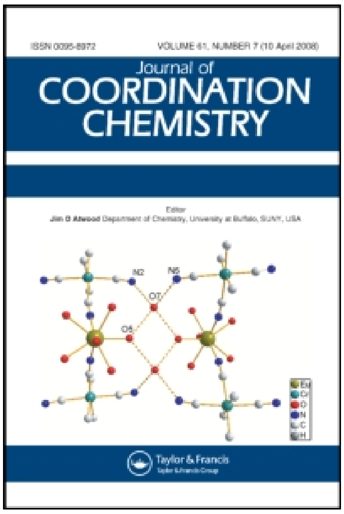

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2D POLYMERIC COPPER(I) COMPLEXES. SYNTHESIS AND CHARACTERIZATIONS OF $[Cu(pyza)_2X]_{\text{<i>n</i>}}$ (*X*CN, NCS AND N_3, AND pyzaPYRAZINECARBOXAMIDE) AND X-RAY CRYSTAL STRUCTURES OF THE CYANO AND THIOCYANATO COMPLEXES

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2D POLYMERIC COPPER(I) COMPLEXES. SYNTHESIS AND CHARACTERIZATIONS OF $[Cu(pyza)_2X]_n$ (X = CN, NCS AND N_3, AND pyza = PYRAZINECARBOXAMIDE) AND X-RAY CRYSTAL STRUCTURES OF THE CYANO AND THIOCYANATO COMPLEXES

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Three new copper(I) complexes of the type $Cu(pyza)_2X$, (X = CN(1), NCS(2) and N_3; pyza = pyrazinecarboxamide) have been prepared and characterized by spectroscopic and single crystal analyses showing 2D polymeric structures. The electronic, IR and Raman spectra of the cyano and thiocyanato complexes are measured and discussed. The structures of **1** and **2** are very similar featuring end-to-end bridging CN or NCS groups, forming chains connected *via* hydrogen bonds between the monodentate pyza of these complexes. Complex **2** displays solid state visible emission spectra when irradiated in the UV region at room temperature.

Keywords: Copper(I) cyano; Thiocyanato and azido complexes; Pyrazinecarboxamide complexes; Crystal structures; IR; Raman and emission spectra

The ability of pyrazine (pyz) and substituted pyrazines to act as bidentate ligands giving rise to oligomeric and polymeric metal complexes is well-established [1]. Such pyrazine-bridged metal complexes are not only of interest because of their magnetic properties, but also because these coordination polymers present potential utility in host-guest chemistry,

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*Corresponding author.

ion exchange, and heterogeneous catalysis [2–5]. However, the vast majority of studies have focused on copper(II)-pyz systems [6–8], and reports on copper(I) complexes of pyrazine and pyrazine derivatives are relatively few, including those of pyrazine itself [9–12], and methylpyrazine [13].

Recently, Moreno *et al.* [12] synthesized and structurally characterized $[Cu(pyz)Cl]_n$; we studied the corresponding 1 : 1 thiocyanato and azido complexes [14]. The structures of these three copper(I) complexes contain two dimensional layers formed by two perpendicular mono-dimensional zigzag chains; the first has pyrazine as a bridging ligand and the second contains bridging X anions. Now, we have isolated good quality crystals of copper(I) complexes of pyrazinecarboxamide (hereafter abbreviated as pyza) of the type $Cu(pyza)_2X$ for $X = CN$, NCS and N_3. In the present paper we report the synthesis and characterizations of these new complexes as elucidated by spectroscopic methods along with the structure determination of the cyano and thiocyanato complexes.

EXPERIMENTAL

Pyrazinecarboxamide was obtained from Aldrich and other chemicals are of analytical grade quality.

