Mixed ligand binuclear copper(I) complexes containing Cu$_2$N$_8$ chromophores. Observation of emissions from MLCT excited states involving two different ligands

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Using the 1:2 condensate (L) of diethylenetriamine and benzaldehyde as the main ligand, binuclear copper(I) complexes [Cu$_2$L$_2$(4,4'-bipyridine)](ClO$_4$)$_2$·0.5H$_2$O (1a) and [Cu$_2$L$_2$(1,2-bis(4-pyridyl)ethane)](ClO$_4$)$_2$ (1b) are synthesised. The two metal ions in 1a are bridged by 4,4'-bipyridine and those in 1b by 1,2-bis(4-pyridyl)ethane. From the X-ray crystal structure of 1a, each metal ion is found to be bound to three N atoms of L and one of the two N atoms of the bridging ligand in a distorted tetrahedral fashion. The Cu(I)–N bond lengths in 1a lie in the range of 1.998(5)–2.229(6) Å. Electrochemical studies in dichloromethane (DCM) show that the Cu$_2$N$_8$ moieties in 1a and 1b are composed of two essentially non-interacting CuN$_4$ cores with Cu$^{1+}$ potential of 0.44 V vs. SCE. While 1a displays metal induced quenching of the inherent emission of 4,4'-bipyridine in DCM solution, 1b exhibits two weak emission bands in DCM solution at 425 and 477 nm (total quantum yield = 3.59 x 10$^{-5}$) originating from MLCT excited states. With the help of Extended Hückel calculations it is established that the higher energy emission in 1b is from Cu(I) → bridging-ligand charge transfer excited state and the lower energy one in 1b from Cu(I) → L charge transfer excited state.

Materials and Methods
Deuterated dimethylsulphoxide (DMSO-d$_6$) (99.9 atom % D) was purchased from Aldrich. [Cu(CH$_3$CN)$_4$]ClO$_4$ was prepared by a reported procedure.$^{13}$ C, H and N analyses were performed using a Perkin-Elmer 2400II analyser. Copper was estimated gravimetrically as CuSCN. FTIR spectra (KBr disc; 4000-400 cm$^{-1}$) were recorded on a Nicolet Magna-IR spectrophotometer (series II). UV-vis spectra on a Shimadzu UV-160A spectrophotometer and NMR spectra (in DMSO-d$_6$; reference, TMS) by Brucker DPX300 spectrometer. Solution conductivity was measured by a Systronics (India) direct conductivity meter (model 304). Cyclic voltammetry was performed using EG&G PARC electrochemical analysis system (model 250/5/0) under dry nitrogen atmosphere in conventional three electrode configurations in purified dichloromethane (DCM) with tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. A planar EG&G PARC G0229
glassy carbon milli electrode was used as the working electrode in cyclic voltammetry. Under the experimental conditions employed here, the ferrocene-ferrocenium couple appears at 0.47 V vs. SCE (saturated calomel electrode) with a peak-to-peak separation of 90 mV at scan rate \( v = 50 \, \text{mV s}^{-1} \). All photoluminescence studies were carried out in air using a Spex Fluorolog spectrofluorimeter. The quantum yields (\( \Phi \)) of the emissions of various compounds involved in the present study have been determined against quinine sulphate\(^{14} \) in 0.1 \( N \) \( H_2SO_4 \). AM1 and Extended Hückel calculations were performed by using HyperChem package purchased from Hypercube Inc., Canada.

**Syntheses**

\( L \)-Benzaldehyde (5.1 cm\(^3\), 50 mmol) and freshly distilled diethylenetriamine (dien) (2.7 cm\(^3\), 25 mmol) were taken in 40 cm\(^3\) of anhydrous methanol and refluxed for 6 h. Then the reaction mixture was evaporated on a water bath to 10 cm\(^3\) to obtain a colourless extract was evaporated at room temperature under reduced pressure to obtain a white viscous mass which was kept in vacuo over fused \( \text{CaCl}_2 \) for two days; yield: 5.53 g (79%). Elemental analyses were consistent with the stoichiometry \( \text{C}_{18}\text{H}_{21}\text{N}_3 \) [Found: C, 76.31; H, 8.16; N, 14.87. Calc: C, 77.37; H, 7.58; N, 15.04\%]. FTIR data (cm\(^{-1}\)): 1645(vs) (C=\( \equiv \)N). UV/vis (DCM): \( \lambda_{\text{nm}} (\varepsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \): 245 (22 100).

