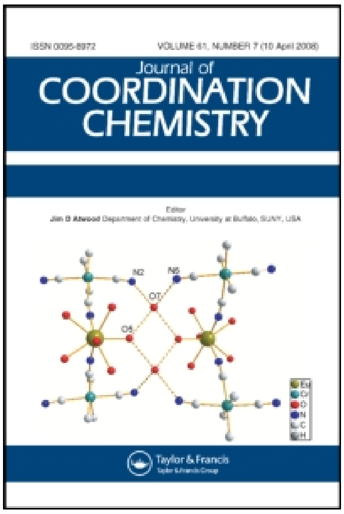

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REACTIONS OF CuX (X = SCN AND CN) WITH 2-BENZOYLPYRIDINE. SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF [9-OXO-INDOLO[1,2-*a*] PYRIDINIUM] DITHIOCYANATOCUPRATE(I) AND POLYMERIC μ-CYANO(2-BENZOYLPYRIDINE) COPPER(I)

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REACTIONS OF CuX (X = SCN AND CN) WITH 2-BENZOYLPYRIDINE. SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF [9-OXO-INDOLO[1,2-*a*] PYRIDINIUM] DITHIOCYANATOCUPRATE(I) AND POLYMERIC μ-CYANO(2-BENZOYLPYRIDINE) COPPER(I)

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When a mixture of excess CuSCN and 2-benzoylpyridine (2-Bzpy) stands in an ethanolic medium for about ten days in contact with air, the intramolecular oxidative cyclization of 2-Bzpy occurs with formation of the ionic compound [9-oxo-indolo[1,2-*a*]pyridinium]$^+$ $[Cu(SCN)_2]^-$ (**1**). In contrast, interaction of CuCN and 2-Bzpy in ethanol leads to formation of the polymer $[Cu(CN)(2\text{-Bzpy})]_n$ (**2**). The reaction of Cu(II) and 2-Bzpy in presence of excess SCN^- in ethanol affords (**1**) and the green monomer $[Cu(SCN)_2(2\text{-Bzpy})_2]$ (**4**). These complexes, along with the 1:1 CuSCN complex of 2-Bzpy (**3**) are studied by IR, Raman and electronic spectroscopic methods and X-ray structural analysis of (**1**) and (**2**). Crystals of (**1**) are monoclinic, space group $P2_1/n$ (No. 14), with a = 5.887(1), b = 36.142(7), c = 7.083(1) Å, B = 109.56(1)°, Z = 4, and R_F = 0.033 for 2487 observed MoKα data, (**2**) monoclinic, space group $P2_1/c$ (No. 14), a = 14.393(3), b = 8.881(2), c = 9.287(2) Å, B = 103.80(3)°, Z = 4, and R_F = 0.036 for 2030 observed MoKα data. The structure of (**1**) consists of a packing of [9-oxo-indolo [1,2-*a*]pyridinium]$^+$ cations and $[Cu(SCN)_2]^-$ anions. Puckered layers are formed by the $[Cu(SCN)_2]^-$ component with four-coordinate Cu(I) and one tridentate μ(N,S,S)-thiocyanato ligand. Complex (**2**) features distorted tetrahedral Cu(I) geometry, formed by a bidentate chelating 2-Bzpy and linear C- and N-bonded bidentate cyano groups, which link adjacent copper centers to form zigzag chains extending along the *c* axis. Complexes (**1**) and (**2**) do not fluoresce at room temperature.

KEY WORDS: Copper(I), 2-Benzoylpyridine, polymer, structures

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INTRODUCTION

It has been reported[1-4] that 2-benzoylpyridine acts as either a mono- or bidentate ligand in first-row transition metal complexes depending on the central metal ion, the anion and the solvent. Recent X-ray studies, however, have shown that 2-benzoylpyridine functions as an N,O-coordinating ligand in all previous structurally characterized complexes.[5-8]

Complexes of Cu(I) halides with unidentate nitrogen donor ligands have been observed to display a wide variety of stoichiometries, structures,[9,10] and emission characteristics[11] in the solid state. Structures of the type CuX(L-L), in which L-L is a bidentate ligand with hetero donor atoms, have also been reported.[12-14] Copper(I) pseudohalide complexes of both types of ligands, however, have received little attention in comparison to their corresponding halide complexes. Copper(I) cyano complexes have been structurally characterized primarily as alkali metal salts.[15-18] In these complexes the anions usually exhibit a polymeric structure, *e.g.* the anion present in $K[Cu(CN)_2]$ forms an infinite spiral[15] and a planar hexagonal network is formed in $K[Cu_2(CN)_3]\cdot H_2O$.[16] Infinite zigzag chains of CuCN have been found in structures of some 1:1 Cu(I) cyanide-organic nitrogen donor ligand complexes.[19,20]

In a previous paper[21] we reported that when a mixture of excess CuI and 2-benzoylpyridine (hereafter abbreviated as 2-Bzpy) was allowed to stand in an ethanolic medium in contact with air for two weeks, an intramolecular oxidative cyclization of 2-Bzpy occurs with formation of the ionic compound [9-oxo-indolo [1,2-*a*]pyridinium]$^+$ $[CuI_2]^-$. The structure of this complex as determined by X-ray crystallography, consists of a packing of [9-oxo-indolo[1,2-*a*] pyridinium]$^+$ cations and CuI_2^- species, with four Cu-I distances varying from 2.669(2) to 2.705(2) Å. We have subsequently extended the investigation to similar reactions between other Cu(I) salts and 2-Bzpy. In the case of CuSCN we isolated the ionic compound [9-oxo-indolo[1,2-*a*]pyridinium]$^+$ $[Cu(SCN)_2]^-$ (**1**); the interaction between CuCN and 2-Bzpy afforded the 1:1 complex (**2**). For comparison we descibe the 1:1 CuSCN complex of 2-Bzpy. The 1:2 $Cu(SCN)_2$ complex of 2-Bzpy was coprecipitated with complex (**1**). As this latter Cu(II) complex has not yet been reported, we described its preparation and properties here.

