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New photoluminescent Cu^IN_4 chromophores. Stabilisation of copper(I) by unconjugated diimines

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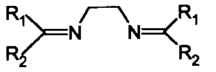
Received 19th November 1999, Accepted 16th December 1999

Two new photoluminescent homoleptic distorted tetrahedral Cu^IN_4 chromophores with $Cu^{II/I}$ potentials of 0.66–0.81 V *vs.* SCE are isolated by using two unconjugated diimines (2:1 condensates of $R_1R_2C{=}O$ and ethylenediamine; R_1 = Ph, R_2 = H; R_1 = R_2 = Ph) as ligands.

Cu^IN_4 chromophores which exhibit photoluminescence in solution are known only in copper(I) complexes of substituted 1,10-phenanthrolines (1,10-phen).[1,2] Herein we report new photoluminescent Cu^IN_4 chromophores isolated with unconjugated diimines L_1 and L_2.



L_1: R_1 = Ph and R_2 = H
L_2: R_1 = R_2 = Ph

The ligands L_1 and L_2 are synthesised by condensing ethylenediamine (en) with benzaldehyde and benzophenone respectively in anhydrous methanol.† Their copper(I) complexes $[Cu(L_1)_2]ClO_4$ (**1**) and $[Cu(L_2)_2]ClO_4$ (**2**) are prepared by reacting the ligands with $[Cu(CH_3CN)_4]ClO_4$ in anhydrous methanol under N_2 atmosphere.‡ Complexes **1** and **2** are respectively yellow and brick-red in colour. The green copper(II) complexes obtained by reacting the ligands with $Cu(ClO_4)_2 \cdot 6H_2O$ in 2:1 molar proportions in anhydrous ethanol are readily hydrolysed to yield violet bis-en complexes of copper(II) and hence we have not been able to characterise them. Complexes **1** and **2** are stable in air in the solid state for 2–3 weeks. However, their solution stability in air depends on the solvent; while in CH_2Cl_2 these are stable for at least 24 h, in CH_3OH **1** is stable for about 2 h and **2** is stable for about 6 h. On standing in air, a methanol solution of **1** or **2** slowly turns violet through green. The violet colour arises due to the formation of the bis-en complex of copper(II).

The structure of the cation in **1** as determined by X-ray crystallography§ is shown in Fig. 1. There are two cations each with *C*2 symmetry in the asymmetric unit but they have very similar structures. The metal coordination spheres are distorted tetrahedra with each metal bonded to four N atoms from two separate ligands. In a cation, the two Cu–N bond lengths for a particular ligand differ by 0.022–0.036 Å. In **1**, the average Cu–N bond length is 2.073 Å with an average dihedral angle (τ) of 73.1° between the two CuN_2 coordination planes (for D_{2d} symmetry, this angle τ is 90°). The average bite angle of the ligand in **1** is 85.3°. Interestingly, the two phenyl rings of a particular ligand in a cation span in the same direction. The structure of the cation in **2** is shown in Fig. 2. The metal coordination sphere is more distorted than in **1** presumably due to more steric crowding. The Cu–N distances in **2** range from 2.014(4) to 2.183(4) Å with τ of 63.9(2)°. The average bite angle of the ligand in **2** is 85.3°.

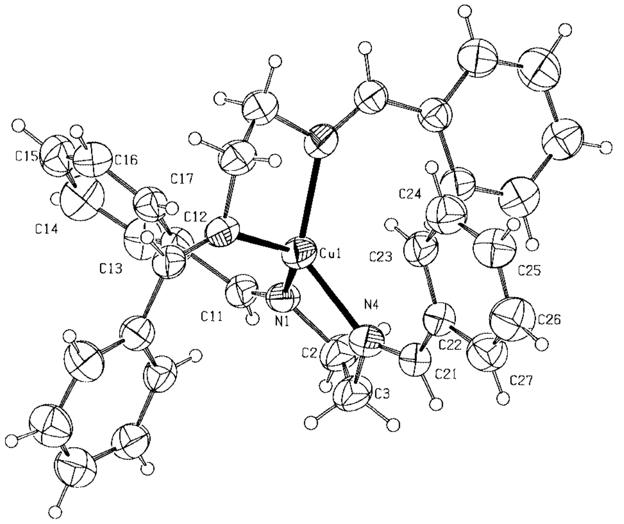


Fig. 1 The structure of the cation in **1** with ellipsoids at 30% probability. In one of the cations (see text), Cu1–N1 2.058(5), Cu1–N4 2.094(6) Å and τ (see text) 80.8(2)° and in the other cation, Cu2–N5 2.082(5), Cu2–N8 2.060(6) Å and τ 65.4(2)°.