$[Cu(pyza)_2(CN)]_n$, (1)

This complex was prepared by mixing an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (2 mmol) and KCN in presence of L(+)-ascorbic acid. The precipitated CuCN was washed several times with water and then dissolved in excess concentrated aqueous KCN and filtered. To the filtrate, an ethanol solution of pyza (3 mmol) was added dropwise, and the clear mixture allowed to stand in open air for several days. The complex was deposited as shiny red fine crystals, which were filtered off. Good quality bright red crystals of the complex were obtained by allowing the clear colorless filtrate to stand over *ca.* 10 days. Yield, 80%. Anal. Calc. (%); C; 40.5; H, 3.1; N, 30.1; Cu, 19.5. Found: C, 40.2; H, 3.3; N, 29.7; Cu, 19.9.

$[Cu(pyza)_2(NCS)]_n$, (2)

This complex was prepared by a method similar to that given above for complex **1**, in which a saturated aqueous solution of NaNCS was added to a suspension of CuNCS until complete dissolution, followed by addition of pyza (in 2:1 molar ratio to copper) dissolved in ethanol. The final clear mixture was allowed to stand over several days until the complex deposited as red crystals suitable for X-ray diffraction. Yield, 60%. Anal. Calc. (%): C, 35.9; H, 2.8; N, 25.1; Cu, 17.3; S, 10.4. Found: C, 35.7; H, 2.8; N, 25.0; Cu, 17.7; S, 10.8.

$[Cu(pyza)_2(N_3)]_n$, (3)

This complex was prepared by mixing a suspension of CuN_3 with pyza (1:3 molar ratio of Cu:pyza) dissolved in ethanol, and boiling the mixture gently. The final mixture was allowed to stand over several days to produce fine needle-like crystals of the complex not suitable for X-ray analysis. Anal. Calc.: C, 34.1; H, 2.9; N,35.8; Cu, 18.1. Found: C, 33.9; H, 2.8; N, 35.4, Cu, 18.6.

Physical Measurements

The experimental procedures and instruments used for different physical measurements are as described previously [14].

X-ray Crystal Structure Analysis

A modified STOE four circle diffractometer was used for single crystal X-ray measurements. Data were collected at 298(2) K using graphite crystal-monochromatized Mo-Kα radiation ($\lambda = 0.71069$ Å) and the ω-scan technique. The intensities were corrected for Lorentz-polarization effects and for absorption. Crystallographic data and processing parameters are given in Table I. The structures were solved by direct methods and subsequent Fourier analyses (Full-matrix least-squares refinements based on F^2). Anisotropic displacement parameters were applied to non-hydrogen atoms. The hydrogen atoms were assigned with isotropic displacement factors and included in the final refinement cycle by use of geometrical restraints. Analytical expression of neutral atom scattering factors were incorporated. The program DIFBAS [15] and SHELXTL/PC program package [16] were used for computations. Selected bond distances and angles are given in Tables II and III.

TABLE I Crystallographic data and processing parameters

Compound	**1**	**2**
Empirical formula	$C_{11}H_{10}CuN_7O_2$	$C_{11}H_{10}CuN_7O_2S$
Formula mass	335.80	367.86
Color	red	orange-red
System, space group	Monoclinic, P2/*n*	Monoclinicic P2$_1$/*m*
a (Å)	4.970(2)	5.293(2)
b (Å)	5.360(2)	21.946(8)
c (Å)	24.519(9)	6.011(3)
β (°)	91.07(3)	96.21(3)
V (Å^3)	639.9(4)	694.1(5)
Z	2	2
μ(MoKα) (mm^{-1})	1.724	1.742
Normal transmission factors	1.000-0.257	1.000-0.332
D_{calc}/D_{obs} (Mg/m^3)	1.743/1.73(3)	1.760/1.75(3)
Approx. crystal size (mm)	0.40 × 0.12 × 0.10	0.50 × 0.12 × 0.06
θ range of data collection (°)	3.32-27.00	3.41-24.99
Reflections collected	1774	1698
Independ. refl./R_{int}	1396/0.0201	1244/0.0274
Parameters	105	122
Goodness-of-Fit on F^2	1.096	1.079
$R1/wR2$ [$I > 2\sigma(I)$]	0.0349/0.0877	0.0342/0.0797
Largest peak/hole (e/Å^3)	0.451/-0.464	0.249/-0.407

