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Three coordinate copper(I) complexes. Synthesis, spectral, and structural study of copper(I) complexes of 4-benzoylpyridine and X-ray crystal structure of the dimer [CuCl(4-benzoylpyridine)]$_2$

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Abstract—Yellow to red–brown copper(I) complexes of the type CuXL for X = Cl, Br,I, CN, SCN and N_3 and $CuXL_2$ for X – NO_3 and ClO_4, where L = 4-benzoylpyridine, have been synthesized and characterized. All complexes exhibit MLCT bands in the visible region and the neutral complexes gave non-conducting solutions in DMF. The IR and Raman spectral data suggest monodentate 4-Bzpy, bridging halides or pseudohalides, *bidentate* nitrate and perchlorate in the respective complexes in the solid state. The structure of the 1:1 chloride complex, as determined by X-ray crystallography, features a discrete centrosymmetric [CuCl(4-benzoylpyidine)]$_2$ molecule with a Cu···Cu distance of 2.953 Å. Each copper atom in the dimeric molecule is trigonally planar coordinated by two μ-chlorine atoms and the nitrogen atom of 4-benzoylpyridine. All the isolated complexes display emission spectra in the solid state at room temperature. The neutral halide or pseudohalide complexes show one emission band with λ^{em}_{max} in the range 586–642 nm which is independent of the excitation wavelength and is related to MLCT or XLCT excited state. The 1:2 nitrate and perchlorate complexes exhibit their λ^{em}_{max} around 468–504 nm. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: copper(I) complexes; 4-benzoylpyridine; crystal structure; vibration spectra; luminescence spectra.

Copper(I) usually forms four-coordinate tetrahedral complexes [1], compounds with lower coordination numbers are known but are less common [2]. Structural evidence has been reported for some trigonal planner three-coordinate copper(I) complexes, e.g., $[Cu(C_6H_7N)_3]^+$ [3], $[Cu(CN)_3]^-$ [4] and $[Cu(CN)_2]^-$ [5]. On the other hand, copper(I) halides form complexes with unidentate nitrogen donor ligands which display a variety of stoichiometries, structures [6] and emission characteristics [7] in the solid state. In some instances, CuX–ligand clusters of the same stoichiometry (1:1:1) exist in more than one crystaline format.

For example, [CuI(py)]$_4$ is a cube, whereas [CuI(py)]$_n$ is a pleated sheet polymer [8]. Similarly, $[CuI(CH_3CN)]_n$, a pleated sheet and $[CuI(CH_3CN)]_4$-dibenzo-18-crown-6, a distorted cubic structure with second sphere interactions between crown ether and acetonitrile methyl hydrogens, are both of stoichiometry Cu:I:CH_3CN of 1:1:1 [9]. These families of structures are of particular interest because the emission behaviour of the solid state material varies with structure. Thus, [CuI(py)]$_n$ displays broad band emission at room temperature and shows no shift of λ_{max} at cooling, whereas [CuI(py)]$_4$ displays two emission maxima corresponding to differing excitation maxima [10].

Recently, we isolated and characterized two types of copper(I) complexes of 2-benzoylpyridine; red to dark brown CuXL type complexes, for X = Cl, Br, I, CN, SCN and N_3, and orange yellow (CuX)$_2$L complexes for X = Cl and Br and structurally characterized those of the first type for X = Br, I and CN [11]. In all

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complexes of the first type, 2-benzoylpyridine behaves as a bidentate ligand and all of them display no emission when excited in the UV region at room temperature. Both complexes of the second type contain *monodentate* 2-benzoylpyridine ligand, as inferred from their IR spectra and display visible emission when excited in the UV region at room temperature. Further work led to the isolation of copper(I) complexes of 4-benzoylpyridine (hereafter abbreviated as 4-Bzpy). These complexes exhibit solid state emission at room temperature. We have now performed an X-ray structure determination of the title complex for which suitable crystals are available.

EXPERIMENTAL

4-Benzoylpyridine was obtained from Aldrich company and the other chemicals were of analytical grade quality.

