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Synthesis, vibrational and emission spectra of some copper(I) complexes of 3- and 4-benzoylpyridine ligands and X-ray crystal structure of $[(4-benzoylpyridine)_2H]^+ \cdot I^-$

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Abstract

The synthesis and characterization of some copper(I) complexes of the type CuLX, where X=Cl, Br, I, CN and SCN, for L=3-benzoylpyridine and a new red 1:1 copper(I) iodide complex of 4-benzoylpyridine in addition to a yellow compound; [(4-benzoylpyridine)₂H] · I (1) are described. The IR and Raman spectral results suggest bridging halide and pseudohalide groups in the 3-benzoylpyridine complexes and reflect the influence of the protonation of the 4-benzoylpyridine on its vibration frequencies. The yellow complexes display emission spectra with λ_{max} in the region 465–580 nm, whereas the red complex of 4-Bzpy emits at $\lambda_{max} = 631$ nm. The X-ray structure determination has shown compound (1) to contain a discrete dimeric cation [(4-benzoylpyridine)₂H]⁺ and an iodide anion. In the cation, a centrosymmetric pair of 4-benzoylpyridine is dimerized via a hydrogen bond of the type N...H...N with a short N...N distance of 2.654(11) Å. The iodide ion is located at the origin of the unit cell. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Copper(I) complexes; 3- and 4-benzoyl pyridine; [(4-benzoylpyridine)₂H] I; Vibration spectra; Emission spectra; Crystal structure.

1. Introduction

In a series of publications [1a,1b,2] (and references cited therein) and [3a,3b], Hardt et al., have reported that copper(I) halides react with various nitrogen bases, e.g. pyridine, picoline, etc. to form compounds that are flourescent at room temperature and to change their fluoresence color reversibly on cooling with liquid nitrogen. However, in some instances CuX-ligand clusters of the same stoichiometry (1:1:1) exists in more than one crystalline format. For example, $[CuI(py)]_4$ is a cube whereas [CuI(py)]n is a pleated sheet polymer [4,5]. These families of structures are of particular interest because the emission behavior 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 different excitation maxima [6].

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 N₃, and orange-yellow (CuX)₂L complexes for X = Cl and Br, and structurally characterized those of the first type for X = Br, I and CN [7,8a,8b]. All complexes of the first type display no emission spectra when excited in the UV region at room temperature. Whereas complexes of the second type display visible emission. On the other hand, copper(I) complexes of 4-benzoylpyridine which are yellow display emission spectra at room temperature [9]. During our trials to prepare crystals of the yellow 1:1 copper(I) iodide complex of 4-benzoylpyridine we isolated two compounds, a red and a yellow crystalline compounds. Elemental analysis of the yellow crystals revealed that it does not contain copper and is formulated as [(4-benzoylpyridine)₂H] I. As these crystals were suitable for X-ray analyses we determined its crystal structure. The syntheses and characterization of these compounds and of the copper(I) complexes of 3-benzoylpyridine which display emission spectra at room temperature are the subject of the present paper.

2. Experimental

3-Benzoylpyridine (3-Bzpy) and 4-benzoylpyridine (4-Bzpy) were obtained from Aldrich company and the other chemicals are of analytical grade quality.

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2.1. Preparation of complexes

CuI(4-Bzpy): this complex was prepared by mixing Cu(NO₃)₂·3H₂O and 4-Bzpy in a 1:6 molar ratio in acetone followed by addition of L(+)-ascorbic acid with several drops of water. Upon addition of KI (1:1 molar ratio with respect to copper) dissolved in the least amount of water some yellow 1:1 complex was precipitated. The final heterogeneous mixture was boiled for *ca*. 20 min, and then filtered. The red filtrate was allowed to stand over night to deposit red needles-like crystals of the complex.

2.2. $[(4-bezoylpyridine)_2H] \cdot I(1)$

Upon addition of an aqueous solution of KI to an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ in the presence of L(+)-ascorbic acid a white precipitate of copper(I) iodide if formed. Solid KI was then added until a clear solution was obtained. To this solution, an excess amount of 4-Bzpy (four folds with respect to copper) in acetone was added upon which the solution turns yellow. This solution was allowed to stand in a test tube. After several days a colorless solid of the organic ligand was obtained and filtered off. The filtrate was allowed to stand over two more days to deposite yellow crystals of the compound.