EXPERIMENTAL

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

Preparation of the Compounds

[9-oxo-indolo[1,2-*a*]pyridinium]$[Cu(SCN)_2]$ (**1**)

This compound was prepared by mixing CuSCN (0.490 g, 4 mmol) in aqueous solution (15 cm^3) with 2-benzoylpyridine (0.460 g, 2.5 mmol) dissolved in ethanol (25 cm^3). The heterogeneous mixture was boiled for about 15 min., cooled and allowed to stand in contact with air over a period of about two weeks to produce dark-brown (almost black) well-formed crystals of (**1**). The compound was also obtained by the procedure given under complex (**4**). *Anal.* Calcd. (%). Cu, 17.55; C, 46.46; H, 2.23; N, 11.60; S, 17.71. Found: Cu, 17.32; C, 46.45; H, 2.20; N, 11.37; S, 17.68. Yield 20%.

[Cu(CN)(2-benzoylpyridine)] (**2**)

A stoichiometric amount of an aqueous solution of $CuSO_4 \cdot 5H_2O$ (2.07 g, 6 mmol) was added to an aqueous solution of KCN. The precipitated CuCN was washed several times with water. Then it was dissolved by slow addition of the calculated quantity of KCN under constant stirring, and filtered. To this filtrate, an ethanolic solution of 2-benzoylpyridine (1.83 g, 10 mmol) was added and the final mixture allowed to stand in a cool place for *ca.* one week. The complex was deposited as dark red plates. Alternatively, an ethanolic solution of $Cu(NO_3)_2 \cdot 2H_2O$ (0.725 g, 3 mmol) was mixed with an aqueous solution of KCN (0.198 g, 3 mmol) followed by addition of L(+)-ascorbic acid. To this mixture, an ethanolic solution of 2-benzoylpyridine (0.33 g, 1.80 mmol) was added. After boiling about 20 min., the mixture was allowed to sand over *ca.* 5 weeks. *Anal.* Calcd. (%): Cu 23.29; C, 57.24; H, 3.33; N, 10.26. Found: Cu, 23.43; C, 57.16; H, 3.22; N, 10.05.

[Cu(SCN)(2-benzoylpyridine)] (**3**)

This complex was prepared as described previously,[7] by mixing the components in 1:1 Cu/2-Bzpy molar ratio in ethanolic aqueous medium. The final mixture was boiled for several minutes and allowed to stand overnight. The complex was isolated as red brown crystals. *Anal.* Calcd. (%): Cu, 20.85; C, 51.22; H,,2.98; N, 9.19. Found: Cu, 20.64; C, 52.06; H, 3.12; N, 9.02.

[Cu(SCN)$_2$(2-benzoylpyridine)$_2$] (**4**)

An ethanolic solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.97 g, 4 mmol) was mixed with 2-benzoylpyridine (1.283 g, 7 mmol) dissolved in ethanol. To this mixture, an aqueous solution of KSCN (0.975 g, 10 mmol) was added dropwise. The color of the final mixture changed gradually to brown. This mixture was allowed to stand for *ca.* 4 days to yield dark brown sheets or plates of complex (**1**) and grass green crystals of complex (**4**). This later complex (**4**) was also prepared by direct interaction between the components dissolved in water. *Anal.* Calcd. (%): Cu, 11.64; C, 57.18; H, 3.32; N, 10.26; S, 11.74. Found: Cu, 11.24; C, 57.28; H, 3.43; N, 10.14; S, 11.34.

Analytical and Physical Measurements

The contents of C, H, N and S were determined by means of a LECO CHNS-932 Elemental Analyser, and the content of copper was determined by atomic absorption using a Perkin-Elmer 5100 PC. UV-vis spectra of solutions and DRS of solid samples were performed with a Varian Cary-5 Double Beam Spectrophotometer. Raman spectra were obtained using a Perkin-Elmer System 2000 NIR FT-Raman spectrometer. Other procedures and instruments are as described previously.[21]

X-ray Structure Determination

Both complexes were handled in the same manner. Details of crystal parameters, data collection and structure refinement are given in Table 1. Raw intensities collected on a Rigaku AFC7R four-circle diffractometer at room temperature (294 K) were corrected for absorption using ω-scan data,[22] Patterson superposition yielded the positions of all non-hydrogen atoms, which were subjected to anisotropic refinement. All hydrogens were generated geometrically (C-H bonds fixed at 0.96 Å) and allowed to ride on their respective parent C atoms: they were assigned the same isotropic temperature factors ($U = 0.08$ Å^2) and included in the structure-factor calculations. Computations were performed using the SHELXTL-PC program package[23,24] on a PC 486 computer. Analytic expressions of atomic scattering factors were employed and anomalous dispersion corrections were incorporated.[25]

The final atomic parameters are listed in Table 2. Bond distances and angles are tabulated in Table 3.

Table 1 Data collection and processing parameters.