Preparation of the complexes:

1. CuCl(4-Bzpy) and $CuX(4\text{-}Bzpy)_2$ complexes, X = NO_3 and ClO_4. These complexes were prepared by mixing the corresponding copper(II) salt (4 mmol) dissolved in water with an ethanolic solution of 4-Bzpy ligand (10 mmol) and the subsequent addition of excess L(+)-ascorbic acid. The mixture was boiled for several minutes and allowed to stand over several hours to produce the complexes.
2. CuX(Bzpy), X = Br, I, CN, SCN and N_3. These complexes were prepared by one of the following general procedures.
   (i) An aqueous solution of $Cu(NO_3)_2.3H_{22}O$ (4 mmol) was mixed with KX or NaX, followed by the addition of L(+)-ascorbic acid. An ethanolic solution of the benzoylpyridine ligand (10 mmol) was then added and the mixture stirred for ca. 15 minutes. The final mixture was allowed to stand over several houres or days until a crystalline product separated.
   (ii) A boiled ethanolic solution of benzoylpyridine (10 mmol) was mixed with $Cu(NO_3)_2{\cdot}3H_2O$ (4 mmol) in ethanol and the subsequent addition of L(+)-ascorbic acid resulted in a clear yellow to orange solution. To this solution, an aqueous solution of KX was added dropwise, the mixture was boiled for several minutes and allowed to stand over several hours to produce the complex.

Crystals of the yellow copper(I) chloride complex suitable for X-ray structure analysis were prepared by the procedure given under (i), except that ethanol was used as the medium and a very slow evaporation of the solvent was used.

Elemental analysis results of the isolated complexes are given in Table 1.

Physical measurements

The IR absorption spectra of solid samples were measured as KBr pellets using a Bruker IFS-25 model FT–IR spectrophotometer. Raman spectra were obtained using a Perkin–Elmer System 2000 NIR FT–

Table 1. Analytical data for the copper(I) complexes

Complex	Color	M.P. °C	Analysis; Found (calc)				
			C	H	N	X	Cu
Cu(4–Bzpy)Cl	yellow fine crystals	171–3 dec.	51.2 (51.1)	3.0 (3.2)	4.9 (5.0)	12.4 (12.6)	22.3 (22.5)
Cu(4–Bzpy)Br	yellow fine needles	190–5 dec.	44.2 (44.1)	2.7 (2.8)	4.5 (4.3)	24.3 (24.5)	19.3 (19.5)
Cu(4–Bzpy)I	orange microcryst. powder	216–8 dec.	38.7 (38.6)	2.3 (2.4)	3.6 (3.7)	33.4 (34.0)	16.8 (17.0)
Cu(4–Bzpy)CN	yellow microcrryst powder	176 dec.	57.2 (57.3)	3.3 (3.3)	10.2 (10.3)		23.5 (23.3)
Cu(4–Bzpy)SCN	orange red powder	217 dec.	50.9 (51.2)	3.1 (3.0)	9.0 (9.2)		21.0 (20.8)
Cu(4–Bzpy)N_3	red brown	158 dec.	49.7 (49.9)	3.2 (3.1)	18.8 (19.4)		22.3 (22.0)
Cu(4–Bzpy)$_2$$NO_3$	can yellow needles	 (58.6)	58.0 (3.7)	3.6 (8.5)	8.7	 (12.9)	12.5
Cu(4–Bzpy)$_2$$ClO_4$	can. Yellow needles	208 dec.	54.0 (54.5)	3.2 (3.4)	5.6 (5.3)		11.7 (12.0)

Raman spectrometer. The laser power was ca. 200 mW. Electronic spectra of complexes were measured as solids mulled in Nujol using a varian cary-5 double beam spectrophotometer. The experimental procedures and instruments used for other measurements are as described previously [12].

X-ray structure analysis of dimeric CuCl(4-*benzoylpyridine*) *complex* (1)

Intensity data were collected at 294 K on a MSC/Rigaku RAXIS IIc imaging plate system, with a rotating-anode X-ray source (Mo–Kα radiation, $\lambda = 0.71073$ Å) [13] and corrected for absorption using the ABSCOR program [14]. Information concerning crystallographic data and structure refinement are summarized in Table 4.

The structure was solved by Patterson superposition and Fourier methods. All non-hydrogen atoms were subjected to anisotropic refinement. The aromatic hydrogen atoms were generated geometrically (C–H fixed at 0.96 Å), allowed to ride on their respective carbon atoms and included in structure-factor calculations with assigned isotropic thermal parameters.

All computations were performed on a DEC Micro VAX-II computer with the SHELXTL-PLUS system [15, 16]. Analytical expressions of neutral atom scattering factors, incorporating the real and imaginary components of anomalous dispersion, were employed [17]. Least-squares refinement converged to the *R* indices and other parameters, as listed in Table 4. Selected bond distances and angles are listed in Table 5. Positional parameters, anisotropic thermal parameters, hydrogen atom coordinates, a full list of bond lengths and angles and observed and calculated structure factors have been deposited with the editor as supplementary material; copies are available on request.

