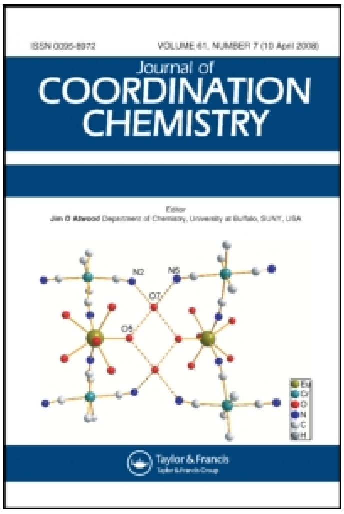

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INTRAMOLECULAR OXIDATIVE CYCLIZATION OF 2-BENZOYLPYRIDINE AND STRUCTURAL CHARACTERIZATION OF [9-OXO-INDOLO[1,2-*A*]PYRIDINIUM] COPPERDIIODIDE AND [Di-μ-bromo-bis(2-BENZOYLPYRIDINE)DICOPPER(I)]

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INTRAMOLECULAR OXIDATIVE CYCLIZATION OF 2-BENZOYLPYRIDINE AND STRUCTURAL CHARACTERIZATION OF [9-OXO-INDOLO [1,2-*A*]PYRIDINIUM] COPPERDIIODIDE AND [Di-μ-bromo-bis(2-BENZOYLPYRIDINE)-DICOPPER(I)]

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When a mixture of excess Cu(I)I and 2-benzoylpyridine (2-Bzpy) stands in an ethanolic medium for two weeks, an intramolecular oxidative cyclization of 2-Bzpy occurs with formation of the ionic complex [(9-oxo-indolo[1,2-a]pyridinium]$^+\cdot CuI_2^-$(1). In contrast the interaction of Cu(I)Br and 2-Bzpy in ethanol leads to formation of the dimer [CuBr(2-Bzpy)}$_2$ (2). The structures of both compounds were established by spectroscopic methods and X-ray diffraction analysis: (1) Space group $P2_1/a$, $a = 6.613(2)$, $b = 16.792(5)$, $c = 12.062(5)$ Å, B = 94.35(3)° and $Z = 4$, (2) Space group $P2_1/n$, $a = 6.896(2)$, $b = 7.551(2)$, $c = 22.454(4)$ Å, B = 93.34(2)° and $Z = 4$. The structure of (1) consists of a packing of [9-oxo-indolo[1,2-a]pyridinium]$^+$ cations and CuI_2^- species with the four Cu–I distances varying from 2.669(2) to 2.705(2) Å. The centrosymmetric [CuBr(2-Bzpy)]$_2$ (2) molecule has a short Cu–Cu distance of 2.696(2) Å.

KEYWORDS: benzoylpyridine, cyclization, copper(I)

INTRODUCTION

Mixing of KI and CuI in the presence of 18-crown-6 or dicyclohexano-18-crown-6 leads to the previously known species CuI_2^- which has been identified by single crystal analysis of CuI_2K(dicyclohexano-18-crown-6) and CuI_2K(18-crown-6).[1] The CuI_2^- anion has symmetrical di-coordinate Cu(I) species where Cu lies on a center of symmetry in both complexes. On the other hand, Baglio *et al.*[2] solved the crystal structures of a number of mixed Cu(I)-Cu(II) complex salts including

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$[Cu(NH_3)_4][CuI_2]_2$. In this latter complex, the CuI_2^- species is polymeric and contains Cu(I) ions which are teterahedrally coordinated to four iodide ions.[2]

Plytzanopoulos *et al.*[3] and others[4–6] have reported complexes formed by first row transition metal ions with 2-benzoylpyridine (hereafter abbreviated as 2-Bzpy) and assigned the coordination geometry mainly on the basis of spectroscopic data. They found that 2-Bzpy acts as either a mono- or bi-dentate ligand in these complexes depending on the central metal ions, the anions and the solvent used. Recent X-ray studies have shown that 2-Bzpy functions as an N,O-coordinating ligand in the polymeric complex $Cu_3(2\text{-Bzpy})_2(N_3)_6$,[7] in the dimeric $[Cu(2\text{-Bzpy})(N_3)_2]_2$[8] complex as well as in the structures of monomeric complexes $[CuX_2(2\text{-Bzpy})_2]$ where X = Br or N_3.[9]

During our attempts to prepare Cu(I) complexes of 2-benzoylpyridine we isolated black crystals of a new complex (1) whose infrared spectrum differs entirely from spectra of the other Cu(I) adducts as well as from that of the parent ligand. Herein we report on the synthesis, characterization and X-ray structures of this complex along with the 1:1 Cu(I) bromide adduct of 2-benzoylpyridine (2).

