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Fluorescent Copper(I) Complexes: Structural and Spectroscopic Characterization of Bis(*p*-toluidine)bis(acetonitrile)tetraiodotetracopper and Bis[(*p*-chloroaniline)(acetonitrile)diiododicopper] Tetrameric Complexes of Mixed-Ligand Character

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The tetrameric copper(I) clusters Cu_4I_4(*p*-toluidine)$_2$(acetonitrile)$_2$ (I) ($Cu_4I_4C_{18}H_{24}N_4$, a = 14.274 (5) Å, b = 7.587 (2) Å, c = 14.239 (5) Å, α = 88.61 (2)°, β = 110.07 (2)°, γ = 88.70 (2)°, D_{calcd} = 2.428 g cm^{-3}, Z = 2, space group $P\bar{1}$, R = 5.8%, 3643 observations) and [Cu_2I_2(*p*-chloroaniline)(acetonitrile)]$_2$ (II) (asymmetric unit $Cu_2I_2C_8H_9N_2Cl$, a = 15.952 (6) Å, b = 23.714 (11) Å, c = 7.596 (3) Å, β = 92.00 (3)°, D_{calcd} = 2.542 g cm^{-3}, Z = 8, space group $C2/c$, R = 7.3%, 1315 observations) both display distorted cubic cluster geometry with copper and iodine atoms at alternate corners and a nitrogen donor ligand filling the fourth coordination site on each copper atom. In I the cluster displays no crystallographic symmetry element whereas in II a twofold axis penetrates opposite faces of the cube relating the copper atoms in pairs. Neither cluster displays a change in emission spectrum with temperature in the solid state.

Introduction

Copper(I) halides react with Lewis bases to produce complexes of wide variation in stoichiometry[1] and structural format. While the Cu_2X_2 rhomb with copper and halide atoms at alternate corners of a distorted square is common to all complexes, this basic building block may exist in isolation[2] or in combinations of rhombs sharing edges to form chairs,[3] cubes,[4] polymers,[5] and clusters of higher nuclearity or complexity.[6] Cluster compounds of stoichiometry [Cu^IIL]$_4$ most commonly display a pseudocubic arrangement with metal and halide occupying alternate corners of a distorted cube, the electron-donating ligand occupying the remaining coordination site of the approximately tetrahedral copper atoms and thus projecting along the diagonals of the cube. Some clusters of this type have been reported to fluoresce in the solid state, and the emission may or may not be temperature-dependent. Empirical evidence links this thermochromic behavior with the absence of a crystallographic symmetry element in the cluster.[7] Thus for a series of clusters with nitrogen donor ligands, changes in the emission maximum with temperature have been noted for (CuIpy)$_4$[8] and for (CuImorph)$_4$[9] (py = pyridine, morph = morpholine) in which the cluster displays no crystallographic symmetry element or a twofold axis, respectively, but not for (CuIpip)$_4$ (pip = piperidine) in which a $\bar{4}$ crystallographic symmetry element relates all Cu-ligand bonds.[10] The wavelength of the fluorescent emission is reported to change with the identity of the halide, with the identity of the Lewis base, and in one case with the presence of a crown ether in the unit cell. The product of the reaction of CuI and acetonitrile reportedly displays yellow emission at 298 K and green emission at 77 K. Prepared in the presence of dibenzo-18-crown-6, the solid product is said to fluoresce yellow at 298 K and pink at 77 K.[11] However, (CuICH$_3$CN)$_x$ is a pleated-sheet polymeric structure in the solid state with edge-sharing rhombohedra of alternating copper and iodine atoms extending in infinite array, whereas $Cu_4I_4(CH_3CN)_4 \cdot Bz_2$-18C6 ($Bz_2$-18C6 = dibenzo-18-crown-6) crystallizes in a distorted-cube format with second-sphere interactions between crown ether and the hydrogen atoms of the acetonitrile methyl groups.[12] The complexity of the differences between the two structures makes comparison of their reported fluorescence difficult.

We have prepared mixed-ligand clusters of the type $Cu_4I_4L_2L'_2$ to eliminate the possibility of a $\bar{4}$ internal symmetry element in the cluster. We have determined the single-crystal X-ray structures of Cu_4I_4(*p*-tld)$_2$(CH_3CN)$_2$ (I) and [Cu_2I_2(*p*-ClAn)(CH_3CN)]$_2$ (II) (*p*-tld = *p*-toluidine, *p*-ClAn = *p*-chloroaniline) and measured the variation of emission spectra with temperature for the solid-state materials to ascertain the importance of lack of a $\bar{4}$ symmetry element in the thermochromicity of emission.

Experimental Section

Cu_4I_4(*p*-tld)$_2$(CH_3CN)$_2$ (I). Copper iodide (0.48 g, 0.0025 mol) and *p*-toluidine (0.258 g, 0.0025 mol) were added to acetonitrile, and the solution was heated under reflux in an argon atmosphere for 3 h. The resulting light brown solution was allowed to cool under an argon atmosphere and then cooled to 5 °C for 48 h whereupon light brown rhombohedral crystals formed which fluoresced yellow-orange at room temperature.