RESULTS AND DISCUSSION

The reaction between copper(I) salts and 4-Bzpy afforded the complexes given in Table 1. 4-Benzoylpyridine, therefore behaves differently from ethyl isonicotinate which affords copper(I) halide complexes of the type CuL_nX, where $n = 1$ and 2, and complexes of the type $[CuL_n]X$, where $n = 2$, 3 and 4 for $X = NO_3$ and ClO_4 [18]. All the isolated complexes are colored and sufficiently stable against air-oxidation when well-dried. In acetone and DMF, the neutral complexes gave non-conducting solutions, whereas the nitrate and perchlorate complexes behave as 1:1 electrolytes [19] with molar conductivities in the range 125–140 $\Omega^{-1}\,cm^{-2}\,mol^{-1}$ in acetone. Thus, the last two complexes may be formulated as $[CuL_2]X$, possessing ionic structures in acetone.

IR and Raman spectra

The IR and Raman spectra (Table 2) of free 4-Bzpy and its copper(I) complexes are similar except the systematic shifts of the vibration bands related to the pyridine moiety as expected for N-ligating pyridine ligands [20]. The carbonyl stretching vibrations appear almost at the same positions in complexes as well as in free 4-Bzpy. In the far IR region, 200–400 cm^{-1}, no bands could be attributable to terminal νCu–Cl or νCu–Br, suggesting bridging halide atoms whose copper–halogen absorption bands are expected below 200 cm^{-1} [21]. For 1:1:1 Cu: bridging halide: monodentate ligand, there are several possible structures including dimer, cubane, stepped cubane, stair and split stair [7].

As seen from Table 3, the ν_2 vibration mode of the perchlorate group in $Cu(4\text{-}Bzpy)_2ClO_4$ is split into three peaks at 1148, 1110, 1048 cm^{-1} (IR) and 1160, 1049, 1025 cm^{-1} (Raman). For the ν_3 mode, at least two peaks are observed in the IR spectrum, but only one peak in the Raman. These results are consistent with a *bidentate* perchlorate group [21]. The spectral results of the nitrate 1:2 complex are consistent with a *bidentate* nitrato group [21]. A distorted tetrahedral structure is therefore assigned for the monomeric perchlorato and nitrato complexes.

The 1:1 azide complex shows a very strong band at 2030 cm^{-1} (IR) and a weak line at 2070 cm^{-1} (Raman) associated with the $\nu_{as}(N_3)$mode. In the 1350–1250 cm^{-1} region, we would not assign any absorption band related to the $\nu_s(N_3)$mode due to the absorption bands of the ligand and, therefore, the IR spectra could not tell us whether the azide group is symmetric or asymmetric in this complex. For symmetric azide groups, the $\nu_s(N_3)$mode is expected to be IR inactive but Raman active. The Raman spectrum of the azide complex shows a medium to strong band at 1336 cm^{-1}, suggesting symmetric azide. As symmetric azide groups of the type μ-1,3 bridging in the complex $[Cu(Ph_3P)_2(N_3)]_2$ exhibit a $\nu_{as}N_3$ band at 2053 cm^{-1} [22], we may assign bridging azides of the type μ-1,1,3 in this complex since azido ligands of this type usually absorb around 2040–2020 cm^{-1} [23, 24]. For the 1:1 thiocyanato complex, a single νCN band is observed above 2100 cm^{-1}, a result which is suggestive of bridging thiocyanato groups [25]. The anionic complex, $[Cu(SCN)_2]^-$, which contains two independent thiocyanato groups; a terminal and a μ-N,S,S shows two νCN bands at 2105 and 2085 cm^{-1}. The later band is related to the terminal N-thiocyanate, whereas the former is due to the second group [12]. We may assign μ-N,S,S bridging thiocyanate in the 1:1 complex. The results given for the 1:1 cyano complex with such higher νCN bands compared with those for terminal cyanides [2075–2095 cm^{-1}.] [26], or the bridging –CN– group [2100–2105 cm^{-1}.] [27], suggest a structure similar to that of $CuCN{\cdot}NH_3$ [28], in which the cyano group acts as a *tridentate* ligand.