\[ \text{Cu}_2\text{La}(4,4^{'-}\text{bpy})(\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O} (1a) \]—L (0.56 g, 2 mmol) and 4,4′-bipyridine (4,4′-bpy) (0.16 g, 1 mmol) were dissolved in 20 cm\(^3\) of anhydrous degassed methanol. To this solution, freshly prepared \[ \text{Cu(CH}_3\text{CN})_4\text{ClO}_4 \] (0.66 g, 2 mmol) was added under dry \( \text{N}_2 \) atmosphere and stirred for 15 min. The reddish brown compound precipitated was filtered, washed with 10 cm\(^3\) of diethylether and stored in vacuo over fused \( \text{CaCl}_2 \). It was recrystallised from a 1:3 mixture of DCM and petroleum ether (40-60°C); yield: 0.28 g (52\%). Elemental analyses were consistent with the stoichiometry \( \text{Ca}_6\text{H}_3\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_5 \) [Found: C, 52.02; H, 5.14; N, 10.49; Cu, 11.85. Calc: C, 53.91; H, 5.09; N, 10.48; Cu, 11.89\%]. FTIR data (cm\(^{-1}\)): 1630(m), 1605(m) (C=\( \equiv \)N); 1145 (m), 1115 (s), 1087(vs), 630 (m) (\text{ClO}_4\text{)}. \( \Delta_\varepsilon/\text{mho cm}^2 \text{ mol}^{-1} \) (CH\(_3\text{OH}) \): 203 (1:2 electrolyte). UV/vis (DCM): \( \lambda_{\text{nm}} (\varepsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \): 247 (41 100), 306sh (7 400), 350sh (5 000).

Caution—Though we have not met with any incident during our studies, care should be taken in handling the metal complexes as perchlorate salts are potentially explosive. These should not be prepared and stored in larger amounts.

**X-ray crystallography**

Reddish orange single crystals of 1a were grown by the direct diffusion of petroleum ether (40-60°C) into a dilute DCM solution of the complex. Diffraction data were collected at 293(2) K with Mo-K\( \alpha \) radiation using the MARresearch Image Plate System. The crystals were positioned at 70 mm from the Image Plate. 100 frames were measured at 2° intervals with a counting time of 2 mins. Data analysis was carried out with the XDS program\(^{15} \) to provide 6526 independent reflections [\( R(\text{int}) = 0.0435 \)]. The structure was solved using direct methods with the SHELXS-86 program.\(^{16} \) Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. An empirical absorption correction was carried out using DIFABS.\(^{17} \) The structure was refined on \( F^2 \) using SHELXL-93\(^{18} \) to \( R_1 = 0.0716 \) and \( wR_2 = 0.2264 \) for 2607 reflections with \( I > 2\sigma(I) \). The positional parameters along with equivalent isotropic thermal parameters for the non-hydrogen atoms in 1a are given in Table 1.
Table I—Final coordinates (in Å) and equivalent isotropic displacement parameters (in Å²) for the non-hydrogen atoms in 1a*  

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<th>Atom</th>
<th>x</th>
<th>y</th>
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*Ueq is 1/3 of the trace of the orthogonalised U tensor. Starred atom sites have a S.O.F less than 1.0. For atom labelling scheme, see Fig. 3.

Crystal data
The cell constants and crystallographic data are: Mol. Formula C46H39ClCu2N6O2S; mol. wt. 1049.92; monoclinic; space group C2/c; a = 17.06(3) Å; b = 16.08(3) Å; c = 17.84(3) Å; β = 102.64(1)°; V = 4775(14) Å³; Z = 4; F(000) = 2172; Dc = 1.461 g cm⁻³; μ = 1.065 mm⁻¹.

Results and Discussion
The tridentate N-donor ligand used in the present work is the 1:2 condensate (L) of dien and benzaldehyde. Its ¹H NMR spectrum is found to be very rich. Though we have not been able to decipher it, it is evident that it does not correspond to the structure I shown in Chart 1. However, its ¹³C NMR spectrum and the DEPT (dynamic enhancement by polarisation transfer) 135 spectrum (Fig. 1) are found to be consistent with the structure II in Chart 1. The ¹³C NMR spectra clearly show presence of two methine carbon atoms of considerably different types and four methylene carbon atoms in L. Of the two methine carbon atoms, one is identified as an imino carbon (C6) from its δ value of 162.05 ppm. The other methine carbon atom which appears at a much higher field of 83.81 ppm is assigned as C1. For comparison, we mention that the alky quaternary carbon atom in 8,8a-diphenyl-1,2,3,5,6,8a-hexahydroimidazo[1,2-alpyrazine, which has a chemical environment very similar to that of C1, resonates at 82.08 ppm in CDCl₃ (ref. 19). Since the chemical environments of C6 and C1 are quite different, the two quaternary aromatic C atoms appear separately at 137.02 and 142.23 ppm. Thus we assign structure II (Chart 1) to L. It should be noted that two closely spaced resonances are observed for each of C4, C5 and C6 in Fig. 1. This is because two isomers are possible for II depending on the orientation of the phenyl group on C6 relative to the two H atoms on C5. From our AM1 calculations²⁰, the energy difference between these two isomers (Fig. 2) in the gas phase is found to be only 1.4 kcal mol⁻¹.

