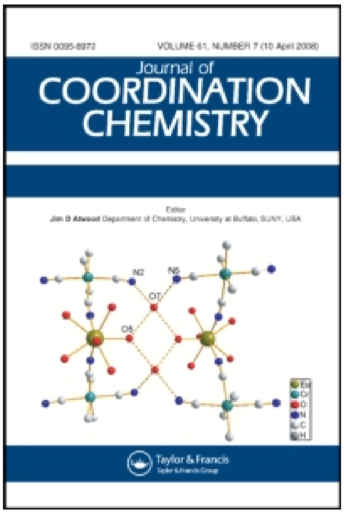

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STRUCTURE AND LUMINESCENCE PROPERTIES OF THE Cu(I) COMPLEXES $CuX(C_5H_5NS)_2$ (X = Cl, SCN)

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Two novel copper(I) halide adducts, $[CuSCN(C_5H_5NS)_2]_2$ (**1**) and $[CuCl(C_5H_5NS)_2]_2$ (**2**), were synthesized and the crystal structure of complex **2** was solved by direct methods. Crystal data: $C_{22}H_{20}N_6S_6Cu_2$; $M = 676.8$, monoclinic; space group *Cc*; $a = 15.020(4)$, $b = 9.9514(13)$, $c = 19.723(6)$ Å, $\beta = 112.178(10)°$; $V = 2729.9(11)$ Å^3; $Z = 4$; $D_c = 1.669$ mg m^{-3}; $R = 0.036$. The structure shows that in distorted tetrahedral Cu_2S_2 dimers, two bridged pyridine-2-thione groups are held in a weak, face-to-face π-stack. The luminescence behaviour of the complex has been studied.

Keywords: Pyridine-2-thione; copper(I); π-stacking; photoluminescence; X-ray structure

INTRODUCTION

Photochemistry of d^{10} metal complexes has been the subject of numerous studies for more than twenty years, but the rich luminescence spectroscopy of copper(I) complexes continues to attract attention because of their diverse structural motifs.[1–3] The copper(I) halide adducts $CuXL_2$ (X = halide, L = ligand) are particularly fascinating for the variety of structural formats which can be altered by varying the reagent stoichiometry,

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crystallization conditions and the reaction medium.[4] Heterocyclic thiones as ligands in copper(I) complexes have attracted considerable attention because of their relevance to biological systems,[5] but their photoluminescence properties have received little attention.[6] Herein we chose 2(1H)-pyridinethione (HL) as ligand to study the luminescense spectroscopy of copper(I), because its flexibility based on thionate tautomerism $[\text{-N=C(S}^-)\text{-}] \leftrightarrow [\text{-NH(C=S)-}]$ can afford various coordination modes; many of its copper(I) complexes have been synthesized, including $[Cu(C_5H_5NS)]_2Cl_2$,[7] $[Cu(C_5H_5NS)_2]_2X_2$ (X = Cl, Br),[4,7] $[Cu_6(C_5H_4NS)_6]$.[8] In this paper, we report the novel crystal structure of the dimer complexes $[CuX(C_5H_5NS)_2]_2$ (X = Cl, SCN) as well as study of their photoluminescence and electrochemical behaviour.

EXPERIMENTAL

All starting materials were commercially available and used without further purification. The solvent used was of AR grade.

Synthesis

CuSCN$(C_5H_5NS)_2$ (1)

A solution of pyridine-2-thione (0.222 g, 2 mmol) in 30 cm^3 of distilled water was added dropwise with stirring to a solution of HCl (0.06 cm^3, 12 M). Then was added, gradually, with stirring, solid CuSCN (0.061 g, 0.5 mmol). The mixture was stirred for 2 h, filtered. The filtrate was left to stand in air for several weeks, when a large quantity of orange crystals formed (yield 62%). The product was characterized by elemental analysis. Found: C, 38.61; H, 3.09; N, 12.35% Calc. for $C_{11}H_{10}N_3S_3Cu$: C, 38.4; H, 2.9; N, 12.13%.

CuCl$(C_5H_5NS)_2$ (2)

This was prepared analogously to **1** through replacing CuSCN with CuCl or $CuCl_2$. Found: C, 37.64; H, 3.44; N, 8.65%. Calc. for $C_{10}H_{10}N_2S_2Cu$: C, 38.4; H, 2.9; N, 8.72%.