EXPERIMENTAL

Materials and Measurements

2-Benzoylpyridine was purchased from Aldrich. The other chemicals were of analytical grade quality. Infrared spectra were recorded from KBr pellets in the range 4000–200 cm^{-1} on a Perkin Elmer 580-B Spectrophotometer. Electronic spectra of solid samples mulled in nujol were measured over the range 200–850 nm using a Pye Unicam SP 8000 Spectrophotometer. Magnetic susceptibility measurements were performed on a modified Faraday balance (SUS 10, manufactured by A. Paar, Graz, Austria). The equipment was calibrated with freshly prepared $HgCo(NCS)_4$. Microanalysis of carbon, hydrogen and nitrogen was performed at the Mikro Analytische Lab., Institut fur Physikalishce Chemie, Wein, Austria. Copper content was determined using a Perkin-Elmer 5000 atomic absorption spectrophotometer. Halogen contents were determined gravimetrically after decomposition of the complex.

Preparation of Compounds

[9-oxo-indolo[1,2-*a*]pyridinium]·CuI_2 (1). A mixture of freshly prepared Cu(I)I (0.38 g, 2 mmol) in *ca.* 3 mL water and 2-benzoylpyridine (0.22 g, 1.2 mmol) in 20 mL ethanol was boiled for about 10 minutes and allowed to stand for 10 days. The colourless solution above CuI changed gradually to orange-red and well-developed black crystals started to deposit on the surface of CuI. Alternatively, an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.43 g, 1.8 mmol) was mixed with 2-benzoylpyridine (0.23 g, 1.3 mmol) in 15 mL ethanol followed by addition of excess L(+)-ascorbic acid, upon which the colour of the solution changed immediately to red. NaI (0.31 g, 2 mmol) was taken then added and the heterogeneous mixtured boiled for several minutes and allowed to stand for more than two weeks to produce black crytals of the complex. Anal calcd for $C_{12}H_8CuI_2NO$ (%): C, 28.85; H, 1.61; N, 2.80; Cu, 12.72; I, 50.81. Found: C, 28.42; H, 2.12; N, 3.00; Cu, 13.02; I, 50.33.

[CuBr(2-benzoylpyridine)]$_2$ (2)

An ethanolic solution (15 mL) of 2-benzoylpyridine (0.64 g, 3.5 mmol) was mixed with $Cu(NO_3)_2 \cdot 3H_2O$ (0.55 g, 2.3 mmol) in 10 mL ethanol followed by addition of excess L(+)—ascorbic acid. To this solution an aqueous solution of KBr (0.298 g, 2.5 mmol, in 2 mL water) was added dropwise and the mixture allowed to stand overnight to produce dark brown crystals of the complex. Anal calcd for $C_{12}H_9BrCuNO$(%): C, 44,13; H, 2.78; N, 4.28; Cu, 19.44; Br, 24.46. Found: C, 43.84; H, 3.05; N, 4.17; Cu, 19.10; Br, 24.52.

Crystallographic Data Collection and Structure Determination

Information concerning crystallographic data collection and structure refinement is summarized in Table 1. Data collection was performed in the ω-scan mode[10] on a

Table 1 Data collection and processing parameters.