Reaction of L with [Cu(CH₃CN)₄]ClO₄ in anhydrous methanol in 1:1 molar proportion under N₂ atmosphere leads to a yellow reaction mixture from which no definite compound can be isolated. However, when the reaction is carried out in presence of 4,4'-bpy in 0.5 molar proportion, a reddish brown precipitate is obtained. Recrystallisation of this precipitate from a 1:3 mixture of DCM and petroleum ether (40-60°C) yields [CuL₂(4,4'-bpy)][ClO₄]₂.0.5H₂O (1a).

![Chart 1—Two possible structures of L together with the numbering scheme for some of the C atoms in structure II](image)
Fig. 1—(a) Normal $^{13}$C NMR spectrum (300 MHz) of L in DMSO-d$_6$ (reference, TMS) with some possible assignments; the resonances around 40 ppm are due to the solvent. (b) DEPT 135 spectrum of L in the same solvent highlighting the phase differences between the methylene C atoms and the methine ones. It should be noted that the aromatic quaternary C atoms resonating at 137.02 and 142.23 ppm in the normal $^{13}$C NMR spectrum [(a)] do not appear in the DEPT spectrum [(b)]. For the identifications of the various C atoms, see structure II of L in Chart 1.

![Fig. 1 NMR spectra](image)

Fig. 2—Line drawings of the stereo views of the two isomers corresponding to structure II of L (Chart 1) as optimised by AM1 method. Isomer A is calculated to be more stable than B in the gas phase by 1.4 kcal mol$^{-1}$.

![Fig. 2 Stereo views](image)

From X-ray crystallography, the structure of 1a is found to consist of discrete [Cu$_2$L$_2$(4,4'-bpy)]$^{2+}$ cations and two ClO$_4^-$ anions together with a water molecule on a two-fold axis with 50% occupancy. The cation, which contains a crystallographic two-fold axis, is shown in Fig. 3. Interestingly, coordinated L has the structure I of Chart 1. Evidently, upon coordination the five membered ring in L opens up to assume structure I. Each metal center in the cation has a very distorted tetrahedral N$_4$ coordination sphere. 4,4'-bpy serves as a bridge between the two copper atoms, each of which is bonded to three nitrogen atoms of an L fragment. With the amino N, the metal forms a bond [2.229(6) Å] much longer than those with the imino ones [2.077(5) and 2.034(5) Å] or that with the pyridyl one [1.998(5) Å]. The angle between the two pyridine rings in the coordinated 4,4'-bpy unit is 49.6°.

When L, [Cu(CH$_3$CN)$_4$]ClO$_4$ and 1,2-bpye are reacted in 1:1:0.5 molar proportion in a manner similar to that adopted to synthesise 1a, deep yellow [Cu$_2$L$_2$(1,2-bpye)][ClO$_4$]$_2$ (1b) is obtained. So far, we have not been able to grow single crystals of 1b.
suitable for X-ray crystallography. However, by comparing its $^1$H NMR spectrum with that of 1a (Fig. 4), we conclude that 1b has a structure essentially similar to that of 1a, i.e. we have a Cu$_2$N$_8$ chromophore in 1b also with L assuming structure I and 1,2-bpy acting as a bridge between the two copper atoms by coordinating through the pyridyl N’s.

The two complexes 1a and 1b are stable towards aerial oxidation in the solid state for about a month. However, their solution stability in air depends on the solvent. In DCM, 1a is stable for about 20 min while 1b is so for only 10 min. These are less stable in polar solvents like methanol, DMSO etc.