Table 2. Infrared and Raman spectra (cm^{-1}) of 4-benzoylpyridine and copper(I) complexes

4-Bzpy IR	Raman	Cu(4-Bzpy)Cl IR	Raman	Cu(4-Bzpy)I IR	Raman	Assignments
	222 ms		232 w		229 wm	νCu–N(L)
	222 ms		242 w		253 w	
	289 ms		311 vw		314 w	
			370 vw		376 w	
	383 wm		386 w		390 w	
	407 w	426 w	430 w	423 w	425 w	ring, pyridine/phenyl
472 m	425* vw	451 w	465 vw	454 w	460 w	
568 w	571 wm	580 wm	582 w	583 w	584 w	
	618 wm	615 vw	619 w	616 w	614 w	ring
638 vs	640 w	645 s	648 w	646 m	646 wm	ring
	663 wm		668 w	693 m	660 w	
695 vs		694 vs		693 m		ring
	722 ms	720 w	729 wm	720 w	720 wm	ring
745 s	748 m	745 wm	750 m	745 w	750* wm	
782 ms	787 wm	790 m		792 wm		
847 ms		845 m	842 vw	849 w	850 w	407 + 425
	865 w	860 ms		860 w	870 w	ring
899 w		903 vw	895 vw			
943 ms		942 ms	950 w	942 wm	945 w	
	995 vs	996 w	1001 s	997 ms	1001 ms	
996 wm	1001 vs	1019 vw	1018 vs		1017 vs	ring breathing
1027 wm	1028 m	1072 wm	1065 ms	1060 wm	1051 vs	ring breathing
1074 m	1064 m	1152 m	1152 s	1153 wm	1151 s	ring
1149 m	1154 vs	1180 m	1185 ms	1178 w	1172 wm	ring
1177 wm	1178 m	1217 w	1212 m	1218 w	1220 m	ring
1230 m	1215 m	1278 vs	1280 w	1279 ms	1280 w	ring
1280 vs	1284 wm	1300 s	1310 w	1310 wm		
1400 m		1404 ms	1405 w			
1433 m	1415 vw	1439 m	1442 w	1437 m	1440 w	ring
	1500	1532 wm		1535 wm		
1534 m	1574 w	1570 m	1585 m	1584 m	1585 wm	ring
1584 ms		1583 ms	1598 vs		1597 vs	ring
	1594 vs		1606 vs	1609 w	1605 s	
1642 vs	1655 vs	1650 vs	1658 vs	1649 vs	1659 vs	νC=O

w weak, m medium, s strong, v very.

Table 3. Vibrational frequencies (cm^{-1}) of the perchlorate, nitrate, cyanide and thiocyanate anions

	CO_4 or NO_3						νCN or $\nu_{as}(N_3)$		νCS or $\nu_s(N_3)$	
	ν_1		ν_2		ν_3					
Compound	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman
$Cu(4\text{-}Bzpy)_2ClO_4$	934 sh	932 ms	1148 vs	1160 s	638 s	662 wm				
		1110 vs	1049 s	625 s						
		1084 vs	1025 s							
$Cu(4\text{-}Bzpy)_2NO_3$			1370 s	1370 vs						
Cu(4-Bzpy)CN							2164 ms	2166 vs		
						2130 vs	2132 vs			
Cu(4-Bzpy)SCN							2105 vs	2119 w	745	790 m
$Cu(4\text{-}Bzpy)N_3$							2030 vs	2070 w	–	1336 m

Table 4. Data collection and processing parameters

Empirical formula	$C_{12}H_9ClCuNO$
color, habit	yellow plate
Crystal size	$0.04 \times 0.20 \times 0.20$
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	3.58(1)
b (Å)	8.565(1)
c (Å)	16.276(2)
α (°)	95.02(1)
β (°)	92.12(1)
γ (°)	101.10(1)
volume (Å^3)	524.9(3)
Z	2
Formula weight	282.2
Density (calc)	1.785 Mg/m^{-3}
Absorption coefficient	2.306 mm^{-1}
F(000)	284
Diffractometer	Rigaku RAXIS IIc
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71073$) Å
Temperature (K)	294
Collection range	$-4 \leqslant h \leqslant 4,\ -10 \leqslant k \leqslant 10$ $20 \leqslant 1 \leqslant 0$
2θ range	3.0 to 55.0°
Independent reflections	1768 ($R_{int} = 2.69\%$)
Observed reflections	1593 ($F > 4.0\sigma(F)$)
Extinction correction	$\aleph = 0.0025(12)$, where $F^* = F[1 + 0.002\ \aleph F^2/\sin(2\theta)]^{-1/4}$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0003F^2$
Number of parameters, p	146
Final R indices (obs. data)	$R = 6.01\%$, $wR = 6.59\%$
R indices (all data)	$R = 7.10\%$, $wR = 33.93\%$
Goodness-of-fit, S	1.94
Largest and mean Δ/σ	0.002, 0.000
Residual extrema	0.69 to -0.88 eÅ^{-3}

