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2-(2′-Thienyl)pyridine versus 2,2′-bipyridyl binding mode in copper(II) complexes

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Abstract

2-(2′-Thienyl)pyridine (pyth) and its acetylated derivative (apyth) (**III**) react with copper chloride to give compounds of formulae [Cu(pyth)$_2$Cl$_2$] (**I**) and [Cu(apyth)$_2$Cl$_2$] (**II**). The crystal structures of **I**, **II** and **III** have been determined by X-ray methods. In both copper complexes the metal atom is surrounded by two N atoms (Cu–N, 2.025(5) Å in **I** and 2.021(2) Å in **II**) from two ligands molecules and two Cl atoms (2.265(2) Å in **I** and 2.264(1) Å in **II**) in a typical square planar environment. Two thiophene S atoms (Cu–S, 2.968(2) Å in **I** and 2.904(1) Å in **II**) complete the coordination sphere, making the complex elongated octahedral. By contrast, in all complexes of general formula [Cu(bipy)$_2$X]X, (bipy = 2,2′-bipyridyl) the coordination environment around copper is quasi-trigonal bipyramidal, the pyridine rings in each bidentate ligand being almost coplanar, and one anion does not participate to coordinative bonding.

Introduction

The various modes of thiophene coordination in transition metal complexes have been reviewed in a recent report [1]. They include simple η^1, S-, η^4- or η^5-bonding or more complicated bridging situations, derived from combinations of these modes. In contrast to alkyl sulfides or tetrahydrothiophene, thiophene is a very weak sulfur donor ligand and few S-bound thiophene complexes are known. In all these compounds the metal lies out of the thiophene plane in such a way that the sulfur has a trigonal pyramidal environment.

Due to this structural demand of the thiophene moiety, 2,2′-pyridylthiophene (pyth) is not able to act as a planar bidentate ligand in the same manner as 2,2′-bipyridyl (bipy), and only three pyth complexes have been structurally characterized [2–4]. These are rhodium(III), platinum(II) and palladium(II) derivatives of formula [Rh(bipy)(pyth-H)$_2$]Cl [2], [Pt(pyth)(pyth-H)I] [3] and [Pd(pyth)$_2$Br$_2$] [4], respectively. In the first two compounds at least one 2,2′-pyridylthiophene molecule has undergone metallation at the 3-carbon. In the latter, the metal is surrounded by two halogen atoms and two nitrogen atoms from the pyth ligands in a square planar environment; two long M–S apical interactions complete coordination to elongated octahedral.

In this paper we describe the crystal structure of two copper complexes obtained by reaction of copper(II) chloride with pyth and its 5-acetyl derivative (apyth), namely [Cu(pyth)$_2$Cl$_2$] (**I**) and [Cu(apyth)$_2$Cl$_2$] (**II**), as well as that of apyth (**III**). Furthermore, the peculiar binding mode of 2,2′-pyridylthiophene and of its acetyl derivative is compared with that of 2,2′-bipyridyl in copper(II) complexes [5–9], particularly in [Cu(bipy)$_2$Cl]Cl [8].

Experimental

General procedures and materials

Copper(II) chloride and 2,2′-pyridylthiophene (pyth) are commercially available and were used as received; 5-acetyl-2,2′-pyridylthiophene (apyth) was prepared by Friedel-Crafts acylation of pyth [10]. Analytical grade solvents were used. IR spectra were collected on a Nicolet 5PC FT spectrometer; elemental analyses were performed on a Carlo Erba CHNS-O EA1108 equipment.

Preparations

A solution of pyth in methanol/dichloromethane (0.5 g, 3.1 mmol in 30 ml) was added to a methanol solution of copper dichloride hydrate (0.26 g, 1.55 mmol in 40 ml) and the homogeneous mixture was refluxed for 2 h. By slow evaporation of the solvent at room tem-

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perature, it gave well-shaped green prismatic crystals (suitable for X-ray analysis) of the complex [Cu(pyth)$_2$Cl$_2$] (I) in almost quantitative yield. *Anal.* Calc.: C, 48.84; H, 3.35; N, 5.18. Found: C, 48.64; H, 3.28; N, 5.40%. FT-IR bands, cm^{-1}: 1601s, 1563s, 1531ms, 1478vs, 1439m, 1422m, 848m, 764s, 709ms. FT-IR bands of pyth (for comparison), cm^{-1}: 1581s, 1562s, 1534m, 1465vs, 1435s, 1421s, 1156m, 992s, 854s, 779vs, 710vs.

