A new photoluminescent $Cu^{I}_2N_6$ chromophore

Letter

Goutam K. Patra,[a] Israel Goldberg,[a] Sanjoy K. Chowdhury,[b] Bikas C. Maiti,[b] Amitabha Sarkar,[b] Prakriti R. Bangal,[c] Sankar Chakravorti,[c] Nitin Chattopadhyay,[d] Derek A. Tocher,[e] Michael G. B. Drew,[f] Golam Mostafa,[g] Shubhamoy Chowdhury[g] and Dipankar Datta*[g]

[a] *School of Chemistry, Tel Aviv University, 69978 Ramat Aviv, Tel Aviv, Israel*
[b] *Organic Chemistry Division, National Chemical Laboratory, Pune 411 008, India*
[c] *Department of Spectroscopy, Indian Association for the Cultivation of Science, Calcutta 700 032, India*
[d] *Department of Chemistry, Jadavpur University, Calcutta 700 032, India*
[e] *Department of Chemistry, University College London, 20 Gordon Street, London, UK WC1H 0AJ*
[f] *Department of Chemistry, University of Reading, Whiteknights, Reading, UK RG6 6AD*
[g] *Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India. E-mail: icdd@mahendra.iacs.res.in*

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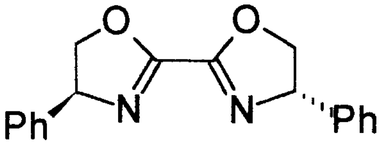
A novel $Cu^{I}_2N_6$ chromophore has been isolated with 2,2′-bis[(4*R*)-phenyl]-1,3-oxazoline (L) in the optically pure triple-stranded helicate $[Cu_2L_3](ClO_4)_2$, which displays photoluminescence in methanol at room temperature (emission maximum $\lambda_{em} = 385$ nm; quantum yield $\phi = 1.6 \times 10^{-4}$; lifetime $\tau \approx 2$ ns) as well as at 77 K ($\lambda_{em} = 430$ nm; $\tau = 0.89 \pm 0.13$ s).

Only the mononuclear homoleptic copper(I) complexes of various derivatives of 1,10-phenanthroline (phen) that contain $Cu^{I}N_4$ chromophores are known to be photoluminescent in fluid solution.[1–3] Homoleptic copper(I) complexes of no other N-donor ligands seem to possess such a property. Recently, we have initiated a search for new N-donor ligands that can give rise to homoleptic photoluminescent copper(I) complexes. So far, we have been successful in synthesising such copper(I) complexes with only two types of ligands. In one case,[4] it is a distorted tetrahedral $Cu^{I}N_4$ chromophore isolated with the 1 + 2 condensate of ethylenediamine and benzophenone, and in another case,[5] it is a $Cu^{I}_2N_8$ chromophore assembled with bis(pyridinal)ethylenediimine. Compared to the $Cu^{I}N_4$ chromophores obtained with the phens, however, the emissions of our $Cu^{I}N_4$ and $Cu^{I}_2N_8$ chromophores in fluid solution are, much weaker. Herein we characterise the structural and photophysical properties of a novel dimeric homoleptic copper(I) complex of 2,2′-bis[(4*R*)-phenyl]-1,3-oxazoline (L), which is a non-aromatic 1,4-diimine.



(L)

Reaction of L with $Cu(ClO_4)_2 \cdot 6H_2O$ in hot ethanol in a 2 : 1 molar proportion in the presence of hydrazine hydrate yields a yellow diamagnetic dimeric copper(I) complex of the type $[Cu_2L_3](ClO_4)_2$ (**1**). This formulation is supported by elemental analyses and FAB mass and ^1H NMR spectra. Complex **1** is quite stable in air—for a week in the solid state and for 3–6 h in solution, depending on the solvent.