Physical Measurements

Elemental analyses were performed on a Perkin-Elmer 240C instrument and electronic spectra were recorded on a Shimadzu UV 3100 spectrophotometer. Luminescence properties were measured on an Aminco Bowman Series 2 spectrophotometer. Cyclic voltammograms were recorded using a Princeton Applied Research model 273 potentiostat (EG&G Ltd.) at room temperature in DMF solution by employing three electrode system consisting of a platinum disc working electrode, a platinum wire auxiliary electrode and a silver–silver chloride reference electrode with 0.1 mol dm^{-3} tetraethylammonium perchlorate as the supporting electrolyte.

X-ray Structure Determination

Single crystal X-ray diffraction data were collected at ambient temperature (23°C) on an Enraf-Nonius CAD-4 diffractometer (monochromatic MoKα radiation, $\lambda = 0.71073$ Å) and were corrected both for absorption using semi-empirical methods and for extinction. Other numerical details of structure determination and refinement are given in Table I. The structure was solved by direct methods (SHELXL-93), hydrogen atoms being placed at their geometrically calculated positions. Final atomic coordinates and thermal parameters along with their estimated standard deviations are listed in Table II, and selected bond distances and angles are given in Table III.

TABLE I Crystal data and structure refinement for **1**

Empirical formula	$C_{22}H_{20}Cu_2N_6S_6$
Formula weight	676.78
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	*Cc*
Unit cell dimensions	$a = 15.020(4)$ Å
	$b = 9.9514(13)$ Å
	$c = 19.723(6)$ Å
	$\beta = 112.178(10)°$
V	2729.9(11) Å^3
Z	4
Calculated density	1.669 mg m^{-3}
Absorption coefficient	2.041 mm^{-1}
F(000)	1388
Crystal size	0.3 × 0.3 × 0.3 mm
θ range for data collection	2.23°–24.97°
Index ranges	$0 \leq h \leq 17, 0 \leq k \leq 11, -23 \leq l \leq 21$
Reflections collected/unique	2499/2499 [*R*(int) = 0.0000]
Radiation	graphite-monochromatized MoKα, $\lambda = 0.71073$ Å
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2499/2/325
Goodness-of-fit on F^2	1.071
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.036$, $wR_2 = 0.101$
R indices (all data)	$R_1 = 0.0481$, $wR_2 = 0.114$
Absolute structure parameter	−0.01(3)
Largest diff. peak and hole	0.664, −0.429 e · Å^{-3}

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1**. *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x/a	*y/b*	*z/c*	*U*(eq)
Cu(1A)	2472.6(9)	4279.8(15)	3414.2(7)	51.1(4)
S(1A)	2801(3)	2043(3)	3545(2)	50.3(9)
C(1A)	3928(9)	1824(11)	4179(6)	36(3)
N(2A)	4474(9)	2886(12)	4510(7)	51(3)
C(3A)	5396(9)	2835(15)	5043(8)	48(4)
C(4A)	5819(11)	1675(15)	5295(8)	48(3)
C(5A)	5279(9)	482(16)	4971(9)	53(4)
C(6A)	4321(10)	565(13)	4420(9)	49(4)
N(1AA)	3478(9)	5631(11)	4028(7)	57(3)
C(2AA)	4182(12)	6080(15)	4343(8)	51(4)
S(3AA)	5223(4)	6735(5)	4875(4)	87.8(14)
S(1B)	2365(2)	4846(3)	2157(2)	41.9(8)
C(1B)	2453(7)	6522(11)	2159(6)	32(2)
N(2B)	1653(8)	7291(10)	1830(7)	40(3)
C(3B)	1587(11)	8717(11)	1787(9)	59(4)
C(4B)	2445(14)	9342(12)	2094(11)	72(5)
C(5B)	1653(10)	8579(16)	3661(7)	60(4)
C(6B)	1687(10)	7331(14)	3634(8)	42(3)
S(1C)	929(2)	4833(4)	3329(2)	44.2(8)
C(1C)	911(10)	6631(12)	3326(7)	49(4)
N(2C)	25(7)	7273(10)	3005(6)	57(3)
C(3C)	41(12)	8718(17)	3029(9)	57(4)
C(4C)	840(11)	9397(14)	3360(9)	58(4)
C(5C)	3336(12)	8611(16)	2477(11)	62(4)
C(6C)	3308(11)	7305(17)	2498(6)	69(5)
Cu(1D)	803.2(8)	4281(2)	2063.3(7)	50.2(4)
S(1D)	484(3)	2056(4)	1938(2)	48.9(9)
C(1D)	−645(10)	1842(13)	1267(7)	43(3)
N(2D)	−1180(7)	2911(9)	960(5)	35(2)
C(3D)	−2062(10)	2818(14)	455(8)	52(3)
C(4D)	−2442(12)	1565(16)	250(9)	58(4)
C(5D)	−1918(12)	467(15)	545(9)	60(4)
C(6D)	−1087(12)	584(11)	1047(9)	50(4)
N(1AE)	−138(9)	5596(11)	1447(5)	49(3)
C(2AE)	−881(10)	6155(14)	1109(8)	44(3)
S(3AE)	−1936(4)	6740(5)	687(4)	106(2)

