properties but they are mostly limited to organic compounds, which are prepared by multi-step syntheses.[4] Recently, Youinou *et al.*[5] have reported the spontaneous formation of a copper(I) tetramer with a significant π-stacking interaction by the reaction of $Cu(CF_3SO_3)_2$ with 3,6-bis(2′-pyridyl)pyridazine (dppn). Herein is described a novel luminescent inorganic cyclophane, showing a weak π–π stacking interaction, obtained by the self-assembly of Cu^I and trithiocyanuric acid.

Treatment of trithiocyanuric acid (H_3L, 100 mg) with 3 equiv. of $CuCl(PPh_3)_3$ (1.5 g) in methanol–dichloromethane (30 ml, 1 : 1 *v*/*v*) in the presence of triethylamine at room temp. for 12 h gave an orange solution, from which the yellow product $[(CuPPh_3)_6L_2]$ was isolated in 90% yield† [eqn. (1)].



(1)

In dichloromethane, $[(CuPPh_3)_6L_2]$ shows an irreversible oxidation wave with E_{pa} at 0.99 V *vs.* SCE. X-Ray quality crystals of $[(CuPPh_3)_6L_2]\cdot 2CHCl_3$ were obtained by slow diffusion of dichloromethane into a chloroform solution.‡ Fig. 1 depicts the structure of $[(CuPPh_3)_6L_2]$ which can be considered as 'cyclophane-like' with six Cu–S bridges. The C–S–Cu angles are close to 99°, which are smaller than those (104–115°) reported for $[Cu(C_5H_4NSH)_3]NO_3$[6] and $[Cu(etu)_3][SO_4]_2$[7] (C_5H_4NSH = pyridine-2-thiol; etu = ethylenethiourea). All six Cu^I atoms are three-coordinate with a distorted Y-shaped planar geometry. [N–Cu–P 137.0(2)–142.2(2)°; S–Cu–P 113.1(8)–118.5(8)° N–Cu–S 103.0(2)–104.2(2)°]. In contrast to other copper(I) clusters such as $[Cu_3(SAr)_3]$[8] and $[Cu_6(mtc)_6]$[9] which show weak $Cu^I\cdots Cu^I$ interactions {SAr = 2-[(*R*)-1-(dimethylamino)ethyl]thiophenol; mtc = di-*n*-propylmonothiocarbamate}, the Cu^I centres are far apart with separations ranging from 3.461(1) to 5.684(1) Å. The C–S bond distances are an average 1.713(7) Å, which is somewhat shorter than those of 1.764(8) and 1.755(8) Å found in $[Cu_6(C_5H_4NS)_6]$ and $[Cu_6(C_9H_6NS)_6]$ (C_9H_6NSH = quioline-2-thiol).[10] These relatively short C–S bond distances suggest an aromatic C=S bond character and similar C=S bond distances have previously been reported.[11]

A striking feature is the virtually parallel orientation of the two triazine rings, which are held in a close proximity of 3.07 Å by the six Cu–S bridges. This separation is much shorter than that of the face-to-face π-stacking interaction in the rigid-rack dinuclear copper(I) complexes of rotaxane type (3.4 Å)[12] and in $[Cu_4(dppn)_4][CF_3SO_3]_4$ (3.47 Å).[5]

The absorption spectrum of the free ligand H_3L shows a broad absorption at 290 nm (ε_{max}^{290} 12100 dm^3 mol^{-1} cm^{-1}). The complex displays intriguing spectroscopic and emission properties. As shown in Fig. 2, the absorption energy of the complex is considerably red-shifted from that of the free ligand and its deprotonated form (prepared by mixing H_3L and NaOMe in MeOH). It shows a broad absorption at 355 nm and a long tailing to 500 nm (ε_{max}^{355} 20300; ε_{max}^{430} 11000 dm^3 mol^{-1} cm^{-1}), which could be due to a metal-to-ligand (Cu → L) charge-transfer transition and/or the π → π* transition of the two stacked triazine rings that are separated by 3.07 Å. The complex shows room-temperature photoluminescence both in the solid state and in fluid solution. The emission at 562 nm in the solid state (lifetime, 0.59 μs at 298 K) and at 580 nm in dichloromethane (lifetime, 0.82 μs at 298 K) are higher in energy than emissions of other copper(I) complexes with sulfur donor ligands. For example, $[Cu_6(SNBu^t)_6]$[13] and $[Cu_6(mtc)_6]$[14]