	1	2
Molecular formula	$C_{12}H_8NOI_2Cu$	$C_{12}H_9NOBrCu$
Molecular weight	499.54	326.65
Color and habit	dark-black needle with (001) well-developed	dark brown, prism
Crystal size (mm^3)	0.36 × 0.16 × 0.52	0.20 × 0.35 × 0.40
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$ (No. 14)	$P2_1/n$ (No. 14)
Unit cell parameters		
a(Å)	6.613(2)	6.896(2)
b(Å)	16.792(6)	7.551(2)
c(Å)	12.062(5)	22.454(4)
B(°)	94.35(3)	93.34(2)
V(Å^3)	1335.5(1)	1167(1)
Z	4	4
F(000)	920	640
Density(calcd)(g cm^{-3})	2.480	1.859
Radiation	graphite-monochromatized Mo*K*α,	$\lambda = 0.17073$ Å
Standard reflections	(2, −1, 4); (1, −2, 2)	(−1, 3, 7); (2, −1, 4)
Intensity variation(%)	±0.9	±1.1
Absorption cofficient(mm^{-1})	6.24	5.27
Maan ur	0.17	0.65
Transmission factors	0.433 to 0.880	0.128 to 0.263
Scan type and rate (° min^{-1})	ω-scan; 3.02–15.60	3.08–29.30
Scan range (°)	0.60 below Kα_1 to 0.85	above Kα_2
Background counting	stationary counts for one-fifth of scan time at each end of scan range	
2σ range (°)	3.0–55.0	3.0–50.0
Unique data measured	2495	2037
Obs. data	1805	1466
No. of variables, p	155	115
Weighting scheme, w	$[\sigma^2\|F_o\| + 0.0004\|F_o\|^2]^{-1}$	$[\sigma^2\|F_o + 0.0005\|F_o^2]^{-1}$
R_F	0.035	0.042
wR	0.040	0.052
S	1.24	1.51
Residual extrena in final difference map (eÅ-3)	+ 0.99 to −0.59	+ 0.76 to −0.48
$R_F = \Sigma\|\|F_o - \|F_o\|\|/\Sigma\|F_o\|$	$wR = [\Sigma w^2(\|Fo\| - \|Fc\|)^2/\Sigma w^2\|F_o\|^2]^{1/2}$	
$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(n-p)]^{1/2}$		

Nicolet R3m/V diffractometer using Mo-K_α radiation (λ = 0.71073 Å) at 293 K. Unit-cell parameters were calculated from least-squares fitting on the 2θ angles for 25 selected strong reflections. The intensity data were processed with a learnt-profile procedure,[11] and an empirical absorption correction based on ψ-scan data were also applied.

The heavy atoms were located by the Patterson method and the remaining non-hydrogen atoms were derived from subsequent Fourier difference syntheses. All non-hydrogen atoms were refined anisotropically by full-matrix least squares. The hydrogen atoms of the organic ligand were placed in calculated positions with C—H 0.96 Å assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms.

All calculations were carried out on a DEC MicroVAX-II computer using the SHELXTL-PLUS program package.[12] Analytical expressions for neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[13] Final atomic coordinates for the two crystal structures, along with their estimated standard deviations, are presented in Tables 2 and 3.

Additional material consisting of hydrogen atom coordinates, displacement parameters, observed and calculated structure factors is available from M.A.S.G. and T.C.W.M.

RESULTS AND DISCUSSION

Synthesis and Properties

The interaction between Cu(I)Br and 2-benzoylpyridine in a molar ratio of 1:>1 in aqueous/ethanolic or ethanol medium afforded a 1:1 Cu(I) bromide-2Bzpy complex (2). Allowing a similar mixture to stand over two to three weeks led to the formation of the Cu(II) bromide complex of 2-benzoylpyridine that has been previously

Table 2 Atomic coordinates (× 10^5 for Cu and I; × 10^4 for others) and equivalent isotropic temperature factors* (Å^2 × 10^4 for Cu and I; × 10^3 for others) for complex (1).

Atom	*x*	*y*	*z*	U_{eq}
Cu(1)	43182(16)	24969(6)	-3573(8)	643(4)
I(1)	20052(7)	16873(3)	9707(4)	557(2)
I(2)	16869(7)	34212(2)	-15704(3)	481(2)
O(1)	3265(8)	-731(3)	4822(4)	60(2)
N(1)	2092(8)	435(3)	7065(4)	40(2)
C(1)	2779(10)	-214(3)	5427(6)	45(2)
C(2)	2093(10)	614(3)	5168(5)	41(2)
C(3)	1846(10)	1022(4)	4166(6)	53(2)
C(4)	1200(12)	1814(4)	4203(7)	60(3)
C(5)	905(11)	2169(4)	5183(7)	61(3)
C(6)	1107(11)	1769(3)	6216(7)	52(2)
C(7)	1708(10)	985(3)	6156(5)	42(2)
C(8)	1928(10)	571(4)	8143(6)	50(2)
C(9)	2326(11)	-69(4)	8882(6)	63(3)
C(10)	2932(11)	-786(4)	8502(7)	61(3)
C(11)	3158(11)	-898(4)	7374(6)	54(2)
C(12)	2728(10)	-282(3)	6668(6)	43(2)

*U_{eq} defined as one third of the trace of the orthogonalized U tensor.