The same reaction takes place between apyth and copper dichloride under the same conditions affording very similar green crystals of [Cu(apyth)$_2$Cl$_2$] (II). *Anal.* Calc.: C, 47.32; H, 3.09; N, 6.13. Found: C, 47.39; H, 3.11; N, 6.50%. FT-IR bands, cm^{-1}: 1659vs 1595m, 1564mw, 1538m, 1451s, 1436s, 1276vs, 851m, 775s. FT-IR bands of apyth (for comparison), cm^{-1}: 1654vs, 1585ms, 1565m, 1535mw, 1447ms, 1431s, 1281vs, 994ms, 817s, 782vs.

X-ray data collection and structure refinement

The data sets for the three compounds were collected at room temperature on a Siemens AED single-crystal diffractometer equipped with an IBM PS2/30 personal computer using Cu Kα radiation. Information on the crystal system and orientation matrix was obtained via an automatic indexing program. Systematic absences agreed with the centric space groups $P2_1/c$ for **I** and $P2_1/n$ for **II**, and with the acentric space group $P2_12_12_1$ for **III**. The crystal data and experimental conditions for data collection are summarized in Table 1. The orthorhombic cell of compound **III** contains eight molecules so that the asymmetric unit comprises two symmetry independent molecules. For each of the compounds the intensity of one standard reflection, monitored at 50-reflection intervals, showed only random fluctuations. The intensities were processed with the peak profile procedure following a local modification of the Lehmann and Larsen method [11] and the data were corrected for Lorentz and polarization effects. For **I** and **II** a correction for absorption was also applied after isotropic refinement by using the empirical method of Walker and Stuart [12].

For both **I** and **II** the positions of the copper and chlorine atoms were determined from a Patterson map and the rest of the non-hydrogen atoms were found on subsequent difference maps. The structure of **III** was solved by the direct method automatic multisolution routine of SHELX 86 [13]. The chosen solution provided an E-map which revealed the position of most non-hydrogen atoms, the remainder of which were located in a subsequent difference map. The three structures were refined to convergence by full-matrix least-squares based upon F. For **I** and **II** all non-hydrogen atoms were allowed to vibrate anisotropically, while in **III** anisotropic thermal parameters were assigned only to atoms heavier than carbon in order to reduce the number of variable parameters (due to the low reflection power of the crystal there is a paucity of observed reflections). All the hydrogen atoms were located in an inner-data difference map and included in the refinement with individual isotropic parameters except those belonging to the methyl groups in **III**, which were added at idealized positions and allowed to ride on associated carbon atoms with their isotropic thermal parameters constrained to be equivalent. As compound **III** crystallizes in a space group ($P2_12_12_1$) which is free of reflective elements, at the end of the refinement the absolute structure [14] (and hence the structural chirality [15]) was determined by changing the sign of the y coordinate. The inverted model resulted in R and R_w values of 0.0574 and 0.0718, respectively, so indicating that the original model ($R=0.0502$, $R_w=0.0635$) was correct. In the absence of elements of chirality in the molecule, the chirality of the crystal structure has to be due to the spatial arrangement of the molecules. In all cases the function minimized was $\Sigma w(|F_o|-|F_c|)^2$, where a weighting scheme of the type $w=k/[\sigma^2(F_o)+gF_o^2]$ was used during the final stages of refinement. No peaks of chemical significance were present in the final difference map of the three compounds.

Atomic scattering factors for neutral atoms were used and anomalous dispersion terms were included for all non-hydrogen atoms [16]. All calculations were performed on a GOULD 6040 computer using the SHELX 76 [17], SHELX 86 [13], ABSORB [18], PARST [19] and ORTEP [20] program packages. The final atomic parameters for the three compounds are given in Tables 2–4.

Results and discussion

2-(2′-Thienyl)pyridine (pyth) and its acetylated derivative (apyth) (III) react with copper(II) chloride to give compounds of formulae [Cu(pyth)$_2$Cl$_2$] (I) and [Cu(apyth)$_2$Cl$_2$] (II). Under the same conditions, other first-row transition metal chlorides do not react with these ligands. The IR patterns of the two complexes, in the 600–1700 cm^{-1} range, show no substantial differences when compared with those of the corresponding ligands; most bands appear nearly at the same frequency or exhibit small shifts of few wavenumbers towards lower or higher frequency. For instance in **II** the carbonyl stretching and the aromatic out-of-plane bending bands are blue-shifted by 4 and 34 cm^{-1}, respectively, whereas several other strong and medium bands are red-shifted (the maximum being about -10 cm^{-1}).