[Cu_2I_2(*p*-ClAn)(CH_3CN)]$_2$ (II). Copper iodide (0.48 g, 0.0025 mol) and *p*-chloroaniline (0.65 g, 0.0025 mol) were added to 30 mL of acetonitrile, and the resulting solution was allowed to stand in open air (48 h) until crystal formation was observed, whereupon crystallization was completed at 5 °C. Orange emission was observed at room temperature.

Fluorescence. Low-temperature measurements were made with the crystals sealed in capillaries in a CTI cryogenic cooler, which had a resistance heater for temperature control between 12 and 300 K. In this particular work, two detectors were used to cover the wide range of emission spectra. A cooled RCA 31034 photomultiplier tube (PMT) for the visible range and an RCA 7102 PMT cooled at dry ice for the near-infrared region were utilized. Emission spectra were measured on a 0.8-m Spex monochromator, and excitation spectra were taken with a 0.22-m Spex monochromator. The exciting light from a 75-W Xe lamp was chopped at the desired frequency. The intensity of the exciting light from the Xe lamp and a Spex Minimate monochromator was measured with a Spectra Radiometer Model 301 instrument. The excitation spectra were corrected accordingly.

Single-Crystal X-ray Studies. Crystals of Cu_4I_4(*p*-tld)$_2$(CH_3CN)$_2$ (I) and [Cu_2I_2(*p*-ClAn)(CH_3CN)]$_2$ (II) were observed to decompose in air over a 6-h period, and thus crystals of appropriate dimensions (0.4 × 0.4 × 0.5 mm (I); 0.2 × 0.3 × 0.3 mm (II)) were sealed in capillaries under an atmosphere of acetonitrile vapor and mounted on a Syntex P3 automated diffractometer. Unit cell dimensions were determined by least-squares refinement of the best angular positions for 15 independent reflections (2θ > 15°) during normal alignment procedures. Data (7665

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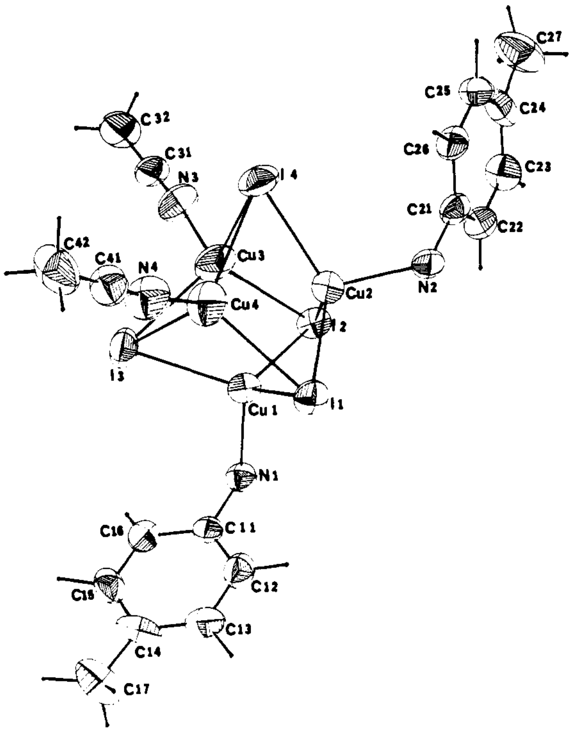

Figure 1. Projection view of $Cu_4I_4(p\text{-tld})_2(CH_3CN)_2$ (I).

Table I. Crystal Data for $Cu_4I_4(p\text{-tld})_2(CH_3CN)_2$ (I) and $[Cu_2I_2(p\text{-ClAn})(CH_3CN)]_2$ (II)

	I	II
formula	$Cu_4I_4C_{18}N_{24}N_4$	$Cu_2I_2C_8H_9N_2Cl$
M_r	1058.2	549.5
a, Å	14.274 (5)	15.952 (6)
b, Å	7.587 (2)	23.714 (11)
c, Å	14.239 (5)	7.596 (3)
α, deg	88.61 (2)	90.0
β, deg	110.07 (2)	92.00 (3)
γ, deg	88.70 (2)	90.0
V, Å^3	1447.12 (77)	2871.8 (22)
$F(000)$	976	2016
μ(Mo Kα), cm^{-1}	71.478	73.91
λ(Mo Kα), Å	0.71069	0.71069
D_{calcd}, g cm^{-3}	2.428	2.542
Z	2	8
obsd reflcns	3643	1315
R, %	5.8	7.3
R_w, %	7.5	9.5
space group	$P\bar{1}$	$C2/c$