TABLE II Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [Å^2 × 10^3]. U(eq) is defined as one third of the trace of the orthogonalized O_{ij} tensor

	x	*y*	*z*	*u*(*eq*)
$[Cu(pyza)_2(CN)]_n$, (**1**)				
Cu(1)	7500	2241(1)	2500	36(1)
N(1)	7179(4)	-304(4)	3201(1)	36(1)
C(1)	5320(5)	151(4)	3579(1)	36(1)
C(2)	4973(4)	-1408(5)	4017(1)	34(1)
N(2)	6446(4)	-3486(4)	4085(1)	43(1)
C(3)	8314(5)	-3916(5)	3710(1)	45(1)
C(4)	8699(5)	-2348(4)	3271(1)	40(1)
C(5)	2850(5)	-782(5)	4432(1)	40(1)
O(1)	1640(4)	1229(4)	4406(1)	53(1)
N(3)	2409(6)	-2507(5)	4803(1)	54(1)
N(4)	3678(4)	3205(4)	2497(1)	33(1)
C(6)	3678(4)	3205(4)	2497(1)	33(1)
$[Cu(pyza)_2(NCS)]_n$, (**2**)				
Cu(1)	2493(1)	2500	7457(1)	35(1)
S(1)	-726(2)	2500	4468(2)	35(1)
C(6)	757(8)	2500	2206(7)	29(1)
N(5)	1653(8)	2500	535(6)	41(1)
N(1)	4675(4)	3274(1)	7065(4)	30(1)
C(1)	4364(6)	3621(1)	5240(5)	30(1)
C(2)	6059(5)	4078(1)	4846(5)	29(1)
N(2)	8130(5)	4193(1)	6254(5)	36(1)
C(3)	8424(7)	3851(2)	8089(6)	39(1)
C(4)	6715(6)	3404(2)	8510(5)	34(1)
C(5)	5546(6)	4461(1)	2782(6)	35(1)
O(1)	3494(4)	4420(1)	1624(4)	51(1)
N(3)	7394(6)	4831(2)	2326(5)	48(1)

TABLE III Selected bond lengths (Å) and angles (°) for (**1**)

Cu(1)—C(6A)	1.932(2)	Cu(1)—N(4)	1.932(2)
Cu(1)—N(1A)	2.201(2)	Cu(1)—N(1)	2.201(2)
N(1)—C(1)	1.331(3)	N(1)—C(4)	1.332(3)
C(1)—C(2)	1.375(3)	C(2)—N(2)	1.334(3)
C(2)—C(5)	1.502(3)	N(2)—C(3)	1.326(3)
C(3)—C(4)	1.380(4)	C(5)—O(1)	1.229(3)
C(5)—N(3)	1.316(3)	N(3)...O(1D)	2.876(3)
N(3)—H(5)	0.851(10)	H(5)...O(1D)	2.035(13)
C(6A)—Cu(1)—N(4)	148.95(13)	C(6A)—Cu(1)—N(1A)	94.98(8)
N(4)—Cu(1)—N(1A)	104.18(9)	C(6A)—Cu(1)—N(1)	104.18(9)
N(4)—Cu(1)—N(1)	94.98(8)	N(1A)—Cu(1)—N(1)	103.42(11)
O(1)—C(5)—N(3)	124.6(2)	O(1)—C(5)—C(2)	119.7(2)
N(3)—C(5)—C(2)	115.7(2)	C(6B)—N(4)—Cu(1)	164.44(7)
N(3)—H(5)...O(1D)	169(4)		

Symmetry codes: (A) $-x+3/2, y, -z+1/2$; (B) $-x+1/2, y, -z+1/2$; (D) $-x, -y, -z+1$.