Table 3 Atomic coordinates ($\times 10^5$ for Cu and Br; $\times 10^4$ for others) and equivalent isotropic temperature factors* ($Å^2 \times 10^4$ for Cu AND Br; $\times 10^3$ for others) for complex (2).

Atom	x	y	z	U_{eq}
Cu(1)	10251(12)	59466(12)	-3820(3)	616(3)
Br(1)	-62(11)	70132(10)	5922(3)	639(3)
O(1)	-339(6)	7384(6)	-1216(2)	59(2)
N(1)	3214(7)	7392(6)	-670(2)	43(2)
C(1)	4923(9)	7611(8)	-363(3)	51(2)
C(2)	6252(10)	8885(10)	-500(3)	60(2)
C(3)	5821(10)	10011(10)	-965(3)	61(2)
C(4)	4118(10)	9774(8)	-1299(3)	54(2)
C(5)	2848(8)	8458(7)	-1147(2)	40(2)
C(6)	926(9)	8117(8)	-1476(3)	47(2)
C(7)	589(8)	8675(8)	-2104(2)	49(1)
C(8)	2039(8)	8657(8)	-2518(2)	53(2)
C(9)	1517(11)	9124(9)	-3111(3)	66(2)
C(10)	-289(12)	9560(10)	-3282(4)	79(2)
C(11)	-1740(13)	9571(10)	-2897(4)	83(2)
C(12)	-1292(11)	9099(9)	-2306(3)	69(2)

*U_{eq} defined as one third of the trace of the orthogonalized U tensor.

described.[9] On the other hand, reaction of Cu(I)I and 2-Bzpy in a similar procedure or the reduction of a mixture of Cu(II) nitrate trihydrate and 2-Bzpy in presence of KI afforded a $[CuI(2\text{-}Bzpy)]_2$ complex.[14] Allowing a mixture of Cu(I) and 2-Bzpy (2:1 molar ratio) to stand more than 10 days led to the deposition of compound (1). Complex (1) is slightly soluble in acetone and ethanol with a change in colour to pale green–yellow, whereas complex (2) is insoluble in both solvents. Complex (2) is diamagnetic but a freshly prepared sample of (1) exhibits a paramagnetic moment of about 0.3 B.M. per Cu. Complex (1) is stable against air oxidation as compared with complex (2) and can be stored over one year without change.

Description of the Structures [9-oxo-indolo[1,2-a]pyridinium]$^+$ CuI_2^- (1)

The structure of the dark-black needles of complex (1) consists of a packing of [9-oxo-indolo[1,2-a]pyridinium]$^+$ cations and polymeric CuI_2^- species (Fig. 1); bond lengths and angles are given in Table 4. Intramolecular oxidative cyclization

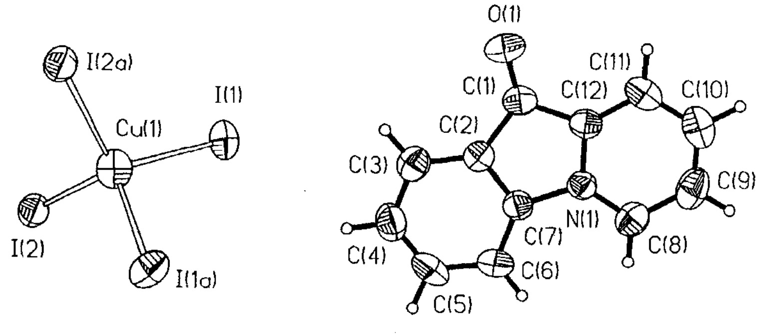


Figure 1 The coordination environment of the Cu(I) atom and the cation in the complex [9-oxo-indolo[1,2-a]pyridinium][CuI_2], *1*, along with the atom numbering scheme.