Table II. Positional Parameters for $Cu_4I_4C_{18}H_{24}N_4$ (I)

atom	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)
I1	0.8191 (1)	0.0413 (1)	0.4994 (1)
I2	1.0005 (1)	0.4584 (1)	0.6809 (1)
I3	0.6743 (1)	0.4661 (2)	0.6249 (1)
I4	0.8750 (1)	0.0341 (2)	0.8256 (1)
Cu1	0.8161 (1)	0.3718 (2)	0.5563 (1)
Cu2	0.9438 (1)	0.1279 (2)	0.6839 (1)
Cu3	0.8531 (2)	0.3752 (3)	0.7569 (2)
Cu4	0.7430 (2)	0.1255 (3)	0.6468 (2)
N1	0.7996 (8)	0.5482 (15)	0.4362 (8)
N2	1.0625 (9)	−0.0503 (16)	0.6994 (8)
N3	0.8711 (12)	0.5097 (20)	0.8777 (11)
N4	0.6224 (12)	−0.0070 (21)	0.6282 (12)
C11	0.7098 (10)	0.5441 (17)	0.3506 (10)
C12	0.7044 (12)	0.4306 (20)	0.2759 (11)
C13	0.6168 (14)	0.4221 (23)	0.1952 (12)
C14	0.5318 (14)	0.5191 (22)	0.1904 (11)
C15	0.5385 (12)	0.6321 (21)	0.2666 (13)
C16	0.6268 (11)	0.6441 (18)	0.3480 (11)
C17	0.4340 (16)	0.5006 (32)	0.1090 (19)
C21	1.1480 (11)	−0.0418 (17)	0.7899 (10)
C22	1.2255 (12)	0.0718 (21)	0.7947 (12)
C23	1.3047 (11)	0.0752 (22)	0.8832 (12)
C24	1.3091 (13)	−0.0190 (21)	0.9677 (13)
C25	1.2331 (13)	−0.1320 (21)	0.9615 (11)
C26	1.1515 (12)	−0.1442 (18)	0.8733 (12)
C27	1.3924 (19)	−0.0018 (32)	1.0674 (15)
C31	0.8700 (13)	0.5827 (21)	0.9438 (11)
C32	0.8702 (18)	0.6763 (31)	1.0309 (13)
C41	0.5545 (12)	−0.0833 (22)	0.6296 (13)
C42	0.4686 (14)	−0.1769	0.6314 (18)
H121	0.7629	0.3510	0.2797
H131	0.6161	0.3372	0.1396
H151	0.4786	0.7034	0.2833
H161	0.6359	0.7386	0.3924
H171	0.3614	0.5408	0.1168
H172	0.4342	0.5678	0.0468
H173	0.4266	0.3755	0.0888
H221	1.2230	0.1485	0.7358
H231	1.3630	0.1564	0.8826
H251	1.2374	−0.2096	1.0223
H261	1.0973	−0.2279	0.8692
H271	1.3785	−0.0664	1.1244
H272	1.4588	−0.0434	1.0641
H273	1.4037	0.1278	1.0839
H321	0.8994	0.7906	1.0303
H322	0.8029	0.6938	1.0321
H323	0.9056	0.6128	1.0808
H421	0.4766	−0.2773	0.6864
H422	0.4181	−0.0925	0.6374
H423	0.4415	−0.2322	0.5668

points (I), 3107 points (II)) were measured at room temperature with use of a variable scan rate and a θ–2θ scan width of 1.2° below Kα_1 and 1.2° above Kα_2 to a maximum 2θ value of 116°. Backgrounds were measured at each side of the scan limit for a combined time equal to the toal scan time. The intensities of 3 standard reflections were remeasured after every 97 reflections, and as the intensities of these reflections showed about 8% variation, corrections for decomposition were made on the basis of the linear decay of the standard intensities. Data were corrected for Lorentz, polarization, and background effects. After removal of redundant and space-group-forbidden data, 3643 (I) and 1315 (II) reflections were considered observed [$I > 3.0\sigma(I)$].

Crystal Data. I: $Cu_4I_4C_{18}H_{24}N_4$, M_r = 1058.2, triclinic, $P\bar{1}$, a = 14.274 (5) Å, b = 7.587 (2) Å, c = 14.239 (5) Å, α = 88.61 (2)°, β = 110.07 (2)°, γ = 88.70 (2)°, V = 1447.1 (8) Å^3, $F(000)$ = 976, D_{calcd} = 2.428 g cm^{-3}, Z = 2, Mo Kα radiation, γ = 0.71069 Å, μ(Mo Kα) = 71.48 cm^{-1}, transmission factors 0.40–0.48. II: $Cu_2I_2C_8H_9N_2Cl$, M_r = 549.53, orthorhombic, space group $C2/c$, a = 15.592 (6) Å, b = 23.714 (11) Å, c = 7.596 (3) Å, β = 92.00 (3)°, V = 2871.8 (22) Å^3, $F(000)$ = 2016, D_{calcd} = 2.542 g cm^{-3}, Z = 8, Mo Kα radiation, λ = 0.71069 Å, μ(Mo Kα) = 73.91 cm^{-1}, transmission factors 0.45–0.52. Solution of the structures was achieved with use of both direct and Patterson methods. The correctness of E-factor maps calculated by using MULTAN80[13] was assessed by checking for the appearance of suitable cross vectors in a Patterson map. Refinement of scale factor, positional, and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence.[14] Hydrogen positional parameters for the p-toluidine (I) and the p-chloroaniline (II) moieties were determined from a difference Fourier synthesis. These hydrogen parameters were included in the final cycles of refinement. The hydrogen atoms were assigned isotropic thermal parameters of U = 0.03 Å^2. All parameters associated with hydrogen atoms were held invariant. The hydrogen atoms of the acetonitrile groups were not located for I or II. The final cycle of refinement [function minimized, $\sum(|F_o| - |F_c|)^2$] led to a final agreement factor R = 5.8% (I), 7.3% (II) [$R = (\sum||F_o| - |F_c||/|F_o|) \times 100$]. Anomalous dispersion corrections were made for Cu and I. Scattering factors were taken from Cromer and Mann.[15] Weighting schemes were applied ($w = 1/F_o$ if $F_o > 10.0$): R = 5.8%, R_w = 7.5% (I); R = 7.3%, R_w = 9.5% (II). The average values of weighted ΔF for equally populated groups of reflections partitioned according to sin θ differed by a factor of 3.5 (I), 2.1 (II). Projection views of the molecules I (Figure 1) and II (Figure 2) are based on the crystal data of Table I and the positional parameters of Tables II and III. Derived bond angles and