Direct diffusion of benzene into a moderately concentrated solution of **1** in dichloromethane yields yellow single crystals of the 1.5 : 1 **1** : CH_2Cl_2 solvate (the crystals lose the solvent molecules rapidly, and need to be contained in a protective environment to preserve their crystallinity). The structure of the $[Cu_2L_3]^{2+}$ cation as determined by X-ray crystallography of 1.5[**1**]$\cdot CH_2Cl_2$ is shown in Fig. 1. The $[Cu_2L_3]^{2+}$ cation contains a $Cu^{I}_2N_6$ chromophore with each copper atom having a trigonal N_3 coordination. The CuN_3 fragments are not exactly planar; the Cu atoms deviate inward from the plane of the three surrounding atoms by 0.067(1) to 0.102(2) Å. The Cu–N distances lie in the range 1.950(6)–1.993(5) Å (in two crystallographically independent entities) with an average of 1.97 Å. Elsewhere we have indicated that the ideal Cu^{I}–N bond length in a symmetric $Cu^{I}N_3$ moiety should be 1.98 Å.[6] The average Cu–Cu distance in **1** is 2.56 Å, while the non-bonding N···N distances within the individual ligands vary from 2.974(5) to 3.016(6) Å. Examples of copper(I) dimers with Cu–Cu separations as short as 2.45 Å are known.[7]

Fig. 1(A) and (B) also show that **1** is a triple-stranded helicate. The five crystallographically independent bisoxazoline ligands are twisted about the central C–C bond to different extents, while the two phenyl groups of a particular L are always *trans*-axial to one another. The resulting conformation is characterised by partial overlap between the individual phenyl substituents and the 1,3-oxazoline rings (each phenyl ring lies in close proximity to a different oxazoline fragment at mean interplanar distances between 3.4 and 3.7 Å). This suggests possible π–π interactions between corresponding unsaturated fragments, which induce and stabilise the observed helical structure. So far, only one authentic example of such a triple-stranded copper(I) helicate in which the metal has an N_3 coordination sphere is known.[8]

As helicates are inherently chiral, use of an optically pure ligand can in principle generate two diastereomers. But in several reports it has been found that with an optically pure helicand, one of the two possible diastereomers is preferentially formed.[9–13] Our ligand L (the helicand) is optically pure [of the (*R*,*R*) type]. Since 1.5[**1**]$\cdot CH_2Cl_2$ crystallises in the space group $P2_12_12$ (the two crystallographically independent moieties in the asymmetric unit have the same chirality),

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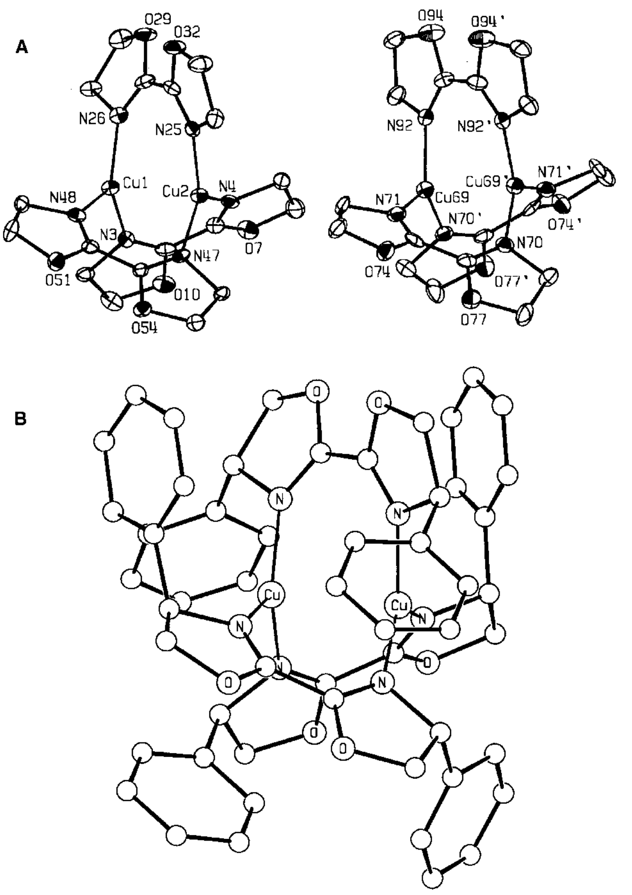