The electrochemical behaviour of 1a and 1b has been studied by cyclic voltammetry at a glassy carbon electrode in purified DCM under dry N$_2$ atmosphere. Complex 1b displays a quasireversible voltammogram with a half-wave potential of 0.44 V vs. SCE; the peak-to-peak separation is 120 mV at $v = 50$ mV s$^{-1}$ (Fig. 5). Comparison of the observed peak currents with those of the ferrocene-ferrocenium couple at the same scan rates shows that in 1b we have two one-step one-electron transfers, not a one-step two-electron transfer. This indicates that the two copper centers behave independent of each other, i.e. there is no interaction between them even in the oxidised state.$^{21}$ This was, however, anticipated in
with same redox potentials. However, in the case of 1a, while a single anodic wave is observed, the cathodic response is composed of two waves of unequal current heights (Fig. 5). The nature of the cathodic response suggests that for 1a the oxidised species generated in the electrode process is not at all stable. Consideration of the anodic peak currents indicates that in 1a also couple (1) is operative, i.e. the two metal ions are non-interacting in 1a also irrespective of the oxidation state. In dinuclear copper(II) complexes, 4,4'-bpy as a bridge is known to bring about only very weak interactions between the two metal centers. For example, the intramolecular exchange coupling constant \([\text{Cu}_2(\text{dien})_2(4,4'-\text{bpy})(\text{ClO}_4)_2](\text{ClO}_4)_2\), where 4,4'-bpy connects the two copper(II) centers\(^2\), is as low as \(-1 \text{ cm}^{-1}\). As such, the crystallographically observed non-coplanarity of the two pyridine rings in the 4,4'-bpy fragment precludes the possibility of any significant interaction between the two copper atoms in 1a.

Our electrochemical results show that the complexes 1a and 1b are composed of essentially two non-communicating CuN\(_4\) chromophores. Such a chromophore, at least in 1b, has a Cu\(^{10+}\) potential of 0.44 V vs. SCE which is quite high when one compares it with that (0.06 V vs. SCE in aqueous medium)\(^2\) in [Cu(py)_3]\(^+\) (py \equiv pyridine). It is now well understood that Cu\(^{10+}\) potential of a CuN\(_4\) core increases with the \(\pi\)-acidity of the N-donor ligand involved and the extent of tetrahedral distortion in the corresponding CuN\(_4\) moiety. In our complexes, apart from the py fragments, the imino functions are capable of acting as \(\pi\)-acids. There is evidence for appreciable \(\pi\) back bonding between a C=N fragment and copper(I) in the IR spectra; the C=N stretching frequency of 1645 cm\(^{-1}\) in the free ligand is lowered to \(-1630 \text{ cm}^{-1}\) in 1a and 1b.

In the electronic spectra in DCM, the ligand L displays a relatively narrow band at 245 nm with a high intensity (\(\varepsilon\)) of 22 100 dm\(^3\) mol\(^{-1}\) cm\(^{-1}\) due to \(\pi \rightarrow \pi^*\) transition localised on the imino fragment. The intraligand charge transfer band in 4,4'-bpy appears at 238 nm in DCM with an \(\varepsilon\) of 12 800 dm\(^3\) mol\(^{-1}\) cm\(^{-1}\). However, such a band in 1,2-bpye is found to be much weaker (\(\varepsilon\) \(=\) 3 000 dm\(^3\) mol\(^{-1}\) cm\(^{-1}\)) with the position shifted towards longer wavelength (\(\lambda_{\text{max}} = 256 \text{ nm}\)). These ligand centered transitions are found to occur in the copper(I) complexes 1a and 1b as an intense and somewhat broad band around 246 nm.

The two metal complexes show additional charge transfer band(s) around 350 nm as shoulder(s) which can be assigned as MLCT one(s).

As a part of our on-going program on the search for the N-donor ligands other than the phenanthrolines that can yield photoluminescent copper(I) complexes\(^8,10,11,12\), we have studied the emission properties of 1a and 1b. Our ligand L does not emit light in DCM at room temperature upon excitation at 350 nm. One of the lessons from the studies on the photophysics of the copper(I)-bisphenanthrolines is that the copper(II) center generated in the photoexcited state has to be stable enough. An idea about this aspect can be had beforehand from electrochemical measurements. For example, since in cyclic voltammetry we have found that [Cu_L\(_2\)(4,4'-bpy)]\(^+\) generated in the electrode process (1) is unstable, we do not expect to observe any photoluminescence from an MLCT excited state in the case of 1a. This is indeed found to be true. Our studies show that upon excitation at 350 nm (within the MLCT envelope) in DCM at room temperature, 1a displays severe quenching of the inherent emission of the 4,4'-bpy fragment (Fig. 6); \(\Phi\) in 4,4'-bpy is 1.83 (emission maxima \(\lambda_{\text{em}} = 413 \text{ nm}\)) and that in 1a 1.73x10\(^{-5}\) (\(\lambda_{\text{em}} = 478 \text{ nm}\)). The quenching is metal induced. It should be noted that quenching of fluorescence of an organic fluorophore by a metal ion
is a very common phenomenon; only a very few cases are known\textsuperscript{24} where some metal ions enhance the fluorescence of the organic fluorophore. However, the situation in Ib is quite different where the corresponding copper(II) species is found to be stable in cyclic voltammetry. Moreover, 1,2-bpye does not fluoresce like 4,4'-bpy upon excitation at 350 nm. Thus upon excitation at 350 nm (within the MLCT envelope) in DCM at room temperature, complex Ib shows two weak and somewhat well-resolved emission bands with maxima at 425 and 477 nm (total $\Phi = 3.59 \times 10^{-5}$; Fig. 7). Owing to poor $\Phi$, we have not
been able to determine the lifetimes of these emissions.