	1	2
Molecular formula	$C_{14}H_8N_3OS_2Cu$	$C_{13}H_9CuN_2O$
Molecular weight	361.9	272.76
Color and habit	black, plate	red plate
Crystal size (mm^3)	0.04 × 0.12 × 0.14	0.05 × 0.20 × 0.30
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
Unit cell parameters		
a(Å)	5.887(1)	14.393(3)
b(Å)	36.142(7)	8.881(2)
c(Å)	7.083(1)	9.287(2)
β(°)	109.36(1)	103.80(3)
V(Å^3)	1422(1)	1152.8(6)
Z	4	4
F(000)	728	5528
Density(calcd)(g cm^{-3})	1.690	1.572
Radiation	graphite-monochromatized MoKα	λ - 0.71073 Å
Standard reflections	(0, -6, 1); (-1, 8, 1)	($\bar{3}$, 1, 1); ($\bar{2}$, 0, 2); ($\bar{2}$, 0, 1)
Intensity variation(%)	± 1.1%	± 0.5%
Absorption cofficient (mm^{-1})	1.83	1.88
Mean ur	0.10	0.138
Transmission factors	0.333 to 0.393	0.770 to 1.000
Scan type and rate (° min^{-1})	ω-scan; 2.00–20.00	2.0–16.0
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	
2θ range (°)	3.0 to 50.0	3.0 to 50.0
Unique data measured	2487	2030
Obs. data	1021	1635
No. of variables, p	190	155
Weighting scheme, w	$[\sigma^2\lvert F_o\rvert + 0.0020\ \lvert F_o\rvert^2]^{-1}$	$[\sigma^2\lvert F_o\rvert + 0.001\lvert F_o\rvert^2]^{-1}$
R_F	0.033	0.036
wR	0.038	0.047
S	0.57	1.96
Residual extrema in final difference map (eÅ^{-3})	+ 0.25 to - 0.33	+ 0.31 to - 0.57
$R_F = \Sigma\lvert\,\lvert F_o - \lvert F_o\rvert\,\rvert/\Sigma\lvert F_o\rvert$	$wR = [\Sigma w^2(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w^2\lvert F_o\rvert^2]^{1/2}$	$S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n - p)]^{1/2}$

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

[9-oxo-indolo[1,2-*a*] $^+$ $[Cu(SCN)_2]^-$ (1) Atom	*x*	*y*	*z*	U_{eq}
Cu(1)	13403(15)	21431(3)	30645(16)	429(4)
O(1)	11161(10)	586(2)	10393(10)	71(3)
N(1)	6867(10)	1181(2)	7357(8)	33(2)
C(1)	9350(14)	729(2)	9265(13)	45(3)
C(2)	6991(13)	563(2)	8198(12)	46(3)
C(3)	6161(18)	207(2)	8134(15)	61(4)
C(4)	3826(20)	137(3)	6881(17)	77(5)
C(5)	2402(16)	412(3)	5763(15)	71(5)
C(6)	3244(14)	772(2)	5806(13)	52(4)
C(7)	5537(14)	834(2)	7037(12)	45(3)
C(8)	6117(14)	1505(2)	6510(12)	44(3)
C(9)	7684(13)	1800(2)	6988(11)	38(3)
C(10)	9997(13)	1754(2)	8287(11)	42(3)
C(11)	10709(13)	1413(2)	9150(11)	40(3)
C(12)	9131(12)	1122(2)	8654(10)	33(3)
S(1)	-3129(3)	1061(1)	2487(3)	52(1)
C(13)	-1260(13)	1414(2)	3003(11)	36(3)
N(2)	81(10)	1658(2)	3370(9)	42(3)
S(2)	7990(3)	2510(1)	1230(3)	41(1)
C(14)	5681(12)	2334(2)	1769(10)	32(3)
N(3)	4074(9)	2223(2)	2136(9)	38(2)
$[Cu(CN)(2\text{-benzoylpyridine})]_n$ (2) Atom	*x*	*y*	*z*	U_{eq}
Cu(1)	20103(3)	15053(5)	37279(4)	510(2)
N(1)	1984(2)	2378(4)	1808(3)	59(1)
C(1)	1971(2)	2808(4)	624(3)	44(1)
O(1)	3312(2)	-99(3)	4476(3)	52(1)
N(2)	1529(2)	-744(3)	3011(3)	48(1)
C(2)	710(3)	-1010(5)	2036(4)	63(1)
C(3)	498(3)	-2379(5)	1301(5)	72(2)
C(4)	1155(3)	-3507(5)	1580(5)	66(2)
C(5)	2013(3)	-3264(4)	2609(4)	54(1)
C(6)	2178(2)	-1868(4)	3296(4)	44(1)
C(7)	3114(2)	-1440(4)	4326(4)	44(1)
C(8)	3779(2)	-2587(4)	5125(3)	45(1)
C(9)	3466(3)	-3911(4)	5682(4)	53(1)
C(10)	4118(3)	-4869(4)	6541(4)	60(2)
C(11)	5084(3)	-4544(4)	6842(4)	61(1)
C(12)	5408(3)	-3273(4)	6272(4)	56(1)
C(13)	4760(2)	-2291(4)	5422(4)	50(1)

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

RESULTS AND DISCUSSION

The interaction between CuSCN and a molar excess of 2-benzoylpyridine afforded a 1:1 complex (**3**), but allowing a mixture of the above components in a nearly 2:1 molar ratio in ethanolic medium to stand for about two weeks led to the deposition of complex (**1**). On the other hand reaction between Cu(II) ions and 2-Bzpy in the

Table 3 Bond lengths (Å) and bond angles (°)