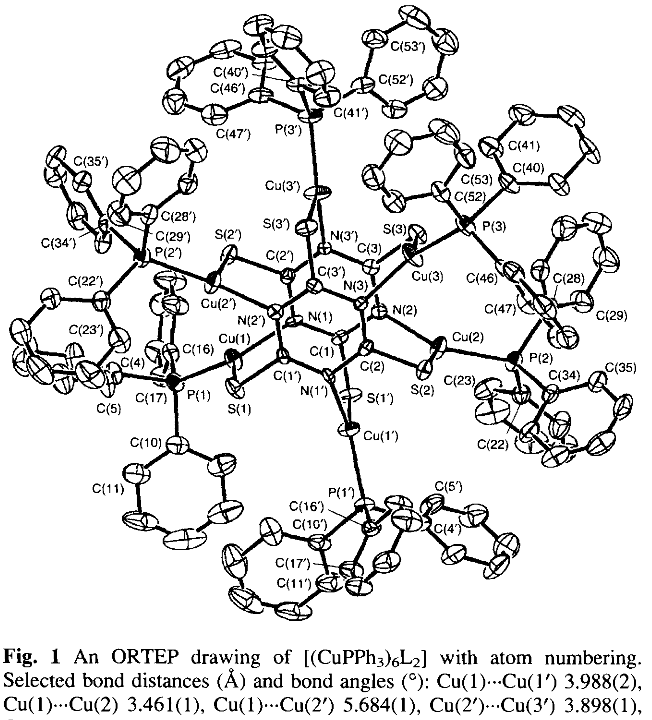


Fig. 1 An ORTEP drawing of $[(CuPPh_3)_6L_2]$ with atom numbering. Selected bond distances (Å) and bond angles (°): Cu(1)···Cu(1′) 3.988(2), Cu(1)···Cu(2) 3.461(1), Cu(1)···Cu(2′) 5.684(1), Cu(2′)···Cu(3′) 3.898(1), Cu(3′)···Cu(3′) 3.498(2), Cu(1)–S(1) 2.299(2), Cu(1)–N(1) 1.991(5), Cu(1)–P(1) 2.186(2), Cu(1′)–S(1) 1.709(6), C(2)–S(2) 1.718(6), C(3)–S(3) 1.710(7); S(1)–Cu(1)–P(1) 118.64(8), S(1)–Cu(1)–N(1) 104.2(2), P(1)–Cu(1)–N(1) 137.0(2), C(1′)–S(1)–Cu(1) 98.1(2), C(2)–S(2)–Cu(2) 99.7(2), C(3)–S(3)–Cu(3) 99.3(2). Symmetry operation(′): −*x*, *y*, 0.5 −*z*.

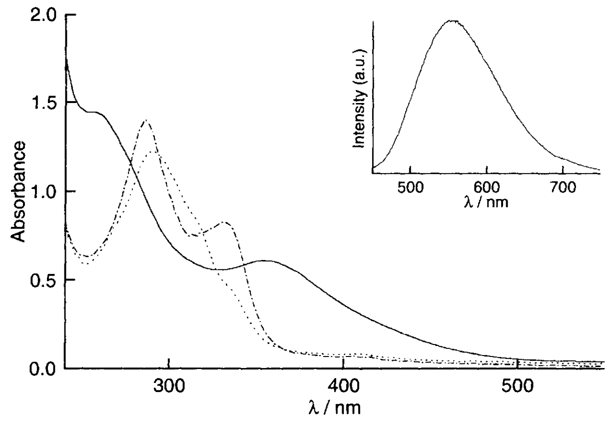


Fig. 2 The electronic absorption spectrum of [$(CuPPh_3)_6L_2$] in CH_2Cl_2 (2.38×10^{-5} mol dm^{-3}) (—), the free ligand H_3L (1.03×10^{-4} mol dm^{-3}) in MeOH (----) and its deprotonated form in MeOH (1.08×10^{-4} mol dm^{-3}) (–·–·–). The inset shows a steady-state emission spectrum of [$(CuPPh_3)_6L_2$] in degassed CH_2Cl_2 at 298 K. (λ_{exc} = 370 nm.)

emit at 755 and 727 nm respectively. It is possible that the emission is either metal-to-ligand (Cu → L) charge transfer in nature or arises from an excimeric π–π interaction of the two triazine rings.

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Footnotes

† Satisfactory elemental analysis of [$(CuPPh_3)_6L_2$] has been obtained. $^{31}P\{^1H\}$ NMR ($CHCl_3$, ref. 85% H_3PO_4) δ 1.55(s).

‡ *Crystal data*: $C_{114}H_{90}Cu_6N_6P_6S_6\cdot 2CHCl_3$, M = 2542.24, monoclinic, space group $C2/c$ (no. 15), a = 31.106(4), b = 18.948(4) c = 23.344(6) Å, β = 123.944(8)°, U = 11414(3) Å^3, Z = 4, D_c = 1.479 g cm^{-3}, μ(Mo-Kα) = 14.82 cm^{-1}, $F(000)$ = 5168, no. of parameters 659, R = 0.050, R_w = 0.053 with a goodness of fit of 2.59 for 4570 observed data with $|F_o| < 3\sigma|F_o|$. A yellow crystal (prism) of dimensions 0.15 × 0.15 × 0.25 mm was used for data collection at 25 °C on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods (SIR92) and difference Fourier techniques and refined by full-matrix least-squares analysis. All calculations were performed on a Silicon Graphics Indy computer using the TeXsan software package. (Crystal Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1992). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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