Fig. 1 (A) The structure of the $[Cu_2L_3]^{2+}$ cation in $1.5[\mathbf{1}]\cdot CH_2Cl_2$ with ellipsoids at 40% probability. For the sake of clarity, the H atoms and the Ph groups on L are omitted. One of the molecules is located on a twofold symmetry axis in the crystal; primed atoms are related to non-primed ones by the symmetry transformation: $\frac{1}{2} - x$, $-y$, z. Selected bond distances (Å) and angles (°): Cu1–N3 1.989(5), Cu1–N26 1.957(5), Cu1–N48 1.979(5), Cu2–N4 1.976(5), Cu2–N25 1.993(5), Cu2–N47 1.970(5), Cu69–N71 1.950(6), Cu69–N92 1.967(5), Cu69–N70′ 1.968(5), Cu1···Cu2 2.561(1), Cu69···Cu69′ 2.552(2); N3–Cu1–N26 121.7(2), N3–Cu1–N48 114.0(2), N26–Cu1–N48 123.6(2), N4–Cu2–N25 121.8(2), N4–Cu2–N47 121.6(2), N25–Cu2–N47 116.3(2), N92–Cu69–N70′ 115.2(2), N92–Cu69–N71 120.8(2), N70′–Cu69–N71 123.2(2). The torsion angles (°) about the central C–C bond in the ligands are: N3–C–C–N4 19.6(9), O7–C–C–O10 17.5(7), N25–C–C–N26 32.7(11), O29–C–C–O32 28.9(9), N47–C–C–N48 13.0(10), O51–C–C–O54 12.1(8), N70–C–C–N71 21.2(10), O74–C–C–O77 20.8(8), N92–C–C–N92′ 18.0(10), O94–C–C–O94′ 13.5(8). (B) A perspective view of the entire $[Cu_2L_3]^{2+}$ cation in $1.5[\mathbf{1}]\cdot CH_2Cl_2$.

it is clear that we have an optically pure helicate in **1**. The ^1H NMR spectrum of **1** at room temperature shows that though the non-aromatic protons are not as well resolved as in the free L, only one of the two possible diastereomers is formed. Thus, in our case also the chirality of the ligand predetermines the handedness of the triple helix in **1**. Incidentally, our complex **1** is, to our knowledge, the first structurally characterised optically pure triple-stranded helicate assembled with a chiral ligand.

The absorption spectrum of L in methanol shows a $\pi \rightarrow \pi^*$ transition at 242 nm with an intensity ε of 8300 $dm^3\ mol^{-1}\ cm^{-1}$. This transition appears at 266 nm in the absorption spectrum of **1** with an ε of 8740 $dm^3\ mol^{-1}\ cm^{-1}$ per L fragment. Complex **1** displays an additional broad and unstructured band having a maximum at 328 nm in methanol ($\varepsilon = 5300\ dm^3\ mol^{-1}\ cm^{-1}$), which we believe is of MLCT origin.

Ligand L is not photoluminescent in methanol at either room temperature or 77 K when excited at 300 nm. Upon excitation at the MLCT band in methanol at room temperature, complex **1** yields a broad, structureless and weak emission band at 385 nm (Fig. 2). This indicates that the MLCT state is emissive. The quantum yield ϕ of the emission is 1.6×10^{-4} against quinine sulfate in 0.1 N sulphuric acid[14] ($\phi = 0.54$). The lifetime τ of the 385 nm emission at room temperature in methanol has been found to be ~2 ns. At 77 K, in methanol glass, this band is red-shifted to 430 nm. Its τ was determined[15] to be 0.89 ± 0.13 s (Fig. 3). The unusually long τ at 77 K indicates that the observed emission in **1** is a phosphorescence.

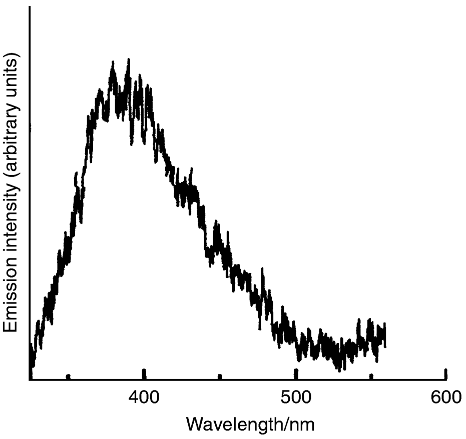

Fig. 2 Emission spectrum of **1** in methanol at room temperature. Excitation wavelength: 300 nm.