2.3. CuX(3-Bzpy), X = Cl, Br, I, CN and SCN

These complexes were prepared by one of the following general procedures

- An aqueous solution of Cu(NO₃)₂⋅3H₂O (4 mmol) was mixed with KX or NaX, followed by the addition of L(+)-ascorbic acid. An ethanolic solution of the 3-benzoylpyridine ligand (10 mmol) was then added and the mixture stirred for ca 15 min. The final mixture was allowed to stand over several hours or days until a crystalline product separated.
- 2. A boiled ethanolic solution of 3-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 and the mixture was boiled for several minutes and allowed to stand over several hours to produce the complex.

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

2.4. Physical measurements

The IR spectra of solid samples were measured as KBr pellets using a Bruker FTIR spectrophotometer. Raman spectra were obtained using a Perkin-Elmer System 2000 NIR FT-Raman spectrometer. The laser power was about 50 mW. Electronic spectra of complexes were obtained for solids mulled in Nujol using a Varian Cary-5 double beam spectrophotometer. The emission spectra of the solid samples were obtained using a Aminco Bowman 2 apparatus. The apparatus was calibrated for solid sample measurements by using an authentic compound. The experimental procedures and instruments used for other measurements are as described previously [9].

2.5. X-ray crystal structure analysis

A modified STOE four circle diffractometer was used for single crystal X-ray measurements. Orientation matrix and lattice parameters were obtained by leastsquares refinement of the diffraction data. Data were collected at 298(2) K, using graphite crystal–mono-chromatized MoK α radiation ($\lambda = 0.71069$ Å) and the ω -scan technique. The intensities were corrected for Lorentzpolarization effects and for absorption. Crystallographic data are given in Table 2.

The structure was solved by direct methods and subsequent Fourier analysis. Anisotropic displacement parameters were applied to nonhydrogen atoms in fullmatrix least-squares refinements based on F^2 . The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement cycles by use of geometrical restraints. Analytical expressions of neutral atom scattering factors were employed and anomalous dispersion corrections were incorporated. The program DIFABS [10] and the SHELXT/PC [11] program package were used for computations. Selected bond distances and bond angles are given in Table 4. Additional material consisting of fractional atomic coordinates, displacement parameters, observed and calculated structure factors and a complete lists of bond distances and angles has been deposited with the Editor.

3. Results and discussion

The results of the preparation of the complexes given in Table 1 suggest that 3-benzoylpyridine behaves very similar to ethyl nicotinate [12] and forms only 1:1 complexes with CuX, for X = Cl, Br, I, CN and SCN, whereas the copper(I) perchlorate, nitrate and azide complexes are too easily oxidized to be isolated. In a previous paper we reported that 4-benzoylpyridine forms 1:1 complexes with copper(I) halides and pseudohalides and 1:2 with the nitrate and perchlorate, and described the crystal structure of the 1:1 chloride complex [9]. However, when we tried to prepare crystals suitable for X-ray diffraction of the corresponding yellow 1:1 copper(I) iodide complex we isolated a new red complex formulated as Cu(4-Bzpy)I, in addition to a yellow crystalline compound formulated as [(4-benzoylpyridine)₂H] I.

Table 1
Analytical data

Complex	Color	M.P. (°C)	Analytical; found/calc.				
			C	Н	Ν	Х	Cu
CuCl(3-Bzpy)	yellow needle-like crystals	124–6	51.4	3.3	5.2	12.8	22.2
		dec.	(51.1)	(3.2)	(5.0)	(12.6)	(22.5)
CuBr(3-Bzpy)	yellow microcryst. powder	175-7	44.0	2.9	4.2	24.8	19.0
		dec.	(44.1)	(2.8)	(4.3)	(24.5)	(19.5)
CuI(3-Bzpy)	pale yellow cryst. powder	170	38.5	2.4	3.7	34.2	17.2
		dec.	(38.6)	(2.4)	(3.7)	(34.0)	(17.0)
CuCN(3-Bzpy)	yellow powder		57.0	3.4	10.5		23.1
			(57.3)	(3.3)	(10.3)		(23.3)
CuSCN(3-Bzpy)	yellow fine needles		51.3	2.8	9.2		20.4
			(51.2)	(3.0)	(9.2)		(20.8)
CuI(4-Bzpy)	red needle-like crystals		38.4	2.3	3.7	34.1	16.9
			(38.6)	(2.4)	(3.7)	(34.0)	(17.0)
$(4-Bzpy)_2H] \cdot I$	yellow crystals		57.4	3.9	5.6	25.12	
			(58.3)	(4.2)	(5.6)	(25.7)	