[9-oxo-indolo-[1,2-*a*]pyridinium][Cu(SCN)$_2$] (1)			
(i) Coordination geometry about Cu atoms			
Cu(1)-N(2)	1.943(6)	Cu(1)-N(3)	1.951(7)
Cu(1)-S(2a)	2.373(2)	Cu(1)-S(2b)	2.471(2)
N(2)-Cu(1)-N(3)	124.0(3)	N(2)-Cu(1)-S(2a)	106.6(2)
N(3)-Cu(1)-S(2a)	111.2(2)	N(2)-Cu(1)-S(2b)	114.0(2)
N(3)-Cu(1)-S(2b)	96.4(2)	S(2a)-Cu(1)-S(2b)	102.6(1)
(ii) thiocyanato groups			
S(1)-C(13)	1.643(8)	C(13)-N(2)	1.156(10)
S(2)-C(14)	1.656(8)	C(14)-N(3)	1.134(10)
Cu(1)-N(2)-C(13)	157.2(5)	S(1)-C(13)-N(2)	179.0(7)
Cu(1)-N(3)-C(14)	166.8(6)	S(2)-C(14)-N(3)	178.1(7)
(iii) [9-oxo-indolo-[1,2-*a*]pyridinium]$^+$			
O(1)-C(1)	1.217(9)	N(1)-C(7)	1.453(10)
N(1)-C(8)	1.326(9)	N(1)-C(12)	1.361(8)
C(1)-C(2)	1.471(10)	C(1)-C(12)	1.478(10)
C(2)-C(3)	1.371(11)	C(2)-C(7)	1.380(10)
C(3)-C(4)	1.390(13)	C(4)-C(5)	1.370(13)
C(5)-C(6)	1.389(13)	C(6)-C(7)	1.362(10)
C(8)-C(9)	1.376(10)	C(9)-C(10)	1.377(9)
C(10)-C(11)	1.379(11)	C(11)-C(12)	1.367(10)
C(7)-N(1)-C(8)	127.6(6)	C(7)-N(1)-C(12)	109.2(5)
C(8)-N(1)-C(12)	123.1(6)	O(1)-C(1)-C(2)	129.4(7)
O(1)-C(1)-C(12)	125.1(7)	C(2)-C(1)-C(12)	105.5(6)
C(1)-C(2)-C(3)	131.8(7)	C(1)-C(2)-C(7)	108.0(6)
C(3)-C(2)-C(7)	120.2(7)	C(2)-C(3)-C(4)	117.3(7)
C(3)-C(4)-C(5)	121.5(9)	C(4)-C(5)-C(6)	121.4(8)
C(5)-C(6)-C(7)	116.1(7)	N(1)-C(7)-C(2)	108.9(6)
N(1)-C(7)-C(6)	127.6(7)	C(2)-C(7)-C(6)	123.5(7)
N(1)-C(8)-C(9)	118.6(6)	C(8)-C(9)-C(10)	120.3(7)
C(9)-C(10)-C(11)	119.5(7)	C(10)-C(11)-C(12)	119.5(6)
N(1)-C(12)-C(1)	108.4(6)	N(1)-C(12)-C(11)	119.0(6)
C(1)-C(12)-C(11)	132.6(6)		

Symmetry transformation: a ($x - 1, y, z$); b ($x - .5, .5 - y, .5 + z$)

presence of excess SCN$^-$ in ethanolic medium afforded complex (**1**), in which the Cu(II) ion is reduced to Cu(I) while 2-Bzpy is oxidatively cyclized, in addition a green Cu(II) complex formulated as [Cu(2-Bzpy)$_2$(NCS)$_2$] was formed. The above reaction in aqueous solution afforded the green Cu(II) complex only. Similar reactions in the case of CuCN led only to the formation of 1:1 complex (2) regardless of the molar ratio of the components used, the medium of reaction, or the period of time over which the reaction mixture was allowed to stand. All the above Cu(I) complexes are stable against air oxidation and exhibit diamagnetic properties. Compound (**1**) is slightly soluble in acetone with a change in color to a pale yellow-green solution. The Cu(II) complex is soluble in DMF giving rise to non-conducting solutions.

Table 3 (*Continued*)

[Cu(CN)(2-benzoylpyridine)]$_x$ (2).			
(i) Coordiantion geometry about Cu atoms			
Cu(1)-N(1)	1.936(3)	Cu(1)-O(1)	2.324(2)
Cu(1)-N(2)	2.167(3)	Cu(1)-C(1a)	1.877(3)
N(1)-Cu(1)-O(1)	111.0(1)	N(1)-Cu(1)-N(2)	98.7(1)
O(1)-Cu(1)-N(2)	72.7(1)	N(1)-Cu(1)-C(1a)	137.4(1)
O(1)-Cu(1)-C(1a)	96.6(1)	N(2)-Cu(1)-C(1a)	120.6(1)
(ii) cyano group			
N(1)-C(1)	1.160(5)		
Cu(1)-N(1)-C(1)	175.7(3)	N(1)-C(1)-Cu(1b)	177.4(3)
(iii) 2-Benzoylpyridine ligand			
O(1)-C(7)	1.225(4)	N(2)-C(2)	1.326(4)
N(2)-C(6)	1.349(4)	C(2)-C(3)	1.392(6)
C(3)-C(4)	1.359(6)	C(4)-C(5)	1.386(5)
C(5)-C(6)	1.389(5)	C(6)-C(7)	1.503(4)
C(7)-C(8)	1.472(4)	C(8)-C(9)	1.401(5)
C(8)-C(13)	1.396(5)	C(9)-C(10)	1.373(5)
C(10)-C(11)	1.381(6)	C(11)-C(12)	1.375(6)
C(12)-C(13)	1.379(5)		
Cu(1)-O(1)-C(7)	114.4(2)	Cu(1)-N(2)-C(2)	122.8(3)
Cu(1)-N(2)-C(6)	117.8(2)	C(2)-N(2)-C(6)	117.6(3)
N(2)-C(2)-C(3)	123.1(4)	C(2)-C(3)-C(4)	119.3(3)
C(3)-C(4)-C(5)	118.8(4)	C(4)-C(5)-C(6)	118.9(3)
N(2)-C(6)-C(5)	122.4(3)	N(2)-C(6)-C(7)	114.3(3)
C(5)-C(6)-C(7)	123.2(3)	O(1)-C(7)-C(6)	117.9(3)
O(1)-C(7)-C(8)	120.6(3)	C(6)-C(7)-C(8)	121.5(3)
C(7)-C(8)-C(9)	122.6(3)	C(7)-C(8)-C(13)	118.3(3)
C(9)-C(8)-C(13)	118.9(3)	C(8)-C(9)-C(10)	119.9(4)
C(9)-C(10)-C(11)	120.2(4)	C(10)-C(11)-C(12)	120.7(3)
C(11)-C(12)-C(13)	119.6(4)	C(8)-C(13)-C(12)	120.5(3)

Symmetry transformations: a (x, $.5 - y$, $.5 + z$); b (x, $.5 - y$, $-.5 + z$).