No fluorescent $Cu_2{}^IN_6$ or Cu^IN_3 chromophores are known with which we can compare the photophysical properties of **1**. The Cu^IN_4 chromophores isolated with the derivatives of 1,10-phenanthroline are known to display a single emission band, the nature of which (*i.e.*, whether due to fluorescence or phosphorescence) is not yet clear.[1–3]

Experimental

All the steady state photoluminescence studies were performed in air using a Hitachi F-4500 spectrofluorimeter. The emission lifetime at room temperature was estimated using a nanosecond nitrogen flashlamp set-up (Edinburgh Instruments 199 fluoresence spectrometer) exploiting the time-correlated single photon counting technique. The emission lifetime measurements at 77 K were performed using the phosphoroscope set-up of the Hitachi F-4500 spectrofluorimeter.

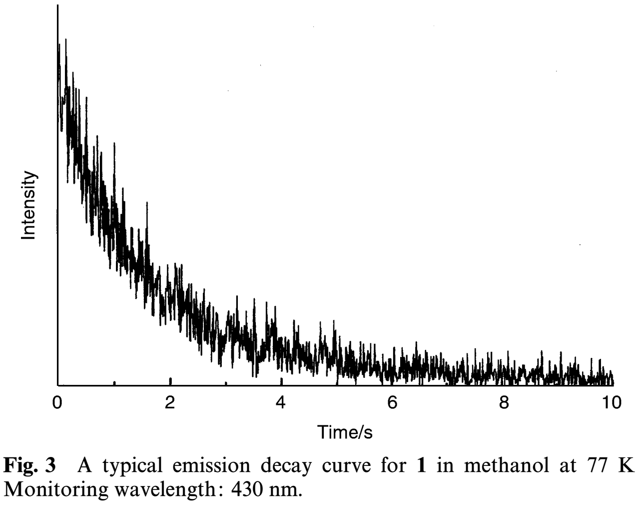

Fig. 3 A typical emission decay curve for **1** in methanol at 77 K. Monitoring wavelength: 430 nm.

Syntheses

2,2′-Bis[(4*R*)-phenyl]-1,3-oxazoline (L). The ligand L was prepared by following the hints given in ref. 16. Diethyl oxalate (4.07 ml, 30 mmol) was added to 8.22 g (60 mmol) of (*R*)-phenylglycinol. The resulting solution was refluxed for 4 h. The reaction mixture became semi-solid. After cooling to room temperature to solidify the *N*,*N*′-bis[(2*R*)-phenyl-1-hydroxyethyl]-1,2-ethanediamide, it was washed with petroleum ether, dried *in vacuo* over fused $CaCl_2$ and pulverised. Yield 19.6 g (92%). This *N*,*N*′-bis[(2*R*)-phenyl-1-hydroxyethyl]-1,2-ethanediamide (14.75 g, 45 mmol) was added to 30 ml of freshly distilled thionyl chloride and refluxed for 2 h. Then the reaction mixture was cooled to room temperature and the thionyl chloride removed by distillation. The last traces of thionyl chloride were removed by azeotropic distillation using benzene. The resulting solid was dissolved in a minimum volume of ethyl acetate to which petroleum ether was added dropwise with constant stirring until the mixture became turbid. Then it was kept in a refrigerator overnight. The amorphous solid so obtained is *N*,*N*′-bis[(2*R*)-phenyl-1-chloroethyl]-1,2-ethanediamide, which was filtered, washed with a small amount of petroleum ether and dried *in vacuo* over fused $CaCl_2$. Yield 11.3 g (69%). CH_2Cl_2 (60 ml) and 1 g of tetrabutylammonium bromide were added to 3 g (75 mmol) of sodium hydroxide dissolved in the minimum volume of water and stirred vigorously for 30 min. To the resulting mixture, 11.3 g (30.9 mmol) of *N*,*N*′-bis[(2*R*)-phenyl-1-chloroethyl]-1,2-ethanediamide was added in small portions over a period of 1 h at room temperature with constant stirring. After the addition of the bischlorodiamide was complete, the reaction mixture was further stirred at room temperature for 3 h. Then the reaction mixture was diluted by adding 50 ml of water and extracted with CH_2Cl_2 (5 × 20 ml). The CH_2Cl_2 extract was dehydrated by adding anhydrous sodium sulfate and the solvent was removed completely at room temperature under reduced pressure to obtain a solid, reprecipitation of which from a CH_2Cl_2–petroleum ether mixture afforded pure L. Yield 7.2 g (80%). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ_H: 4.38t, 4.87t, 5.47t (1 × 3 × 2 H, non-aromatic, $J = 10$ Hz), 7.27–7.38 (5 × 2 H, aromatic).