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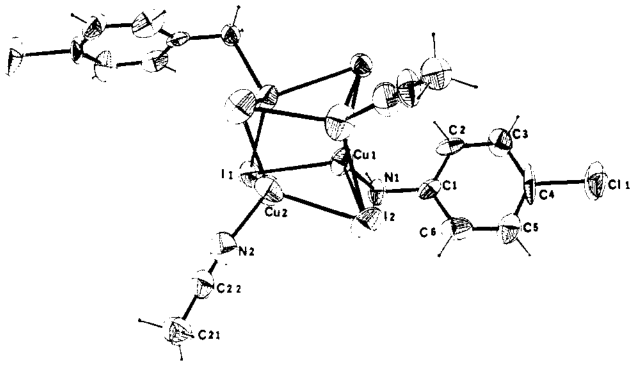

Figure 2. Projection view of $[Cu_2I_2(p\text{-}ClAn)(CH_3CN)]_2$ (II).

Table III. Positional Parameters for $Cu_2I_2C_8H_9N_2Cl$ (II)

atom	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)
I1	0.4061 (1)	0.4115 (1)	0.5425 (3)
I2	0.3960 (2)	0.2773 (1)	0.9622 (4)
Cu1	0.4352 (3)	0.3806 (2)	0.8709 (6)
Cu2	0.4436 (3)	0.3006 (2)	0.6260 (7)
Cl1	-0.0033 (6)	0.4161 (6)	1.0005 (18)
N1	0.3680 (15)	0.4315 (11)	1.0584 (35)
N2	0.3739 (21)	0.2490 (16)	0.4853 (47)
C1	0.2778 (19)	0.4298 (13)	1.0465 (38)
C2	0.2337 (23)	0.4656 (13)	0.9254 (41)
C3	0.1492 (24)	0.4629 (15)	0.9091 (52)
C4	0.1055 (20)	0.4211 (19)	1.0176 (59)
C5	0.1443 (23)	0.3859 (16)	1.1417 (50)
C6	0.2324 (25)	0.3892 (15)	1.1474 (47)
C21	0.3095 (24)	0.1692 (16)	0.3136 (52)
C22	0.3435 (24)	0.2131 (18)	0.4062 (56)
H2	0.2680	0.4920	0.8572
H3	0.1199	0.4883	0.8363
H5	0.1098	0.3602	1.2121
H6	0.2638	0.3630	1.2150
H11	0.3861	0.4705	1.0370
H12	0.3825	0.4197	1.1728
H211	0.3144	0.1767	0.1893
H212	0.2490	0.1653	0.3522
H213	0.3369	0.1315	0.3467

distances (Table IV) were based on the same final data.