TABLE IV Selected bond lengths (Å) and angles (°) for (**2**)

Cu(1)—N(1)	2.082(3)	Cu(1)—N(1A)	2.082(3)
Cu(1)—N(5B)	1.949(4)	Cu(1)—S(1)	2.338(2)
S(1)—C(6)	1.642(4)	C(6)—N(5)	1.156(6)
N(5)—Cu(1C)	1.949(4)	N(1)—C(1)	1.331(4)
N(1)—C(4)	1.341(4)	C(1)—C(2)	1.383(4)
C(2)—N(2)	1.335(4)	C(2)—C(5)	1.499(4)
N(2)—C(3)	1.329(4)	C(3)—C(4)	1.376(5)
C(5)—O(1)	1.228(4)	C(5)—N(3)	1.323(4)
N(3)—H(4)	0.851(10)	N(3)—H(5)	0.840(10)
N(3)—O(1D)	2.884(4)	H(4)—O(1D)	2.041(12)
N(5B)—Cu(1)—N(1)	107.09(10)	N(5B—Cu(1)—N(1A)	107.09(10)
N(1)—Cu(1)—N(1B)	109.36(14)	N(5B—Cu(1)—S(1)	120.47(13)
N(1)—Cu(1)—S(1)	106.27(7)	N(1A)—Cu(1)—S(1)	106.27(7)
C(6)—S(1)—Cu(1)	105.2(2)	N(5)—C(6)—S(1)	175.7(4)
C(6)—N(5)—Cu(1C)	169.1(4)	N(3)—H(4)—O(1D)	170.7(3)

Symmetry codes: (A) $x, -y+1/2, z$; (B) $x, y, z+1$; (C) $x, y, z-1$; (D) $-x+1, -y+1, -z$.

RESULTS AND DISCUSSION

The reactions between copper(I) cyanide, or copper(I) thiocyanate dissolved in excess Na*X* or K*X* with excess pyza resulted in the formation of crystalline complexes of the type $\mathrm{Cu(pyza)_2}X$, whereas mixing of copper(I) azide and excess pyza afforded an azido complex of the above formula. These diamagnetic complexes are colored and sufficiently stable against air oxidation. They are insoluble in common polar and non-polar solvents, but soluble in DMF or DMSO giving rise to non-conducting solutions. The solubility of these complexes in deuterated DMF, however, is not sufficient for NMR measurements.

Structures

Figure 1 illustrates the principle structural features along with the atom numbering scheme for complex **1**; Table II lists selected bond lengths and bond angles. In the asymmetric unit of **1** each copper atom is coordinated by three nitrogen atoms, two from pyza ligands, N(1)[Cu—N = 2.201(2) Å], and the third from a cyano bridge [Cu—N = 1.932(2) Å]. The fourth coordination site is occupied by a carbon of a second cyano bridge. Thus the cyano ligands bridge copper centers from both sides forming a zigzag chain along the short *c*-axis of the unit cell (Fig. 2); pyza behaves as a monodentate ligand. The Cu—C and Cu—N(CN) bond lengths are similar to corresponding values found in many polymeric copper(I) cyano complexes [17]. The copper atom, located at a special position 1/4, is in a distorted tetrahedral chromophore CuN_3C. Two pyza ligands from adjacent $(CuCN)_n$ chains form a nearly planar hydrogen bonded dimer, thus a 2D network structure is resulted.

The principle structure features of **2**, along with the atom labeling scheme are illustrated in Figure 3. In this structure each distorted tetrahedral copper