Structure of the 1:1 *copper*(*I*) *chloride complex*

The structure determination has shown the title complex as [CuCl(4-benzoylpyridine)]$_2$ (Figures 1 and 2), another example of a metal–halide monodentate ligand with hetero atoms of the stoichiometry CuClL, to be structurally characterized. This dinuclear complex is disposed about a crystallographic inversion center with a planar Cu_2Cl_2 rhombohedral core of alternating copper and chlorine atoms. The Cu–Cl distance of 2.291(2) and 2.323(2) Å are shorter than those usually observed for [CuClL]$_n$ polymeric pleated sheets where each copper has three chlorine neighbours [av. 2.410 Å] [29–31]. The Cu–N bond length is a little shorter than that found (2.035(4) Å) in [CuI(2-benzoylpyridine)]$_2$ [11], but very close to the corresponding value of 1.995(7) Å found in [CuClL], where L is isonicotinic acid [32].

The structure of the title complex with a trigonal planar geometry about each copper atom is one of the rare examples of copper(I) chloride complexes of nitrogen donor ligands of such stoichiometry having three coordinate copper atoms. Three coordinate copper(I) complexes are known for [CuL$_3$]$^+$, L is 2-picoline [3], [CuXL$_2$], for X = Cl or I [33] and [CuIL]$_2$ for L = 2,6-dimethylpyridine [31], in all of these examples, the steric hinderance of the methyl group(s) in the pyridine ring is the reason for such coordination number 3 and not the usual tetrahedral geometry. In case of complex (1), however, there is no such steric hindrance. The existence of a bulk group, such as a benzoyl in position 4 in the pyridine ring is responsible for the formation of a dimer complex with three coordinate copper, rather than polymeric pleated structure with four coordinate copper atoms. This explains why we could not isolate copper(I) halide complexes of this ligand with ligand content higher than 1:1:1. The Cu···Cu separation of 2.953 Å in the present structure is comparable with the corresponding value found (2.995(3) Å) in the structure of [CuCl(2,4-dimethylpyridine)$_2$]$_2$ [34], but shorter than that found (3.145(3) Å) in the structure of [CuCl(2-Picoline)$_2$] [34].

Table 5. Bond lengths (A°) and bond angles(°) for [CuCl(4-benzoylpyridine)]$_2$ complex

Cu(1)–Cl(1)	2.291(2)	Cu(1)–N(1)	1.992(4)
Cu(1)–Cl(1A)	2.323(2)	N(1)–C(5)	1.343(6)
N(1)–C(1)	1.330(6)	C(1)–C(2)	1.369(7)
O(1)–C(6)	1.207(5)	C(3)–C(4)	1.381(7)
C(2)–C(3)	1.394(6)	C(4)–C(5)	1.371(7)
C(3)–C(6)	1.494(7)	C(7)–C(8)	1.393(6)
C(6)–C(7)	1.479(6)	C(8)–C(9)	1.380(6)
C(7)–C(12)	1.388(7)	C(10)–C(11)	1.373(7)
C(9)–C(10)	1.366(9)	C(11)–C(12)	1.375(7)
Cu(1)–Cu(1A)	2.953		
Cl(1)–Cu(1)–N(1)	120.4(1)	Cl(1)–Cu(1)–Cl(1A)	113.5(1)
N(1)–Cu(1)–Cl(1A)	117.3(1)	Cu(1)–N(1)–C(1)	120.2(3)
Cu(1)–Cl(1)–Cu(1A)	113.5(1)	C(1)–N(1)–C(5)	117.0(4)
Cu(1)–N(!)–C(5)	122.7(3)	C(1)–C(2)–C(3)	119.2(4)
N(1)–C(1)–C(2)	123.7(4)	C(2)–C(3)–C(6)	118.2(4)
C(2)–C(3)–C(4)	117.3(4)	C(3)–C(4)–C(5)	119.8(4)
C(4)–C(3)–C(6)	124.1(4)	O(1)–C(6)–C(3)	118.6(4)
N(1)–C(5)–C(4)	123.0(5)	C(3)–C(6)–C(7)	120.6(4)
O(1)–C(6)–C(7)	120.8(4)	C(6)–C(7)–C(12)	119.1(4)
C(6)–C(7)–C(8)	121.5(4)	C(7)–C(8)–C(9)	119.1(5)
C(8)–C(9)–C(10)	121.0(5)	C(9)–C(10)–C(11)	120.4(5)
C(8)–C(7)–C(12)	119.3(4)	C(7)–C(12)–C(11)	120.6(4)
C(10)–C(11)–C(12)	119.6(5)		

* Symmetry transformation: a $(-x,-y,-z)$.