Discussion

Both $Cu_2I_2(CH_3CN)_2(p\text{-}tld)_2$ (I) and $[(Cu_2I_2(CH_3CN)(p\text{-}ClAn)]_2$ (II) crystallize in a distorted-cubic format; however, I shows no internal symmetry element and thus has four independent Cu–ligand bonds (two each of two different types), whereas a twofold axis relates the halves of the cubic cluster II, making the acetonitrile-bound copper atoms equivalent, as also the bonds between a second pair of copper atoms and the *p*-chloroaniline groups ligated to them. Copper–ligand distances are equivalent in I and II [Cu–aniline derivative average 2.09 (1) Å (I), 2.13 (3) Å (II); Cu–acetonitrile average 1.96 (2) Å (I), 1.99 (2) Å (II)], as are Cu–I distances: average 2.689 (3) Å (I), 2.690 (6) Å (II). Cu–I bonds are relatively unchanging in Cu–I cubic clusters (Table V), averaging 2.698 Å. Copper–copper distances in I and II [2.699 (3), 2.682 (7) Å] are comparable to those found in other nitrogen-donor cubic $(CuIL)_4$ systems [$(CuIpy)_4$, 2.691 (5) Å;[8] $(CuImorph)_4$, 2.65 (3) Å;[9] $(CuIpip)_4$, 2.657 (2) Å;[10] $[CuI(3\text{-}pic)]_4$, 2.647 (4)–2.746 (4) Å;[16] $(CuICH_3CN)_4$·Bz_2-18C6, 2.770 (5) Å[12]] (pic = picoline) but shorter than those observed in the $(CuX(Et_3P))_4$ series [X = Cl, 3.211 (2) Å; X = Br, 3.184 (2) Å;[17] X = I, 2.927 (2) Å[18]]. These copper–copper distances are indicative of only weak interactions between metal atoms, being significantly shorter than the Cu–Cu metal distance of 2.56 Å. However, later comments will show that these Cu–Cu distances seen in $(CuIL)_4$ systems may be considered representative of some metal–metal involvement. The angles at copper remain relatively constant despite variations in the space-filling character of the ligand and variation within the group (Table V) of hybridization of the nitrogen donor atom: sp^3-hybridized nitrogen in C, D, F (I), and G (II); sp^2-hybridized nitrogen in A, B, and H; sp-hybridized nitrogen in E, F (I), G (II), and I.

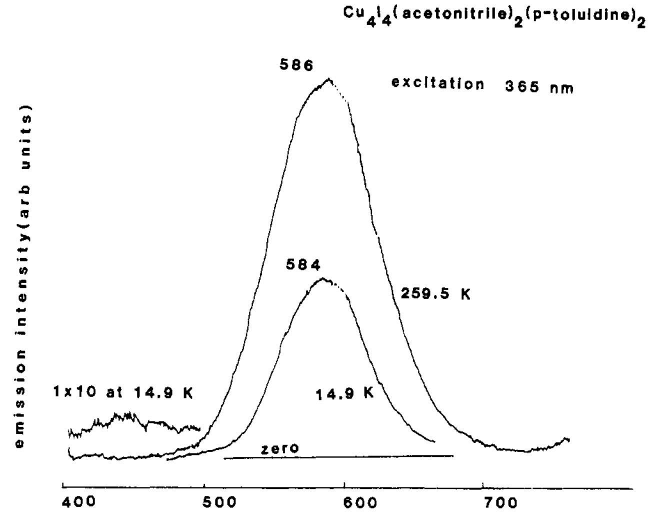

Figure 3. Emission spectra of I at 15 and 223.5 K.

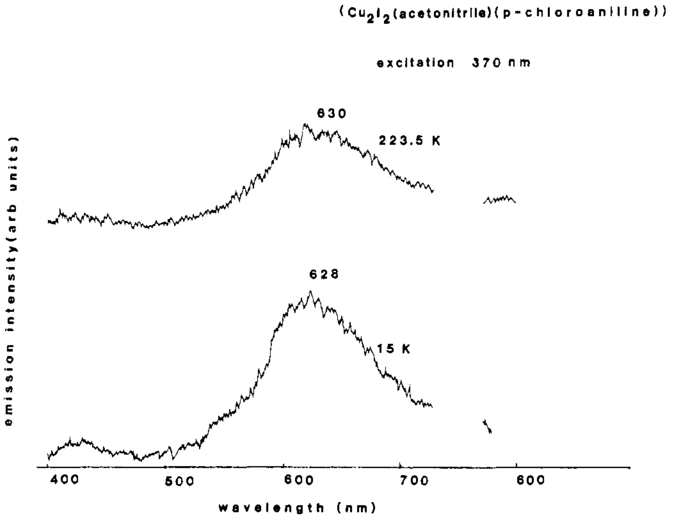

Figure 4. Emission spectra of II at 14.9 and 259.5 K.

Emission spectra for I and II were measured with single crystals of these complexes sealed in capillaries that had previously been found to be nonemitting under the conditions of the experiment. The emission spectra for I and II were produced by exciting into the absorption maxima, 365 nm (I) and 370 nm (II). Emission was broad and featureless over the range 259.5–14.9 K, displaying maxima at 586 nm (I) and 630 nm (II) over this range and a minor shoulder in the 420–450-nm range in each case at low temperatures. Increase of intensity with decrease of temperature and a minor sharpening of the more intense emission band was noted. In each case the emission band is strongly Stokes shifted from the absorption maximum but only insignificant temperature shifts of the band were noted. Thus the presence or absence of a symmetry element in the cubic clusters of $(CuIL)_4$ is not the deciding factor in the thermochromicity of the systems.