Description of the Structures

[9-oxo-indolo[1,2-*a*]pyridinium]$^+$ [Cu(SCN)$_2$]$^-$ (1)

Figure 1 illustrates the essential structural features of complex (**1**) which consists of a packing of [9-oxo-indolo[1,2-*a*]pyridinium]$^+$ cations and polymeric [Cu(NCS)$_2$]$^-$ species; bond distances and angles are given in Table 3. 2-Benzoylpyridine is thus oxidatively cyclized at the nitrogen atom of the pyridine moiety and C(7) of the phenyl ring. The N(1)-C(7) bond length of 1.435(3) is longer than the two neighboring N(1)-C(8) and N(1)-C(12) bonds of 1.326(9) and 1.361(8)Å, respectively. The bond lengths and angles for this cation are very similar to corresponding values given for [9-oxo-indolo[1,2-*a*]pyridinium]$^+$ [CuI$_2$]$^-$.[21] The cyclization of 2-Bzpy manifests itself in substantial differences in bond lengths and bond angles for the cation as compared to corresponding values in similar 2-benzoylpyridine complexes. Thus, for example, the lengths of C(1)-C(12), C(2)-C(7), C(6)-C(7) and N(1)-C(8) bonds decrease from 1.500(8), 1.396(8), 1.402(9) and 1.341(8) Å in [Cu(2-Bzpy)Br]$_2$,[21] to 1.361(8), 1.380(10), 1.362(10) and 1.326(9) Å in the cation. The C-C bonds which are far from the cyclization positions either increase or are not affected, *e.g.* the C(6)-C(5) bond length increases from 1.359(12) Å, in

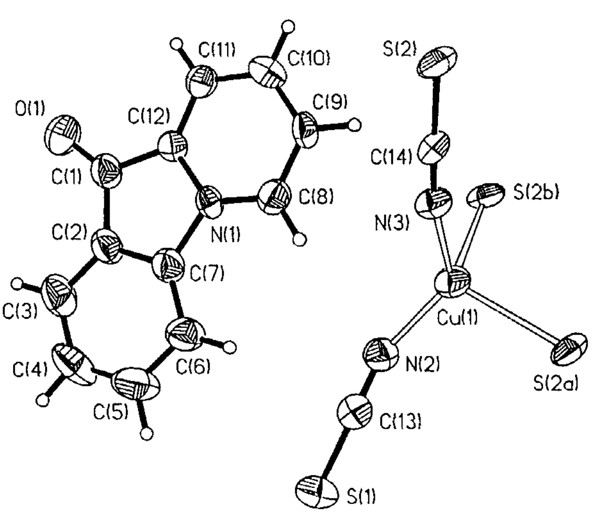

Figure 1 The coordination environment of the copper(I) atom and the cation in the complex [9-oxo-indolo(1,2-*a*]pyridinium]$^+$. $[Cu(SCN)_2]^-$, (**1**), along with the atom numbering scheme.

$[CuBr(2\text{-}Bzpy)]_2$ to 1.389 (12) Å in the cation. Similar trends are observed for bond angles, *e.g.*, the C(1)-C(12)-N(1) and N(1)-C(8)-C(9) angles decrease from 114.0(5) and 123.2(6) to 108.4(6) and 118.6(6)°, whereas the C(12)-N(1)-C(8) angle increases from 116.9(5)° to 123.1(6)°, in $[Cu(2\text{-}Bzpy)Br]_2$ and the cation, respectively. In the polymeric $[Cu(SCN)_2]^-$ species, each copper atom is coordinated by two nitrogen atoms [Cu—N_{av} = 1.947 Å] and two sulpher atoms from bridging thiocyanato groups at Cu—S distances of 2.373(2) and 2.471(2) Å. Figures 2 and 3 show the crystal structure of the complex and the coordination about the copper centers in the $[Cu(SCN)_2]^-$ species. It is clear from Figure 3 that one independent

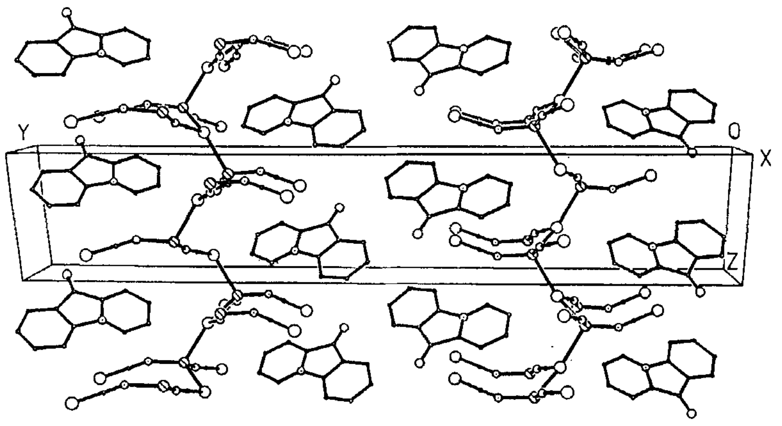

Figure 2 Perspective view of the crystal structure of complex (**1**) showing the packing of the molecules.