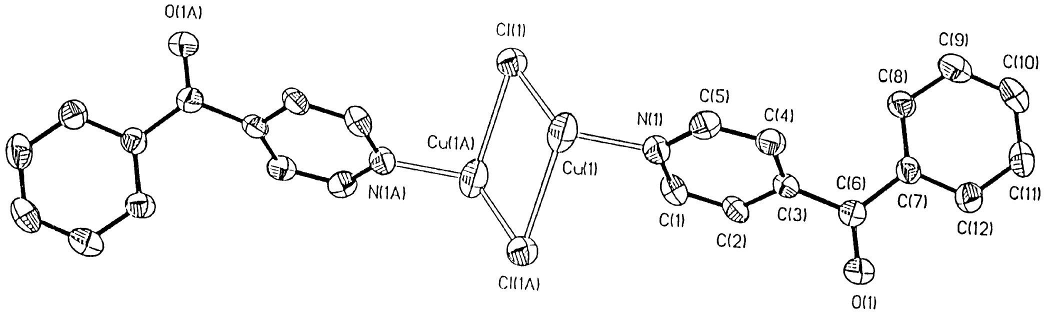

Fig. 1. Perspective view of the structure of the [CuCl(4-benzoylpyridine)]$_2$ *dimer with atom labeling scheme.*

Electronic absorbtion spectra

The electronic absorption spectra of the solid complexes mulled in Nujol (Table 6 and Fig. 3) exhibit a strong absorption band in the visible region due to charge transfer transitions from Cu (I) d^{10} to the empty π^* orbital on the pyridine ligand. The MLCT bands is dependent on the nature of the counter ion, as found for other copper(I) complexes [35]. That the position of the MLCT bands appear at lower energies in the case of the red–brown 1:1 azide and thiocyanate complexes reflects the influence of these anions on the MLCT. These ligands enhance the MLCT transitions, particularly the azide one.

Emission spectra

Table 6 and Figs 4–6 summarize the results of the emission and excitation spectra of the isolated copper(I) complexes in the solid state at room temperature. The following points are observed. (1) The emission spectra of the 1:1 halide and pseudohalide complexes exhibit a single slightly asymmetric band in the range 586–642 nm, whereas the 1:2 nitrate and perchlorate complexes show their emission bands in the range 468–504 nm with more than one maxima. (2) The emissions, as well as the excitation spectra of the nitrate and perchlorate complexes, could not be distinguished from each other. (3) The luminescence

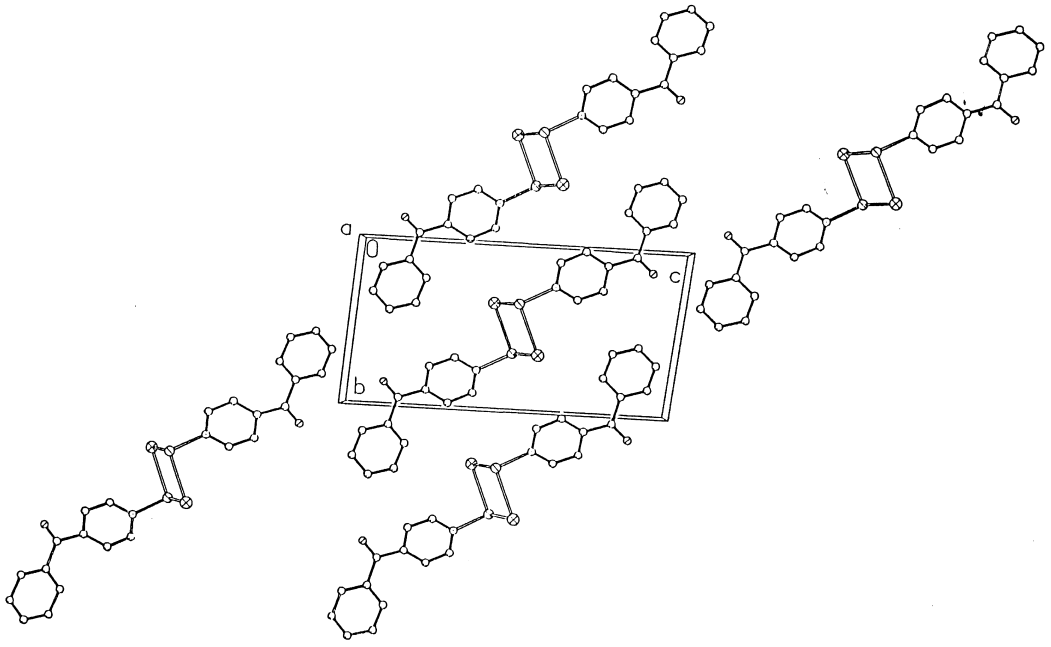

Fig. 2. Paking in the unit cell of $[CuCl(4\text{-benzoylpyridine})]_2$ dimer.