Previous workers have measured the emission spectra for solid copper(I) systems for which single-crystal X-ray data are also known and have assigned the electronic emissions of the emitting states.[19] Emissions are generally understood to involve ligand-

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Table IV. Bond Distances (Å) and Angles (deg) for I and II[a]

I		II		I		II	
Cu1–I1	2.657 (2)	Cu1–I1	2.657 (5)	Cu4–N4	1.95 (2)		
Cu1–I2	2.726 (2)	Cu1–I1′	2.737 (5)	N1–C11	1.43 (2)	N1–C1	1.44 (4)
Cu2–I1	2.726 (2)			N2–C21	1.44 (2)		
Cu2–I2	2.656 (2)			C11–C12	1.38 (2)	C1–C2	1.45 (4)
Cu3–I3	2.662 (3)	Cu2–I2	2.676 (6)	C11–C16	1.38 (2)	C1–C6	1.41 (5)
Cu3–I4	2.717 (3)	Cu2–I2′	2.679 (6)	C21–C22	1.40 (2)		
Cu4–I3	2.715 (3)			C21–C26	1.38 (2)		
Cu4–I4	2.659 (2)			C12–C13	1.38 (2)	C2–C3	1.36 (5)
Cu1–I3	2.625 (3)	Cu1–I2	2.615 (5)	C15–C16	1.40 (2)	C5–C6	1.41 (6)
Cu2–I4	2.620 (3)	Cu2–I1	2.775 (6)	C22–C23	1.37 (2)		
Cu3–I2	2.754 (3)			C25–C26	1.40 (2)		
Cu4–I1	2.756 (3)			C13–C14	1.38 (3)	C3–C4	1.45 (6)
Cu1–Cu2	2.730 (2)	Cu1–Cu1′	2.716 (6)	C14–C15	1.38 (2)	C4–C5	1.42 (6)
Cu3–Cu4	2.664 (3)	Cu2–Cu2′	2.650 (8)	C23–C24	1.37 (2)		
Cu1–Cu3	2.721 (3)	Cu1–Cu2	2.656 (7)	C24–C25	1.37 (2)		
Cu1–Cu4	2.672 (3)	Cu1–Cu2′	2.708 (7)	C14–C17	1.49 (2)	C4–C11	1.75 (3)
Cu2–Cu3	2.679 (3)			C24–C27	1.51 (2)		
Cu2–Cu4	2.730 (3)			N3–C31	1.11 (2)	N2–C22	1.16 (6)
Cu1–N1	2.09 (1)	Cu1–N1	2.13 (3)	N4–C41	1.15 (2)		
Cu2–N2	2.09 (1)			C31–C32	1.45 (3)	C22–C21	1.38 (6)
Cu3–N3	1.96 (2)	Cu2–N2	1.99 (4)	C41–C42	1.44 (3)		
I		II		I		II	
I1–Cu1–I2	110.51 (7)	I1–Cu1–I1′	110.2 (2)	Cu3–I4–Cu4	59.40 (7)		
I1–Cu2–I2	110.56 (6)			Cu1–I1–Cu4	59.12 (7)	Cu1–I1–Cu2	58.5 (2)
I3–Cu3–I4	115.18 (9)	I2–Cu2–I2′	115.4 (2)	Cu1–I2–Cu3	59.53 (6)		
I3–Cu4–I4	115.30 (9)			Cu2–I1–Cu4	59.74 (7)		
I1–Cu1–I3	117.38 (8)	I2–Cu1–I1	117.3 (2)	Cu2–I2–Cu3	59.32 (7)		
I2–Cu1–I3	112.30 (8)	I2–Cu1–I1′	113.7 (2)	Cu1–I3–Cu3	61.95 (8)	Cu1–I2–Cu2	60.0 (2)
I1–Cu2–I4	112.08 (8)			Cu1–I3–Cu4	60.03 (7)		
I2–Cu2–I4	117.27 (8)			Cu2–I4–Cu3	60.23 (7)		
I2–Cu3–I4	110.86 (10)	I1–Cu2–I2	110.8 (2)	Cu2–I4–Cu4	62.28 (8)		
I2–Cu3–I3	110.28 (8)	I1–Cu2–I2′	110.5 (2)	Cu1–N1–C11	118.0 (9)	Cu1–N1–C1	115 (2)
I1–Cu4–I3	111.12 (10)			Cu2–N2–C21	116.6 (9)		
I1–Cu4–I4	109.91 (9)			Cu3–N3–C31	172 (2)	Cu2–N2–C22	169 (3)
Cu1–I1–Cu2	60.93 (6)	Cu1–I1–Cu1′	60.4 (1)	Cu4–N4–C41	171 (2)		
Cu1–I2–Cu2	60.95 (5)			N3–C31–C3i	179 (2)	N2–C22–C21	178 (4)
Cu3–I3–Cu4	59.39 (7)	Cu2–I2–Cu2′	59.1 (2)	N4–C41–C42	179 (2)		

[a] Comparable distances in the two structures are listed side by side.