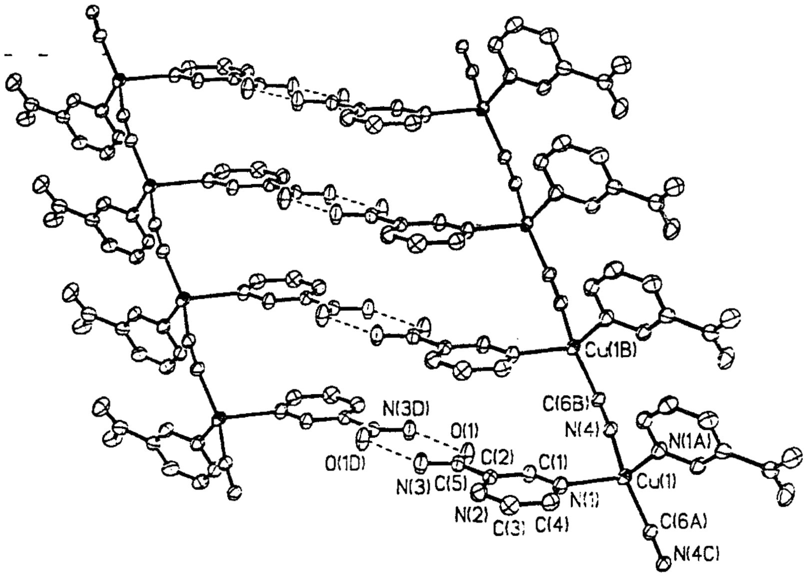

FIGURE 1 [Cu(pyza)$_2$(CN)] (**1**): A section of the layer structure together with the atom labeling scheme. Broken lines indicate hydrogen bonds. Carbon and nitrogen atoms of the disordered cyano ligands are occupying the same general crystallographic positions, with 50% occupancy, respectively.

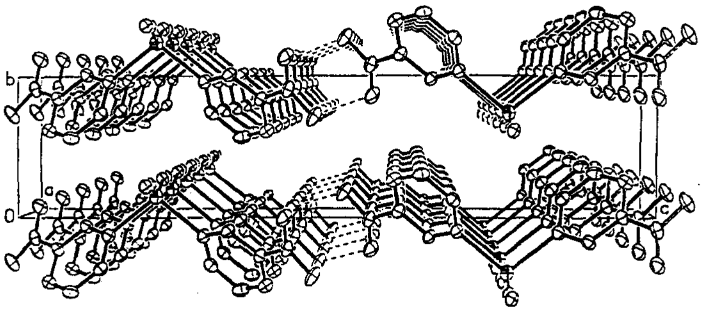

FIGURE 2 Packing view of [Cu(pyza)$_2$(CN)] (**1**): Chains of copper(I) tetrahedra are formed by bridging cyano ligands. These chains of polyhedra (oriented along the *a*-axis) are linked by N—H...O type hydrogen bonds along the *c*-axis of the unit cell.

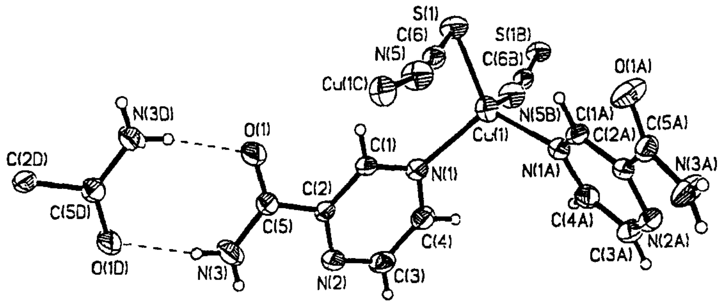

FIGURE 3 Perspective view with atom labelling scheme of [Cu(pyza)$_2$(NCS)] (**2**): Broken lines indicate hydrogen bonds.

center is coordinated by two pyza ligands *via* their nitrogen atoms, N(1) [Cu—N = 2.082(3) Å] and a nitrogen atom [Cu—N = 1.949(4) Å] and a sulfur atom [Cu—S = 2.338(2) Å] from two μ-1,3 thiocyanate bridges. The Cu—NCS—Cu zigzag chains are linked by dimeric hydrogen bonds of the type N—H...O between pyza ligands, giving rise to a 2D network structure (Fig. 4). The Cu—N and Cu—S bond distances match very well corresponding distances [1.886–2.016 Å and 2.318–2.662 Å, respectively] reported for polymeric four-coordinate copper(I) complexes containing μ-1,3 thiocyanato bridges [18].