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

Cu(1)-I(1)	2.669(2)	Cu(1)-I(2)	2.682(2)
Cu(1)-I(1a)	2.677(2)	Cu(1)-I(2a)	2.705(2)
I(1)-Cu(1a)	2.677(2)	I(2)-Cu(1a)	2.705(2)
O(1)-C(1)	1.194(8)	N(1)-C(7)	1.442(8)
N(1)-C(8)	1.332(9)	N(1)-C(12)	1.373(8)
C(1)-C(2)	1.489(8)	C(1)-C(12)	1.504(10)
C(2)-C(3)	1.389(10)	C(2)-C(7)	1.385(9)
C(3)-C(4)	1.399(10)	C(4)-C(5)	1.351(11)
C(5)-C(6)	1.414(11)	C(6)-C(7)	1.378(8)
C(8)-C(9)	1.409(10)	C(9)-C(10)	1.360(11)
C(10)-C(11)	1.392(11)	C(11)-C(12)	1.356(9)
I(1)-Cu(1)-I(2)	104.2(1)	I(1)-Cu(1)-I(1a)	106.6(1)
I(2)-Cu(1)-I(1a)	113.8(1)	I(1)-Cu(1)-I(2a)	114.6(1)
I(2)-Cu(1)-I(2a)	114.4(1)	I(1a)-Cu(1)-I(2a)	103.3(1)
Cu(1)-I(1)-Cu(1b)	76.4(1)	Cu(1)-I(2)-Cu(1b)	75.7(1)
C(7)-N(1)-C(8)	127.5(5)	C(7)-N(1)-C(12)	109.7(5)
C(8)-N(1)-C(12)	122.7(5)	O(1)-C(1)-C(2)	130.0(6)
O(1)-C(1)-C(12)	125.5(6)	C(2)-C(1)-C(12)	104.5(5)
C(1)-C(2)-C(3)	131.1(6)	C(1)-C(2)-C(7)	108.2(5)
C(3)-C(2)-C(7)	120.7(6)	C(2)-C(3)-C(4)	117.2(7)
C(3)-C(4)-C(5)	120.8(7)	C(4)-C(5)-C(6)	123.5(6)
C(5)-C(6)-C(7)	114.6(7)	N(1)-C(7)-C(2)	109.5(5)
N(1)-C(7)-C(6)	127.4(6)	C(2)-C(7)-C(6)	123.2(6)
N(1)-C(8)-C(9)	117.5(6)	C(8)-C(9)-C(10)	120.5(7)
C(9)-C(10)-C(11)	120.3(7)	C(10)-C(11)-C(12)	118.6(6)
N(1)-C(12)-C(1)	108.1(5)	N(1)-C(12)-C(11)	120.3(6)
C(1)-C(12)-C(11)	131.6(6)		

Symmetry transformation: a (.5 + x, .5 + y, z)
b (− .5 + x, .5 + y, z).

of 2-benzoylpyridine occurs at the nitrogen atom of the pyridine moiety and C(7) of the phenyl ring with a N(1)—C(7) bond length of 1.442(8) Å. This bond is longer than the two neighbour bonds of 1.332(9) and 1.373(8) Å for N(1)—C(8) and N(1)—C(12), respectively. The copper and iodine atoms constitute columns of edge-sharing CuI_4 tetrahedral running parallel to the *a* axis (Fig. 2). This is similar to the corresponding CuI_2^- species found in the structure of $[Cu(NH_3)_4][CuI_2]_2$, except that two iodide rows from the chains also interact with a Cu(II) and are nearly perpendicular to the tetraammine Cu(II) plane.[2] The I-Cu-I and Cu-I-Cu angles in this later species are from 98.5(5) to 118.9(5)° and 76.2(5), 76.4(1)° respectively, as compared to corresponding values from 104.2(1) to 114.6(1)° and 75.7(1), 76.4(1)°, in complex (1). The Cu—I distances (Table 4) in the present structure are much longer than those reported (2.394(2) and 2.383(1) Å) in the previously described linear CuI_2^- species.[1] These Cu—I bond lengths, however, closely corresponded to the distances observed in CuI complexes in which Cu is bound to two iodines in the dimeric Cu_2I_2 units, *e.g.*, av. = 2.686Å in $[CuI(quinoline)_2]_2$,[15] av. = 2.655 Å in $[Cu_2I_2(3\text{-Me-pyridine})_4]$,[16] and av. = 2.683 Å in $[CuI(2\text{-benzoylpyridine})]_2$.[14] Compared to complexes in which Cu links four iodine atoms, the Cu—I bond lengths in the present CuI_2^- species are shorter than those (av. = 2.711 Å) in the complex $(Cu_4I_6)K_2(15\text{-crown-}5)$[17] and av. = 2.72 Å in $[Cu(NH_3)_4][CuI_2]_2$.[2]

[CuBr(2-benzoylpyridine)]$_2$ (2)