Table V. Structural Parameters for $(CuIL)_4$ Systems and Comparison $(CuIL)_\infty$ Systems (L = Nitrogen-Donor Ligand)

code	formula[a]	Cu–Cu, Å	Cu–X, Å	Cu–N, Å	X–Cu–X, deg	Cu–X–Cu, deg	ref
			Tetrameric Cubes				
A	$(CuIpy)_4$	2.691 (5)	2.629 (4)–2.790 (4)	2.04 (2)	110.4 (1)–120.2 (1)	57.7 (1)–61.1 (1)	8
B	$[CuI(3\text{-pic})]_4$	2.647 (4)–2.746 (4)	2.641 (3)–2.771 (3)	2.04 (2)	109.3–118.0	57.9–61.6	16
C	$(CuImorph)_4$	2.65 (3)	2.76 (1)	2.02 (4)			9
D	$(CuIpip)_4$	2.657 (2)	2.701 (2)	2.052 (7)	113.48 (4)	58.93 (5)	10
E	$(CuICH_3CN)_4{\cdot}Bz_2\text{-}18C6$	2.770 (5)	2.692 (4)	2.00 (2)	107.7 (1)–116.2 (1)	60.1 (1)–64.7 (1)	12
F	$Cu_4I_4(CH_3CN)_2(p\text{-tld})_2$	2.699 (3)	2.689 (3)	2.09 (1)–1.96 (2)	109.91 (9)–117.38 (8)	59.12 (7)–62.28 (8)	*b*
G	$[Cu_2I_2(CH_3CN)(p\text{-ClAn})]_2$	2.682 (7)	2.690 (6)	2.13 (3)–1.99 (2)	110.2 (2)–117.3 (2)	58.5 (2)–60.4 (1)	*b*
			Polymers				
H	$(CuIpy)_\infty$	2.875 (2)	2.641 (1)–2.689 (1)	2.038 (6)	104.0 (1)–115.2 (1)	65.3–104.0 (1)	24
I	$(CuICH_3CN)_\infty$	3.022 (10)–4.298 (13)	2.658 (8)	1.97 (2)	107.0 (3)–111.5 (3)	69.0 (2)–107.0 (4)	12

[a] Abbreviations: py, pyridine, pic, picoline; morph, morpholine; pip, piperidine; Bz_2-18C6, dibenzo-18-crown-6; *p*-tld, *p*-toluidine; *p*-ClAn, *p*-chloroaniline. [b] This work.

centered, metal–ligand charge-transfer (MLCT) or metal-centered transitions. These studies have shown that ligand-centered emissions from coordinated ligands are shifted by less than 1000 cm^{-1} from those of the uncoordinated ligands. Clearly neither the acetonitrile or substituted-aniline moieties can be responsible for the emissions observed.

Metal-to-ligand charge-transfer emissions have been identified in copper(I) systems. From work on glassy Cu(I) complexes, $[Cu(PPh_3)_2(2,2'\text{-bpy})]^+$, $[Cu(\textit{cis}\text{-dppee}_2)]^+$, and $[Cu(2,9\text{-Me}_2\text{-}1,10\text{-phen})]^+$ (bpy = bipyridine, dppee = bis(diphenylphosphino)ethylene, phen = phenanthroline), Buckner and McMillin[20] conclude that the broad featureless emission bands observed (λ_{abs} 356, 398, and 454 nm, respectively; λ_{em}(max) 610, 612, and 710 nm) were derived from more than a single MLCT state. Further work on solid-state $[Cu(PPh_3)_2(phen)]^+BF_4^-$ showed the emission spectrum and decay time to be temperature-dependent. These features suggested a three-level system consisting of two excited states and a ground state, the higher excited state emitting green, decaying rapidly, and coexisting at room temperature with a lower energy excited state which emits yellow and is of longer decay time. This latter excited state is chiefly responsible for the low-temperature emission. Metal-centered transitions were considered less likely in these systems because the expected lifetimes for low-lying tetrahedral $3d^94s^1$ states were longer than those observed.[21] Work on powder samples of similar structure, $[Cu(R_3P)_2$(bidentate nitrogen-donor aromatic ligand)$]^+$, showed similar broad emission envelopes whose

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(20) Buckner, M. T.; McMillin, D. R. *J. Chem. Soc., Chem. Commun.* **1978**, 759.

Table VI. Solid-State Emission Maxima for $(CuIL)_4$ Systems and Comparison $(CuIL)_\infty$ Systems (L = Nitrogen-Donor Ligand)

code	formula[a]	$d^{10} \rightarrow d^9\pi^*$, emiss, nm	metal-Ctrd	ref
	Tetrameric Cubes			
A	$(CuIpy)_4$	436	615	24
B	$[CuI(3\text{-pic})]_4$	457	588	24
C	$(CuImorph)_4$		625	7
D	$(CuIpip)_4$		570	24
E	$(CuICH_3CN)_4\cdot Bz_2\text{-}18C6$		550	11
F	$Cu_4I_4(CH_3CN)_2(p\text{-tld})_2$	458	586	*b*
G	$[Cu_2I_2(CH_3CN)(p\text{-}ClAn)]_2$	420	628	*b*
	Polymers			
H	$(CuIpy)_\infty$	449		24
I	$(CuICH_3CN)_\infty$	540		11

[a] For abbreviations see footnote *a* of Table V. [b] This work.

maxima were blue-shifted at lower temperatures. Correlation of excitation intensities and decay times with temperature suggested that a splitting of the lower excited state of the model into singlet and triplet levels with differing decay times would better explain the observed phenomena.[22] Single-crystal X-ray studies revealed the solid-state materials to consist of isolated copper atoms tetrahedrally coordinated to two phosphorus donor ligands and one bidentate nitrogen donor system of extended aromatic character.[23] The low-lying π^* levels of these are assessible to the metal for MLCT interaction. In the title systems, only the acetonitrile offers suitably situated π^* levels and these are of considerably higher energy. The title systems, however, display further possibilities due to the presence of metal atoms in close proximity to each other.