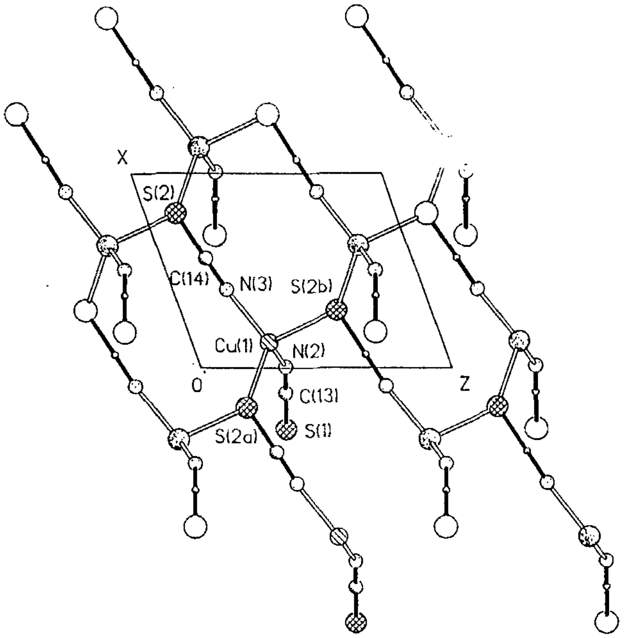

Figure 3 Perspective view showing the coordination environment of copper(I) and the construction of a puckered layer from the μ-(*N,S,S*) linkage of the $[Cu(SCN)_2]^-$ species.

thiocyanato group S(2)-C(14)-N(3) functions as a μ(*N,S,S*) bridging tridentate ligand, in which the sulphur atom links two different copper atoms, whereas the nitrogen atom binds a third copper center, giving rise to a puckered layer whose mean plane corresponds to y = 1/4 and 3/4. The other independent thiocyanate group acts as a monodentate ligand with N(2) linked to a copper atom; N-coordinated ligands of this type protrude on both sides of each layer and serve as partitions for adjacent heterocyclic cations arranged in rows running parallel to the c axis.

$[Cu(CN)(2\text{-benzoylpyridine})]_n$ (2)

The structure of [CuCN(2-benzoylpyridine)] (**2**) consists of zigzag CuCN chains in which each copper atom is in a distorted tetrahedral environment (Figure 4). Three coordination sites are occupied by the nitrogen atom of a bridging cyano group and a bidentate *N,O*-chelating 2-Bzpy ligand. The fourth coordination position at a distance of 1.877(3) Å is occupied by the carbon atom of another bridging cyano group. It is worth noting that Cu-N distance in cyano Cu(I) complexes is usually longer by about 0.1 Å than the Cu-C distance.[16] For the present structure the observed difference is 0.059 Å. The values given here, however, are similar to corresponding values reported for [CuCN(pyridazine)] and [CuCN(4-cyanopyridine)] [Cu-C av. = 1.912 and 1.907 Å, and Cu-N av. = 1.944 and 1.999 Å, for both complexes respectively].[20] The Cu-O distance in the five-membered ring [2.324(2) Å] is a little longer than distances reported for $[CuX(2\text{-Bzpy})]_2$;

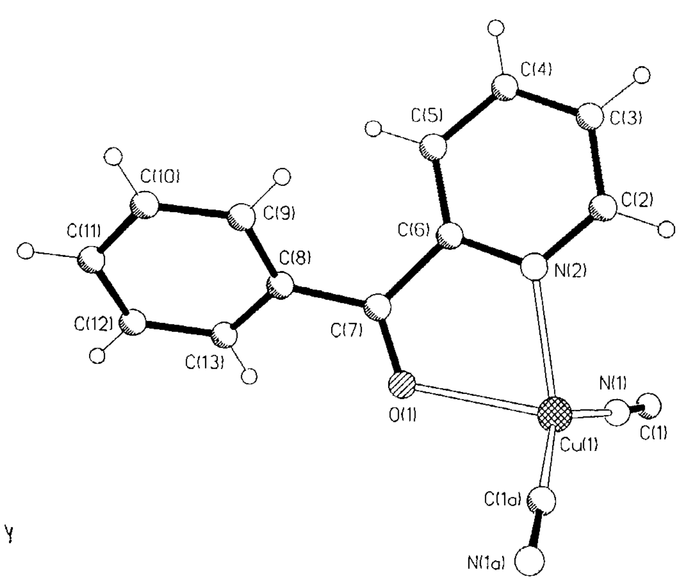

Figure 4 The coordination environment of the copper(I) atom in the complex [Cu(CN)(2-benzolpyridine)]$_n$ (**2**), along with the atom numbering scheme.

2.315(4) Å for X = Br,[21] and 2.467(3) Å, for X = I,[7] but significantly shorter than corresponding values in the structures of [CuX_2(2-Bzpy)$_2$]; 2.404(4) Å for X = Br and 2.467(3) Å for X = N_3.[8] In all these complexes 2-Bzpy acts as a chelating bidentate ligand. The Cu-N distance, however, is much greater than distances reported for the complexes above [av. = 2.003 Å].