Earlier in connection with the electrochemical studies, we have indicated that our complexes 1a and 1b can be considered as composed of two isolated Cu'N₄ chromophores. In the photophysics of Cu'N₄ chromophores, observation of more than one emission band is rare⁴⁻⁹. Two emission bands are observed in some copper(I)-bisphenanthroline at lower temperatures⁴. In these cases, the two bands are thought to arise from a higher lying ¹MLCT and a lower lying ³MLCT states; the energy separation between these two states are expected to lie within 1000-2000 cm⁻¹⁴⁻⁹⁻⁻²⁵⁻²⁶. The energy separation between the two emission bands in 1b is found to be 2565 cm⁻¹ (from Fig. 7) which seems to be rather large. Moreover, in photoluminescent Cu'N₄ chromophores, the emission from the ³MLCT state is thought to be much weaker than that from ¹MLCT⁴⁻⁹. But in 1b the lower energy emission is much stronger than the higher energy one (see Fig. 7). Thus the two emission bands in 1b do not seem to arise from the triplet and singlet configurations of the same MLCT excited state. In order to understand the origin of these two bands in 1b, we have performed Extended Hückel calculations on the [CuL(py)]⁺ fragment of the cation [Cu₂L₂(4,4'-bpy)]²⁺ at the crystallographically determined geometry. The calculated contour diagrams of the HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital) and two next energetically higher MO's, LUMO+1 and LUMO+2, are shown in Fig. 8. As expected, the HOMO has a considerable metal character. The other three subsequent higher MO's are ligand centered. The LUMO is localized on the imino fragment, the N atom of which forms a longer bond [2.077(6) Å] with copper(I) and LUMO+2 on the other imino fragment of L. LUMO+1 is essentially localized on the pyridine moiety. Thus electronic transition from HOMO to any of the three higher MO's can result in MLCT states. We reckon that the 477 nm emission band in 1b arises from the MLCT excited state involving HOMO and LUMO, and 425 nm one from the MLCT excited state involving

Fig. 8—Calculated contour diagrams of (a) HOMO, (b) LUMO, (c) LUMO+1 and (d) LUMO+2 in [CuL(py)]⁺ fragment. LUMO is localized on C11-N1 moiety and LUMO+2 on C71-N7 moiety. See Fig. 3 to identify C11, N1, C71 and N7. Relative energies (in eV): (a) set to 0, (b) 1.13, (c) 1.82 and (d) 2.06.
HOMO and LUMO+1. Another MLCT excited state involving HOMO and LUMO+2 is conceivable, the emission from which is expected to occur at a wavelength shorter than 425 nm. Since in the present case the excitation wavelength is 350 nm, we could not observe it. From the pictorial representations of the various MO’s in Fig. 8, we can say that the higher energy emission band in 1b is from Cu(I) → pyridine charge transfer excited state and the lower energy one from Cu(I) → an imine-fragment (of L) charge transfer excited state. In view of the relative Φ’s of the two emission bands in 1b (Fig. 7), it can be concluded that an imino N is more effective than a pyridyl one in designing new photoluminescent CuN₄ chromo- phores. This seems reasonable as [Cu(py)₄]⁺ is not known to display emission(s). Further, even 2,2’-bipyridine, which is a close kin of 1,10-phenanthroline, has not been able to afford photoluminescent CuN₄ chromophores. On the other hand, in recent times we have been able to provide new examples of photoluminescent homoleptic copper(I) complexes with ligands having unconjugated imino N’s (refs 8,9,11).

Supplementary material

Tables containing listings of positional parameters, thermal parameters, all distances and angles for 1a are available from the authors.

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