Table 2 Crystal data and structure refinement for (1)

Empirical formula	$C_{24}H_{19}IN_2O_2$
Formula weight	494.32
Temperature	298(2) K
Wavelength	0.71069 Å
Crystal system	triclinic
Space group	pĪ
Unit cell dimensions	$a = 6.634(3) \text{ Å}, \alpha = 90.53(3)^{\circ}$
	$b = 9.080(5) \text{ Å}, \beta = 105.64(3)^{\circ}$
	$c = 9.718(5) \text{ Å}, \gamma = 104.69(3)^{\circ}$
Volume, z	543.4(5) Å ³ , 1
Density (calculated)	1.511 Mg/m ³
Absorption coefficient	$1.495 \mathrm{mm^{-1}}$
F(000)	246
Crystal size	$0.28\times0.26\times0.12mm$
θ range for data collection	$3.06-26.00^{\circ}$
Limiting indices	$-8 \leqslant h \leqslant 7, -11 \leqslant k \leqslant 5,$
	$-11 \leq l \leq 11$
Reflections collected	2581
Independent reflections	$2004 (R_{int} = 0.0344)$
Absorption correction	DIFABS
Max. and min. transmission	1.000 and 0.179
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2004/0/134
Goodness-of-fit on F^2	0.984
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0560, wR2 = 0.1140
<i>R</i> indices (all data)	R1 = 0.0900, wR2 = 0.1312
Largest diff. peak and hole	0.608 and $-0.777 \text{e}\text{\AA}^{-3}$

All the isolated complexes of 3-Bzpy are yellow and sufficiently stable, when well dried, against air oxidation. These complexes in addition to the red complex of 4Bzpy are insoluble in many polar and nonpolar solvents, but they are soluble in DMF and DMSO giving rise to nonconducting solutions.

3.1. IR and Raman spectra

The IR and Raman spectra of free 3-Bzpy and some of its copper(I) complexes are collected in Table 3. The spectra of the complexes and free 3-Bzpy are similar except the systematic shifts of the vibrations related to the pyridine moiety as expected for N-bonded pyridine ligands [9]. In the far IR spectra 200–400 cm⁻¹, no bands could be attributed to terminal γ Cu–Cl or Cu–Br, suggesting bridging halide atoms whose copper–halogen absorption are expected below 200 cm⁻¹ [13] (and references cited therein). For 1:1:1 Cu:bridging halogen:monodentate ligand, there are several possible structures including dimer, cubane, stepped cubane, stair and split stair [14a, 14b]. Thus we could not assign definite structures for the present complexes without X-ray structure determination.

The yellow 1:1 copper(I) thiocyanato complex shows a strong band at 2100 cm⁻¹ (IR) and a medium band at 758 cm⁻¹ due to v_{as} CN and v_s CS modes, respectively. Similar bands have been reported for the [CuSCN(gly) (H₂O)]_n (gly=glycinate) containing $\mu(N,S)$ thiocyanato groups [15]. The corresponding 1:1 cyano complex exhibits a medium ν CN band at 2120 cm⁻¹, suggesting a bridging –CN– ligands as found in [CuCN(2-Bzpy)]*n* complex [8a, 8b]. Thus the pseudohalide complexes like the halide ones contain trigonal planner three coordinate copper(I) atoms.

Table 3									
Infrared and	Raman	spectra	(cm^{-1}) c	of 3-benzoylp	yridine a	and sor	ne of i	ts c	copper(I)
complexes									

3-Bzpy IR	Raman	Cu(3-Bzpy)Cl IR	Raman	Assignments
			222s	vCu–N(L)
	231 s		242 w	
	289 ms		292 m	
			370 w	
	405 w		405 w	
	400 w	417 w		ring
431 w	433 wm	442 w	440 w	ring
568 w	572 wm	590 w	583 w	
618 w	619 wm		617 w	ring
651 wm	661 wm	653 m	642 wm	ring
690 m		700s	660 w	ring
703 vs	735 s	741 wm	744 s	
782 s	787 m	779 wm	792 wm	$ring + 2 \times 372$
830 ms	825 w	822 m	830 w	405 + 431
	848 w		850 vw	405 + 440
920 m	918 w	939 m		
947 m	950 wm	952 m	960 w	
996 m	1001 vs	996 m	1000 vs	ring breathing
1035 m	1025 vs	1020 m	1035 vs	ring breathing
1043 m	1039 vs	1049 m	1048 m	
1150 m	1156 s	1154 w	1158 vs	ring
1174 wm	1181 wm	1185 m	1185 wm	
1197 wm	1200 wm	1200 wm	1197 wm	ring
1283 vs	1287 m	1282 s	1288 wm	2×651
1434 m	1450 vs	1439 m	1450 w	ring
1570 s	1585 vs	1584 s	1585 wm	ring
	1597s		1596 vs	ring
1635 vs	1648 vs	1651 vs	1660 vs	vC=O

v very, s strong, m medium, w weak (*) splitted band.