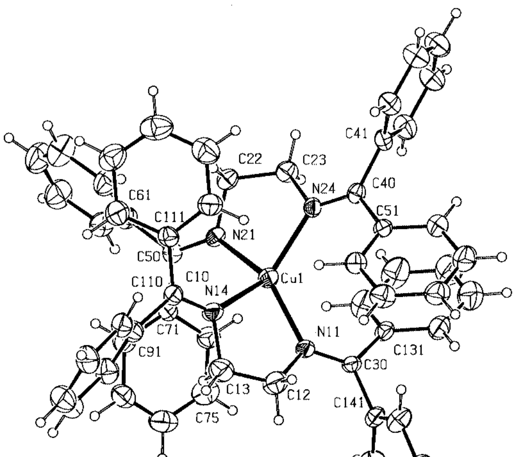


Fig. 2 The structure of the cation in **2** with ellipsoids at 30% probability. Selected bond lengths: Cu1–N11 2.014(4), Cu1–N14 2.183(4), Cu1–N21 2.065(4), Cu1–N24 2.077(5) Å; τ (see text) 63.9(2)°.

The electrochemical behaviour of complexes **1** and **2** has been examined by cyclic voltammetry and coulometry in CH_2Cl_2 at platinum electrodes under an N_2 atmosphere. Complex **1** shows a quasireversible $Cu^{II/I}$ couple with an $E_{1/2}$ of 0.81 V *vs.* SCE (saturated calomel electrode). In cyclic voltammetry, a

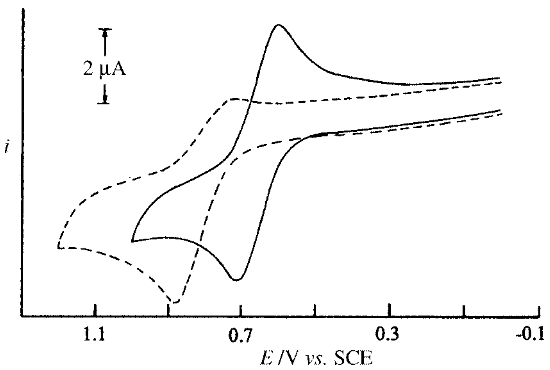


Fig. 3 Cyclic voltammograms of **1** (broken line; concentration $c = 1.03$ mmol dm^{-3}) and **2** (full line; $c = 1.00$ mmol dm^{-3}) in 0.1 mol dm^{-3} dichloromethane in tetrabutylammonium perchlorate at a platinum electrode; scan rate v, 50 mV s^{-1}. Under the same experimental conditions, the ferrocene–ferrocenium couple appears at 0.46 V *vs.* SCE with a ΔE_p of 125 mV at $v = 50$ mV s^{-1}.

peak-to-peak separation (ΔE_p) of 160 mV is observed at a scan rate v of 50 mV s^{-1} (Fig. 3) and the ratio of the anodic and cathodic peak currents (i_{pa}/i_{pc}) approaches unity as the scan rate increases showing that the corresponding copper(II) species is not quite stable on the cyclic voltammetric time scale. This couple is much more reversible in complex **2** with an $E_{1/2}$ of 0.66 V *vs.* SCE ($\Delta E_p = 120$ mV and $i_{pa}/i_{pc} \approx 1$ at $v = 50$ mV s^{-1}; Fig. 3). The Cu$^{II/I}$ potential in a Cu^{I}N$_4$ chromophore is believed to increase with the π-acidity of the ligand(s) and with the extent of tetrahedral distortion occurring in the corresponding Cu^{II}N$_4$ chromophore.[3–5] This has been demonstrated so much in bis-copper(I) complexes of 1,4-diimines [specifically 2,2′-bipyridine,[3] 1,10-phen,[5] 2,2′-biquinoline[6] and N-alkyl/aryl-(2-pyridyl)methanimine[7]] with bulky substituents at steric positions that unconjugated diimines have never been used seriously to stabilise copper(I). To our knowledge, in this regard there is only one report of using an unconjugated diimine earlier where the ligand is di-2-pyridylamine (DPA).[8] [Cu(DPA)$_2$]ClO$_4$ has a Cu$^{I/II}$ potential of −0.2 V *vs.* SCE in dimethylsulfoxide.[8] Incidentally, the corresponding copper(II) complex of DPA, [Cu(DPA)$_2$](ClO$_4$)$_2$, is known to have a pseudotetrahedral Cu^{II}N$_4$ moiety.[9] The π-acidity of a C=N group is likely to be less than that of pyridine.[10] Thus when the $E_{1/2}$ values of **1** and **2** are compared with that of [Cu(DPA)$_2$]ClO$_4$, our results appear to be remarkable. Further studies on the effect of the substituents on the imino C atoms on the relative stability of the Cu^{I}N$_4$ chromophores are ongoing.