Structure determination of complex (2) confirmed the Cu(I)Br:bidentate ligand stoichiometry to be 1:1 as expected, the molecular species is binuclear and disposed about a crystallographic inversion centre with a planar Cu_2Br_2 rhombohedral core of alternating copper and bromine atoms (Fig. 3). Bond lengths and bond angles are given in Table 5. The Cu—Br distances of 2.474(1) and 2.382(1) Å found in complex (2) are shorter than those observed for 1:1 CuBr:L adducts, where L is a monodentate ligand, *e.g.*, 2.571(1) to 2.599(2) Å in the cubane complex [CuBr(P(t-Bu)$_3$)]$_4$,[18] 2.48(1)-2.50(1) Å in [CuBr(MeCN)]$_\infty$ with the ribbon structure,[19] and dimeric complexes [CuBrL$_2$]$_2$, L = 2-methylpyridine (av. = 2.594 Å), L = 2,4-dimethylpyridine (av. = 2.590 Å) and L = quinoline (av. = 2.60 Å).[20] They are also shorter than those of [CuBr(L-L)]$_2$ where L-L = a bidentate ligand, *e.g.*, [CuBr(dmphen)]$_2$ (dmphen = dimethylphenanthroline) (av. = 2.795 Å).[21] Each copper center in the Cu_2Br_2 unit is further coordinated by the carbonyl oxygen at C=O = 2.315(4) Å and the heterocyclic nitrogen (Cu—N = 2.001(5) Å) of 2-Bzpy, thus forming a five-membered chelate ring. The Cu—O distance is a little shorter than that found in [CuI(isopropylquinaldate)]$_2$ (2.33(1) Å) and a little longer than Cu—O (2.26(6) Å) in C[CuI(n-butylquinaldate)]$_2$,[22] but matches very well for that found for [CuI(2-Bzpy)]$_2$ (2.304(1) Å).[14] The Cu—N distance agrees well with those found in the above three complexes [2.04(1), 2.04(2) and 2.035(4) Å, respectively]. Similar Cu-carbonyl oxygen bond lengths in the complex of

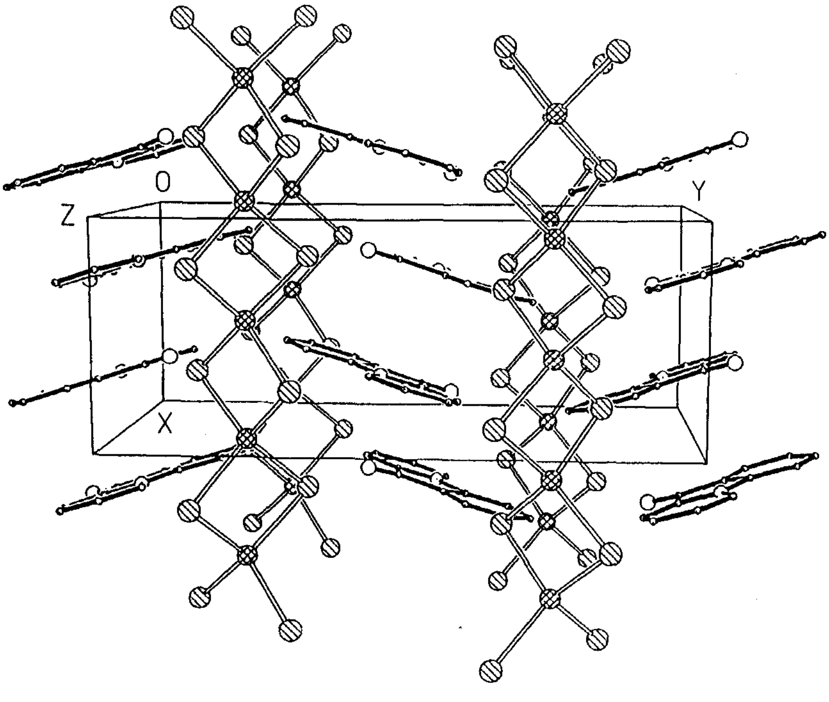


Figure 2 A stereoview of the crystal structure of complex (1).