Table 4 Selected bond lengths (Å) and angles (°) for (1)

N(1)-C(1)	1.331(9)	(1)–C(5)	1.338(9)
C(1)-C(2)	1.380(10)	C(2)–C(3)	1.379(9)
C(3)–C(4)	1.386(9)	C(3)–C(6)	1.506(9)
C(4) - C(5)	1.376(9)	C(6)-0(1)	1.205(8)
C(6)–C(7)	1.479(9)	C(7)–C(8)	1.386(9)
C(7)–C(12)	1.393(9)	C(8)–C(9)	1.378(11)
C(9)-C(10)	1.377(12)	C(10)-C(11)	1.373(13)
C(11)–C(12)	1.380(10)	$N(1)-N(1) \neq 1$	2.654(11)
C(1)–N(1)–C(5)	120.0(6)	N(1)-C(1)-C2)	121.1(7)
C(1)-C(2)-C(3)	119.8(6)	C(2)-C(3)-C(4)	118.4(6)
C(2)-C(3)-C(6)	123.2(6)	C(4)-C(3)-C(6)	118.3(6)
C(5)-C(4)-C(3)	119.1(6)	N(1)-C(5)-C(4)	121.6(6)
O(1)-C(6)-C(7)	122.2(6)	O(1)–C(6)–C(3)	118.6(6)
C(7)-C(6)-C(3)	119.2(6)	C(8)–C(7)–C(12)	118.7(7)
C(8)-C(7)-C(6)	119.2(6)	C(12)-C(7)-C(6)	121.8(6)
C(9)–C(8)–C(7)	120.5(8)	C(10)-C(9)-C(8)	120.0(8)
C(11)–C(10)–C(9) C(11)–C(12)–C(7)	120.5(8)	C(10)-C(11)-C(12)	119.6(9)

Symmetry transformations used to generate equivalent atoms: #1 - x, -y, -z+1.

The IR and Raman spectra of the red 1:1 complex of 4-Bzpy are quite similar to those of the parent ligand, except the systematic shifts of the vibrations related to the pyridine moiety, and did not show any band that could be attributed to terminal Cu-I, a result which is suggestive of bridging iodide atom. As the corresponding yellow 1:1 complex has been demonstrated by X-ray diffraction to be a dimer and posses three coordinate copper(I) atoms [9], one may assume a polymer structure for the new red complex in which the copper atom attains a tetrahedral geometry. The IR spectrum of [(4-benzoylpyridine)₂H] · I compound shows a substantial shifts of the pyridine vibrations to higher frequencies when compared to the corresponding ones of the free ligands. Thus the bands at 1584, 1536, 1149, 638 and 472 cm^{-1} in the IR spectrum of free 4-Bzpy appeared at 1615, 1550, 1164, 645 and $484 \,\mathrm{cm}^{-1}$ in the compound, which are higher than those of the red 1:1 complex. It was pointed out [16] that the shifts of the ring vibrations to higher frequencies, caused by complex formation of pyridine, are smaller for transition metal ions than for the H⁺ ion. Therefore the protonation of the pyridine nitrogen atom in the hydrogen bonded compound is the reason for such large shifts. The appearance of medium broad bands around 3485 and 1955 cm⁻¹ supports the existence of hydrogen bonding of the type $H \dots N \dots H$. These results are confirmed by the structure determination of this compound.