Table 6. Electronic, excitation and emission spectra of solid complexes at room temperature

Complex	λ_{max}^{abs} (a) (nm)	λ_{max}^{em} (b) (nm)	λ_{max}^{ex} (c) (nm)
Cu(4-Bzpy)Cl	370–450	642	359, 397, 468
Cu(4-Bzpy)Br	350–450	600	358, 397
Cu(4-Bzpy)I	400	631	359, 398, 468
Cu(4-Bzpy)CN	420	586	350, 405,469
Cu(4-Bzpy)SCN	400–550	460	357, 397, 468
Cu(4-Bzpy)N_3	400–550		
Cu(4-Bzpy)$_2NO_3$	375	469, 483, 504	334, 359, 402
Cu(4-Bzpy)$_2ClO_4$	375	469, 483, 502	334, 359, 402[3]

(a) Solid samples are measured as Nujol mulls.
(b) Emission maxima (excitation wavelength at λ_{max}^{ex}).
(c) Excitation maxima (monetored at λ_{max}^{em}).

spectra of these solid complexes proved independent of the excitation wavelength at room temperature. (4) It is also observed that the λ_{max}^{em} changes from 642 for the chloride to 631 nm for the iodide complex, i.e., the emission maxima is shifted to a lower energy on going from the iodide complex to the chloride. (5) The 1:1 bromide complex shows its λ_{max}^{em} at 600 nm and its excitation spectrum differs a little from the other halide complexes.

Extensive studies of the emission spectra of a series of $[CuI(py\text{–}X)]_4$ complexes, both in solid state and in solutions at room temperature and at 77 K, have been undertaken [36–38]. These complexes display two emission maxima; a low energy (LE) band (620–698 nm) and a high energy (HE) band (430–540 nm). The LE band was observed for complexes with Cu–Cu distances less than the summed Cu(I) Van der Waals radii (2.8 Å) and considered as a property of the Cu_4X_4 core and involves extensive interactions between the copper(I) centers owing to the σ bonding nature of the LUMO for these clusters with short metal–metal distances [39]. The HE band, which was

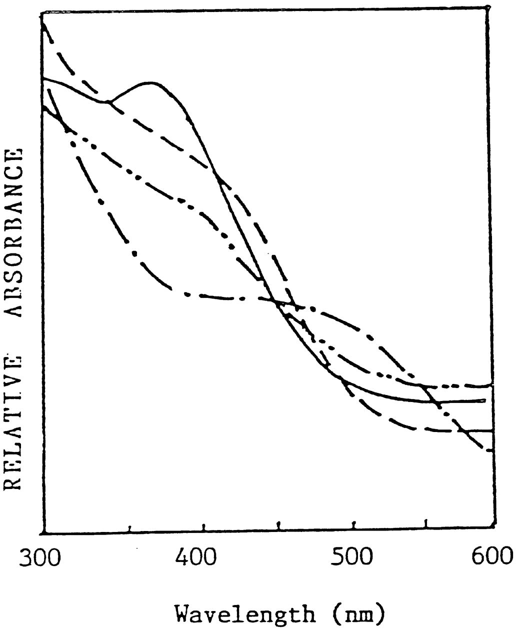

Fig. 3. Electronic absorption spectra of (————) Cu(4-Bzpy)$_2$ClO$_4$; (— — —) Cu(4-Bzpy)Cl; (—··—) Cu(4-Bzpy)I; (—·—) Cu(4-Bzpy)SCN.

also observed for [CuXpy]$_n$, was attributed to metal-to-ligand charge transfer (MLCT) or halide-to-ligand charge transfer (XLCT) [40]. In order to assign the emission spectra of the present complexes, the following points have to be considered. (1) The structure of the chloride complex, as shown by crystal structure analysis is a dimer and not a cubic tetramer. (2) The Cu–Cu distance of 2.953 Å in the chloride complex exceed the 2.8 Å value required for emission due to the Cu–Cu interactions as observed in complexes having the Cu$_4$X$_4$ core. (3) Point 4, given above, is consistent with what has been observed previously [41] that the emission bands for the chloride clusters occur at lower energy than the HE bands of the respective iodide clusters. Thus, the emitting state in the present copper(I) halides or pseudohalide complexes of 4-benzoylpyridine would be triplet MLCT or XLCT excited states. That the position of the emission λ_{max} for the present complexes appear at lower energies (586–642 nm) compared with those of [CuI(py)]$_n$ or the HE bands of [CuI(py)]$_4$ is due to the fact that the HE band energies are quite sensitive to substituents on the pyridine: electron withdrawing substituents shift these to lower values [41, 42]. X-ray powder diffraction has shown the bromide complex to be different from the chloride or iodide, this may explain the difference in their emission and excitation spectra.