Although both structures have very similar features, they are crystallographically different. In **2** the copper center and the thiocyanato ligand are located at mirror planes of the monoclinic space group P2$_1$/*m* (no. 11) occupying special positions $x, 1/4, z$. For **1** only the Cu(I) is located on a crystallographic diad of the monoclinic space group P2/*n* (no. 13) with

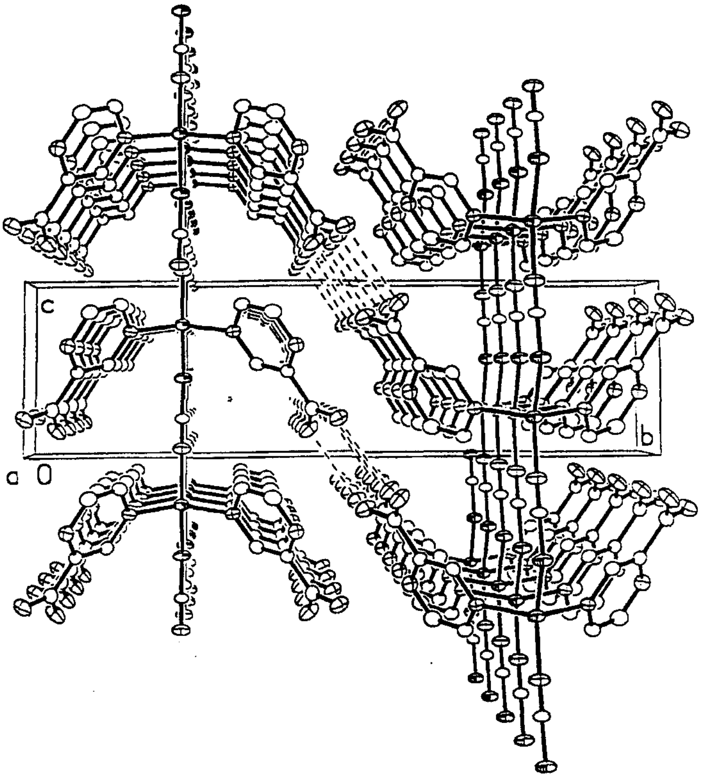

FIGURE 4 Cell plot of [Cu(pyza)$_2$(NCS)] (**2**): Chains of copper(I) tetrahedra are formed by μ(N,S)-bridging thiocyanato ligands. These chains of polyhedra (oriented along the *c*-axis) are linked by N—H...O type hydrogen bonds along the *b*-axis of the unit cell.

coordinates $3/4, y, 1/4$. Thus the C(6) and N(4) atoms of the disordered cyano ligands occupy the same general crystallographic positions with 50% occupancy, respectively.

The Cu—N(L) distances in **2** are shorter than in **1**, indicating a weaker copper-pyza interaction in the cyano complex. These distances in both complexes, however are significantly longer than corresponding Cu—N distances in copper(I) complexes containing terminal pyrazine ligands (Cu—N av. = 1.98 Å [10a]. This may be due to the substituent group in pyza and the dimeric hydrogen bond formation. It is noteworthy to compare the present structures with that of the polymeric [Cu(pyza)(N$_3$)]$_n$ described previously [19]. In the present complexes two coordination sites of the copper atom are occupied by nitrogen atoms from two pyza ligands, and in order to complete a tetrahedral geometry the other two sites should be occupied by a bridging bidentate ligand (CN or NCS). In the 1 : 1 azido complex only one coordination site of the copper atom is occupied by pyza and the other three positions of the tetrahedron must be occupied by one azido ligand, which should behave as a tridentate ligand as found by its structure determination. The azide complex exists as a 3D network consisting of sheets of $[Cu(N_3)]_n$ linked by pyza. Within the sheets each copper(I) is coordinated by three symmetry related azide ligands, thus the azido groups behave as μ-1,1,3 bridges leading to the formation of ten-membered Cu—NNN—CuN—Cu—NNN rings [19].