3.2. Structure of $[(4-benzoylpyridine)_2H] \cdot I$ compound

The crystal structure of the title compound (1) consists of a packing of $[(4-benzoylpyridine)_2H]^+$ cations and $I^$ anions (Fig. 1). The two benzoylpyridine molecules are bridged by a proton to form a dimeric cation through hydrogen bonding of the type N...H...N or N...H– N with a N...N distance of 2.654(11)Å. This dimeric cation is very similar to that observed in the case of $[(methyl quinaldate)_2H]^+.[AuBr_4]^-$, except that the N...N distance of 2.88(1)Å [17], is longer than in (1). Somewhat surprisingly, the bond lengths of the 4-benzoylpyridine molecules in the hydrogen bonded cation are close to those reported for N-coordinated 4-benzoylpyridine in its copper(I) chloride complex [9]. However, the main effect of the coordination to copper(I) manifests itself in the bond angles of 4-benzoylpyridine where the C(1)–N(1)–C(5) and C(2)–C(3)–C(6) angles decrease from 120.0 and 123.2° in (1) to 117.0 and 118.2°, respectively, while the angles N(1)–C(5)–C(4) and N(1)– C(1)–C(2) increase from 121.6 and 121.1° in (1) to 123.0 and 123.7°, respectively in [CuCl(4-benzoylpyridine)]₂ complex [9]. The iodide anion in the present compound is located at the origin of the unit cell (Fig. 2).

3.3. Electronic spectra

The electronic spectra (Table 5) of all copper(I) complexes mentioned here exhibit strong absorption bands in the 370–420 nm range for the yellow complexes of 3-Bzpy and around 520 nm for the 1:1 iodide complex of 4-Bzpy. These bands are due to charge transfer transitions from Cu^I d^{10} to an empty π^* orbital on the benzoylpyridine ligands. The positions of these bands are very similar to those reported for corresponding complexes of other pyridine derivative ligands [18–20].

3.3. Emission spectra

The results of the room temperature emission spectra of the solid copper(I) complexes are collected in Table 5. All these complexes display emission spectra at room temperature with λ_{max}^{em} in the range 468–577 nm for those derived from 3-Bzpy and at 642 nm for the red 1:1 copper(I) iodide complex of 4-Bzpy. The spectrum of each of these complexes consists of a single slightly asymmetric band as seen from Fig. 3.

Previous studies [21–25] of the emission spectra of copper(I) halides of pyridine and pyridine derivatives has shown that these complexes display high energy (HE) band (430–540 nm) and low energy (LE) band (620–



Fig. 1. Prespective view of the structure of the dimer [(4-benzoylpyridine)₂H] · I, along with the atom labelling scheme.



Fig. 2. Packing in the unit cell of $[(4-benzoylpyridine)_2H] \cdot I$.

Table 5
Electronic and emission spectra

Complex	$\lambda_{\max}abs^{a}$ (nm)	$\lambda_{\max}^{em b}(nm)$		
CuCl(3-Bzpy)	410	468		
CuCl(3-Bzpy)	410	578		
CuI(3-Bzpy)	400	546		
CuCN(3-Bzpy)	420	569		
CuSCN(3-Bzpy)	420	577		
CuI(4-Bzpy)(H ₂ O)	520	631		

^aSolid samples are measured as Nujol mulls.

^bEmission maxima (excitation wavelength at 350 nm, except for the bromide; $\lambda^{\text{ex}} = 397$ nm.



λ (nm)

698 nm). The former was observed for $[CuX(py)]_4$ complexes having cubane structure with Cu...Cu distances of less than 2.8 Å, whereas the later band was observed also for polymeric [CuX(py)]n complexes. It was pointed out [26,27a,27b] that the energies of the HE band are quite sensitive to substituent on the pyridine; electron withdrawing substituent shifts these bands to lower

Fig. 3. Emission spectra of solid complexes, (a) Cu(3-benzoylpyridine)Cl, (b) Cu(3-benzoylpyridine)Br, (c) Cu(3-benzoylpyridine) \cdot I and (d) Cu(4-benzoylpyridine) \cdot I.

energy values. The results given in Table 5 suggest that the emission spectra of the complexes of 3-Bzpy experience a

substantial shift to lower energies when compared with corresponding complexes of pyridine [21,22,23a,23b,24,25]. Thus the emission band observed here is the HE band and is attributed to metal-to-ligand charge transfer (MLCT) or halide-to-ligand charge transfer (XLCT) [28]. The position of the λ_{max} of the emission band observed for the 1:1 iodide complex of 4-Bzpy suggests that the HE band is not only sensitive to the nature of substituent group, but also sensitive to its position in the pyridine ring. The results given here suggest that the energies of the emission band decrease in the order py > 3-Bzpy>4-Bzpy. The yellow 1:1 copper(I) iodide complex 4-Bzpy exhibits its emission band at $\lambda_{max} = 631$ nm. Thus the position of the emission band is sensitive to the stereochemistry of the copper(I) complex.

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