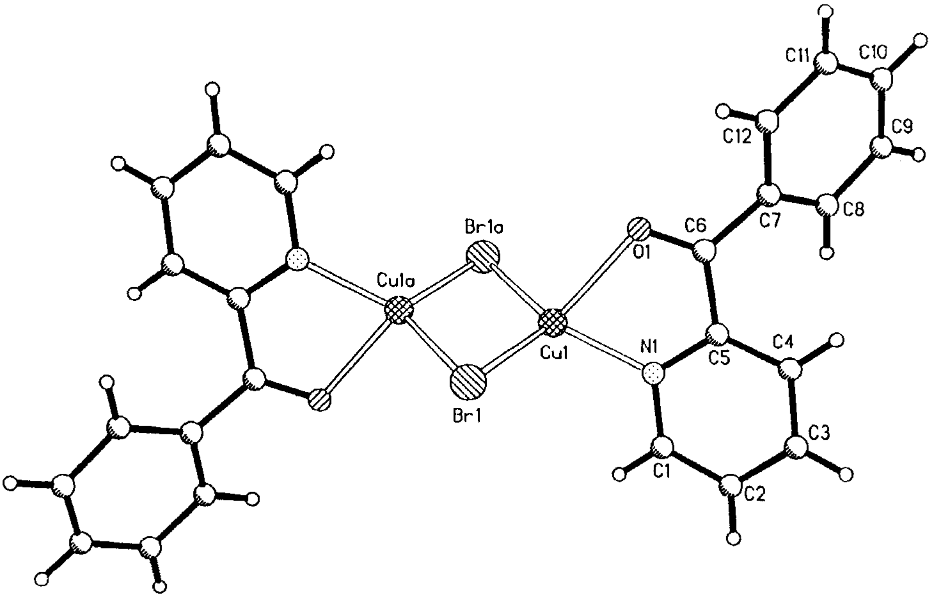


Figure 3 Perspective view showing the coordination environment of the Cu(I) atoms in the complex [CuBr(2-benzoylpyridine)], *2*, along with the atom numbering scheme.

Table 5 Bond lengths (Å) and bond angles (°) for complex (2).

Cu(1)-Br(1)	2.474(1)	Cu(1)-O(1)	2.315(4)
Cu(1)-N(1)	2.001(5)	Cu(1)-Cu(1a)	2.696(2)
Cu(1)-Br(1a)	2.382(1)	Br(1)-Cu(1a)	2.382(1)
O(1)-C(6)	1.212(8)	N(1)-C(1)	1.341(8)
N(1)-C(5)	1.352(7)	C(1)-C(2)	1.376(9)
C(2)-C(3)	1.366(10)	C(3)-C(4)	1.367(9)
C(4)-C(5)	1.380(8)	C(5)-C(6)	1.500(8)
C(6)-C(7)	1.478(8)	C(7)-C(12)	1.386(9)
C(8)-C(9)	1.402(9)	C(9)-C(10)	1.323(11)
C(10)-C(11)	1.359(12)	C(11)-C(12)	1.392(11)
Br(1)-Cu(1)-O(1)	116.0(1)	Br(1)-Cu(1)-N(1)	111.7(1)
O(1)-Cu(1)-N(1)	76.2(2)	Br(1)-Cu(1)-Br(1a)	112.6(1)
O(1)-Cu(1)-Br(1a)	100.3(1)	N(1)-Cu(1)-Br(1a)	131.8(1)
Cu(1)-Br(1)-Cu(1a)	67.4(1)	Cu(1)-O(1)-C(6)	109.5(4)
Cu(1)-N(1)-C(1)	123.9(4)	Cu(1)-N(1)-C(5)	118.1(4)
C(1)-N(1)-C(5)	116.9(5)	N(1)-C(1)-C(2)	123.2(6)
C(1)-C(2)-C(3)	119.2(6)	C(2)-C(3)-C(4)	118.6(6)
C(3)-C(4)-C(5)	119.8(6)	N(1)-C(5)-C(4)	122.1(5)
N(1)-C(5)-C(6)	114.0(5)	C(4)-C(5)-C(6)	123.9(5)
O(1)-C(6)-C(5)	118.8(5)	O(1)-C(6)-C(7)	120.8(5)
C(5)-C(6)-C(7)	120.4(5)	C(6)-C(7)-C(8)	123.4(3)
C(6)-C(7)-C(12)	118.0(5)	C(80)-C(7)-C(12)	118.3(4)
C(7)-C(8)-C(9)	118.2(4)	C(8)-C(9)-C(10)	121.5(7)
C(9)-C(10)-C(11)	122.1(8)	C(10)-C(11)-C(12)	118.3(8)
C(7)-C(12)-C(11)	121.5(7)		