The structure of the present complex may be compared with that of polymeric CuCN(4-cyanopyridine), which also contains zigzag CuCN chains where each copper atom links a nitrogen atom and a carbon atom of two cyano groups with a C-Cu-N angle of 117.3(1)°.[20] This complex, however, differs from complex (**2**) (Figure 5) in that the CuCN chains are connected by bridging bidentate ligands. Because of the long distance between the two nitrogen centers in the 4-cyano-pyridine ligand, the linkage is between two copper atoms in adjacent unit cells.[20]

Spectra

The electronic spectra of the solid Cu(I) complexes (**2**) and (**3**) exhibit a strong broad band around 350–500 nm. This band is undoubtedly due to a charge transfer transition[26] from Cu(I) d^{10} to an empty π^* orbital on 2-benzoylpyridine. The intense band around 340–480 nm 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 thiocyanate chain. The spectrum of Cu(II) complex (**4**) exhibits a strong absorption band around 420 nm, which is due to a LMCT transition from thiocyanate to copper. It shows an asymmetric *d-d* absorption band at 630 nm, which is consistent with a distorted octahedral Cu(II) environment.[27,28] This spectrum is very similar to that reported for the monomer [Cu(N_3)$_2$(2-

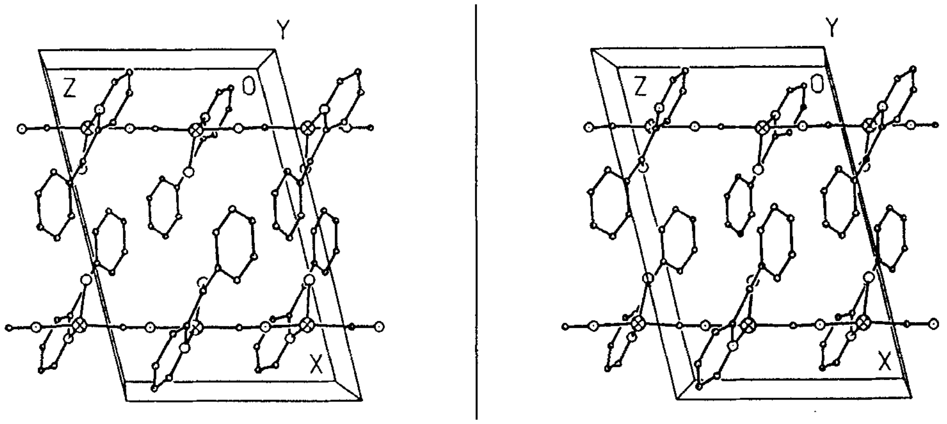

Figure 5 Perspective view of the crystal structure of complex (**2**).

Bzpy)$_2$],[8] suggesting a similar monomeric structure for complex (**4**) with N-thiocyanato groups.

With the exception of (**1**) all other complexes were studied using Raman spectroscopy. Complex (**1**), however, decomposed immediately in the laser beam. Selected vibrational bands are given in Table 4. The IR spectra of complexes (**1**) and (**3**) show two absorption bands at 2105, 2115 cm^{-1} and 2115, 2085 cm^{-1} respectively. Complex (**3**) shows a single feature at 2115 cm^{-1} in its Raman spectrum. X-ray analysis revealed the dimeric nature of [P(CH$_3$)(C$_6$H$_5$)$_2$)$_2$-CuSCN]$_2$.[29] This complex exhibits two cyanide stretching vibration bands at 2112 and 2080 cm^{-1}. Unfortunately, the ν_s(CS) and δ(NCS) bands are masked by ligand bands. Complex (2) exhibits a single cyanide stretching band at 2117 cm^{-1} (IR) and 2118 cm^{-1} (Raman). This band is very similar to that reported for 1:1 CuCN complexes of phenanthroline and bipyridine with polymeric structures.[30] Complex (**4**) shows only one band at 2095 (IR) (2085 (Raman)) in the region usually found for N-bonded thiocyanato groups.[31–33] This result supports our previous conclusion that the 1:2 Cu(II) complex attains an octahedral geometry with N-thiocyanato

Table 4 Some selected vibrational bands (cm^{-1})

2-Bzpy	(1)	(2)		(3)		(4)		
IR	IR	IR	Raman	IR	Raman	IR	Raman	Assignment
	2105 vs 2075 vs	2117 vs	2118 vs	2115 vs 2085 s	2115 vs	2095 vs	2085 vs	ν(CN)
1660 s	1734 vs	1658 vs	1637 vs	1643 s	1647 s	1646 s	1642	ν(C = O)
1580 ms	1600 s, br	1595 s	1597 s	1590 m	1597 ms	1595 s	1594 s	ring
1560 m	1570 m 1480 ms	1580 ms	1567 m	1565 m	1572 wm	1570 m	1565 m	ring
1440 m	1450 ms	1460 m 1450 m	1464 wm	1450*m	1467 m	1440 w	1440 m	ring
	1380 s							
995 s		1020 s	1004 vs	1013 m	1014 s	1020 ms	1025 m	ring
610 ms	650 m	630 s	630 wm	651 ms	639 m	640 w	650 s	ring

v = very, s = strong, m = medium, br = broad, (*) splitted band ligands. Complexes (**2**) to (**4**) show the ν(C = O) vibration band in the range 1658–1642 cm^{-1} in both IR and Raman spectra, as well as a substantial shift of the pyridine vibrations to higher wave numbers when compared with corresponding free ligand bands. Thus these three complexes contain bidentate N,O-chelating 2-Bzpy ligands. The IR spectrum of complex (**1**) differs from the spectra of the other complexes. It exhibits a strong absorption band due to (C = O) at 1734 cm^{-1} and the first two C-C, C-N (phenyl and pyridine moieties) at 1615 and 1580 cm^{-1}, which may be compared with the spectrum of fluoro-9-one.[34] When compared with the spectra of the other complexes, the bands at 700 and 770 cm^{-1} are absent in (**1**) and new bands are observed at 1380, 1360 and 1250 cm^{-1}.

The ESR spectrum of the solid crystalline powder of complex (**4**) is of the axial type; $g_{\perp} = 2.077$ and $g_{\parallel} = 2.262$, with no absorption at low or high fields. This spectrum is consistent with magnetically dilute Cu(II) environments,[35,36] and with the absence of any strong copper–copper interactions.