The ligands L$_1$ and L$_2$ are non-fluorescent in dichloromethane and methanol at room temperature. However, their copper(I) complexes display photoluminescence upon excitation at 350 nm (within the MLCT envelope) in both the solvents at room temperature. In dichloromethane, the two complexes show single broad structureless emission around 430 nm; the quantum yield (φ) is 4×10^{-5} (against quinine sulfate[11] in 0.1 N H$_2$SO$_4$) for complex **1** and 2×10^{-4} for complex **2**. A change of solvent from dichloromethane to methanol does not affect the emission maxima appreciably (430 nm for **1** and 420 nm for **2**; Fig. 4) but leads to a considerable lowering of φ (2×10^{-5} for **1** and 6×10^{-5} for **2**). All the known examples of photoluminescent Cu^{I}N$_4$ chromophores are known to exhibit a single emission band.[1,2] Studies on the copper(I) complexes of substituted 1,10-phens reveal that φ increases as the copper(II) centre generated in the photoexcited state acquires a distorted tetrahedral geometry imposed by steric hindrance of the substituents.[1,2] For example, while [Cu(1,10-phen)$_2$]$^+$ does not show any emission in CH$_2$Cl$_2$ at room temperature, φ of [Cu{2,9-di-(2-methylphenyl)-1,10-phen}$_2$]PF$_6$ under the same condition is 15×10^{-4}. We believe a similar effect is operative in our case also, resulting in three- to five-fold enhancement of φ in **2** compared to **1**; the extra steric influence comes from the additional phenyl groups in L$_2$. This is in accord with our cyclic voltammetric results where the Cu$^{II/I}$ couple in **2** is found to be more reversible than in **1**.

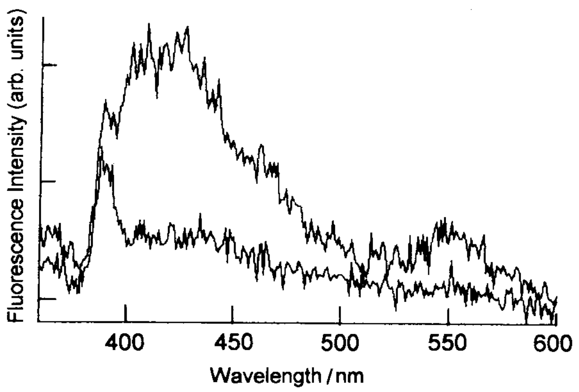


Fig. 4 Emission spectra of **1** (lower trace) and **2** (upper trace) in methanol at room temperature. Excitation wavelength, 350 nm. Absorbances of both the solutions at 350 nm are 0.32.

Interestingly, the emission spectrum of complex **2** shows an additional band around 550 nm in methanol albeit very weak (Fig. 4) which is absent in dichloromethane. Both the emissions in **2** in methanol originate from the MLCT state. The observation of such dual emission is really novel in the photophysics of Cu^{I}N$_4$ chromophores. The high energy emission is possibly a fluorescence while the low energy one a phosphorescence. It should be noted in this context that the exact nature of the single emission band observed in bis-copper(I) complexes of substituted 1,10-phens is not yet known.[1,2] We are presently investigating the factors (*e.g.* nature of the substituents on the imino C atoms, solvent effect, counteranion effect *etc.*) which may increase the emission yield so that we can study the photophysics in detail.

Acknowledgements

M. G. B. D. thanks EPSRC and the University of Reading for funds for the Image Plate System. D. D. thanks the Department of Science and Technology, New Delhi, India and N. C. the Council of Scientific and Industrial Research, New Delhi, India for financial support.

Notes and references

† L$_1$: 15 ml of benzaldehyde (148 mmol) and 5 ml of distilled ethylenediamine (74 mmol) were refluxed in 75 ml of anhydrous methanol for 6 h. Then the reaction mixture was evaporated on a water bath until the volume reduced to *ca.* 20 ml to obtain a viscous liquid. It was cooled in the refrigerator overnight to obtain a yellowish wax-like compound. It was recrystallised from *n*-hexane to obtain large colourless blocks. Yield, 10.34 g (60%); mp 49–52 °C. Anal. Found (calc.): C, 81.37 (81.32); H, 6.76 (6.82); N, 11.78 (11.85)%. IR ν/cm^{-1} (KBr): 1640vs (C=N). UV/VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_3$OH): 245 (24 500).

L$_2$: 10.87 g of benzophenone (60 mmol) and 2 ml of distilled ethylenediamine (30 mmol) were refluxed in 50 ml of anhydrous methanol for 6 h. Then the reaction mixture was evaporated on a water bath until a white semi-solid appeared. This was cooled to room temperature. The compound was recrystallised from *n*-hexane as white blocks. Yield, 8.6 g (85%); mp 43–45 °C. Anal. Found (calc.): C, 86.48 (86.56); H, 6.19 (6.23); N, 7.27 (7.21)%. IR ν/cm^{-1} (KBr): 1625vs (C=N). UV/VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_3$OH): 219 (7700), 252 (17 500).