$[Cu_2L_3](ClO_4)_2$ (1). L (0.12 g, 0.4 mmol) was dissolved in 20 ml of ethanol and 0.01 ml (2 mmol) of hydrazine hydrate was added. The resulting mixture was heated to boiling. To the boiling solution, 0.075 g (0.2 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ dissolved in 5 ml of ethanol was added dropwise with constant stirring. A yellow compound immediately started to appear. The reaction mixture was left in air for 30 min. Then the yellow compound was filtered, washed with 2 ml of ethanol and dried and stored *in vacuo* over fused $CaCl_2$. Yield 0.075 g (25%). The compound is analytically pure. It can be recrystallised from an acetone–petroleum ether mixture. Anal. found (calc. for $C_{54}H_{48}N_6Cl_2Cu_2O_{14}$): C, 53.96 (53.89); H, 3.97 (4.02); N, 6.93 (6.99); Cu, 10.59 (10.56)%. FAB MS: *m*/*z* 1104 ($[Cu_2L_3]ClO_4 + H^+$, 2%), 812 ($[Cu_2L_2]ClO_4 + H^+$, 7%), 712 ($Cu_2L_2 + H^+$, 3%). Λ_M (CH_3OH): 161 Ω^{-1} cm^2 mol^{-1} (1 : 2 electrolyte). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ_H: 4.40br, 4.76br, 5.32br (1 × 3 × 6 H, non-aromatic), 7.26–7.42 (m, 5 × 6 H, aromatic).

Caution! Although we have not encountered any problems in handling **1**, it is noted that perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled only in small quantities with appropriate precautions.

X-Ray crystallography

The X-ray diffraction measurements on $1.5[\mathbf{1}] \cdot CH_2Cl_2$ were carried out at *ca.* 110 K on a Nonius Kappa CCD diffractometer using Mo-Kα radiation. The analysed crystals were coated with a layer of hydrocarbon oil (in order to avoid deterioration) and mounted on a glass fiber. Intensity data were collected on 426 detector frames using 0.6° φ and ω scans, and were corrected for absorption. The structure was solved by Patterson and Fourier methods (DIRDIF-96),[17] and refined by full-matrix least-squares based on F^2 for all reflections (SHELXL-97).[18] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles, and were included in the refinement with isotropic displacement parameters using a riding model. One molecule of the complex is located in a general position, while the other is located on the twofold rotation axis of symmetry at $(\frac{1}{2}, 0, z)$.

Crystal data. $C_{82}H_{74}N_9Cl_5O_{21}Cu_3$ ($1.5[\mathbf{1}] \cdot CH_2Cl_2$): $M_w = 1889.37$, orthorhombic, space group $P2_12_12$, $a = 13.1254(2)$, $b = 48.0683(7)$, $c = 12.8677(2)$ Å, $U = 8118.3(5)$ Å^3, $Z = 4$, $\mu = 1.02$ mm^{-1}, 12 204 unique reflections (1077 refined parameters). Final residuals of the crystallographic refinement: $R_1 = 0.051$ and $wR_2 = 0.112$ for 8848 reflections with $I > 2\sigma(I)$; $R_1 = 0.088$ and $wR_2 = 0.128$ for all data.

CCDC reference number data. See http://www.rsc.org/suppdata/nj/b1/b105442m/ for crystallographic in CIF or other electronic format.

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