RESULTS AND DISCUSSION

Since the single crystal of the complex **2** was not stable, only the structure of the complex **1** was characterized, Figure 1 depicts the structure of CuSCN(HL)$_2$, which is different from [Cu(C$_5$H$_5$NS)]$_2$Cl$_2$,[7] the dimer existing as cation. Each copper(I) atom is bonded to a sulfur atom of one terminal and two bridging pyridine-2-thione ligands. The ligands are all in the thione tautomeric form, and two terminal ligands are similar. The average C–S–Cu angles are close to 106.5°, in agreement with those (104°–115°) reported for [Cu(C$_5$H$_4$NSH)$_3$]NO$_3$[9] and [Cu(etu)$_3$][SO$_4$]$_2$

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

Cu(1A)-N(1AA)	2.044(11)	N(2B)-C(3B)	1.42(2)
Cu(1A)-S(1A)	2.273(4)	S(1C)-C(1C)	1.789(13)
Cu(1A)-S(1C)	2.326(4)	S(1C)-Cu(1D)	2.492(5)
Cu(1A)-S(1B)	2.487(4)	C(1C)-N(2C)	1.39(2)
Cu(1A)-Cu(1D)	2.8883(11)	N(2C)-C(3C)	1.44(2)
S(1A)-C(1A)	1.697(13)	Cu(1D)-N(1AE)	1.972(12)
C(1A)-N(2A)	1.35(2)	Cu(1D)-S(1D)	2.259(4)
N(2A)-C(3A)	1.39(2)	S(1D)-C(1D)	1.725(13)
S(1B)-C(1B)	1.673(12)	C(1D)-N(2D)	1.33(2)
S(1B)-Cu(1D)	2.351(4)	N(2D)-C(3D)	1.33(2)
C(1B)-N(2B)	1.365(14)		
N(1AA)-Cu(1A)-S(1A)	119.8(4)	C(1C)-S(1C)-Cu(1A)	104.5(5)
N(1AA)-Cu(1A)-S(1C)	112.4(4)	C(1C)-S(1C)-Cu(1D)	102.8(4)
S(1A)-Cu(1A)-S(1C)	114.07(15)	Cu(1A)-S(1C)-Cu(1D)	73.58(12)
N(1AA)-Cu(1A)-S(1B)	101.4(4)	N(1AE)-Cu(1D)-S(1D)	120.6(3)
S(1A)-Cu(1A)-S(1B)	105.34(15)	N(1AE)-Cu(1D)-S(1B)	110.6(4)
S(1C)-Cu(1A)-S(1B)	100.73(15)	S(1D)-Cu(1D)-S(1B)	114.02(14)
N(1AA)-Cu(1A)-Cu(1D)	137.4(4)	N(1AE)-Cu(1D)-S(1C)	103.7(3)
S(1A)-Cu(1A)-Cu(1D)	100.42(12)	S(1D)-Cu(1D)-S(1C)	105.01(15)
S(1C)-Cu(1A)-Cu(1D)	55.84(11)	S(1B)-Cu(1D)-S(1C)	99.90(14)
S(1B)-Cu(1A)-Cu(1D)	51.21(9)	N(1AE)-Cu(1D)-Cu(1A)	137.7(3)
C(1A)-S(1A)-Cu(1A)	108.8(4)	S(1D)-Cu(1D)-Cu(1A)	100.10(12)
C(2AA)-N(1AA)-Cu(1A)	160.2(13)	S(1B)-Cu(1D)-Cu(1A)	55.55(11)
C(1B)-S(1B)-Cu(1D)	108.3(4)	S(1C)-Cu(1D)-Cu(1A)	50.58(9)
C(1B)-S(1B)-Cu(1A)	104.4(4)	C(1D)-S(1D)-Cu(1D)	108.2(5)
Cu(1D)-S(1B)-Cu(1A)	73.24(12)	C(2AE)-N(1AE)-Cu(1D)	161.9(11)