‡ **1**: 0.47 g (2 mmol) of the ligand was dissolved in 25 ml of anhydrous, degassed methanol to which 0.33 g of freshly prepared [Cu(CH$_3$CN)$_4$]ClO$_4$ (1 mmol) was added under dry N$_2$ atmosphere. The reaction mixture was stirred for 15 min. The silky yellow compound precipitated was filtered, washed with *n*-hexane and stored *in vacuo* over fused CaCl$_2$. It was recrystallised from a dichloromethane–*n*-hexane mixture as yellow needles. Yield, 0.51 g (80%). Single crystals were grown by direct diffusion of *n*-hexane into a dilute dichloromethane solution of the complex. Anal. Found (calc.): C, 60.52 (60.47); H, 5.02 (5.07); N, 8.75 (8.81); Cu, 10.07 (10.00)%. Λ_M (CH$_3$OH): 108 Ω^{-1} cm^2 mol^{-1} (1:1 electrolyte). IR ν/cm^{-1} (KBr): 1630vs (C=N); 1100vs, 630m, split (ClO$_4$). UV/VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_3$OH): 218 (20 350), 252 (29 650), 311 sh (8250), 366 sh (5000).

2: 0.78 g of the ligand (2 mmol) was dissolved in 35 ml of anhydrous, degassed methanol to which 0.33 g of freshly prepared [Cu(CH$_3$CN)$_4$]ClO$_4$ (1 mmol) was added under dry N$_2$ atmosphere. The reaction mixture was stirred for 15 min. The red compound precipitated was filtered, washed with *n*-hexane and dried *in vacuo* over fused $CaCl_2$. It was recrystallised from a dichloromethane–*n*-hexane mixture as brick-red cuboids. Yield, 0.5 g (55%). Single crystals were grown by direct diffusion of *n*-hexane into a dilute dichloromethane solution of the complex. Anal. Found (calc.): C, 71.45 (71.55); H, 5.12 (5.15); N, 6.05 (5.96); Cu, 6.70 (6.76)%. Λ_M (CH_3OH): 94 Ω^{-1} cm^2 mol^{-1} (1 : 1 electrolyte). IR ν/cm^{-1} (KBr): 1620vs (C=N); 1100vs, 630m, split (ClO_4). UV/VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH_3OH): 215 (29 600), 240 (32 000) 314 sh (5700), 387 sh (3300).

§ *Crystal data*: $C_{32}H_{32}ClCuN_4O_4$ **1**: $M_w = 635.60$, monoclinic, space group *C*2/*c*, $a = 17.75(2)$, $b = 18.316(19)$, $c = 20.84(2)$ Å, $\beta = 113.51(1)°$, $U = 6212$ Å^3, $Z = 8$, $\mu = 0.831$ mm^{-1}, $D_c = 1.359$ g cm^{-3}, 8306 data collected, 5151 unique. $C_{56}H_{48}ClCuN_4O_4$ **2**: $M_w = 939.97$, monoclinic, space group $P2_1/c$, $a = 15.446(17)$, $b = 13.270(15)$, $c = 23.70(3)$ Å, $\beta = 91.58(1)°$, $U = 4856$ Å^3, $Z = 4$, $\mu = 0.555$ mm^{-1}, $D_c = 1.286$ g cm^{-3}, 13 972 data collected, 8013 unique. The data were collected using Mo-Kα radiation using the MARresearch Image Plate System. The crystals were positioned at 70 mm from the Image Plate. 95 frames were measured at 2° intervals with a counting time of 2 min. Data analyses were carried out with the XDS program.[12] The structures were solved using direct methods with the SHELXS-86 program.[13] In **1** there were two molecules in the asymmetric unit, both with crystallographic *C*2 symmetry. The perchlorate anion was in a general position, but was disordered and two sets of oxygen tetrahedra were included each with 50% occupancy. There were no unusual features in the structure determination of **2**. Both the structures were refined on F^2 using SHELXL-93.[14] Final *R* values: for **1** with observed data $I > 2\sigma(I)$, $R1 = 0.0731$, $wR2 = 0.1871$ and for all data $R1 = 0.1736$, $wR2 = 0.2193$; for **2** with observed data $R1 = 0.0837$, $wR2 = 0.1540$ and for all data $R1 = 0.1515$, $wR2 = 0.1733$.

CCDC reference number 186/1769.

See http://www.rsc.org/suppdata/dt/a9/a909224b/ for crystallographic files in .cif format.

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Communication a909224b