In CuX-ligand systems, copper–copper distances of less than 2.8 Å lead to emission at 550–628 nm, attributed to metal–metal interactions.[37] A ligand that permits MLCT and has aromatic ligands packed in parallel planes separated by 3.22–3.28 Å, results in emission spectra.[38–40] Accordingly, complexes (**1**) and (**2**) are expected to demonstrate visible evidence of emission. However, neither (**1**) nor (**2**) display emission at room temperature. This result is similar to that reported for CuI-quinaldate complexes.[41] The non-emitting character of these complexes may be affected by the electron withdrawing benzoyl group which alters the energy levels of the aromatic ring to make the excitation of greater energy or to make other radiationless decay mechanisms more efficient.

CONCLUSIONS

The results of the interactions of copper salts with 2-benzoylpyridine are summarized in Scheme 1. Thus, while CuI and CuSCN catalyze the intramolecular oxidative cyclization of 2-benzoylpyridine giving rise to the [9-oxo-indolo[1,2-*a*] pyridinium]$^+$ cation, CuCN yields only the 1:1 complex (**2**) irrespective of the molar ratio of the components, reaction medium or time of reaction. The cation, which is separated as compound (**1**) is also formed when Cu(II) ions, 2-Bzpy and excess SCN^- ion stand in ethanol for about 2 days, along with the $[Cu(SCN)_2(2\text{-}Bzpy)_2]$ complex (**4**). The above reaction in aqueous medium yields complex (**4**) only. It is questionable why CuCN, which is as stable as CuI or CuSCN, does not catalyse the oxidative cyclization of 2-Bzpy. Such intramolecular oxidative cyclizations of 2-benzoylpyridine in the presence of other metal ions are under current investigations.

Acknowledgement

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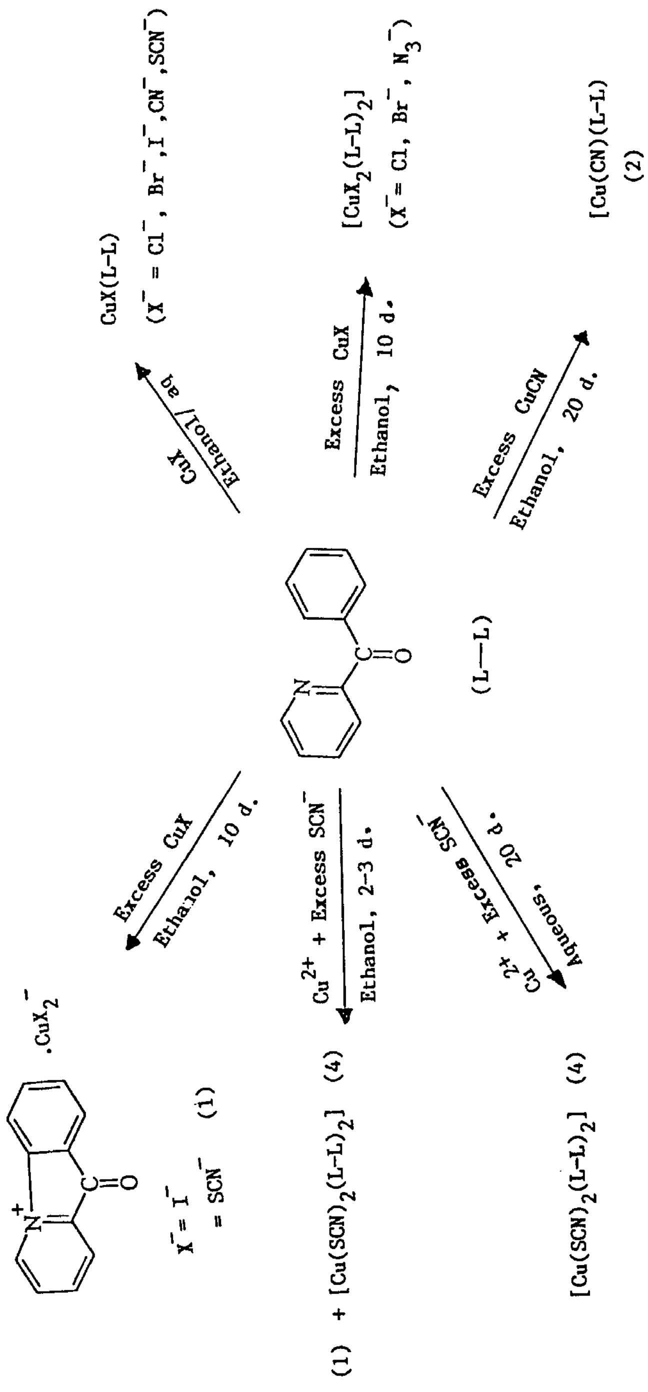
(L—L)
CuX / Ethanol / aq
CuX(L-L)
(X⁻ = Cl⁻, Br⁻, I⁻, CN⁻, SCN⁻)
Excess CuX
Ethanol, 10 d.
[CuX₂(L-L)₂]
(X⁻ = Cl, Br⁻, N₃⁻)
Excess CuCN
Ethanol, 20 d.
[Cu(CN)(L-L)
(2)
Excess CuX
Ethanol, 10 d.
.CuX₂⁻
X⁻ = I⁻
= SCN⁻
(1)
Cu²⁺ + Excess SCN⁻
Ethanol, 2-3 d.
(1) + [Cu(SCN)₂(L-L)₂] (4)
Cu²⁺ + Excess SCN⁻
Aqueous, 20 d.
[Cu(SCN)₂(L-L)₂] (4)

Scheme 1

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