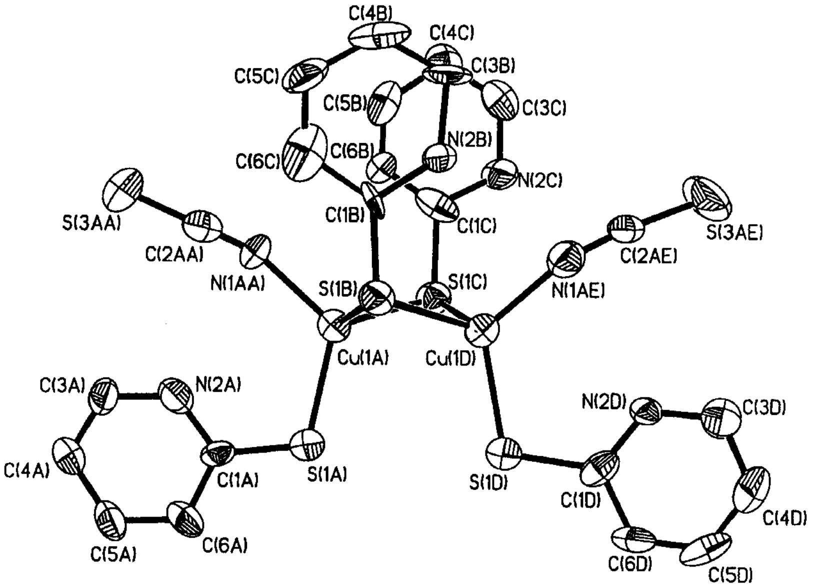

FIGURE 1 The molecular structure of the crystallographically unique unit.

(etu = ethylenethiourea).[10] The geometry of copper(I) shows a distorted tetrahedron [N–S–Cu 100°–120°]. Cu–S distances (2.25–2.49 Å) fall within the range previously reported for copper(I) complexes.[5–10] The S atoms of pyridine-2-thione molecules bridge two Cu atoms forming a distorted tetrahedron with two short Cu–S and two long Cu–S distances, different to the planar Cu_2S_2 core of other dimeric species $[CuCl(HL)_2]_2$, $[CuI(C_5H_5NS)(P\text{–}Tol_3P)]_2$ (Tol_3P: tri-p-tolylphosphine).[5,7] Each bridging sulfur atom exhibits one long and one short Cu–S bonds. The distance between the two copper atoms is 2.888 Å, close to the sum of the ionic radii (1.92 Å).[11] The values of 1.97–2.04 Å for Cu–N (thiocyanate) distances are close to those found for other Cu(NCS) complexes (1.92(1)–2.01(3) Å).[12] In addition, there are weak C–H···S bonds between S atoms from thiocyanate groups and carbons from the pyridyl rings among the units as shown in Figure 2 (H···S: 2.920, 2.925, 2.944 Å).[13] A striking feature is the nearly parallel orientation (dihedral angle 4.8°) of the two bridged pyridine-2-thione groups, which are held in close proximity of (3.70 Å); this separation is consistent with a face-to-face π-stacking interaction. In contrast to the distance of 3.219 Å found in the one-dimensional polymer $[Cu(C_9H_7NS)_2]ClO_4$,[14] it contributes to the stabilization of this crystalline form. C–S bond distances average 1.721 Å, somewhat shorter than those of 1.764 and 1.755 Å found in $[Cu_6(C_5H_4NS)_6]$ and $[Cu_6(C_9H_6NS)_6]$ (C_9H_6NSH = quioline-2-thione).[14,15] These relatively short C–S bond distances suggest aromatic C=S bond character and similar C=S bond distances have previously been reported. However, the S(1C)–C(1C) bond distance of 1.78 Å shows that it is a S–C single bond.

Electronic absorption spectra for complexes **1** and **2** in dichloromethane are characterized by absorption bands at *ca* 294 and 378 nm. The high-energy absorption band at *ca* 294 nm is likely to arise from the pyridyl ring and the absorption band at *ca* 378 nm from the C=S chromophore. Due to charge-transfer absorption, the complexes are bright orange,[16] but we do not observe typical MLCT (metal-to-ligand charge transfer) bands in **1** and **2**, and maybe they are dissociated in solution unlike $[Cu(C_5H_5NS)]_2Cl_2$ and $[Cu(C_5H_5NS)_2]_2Cl_2$ because CuSCN and CuCl precipitation can be observed during several hours.