Emissions due to metal-centered transitions have been observed for Cu(I) doped into a $RbMgF_3$ matrix (emissions at 450 and 575 nm). The associated absorption maximum, 295 nm, was assigned to a $3d^{10} \rightarrow 3d^94s^1$ transition and the appearance of two emission bands believed due to two different Cu(I) sites in the crystal. Since the concentration of Cu in the crystal was at the ppm level, only isolated metal centers were involved.[24]

Emissions observed for the $(CuIpy)_4$ complex were assigned to MLCT $d^{10} \rightarrow d^9\pi^*$ transitions (λ_{max} 370 nm) and to metal-centered transitions: $d^{10} \rightarrow d^9s^1$ (λ_{max} 333 nm). The polymeric $(CuIpy)_\infty$ species with similar copper coordination (3 I and 1 pyridine per copper) displayed only the emission assigned to charge transfer (Table VI). The authors[25] discuss their observations in terms of transitions at a single metal atom. However, it should be noted that $(CuIpy)_4$, which displays MLCT and metal-centered transitions, has Cu–Cu distances of average 2.691 (5) Å whereas the polymeric $(CuIpy)_\infty$ Cu–Cu distances are longer, 2.875 (2) Å. The question of interacting metal centers is thus raised.

Attempts have been made to pinpoint interactive metal–metal distances in d^{10} systems. Molecular orbital calculations based on Cu(I) model systems[26] have shown that Cu_4^{4+} clusters with Cu–Cu distances of 2.83 Å have overlap population 0.32 (binding energy −0.417 eV) and that bonding strength increases as the Cu–Cu distance is diminished (overlap 0.08, binding energy −0.984 eV at Cu–Cu separation 2.57 Å). Inclusion of a ligand in a dimeric model produced a computed Cu–Cu optimum distance of 2.7 Å with Cu–Cu orbital overlap population increasing as Cu–Cu separation diminished. The identification of Cu–Cu distances of 2.8 Å or less as due to interactions is also supported by the maintenance of Cu–Cu distances averaging close to 2.82 Å despite fundamentally different demands of ligand geometry in a series of Cu_8S_{12} species.[27] The tetrameric Cu(I) complexes of Table V all show copper–copper distances of less than 2.8 Å, and despite the range of ligands represented, all show emission at 550–628 nm. The assignment of emission in this range to a metal–metal interaction is supported by the absence of this absorption in polymeric structures of the same stoichiometry and ligand identity in which Cu–Cu distances are longer.

The copper–iodine bond is another potential source of excitation leading to emission. Donor–acceptor pairs (DAP) have been cited as the source of the 420-nm emission in crystalline CuI excited at 337 nm (nitrogen laser). The solid-state material also displays a series of narrow band emissions at lower and higher wavelengths attributed to exciton phenomena.[28] All Cu–I distances in solid CuI are 2.617 Å, only slightly shorter than those of Table V.

Molecules I and II thus have the capability of emitting from excited states due to the ligand alone, to MLCT interactions between metal and acetonitrile, to transitions on isolated metal centers, to coupled metal centers, or to Cu–I DAP phenomena.

For cubic $(CuIL)_4$ systems for which solid-state structure and solid-state emission characteristics are both known, the presence or absence of crystallographically related Cu–L bonds appears unrelated to the temperature dependence of the wavelength of maximum emission. Emission from these species is more properly regarded as being derived from more than one excited state, and populations of the excited states change with temperature. For the $(CuIL)_4$ clusters where L = pyridine, the 436–449-nm absorption may be due to a $d^{10} \rightarrow d^9\pi^*$ transition but the emission of longer wavelength would appear to derive from a metal-centered phenomenon that involves more than one metal center. The title structures as well as other $(CuIL)_4$ clusters are consistent in displaying this emission and also Cu–Cu distances of 2.8 Å or less, which suggests that metal–metal transitions may be responsible. The title structures display a weak absorption in the 420–458-nm range that is apparent only at low temperatures. This may arise from MLCT [the $(CuICH_3CN)_\infty$ polymer shows an absorption at 540 nm] due to the acetonitrile ligand. A definite assignment cannot be made on the basis of the available evidence. For these systems, the Cu–I bond cannot be eliminated as a source of emission.

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Supplementary Material Available: Listings of anisotropic thermal parameters and observed and calculated structure factors for I and II (61 pages). Ordering information is given on any current masthead page.

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