The 1:2 nitrate and perchlorate complexes display their emission spectra in the range 468–504 nm with more than one emission maxima, which differs from the range where the halide complexes emit. This may support the assignments of the emission of the halide complexes as arising from MLCT and XLCT excited states. In the case of the 1:2 complexes, the emission may arise from the MLCT states, There is, however, another possibility for their emission. It was found that when aromatic ligands are packed in parallel planes separated by 3.225–3.279 Å, it results in emission spectra of the ligand alone [42]. As a solution of 4-benzoylpyridine in ethanol displays emission spectra at room temperature with λ^{em}_{max} at 453 nm and a pronounced shoulder around 492 nm, the emission spectra of the nitrate and perchloratye complexes may arise from ligand interactions alone and from MLCT interactions between Cu(I) and 4-benzoylpyridine.

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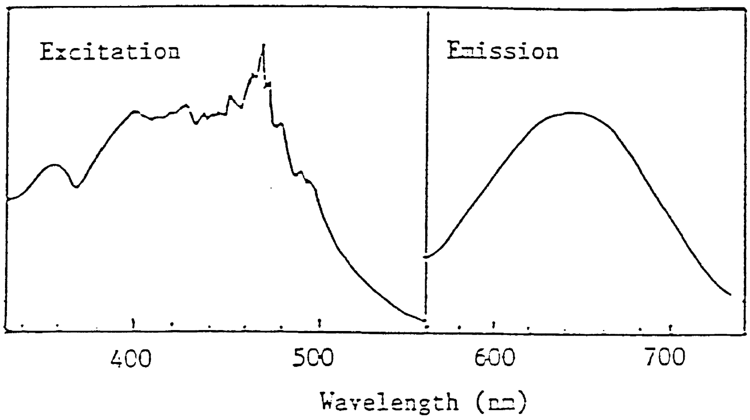

Fig. 4. Excitation and emission spectra of solid [CuCl(4-Bzpy)]$_2$ complex at room temperature.

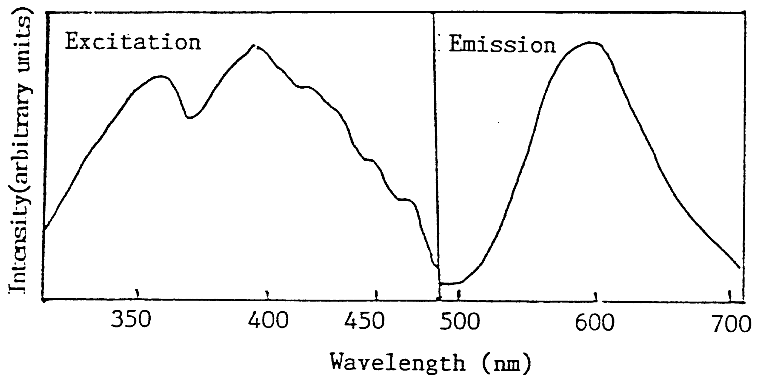

Fig. 5. Excitation and emission spectra of solid CuBr(4-Bzpy) complex at room temperature.

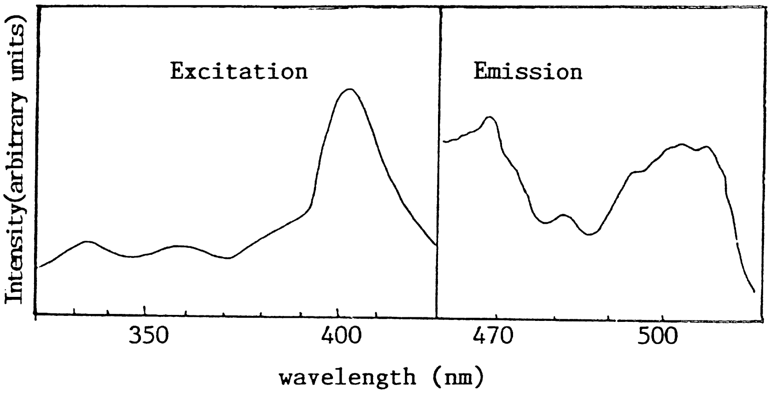

Fig. 6. Excitation and emission spectra of solid Cu(NO_3)(4-Bzpy)$_2$ complex at room temperature.

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