Excitation of solid samples of **1** and **2** produces intense luminescence. Solid samples of **1** and **2** display emission with $\lambda_{max} = 590$ and 589 nm at 298 K, respectively. The emissions are higher in energy than those of other copper(I) complexes with sulfur donor ligands such as $[Cu_6(SNBu^t)_6]$ and $[Cu_6(mtc)_6]$ at 755 and 727 nm, respectively (mtc = di-*n*-propylmonothiocarbamate).[6,8] Because there is no significant shift in emission energy for the

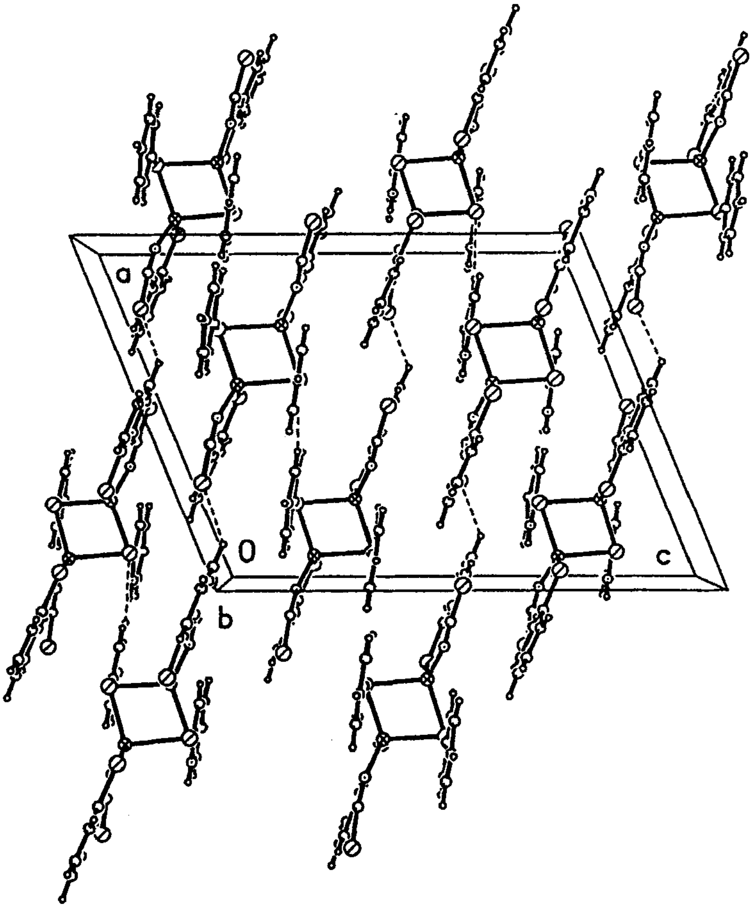

FIGURE 2 Packing diagram viewed down the *b* axis.

related [Cu(HL)$_2$X] (X = Cl, SCN) complexes, the emission is neither MLCT nor LMCT (ligand-to-metal charge transfer) in nature. We tentatively assign it to intraligand fluorescence since a similar emission with $\lambda_{max} = 580$ nm is also observed for the free ligand.[17]

Electrochemical behaviour of the Cu^{I}/Cu^{II} couple for the binuclear complexes was investigated by cyclic voltammetry in DMF. According to the peak separation (ΔE_p) and current ratio (i_a/i_c), the electrochemical behaviour is considered to be *quasi*-reversible,[18] two oxidative waves and two reductive waves ($E_{1/2} = 0.455$, 1.01 V) being found for [CuCl(HL)$_2$]$_2$.[19] However, there are three oxidative waves and three reductive waves

$E_{1/2} = 0.385, 0.663, 1.10$ V) for $[CuSCN(HL)_2]_2$. It is clear that both electrochemical waves found for Cu^ICu^{II} are due to oxidative of Cu^I to Cu^{II}, and the $E_a = 0.69$ V, $E_c = 0.635$ V ($E_{1/2} = 0.663$ V) wave is assigned to the oxidation and reduction of $SCN^-/(SCN)_2$. All $E_{1/2}$ values for the mercaptide complexes are in the range of about +0.3 to +1.1 V (*versus* SCE), being among the highest values reported for the Cu^I/Cu^{II} couple. This is in agreement with previous observations that coordination to mercaptide sulfur produces high values for the Cu^I/Cu^{II} couple.[19]

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Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

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