ORTEP diagrams and atomic labelling schemes for the two complexes are given in Figs. 1 and 2, where the primed atoms are related to the unprimed ones

TABLE 1. Crystallographic data, collection data and refinement procedures

Compound	I	II	III
Formula	$C_{18}H_{14}CuCl_2N_2S_2$	$C_{22}H_{18}CuCl_2N_2O_2S_2$	$C_{11}H_9NOS$
Molecular weight	456.89	540.97	203.26
Crystal size (mm)	0.26×0.44×0.46	0.26×0.67×0.68	0.36×0.67×0.60
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P2_12_12_1$
a (Å)	6.228(1)	7.477(2)	22.642(7)
b (Å)	16.399(4)	13.871(4)	15.319(5)
c (Å)	9.074(2)	10.997(3)	5.712(2)
α (°)	90	90	90
β (°)	100.19(1)	87.16(1)	90
γ (°)	90	90	90
V (Å^3)	912.1(3)	1139.1(6)	1981(1)
Z	2	2	8
D_{calc} (g cm^{-3})	1.664	1.577	1.363
μ (cm^{-1})	65.8	54.3	25.5
$F(000)$	462	550	848
θ Range (°)	3–70	3–70	3–68
No. reflections measured	1967	2380	2103
No. unique reflections	1739	2167	2103
Condition for observed reflections	$I>2\sigma(I)$	$I>3\sigma(I)$	$I>2\sigma(I)$
No. observed reflections	1342	1977	1500
Parameters refined	143	178	201
Max. height in final ΔF map	0.76	0.73	0.27
R, R_w	0.0623, 0.0827	0.0659, 0.0979	0.0502, 0.0635

Features common to the three determinations include the use of Cu Kα radiation (λ=1.54178 Å) and the θ–2θ scan technique.

TABLE 2. Atomic coordinates (×10^4) and equivalent isotropic thermal parameters (Å^2) (one third trace of the diagonalized matrix) with e.s.d.s in parentheses for **I**

Atom	x/a	y/b	z/c	B_{eq}
Cu	0	0	0	3.22(3)
Cl	2177(3)	968(1)	1268(2)	4.41(4)
S	3447(3)	−1224(1)	1038(2)	4.49(4)
N	−666(8)	−422(3)	1967(5)	3.67(12)
C1	−2031(13)	46(4)	2582(7)	4.65(18)
C2	−2801(13)	−164(5)	3849(8)	5.27(21)
C3	−2164(13)	−903(5)	4526(7)	5.40(21)
C4	−801(13)	−1393(4)	3896(7)	4.86(19)
C5	−9(10)	−1146(4)	2620(6)	3.70(14)
C6	1563(10)	−1636(3)	2024(6)	3.61(14)
C7	1931(13)	−2459(4)	2218(7)	4.62(18)
C8	3681(13)	−2744(4)	1559(8)	5.26(21)
C9	4638(12)	−2149(4)	890(8)	4.84(19)

TABLE 3. Atomic coordinates (×10^4) and equivalent isotropic thermal parameters (Å^2) (one third trace of the diagonalized matrix) with e.s.d.s in parentheses for **II**

Atom	x/a	y/b	z/c	B_{eq}
Cu	0	0	0	2.63(2)
S	−1674(1)	780(1)	2227(1)	3.27(2)
Cl	1744(1)	−865(1)	1225(1)	3.65(2)
O	−4631(4)	−200(2)	3517(3)	5.32(9)
N	1454(3)	1187(2)	354(2)	2.89(6)
C1	3107(4)	1245(3)	−196(3)	3.44(8)
C2	4149(5)	2057(3)	−153(3)	3.90(9)
C3	3470(5)	2854(3)	451(4)	3.99(9)
C4	1804(4)	2807(3)	1050(3)	3.71(8)
C5	821(4)	1952(2)	994(3)	3.01(7)
C6	−935(4)	1868(2)	1650(3)	3.02(7)
C7	−2118(5)	2605(2)	1928(3)	3.36(7)
C8	−3688(5)	2261(2)	2560(3)	3.33(7)
C9	−3656(4)	1291(2)	2772(3)	3.05(7)
C10	−4991(5)	654(2)	3378(3)	3.47(8)
C11	−6766(5)	1070(4)	3781(4)	4.71(11)

by the symmetry operation $-x$, $-y$, $-z$. In both cases the crystallographic unit constitutes half a copper atom, one ligand molecule and one chlorine atom. In fact, since both space groups $P2_1/c$ and $P2_1/n$ have four general positions, the two molecules per unit cell are constrained at special positions, with the metal atom lying on a crystallographic centre of inversion. Both structures are built of monomeric units in which the copper atom is surrounded by two N atoms from two ligand molecules and two Cl atoms in typical square planar environment. Two thiophene S atoms, located on opposite sides with respect to the square, complete the coordination sphere, making the complex elongated octahedral.