Symmetry transformation: a (−x, 1−y, −z) bis(10-methylisoalloxazine)[23] with Cu(I) are 2.27(2) and 2.21(2) Å. In this complex a similar (−Cu...N=C−C=O−) five-membered chelate ring exists with both nitrogen and oxygen coordinated to Cu(I) [Cu-N = 1.94(2) and 1.92(2) Å]. The Cu...Cu separation of 2.696(2) Å in complex (2) is much shorter than those of 3.097(1), 3.351(3) and 3.091(3) Å found in $[CuBrL_2]_2$ for L = 2-Mepy, 2,4-diMepy and quinoline,[20] respectively, and 3.140(4) Å in $[CuBr(dmphen)]_2$.[21] This Cu...Cu separation, however, is longer than that (av. = 2.606 Å) found in $Cu_2Br_2(TEED)_2$ (TEED = N,N,N',N−tetraethylethylenediamine).[24]

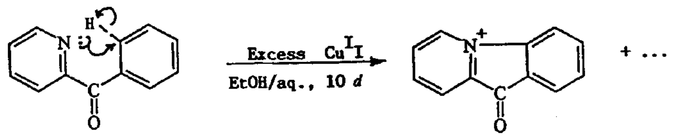
Spectra

The infrared spectrum of the $[CuBr(2\text{-}Bzpy)]_2$ complex (2) shows absorption bands at 1630 vs ($\upsilon_{C=O}$), 1585 m, 1565 m, 1445 m, 1020 m, 655 m (pyridine ring) cm^{-1}. Free 2-benzoylpyridine exhibits corresponding absorption bands at 1660 s, 1580 ms, 1560 m, 1440 m, 995 s, and 610 ms. The substantial shifts of $\upsilon_{C=O}$ band to lower frequency and the pyrdine ring vibrations to higher frequencies upon complexation suggest simultaneous N,O-coordination of 2-Bzpy in complex (2). In the far infrared spectrum (400–200) cm^{-1}) of (2) no bands could be attributed to terminal $\upsilon_{Cu\text{-}Br}$, suggesting briding bromide atoms whose copper bromide absorption bands are expected below 200 cm.$^{-1}$ The infrared spectrum of (1), however, differs substantially from spectra of both free 2-Bzpy and its Cu(I) bromide complex (2). It exhibits $\upsilon_{C=O}$ at 1730 cm^{-1} and the first two C-C, C-N (pheyl and pyridine moieties) at 1610 and 1585 cm^{-1}, which may be compared with the spectrum of fluoro-9-one.[25] When compared with the spectrum of (2), the medium to strong bands at 695 and 775 cm^{-1} disappear from (1) and new bands are observed at 1480 m, 1355 m, and 1250 cm^{-1}.

The electronic spectra of solid complexes (1) and (2) exhibit broad bands around 330–440 nm and 330–480 nm, respectively. The band in complex (2) is undoubtedly a charge transfer transition[26] from Cu(I) d^{10} to an empty π^* orbital on 2-benzoylpyridine. The intense band in the spectrum of complex (1) may be a charge transfer band associated with interaction of the [9-oxo-indolo[1,2-a]pyridinium]$^+$ cation with the cuprous iodide chains.

CONCLUSION

Cu(I) iodide catalyses the intramolecular oxidative cyclization of 2-benzoylpyridine (I) which occurs at the nitrogen atom of the pyridine moiety and C(7) of the phenyl ring giving rise to the [9-oxo-indolo[1,2-*a*]pyridinium]$^+$ cation (II),



(I) (II)

The relative stabilities of Cu(I) and Cu(II) in aqueous solutions depend very strongly on the nature of anion or other ligands present. That the iodide ion favors

Cu(I) may explain why such oxidative cyclization of 2-Bzpy does not occur in case of the chloride or bromide ions. Oxidation of Cu(I) rather than 2-Bzpy is likely to take place with these latter ions. In summary, the interaction between Cu(I) halides and 2-Bzpy afforded (i) 1:1 Cu(I) complexes of the ligand, or (ii) oxidative cyclization of 2-Bzpy giving the [9-oxo-indolo[1,2-*a*]pyridinium]$^+$ cation, or (iii) oxidation of Cu(I) with formation of Cu(II) complexes of 2-Bzpy, depending on the halide ion, the molar ratio of coper to 2-Bzpy and the time of interaction. Excess 2-Bzpy leads to 1:1 complexes with the three halides, but excess Cu(I) over 2-Bzpy with a long time of interaction favors oxidation of Cu(I) for the chloride and bromide anions. To our knowledge, the intramolecular oxidative cyclization of 2-Bzpy catalyzed by Cu(I) is the first to have been reported. Such of reactions in presence of other Cu(I) salts or other metal ions are under investigation.

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