Vibrational Spectra

The IR and Raman spectra of free pyza exhibit the following absorption bands (cm^{-1}, v = very, m = medium, w = weak, s = strong): 3414, 3162 m, and 1610 s (IR) and 3429 vw, 3065 m (R) (υNH_2); 1714 s, (IR), 1672 wm (R) ($\upsilon C{=}O$); 1581 ms, 1054 ms, 619 wm, 412 s (IR); 1576 s, 1051 s, 616 w, 412 m (R) (pyrazine ring) [20]. The spectra of the complexes, on the other hand, show little influence on the NH_2 bands which appear around 3433 s, 3288 m, 1605 m (IR), 3405 vw, 3167 s (R), as well as the C=O bands; around 1708 s (IR), 1673 m (R). These results sugest that the $CONH_2$ group is not involved in bond formation. Vibrations related to the pyrazine moiety are slightly shifted to higher frequencies and appear at 1595 m, 1060 s, 635 ms, 455 ms (IR), 1585 s, 1059 s, 633 ms, 447 wm (R). These shifts indicate a monodentate pyza ligand.

The spectra of complex **1** show very strong and sharp bands at 2099 cm^{-1} (IR), 2093 vs (R) and 766 m (IR), 764 m (R) in addition to 451 m (IR) associated with the asymmetric, symmetric and bending vibration modes, respectively, of the thiocyanate group. Thiocyanate bridges of the μ-1,3 type are expected to exhibit two υ(CN) bands above and below 2100 cm^{-1} as well as two υ(CS) bands [21–25]. Accordingly, the results given above are not consistent with the crystal structure determination of **2**. The appearance of a single υ(CN) band, however, is not unusual and has been observed for many μ-1,3-thiocyanato complexes [26–28]. The IR spectrum of complex **1** exhibits a single medium to strong band at 2097 cm^{-1} due to υ(CN). The position of this band is a little lower frequency than those found for corresponding 1 : 1 CuCN complexes of phenanthroline and bipyridine with polymeric structures [29]. The IR spectrum of complex **3** exhibits a very strong band at 2039 cm^{-1} associated with the as (N_3) mode. The position of this band is very similar to that reported for polymeric $[Cu(pyrazine)N_3]_n$ [14] and $[(PPh_3)_2CuN_3]_2$ [28] containing a μ-1,3 azide bridge. The disappearance of any band in the region 1350–1270 cm^{-1} due to $v_s(N_3)$ supports the μ-1,3 bridging nature of the azide ligand. Other evidence comes from the appearance of a medium to strong band at 1338 cm^{-1} in the Raman spectrum of the complex.

Electronic and Emission Spectra

The electronic spectra of solid complexes exhibit a strong and broad band, 300–550 nm in the visible region due to $Cu^I \rightarrow L$ CT transition (Tab. I). These spectra are similar to those reported for copper(I) complexes of pyrazine [12, 14]. The emission spectra of the solid cyano and thiocyanato complexes at room temperature show that the thiocyanato complex displays an emission spectrum when irradiated in the UV region, consisting of a single slightly asymmetric band at 645 nm (Fig. 5), while the corresponding cyano complex does not flouresce.

CuXL (L = nitrogen donor ligands) systems with a copper–copper distance less than 2.8 Å display emission at 550–630 nm, attributed to metal–metal interactions [29]. A complex that permits MLCT and has aromatic ligands packed in parallel planes separated by 3.32–3.28 Å results in emission spectra [32–34]. Accordingly, complexes **1** and **2** are expected to demonstrate visible evidence of emission of the second type. That the cyano complex whose structure is very similar to the thiocyanato complex does not emit, could not be explained, particularly since several solid copper(I) cyano complexes of pyridine ligands display visible emission spectra when irradiated in the UV region [33, 34].

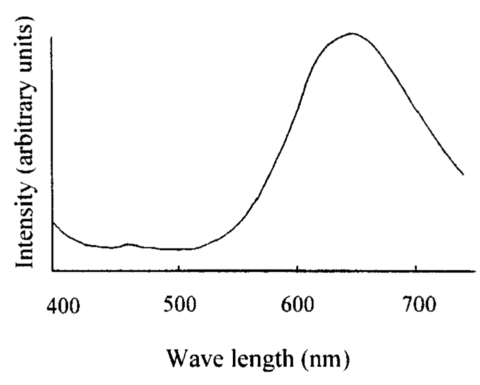

FIGURE 5 Emission spectrum of solid $[Cu(pyza)_2SCN]_n$ complex **2**, (excitation at λ_{max} = 365 nm).

Acknowledgements

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