Disregarding the acetyl group in **II**, a comparison of the structures of the two complexes shows a close resemblance in bond distances and angles as can be

TABLE 4. Atomic fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å^2) (one third trace of the diagonalized matrix) with e.s.d.s in parentheses for **III**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}
Molecule A				
S1	4170(1)	−6792(1)	232(3)	4.80(3)
O1	3534(2)	−5157(3)	1346(10)	7.34(15)
N1	4957(2)	−8277(3)	599(9)	5.60(14)
C1	5336(3)	−8925(4)	1095(12)	5.68(13)
C2	5426(3)	−9625(4)	−398(14)	6.21(15)
C3	5130(3)	−9671(5)	−2369(15)	6.54(16)
C4	4729(3)	−8994(5)	−2976(13)	5.80(14)
C5	4660(2)	−8317(4)	−1405(11)	4.62(11)
C6	4252(2)	−7588(3)	−1854(9)	4.43(10)
C7	3910(3)	−7430(4)	−3766(12)	5.39(12)
C8	3582(3)	−6648(4)	−3550(12)	5.43(13)
C9	3668(2)	−6233(4)	−1493(10)	4.51(10)
C10	3422(3)	−5416(4)	−628(12)	5.46(13)
C11	3023(3)	−4911(5)	−2220(14)	7.22(17)
Molecule B				
S2	3173(1)	1121(1)	1152(3)	4.88(4)
O2	2481(2)	2731(3)	2146(9)	7.96(16)
N2	3967(2)	−385(3)	1649(9)	5.73(14)
C12	4350(3)	−1053(5)	2083(13)	6.15(14)
C13	4451(3)	−1718(4)	583(12)	6.23(14)
C14	4174(3)	−1740(5)	−1546(14)	6.52(15)
C15	3779(3)	−1054(4)	−2056(13)	5.91(14)
C16	3701(2)	−388(4)	−446(10)	4.46(10)
C17	3294(2)	327(3)	−927(9)	4.33(10)
C18	2981(3)	496(4)	−2933(11)	4.91(12)
C19	2631(3)	1252(4)	−2776(11)	5.02(12)
C20	2679(2)	1657(3)	−671(10)	4.59(11)
C21	2392(3)	2460(4)	195(14)	5.72(13)
C22	1959(3)	2887(5)	−1462(15)	7.22(17)

seen from the data quoted in Tables 5 and 6 which further compare these data to those of compound **III**.

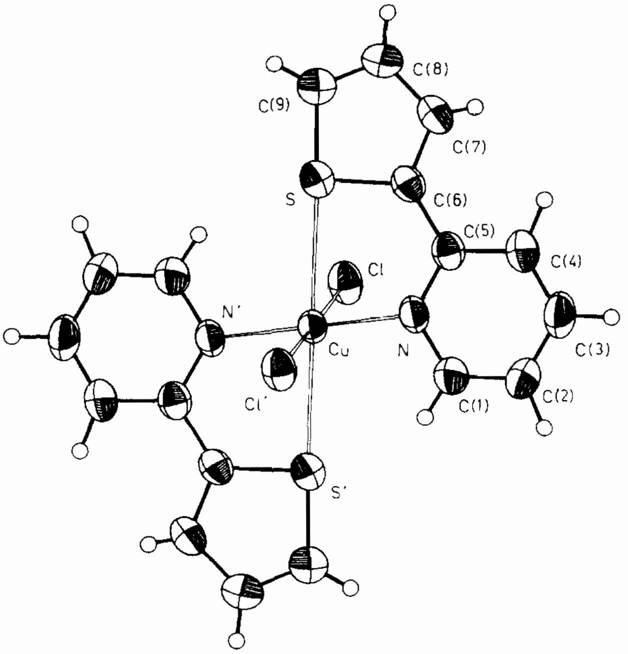

Fig. 1. ORTEP drawing of compound **I** with thermal ellipsoids at the 50% probability level.

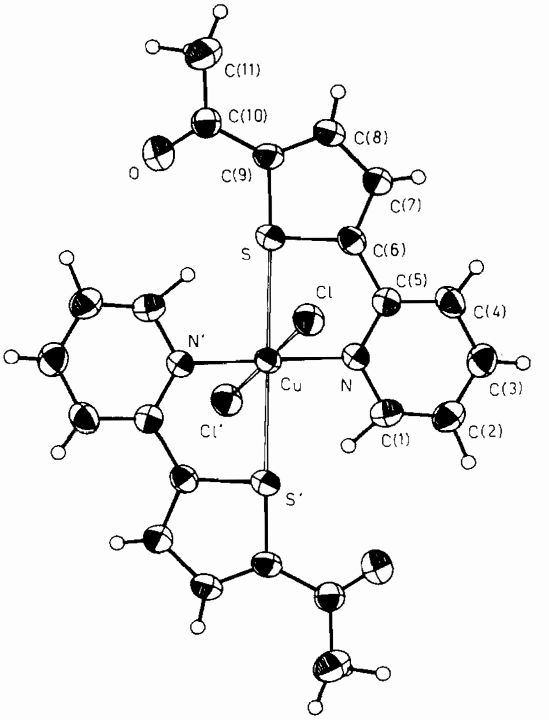

Fig. 2. ORTEP drawing of compound **II** with thermal ellipsoids at the 50% probability level.

A notable structural feature of these compounds is undoubtedly the nature of the thiophene–copper interaction, which occurs through an η^1,S-coordination. The few examples of structurally characterized η^1,S-thiophene complexes which are presently known, include Pt(II) [3], Pd(II) [4], Ru(II) [21–23], Ag(I) [24], Cu(I) [24] and Cu(II) [25] derivatives. Features common to all these compounds (and to the present ones too) are the chelating nature of the involved ligands, which helps to stabilize the metal–sulfur interaction, and the pyramidal environment of the coordinated S atom. In our compounds the angle defined by the Cu–S bond and the vector from S to the midpoint of the C(7)–C(8) bond is 54.8(2)° in **I** and 60.20(7)° in **II**, while the angle between the Cu–S bond and the thiophene ring plane is 28.3(1)° in **I** and 38.18(7)° in **II**. The angle between the Cu–N bond and the pyridine ring plane is 5.0(2)° in **I** and 7.5(1)° in **II**. The organic ligand in both complexes appears to function as an asymmetrically bidentate N, S-donor exactly as previously found in the above mentioned Pt and Pd complexes which are the only 2,2′-thienylpyridine complexes of which we are aware. The coordinating mode of the ligand as well as the Jahn-Teller effect can account for the distortion in the coordination polyhedron.

TABLE 5. Bond distances (Å)[a]

	I	II	III	
			Molecule A	Molecule B
Cu–Cl	2.265(2)	2.264(1)		
Cu–N	2.025(5)	2.021(2)		
Cu–S	2.968(2)	2.904(1)		
N–C(1)	1.339(9)	1.351(4)	1.342(8)	1.365(9)
C(1)–C(2)	1.366(11)	1.371(5)	1.385(8)	1.350(10)
C(2)–C(3)	1.384(11)	1.374(5)	1.313(11)	1.368(11)
C(3)–C(4)	1.365(11)	1.382(5)	1.421(11)	1.409(10)
C(4)–C(5)	1.396(10)	1.398(5)	1.380(9)	1.386(9)
C(5)–N	1.357(7)	1.347(4)	1.330(8)	1.340(8)
C(5)–C(6)	1.443(9)	1.471(4)	1.471(7)	1.457(7)
C(6)–S	1.733(6)	1.718(3)	1.716(6)	1.721(5)
C(6)–C(7)	1.375(9)	1.377(4)	1.360(9)	1.372(8)
C(7)–C(8)	1.412(11)	1.417(5)	1.416(9)	1.406(8)
C(8)–C(9)	1.344(11)	1.366(5)	1.350(9)	1.357(8)
C(9)–S	1.704(7)	1.723(3)	1.730(6)	1.735(5)
C(9)–C(10)		1.469(5)	1.456(8)	1.477(9)
C(10)–O		1.225(4)	1.222(9)	1.206(9)
C(10)–C(11)		1.494(5)	1.497(10)	1.512(10)

[a] Atoms in molecule B of III have been labelled as in molecule A to simplify the comparison.

TABLE 6. Bond angles (°)[a]

	I	II	III	
			Molecule A	Molecule B
N–Cu–Cl	89.4(1)	89.20(7)		
N–Cu–S	74.8(1)	75.39(7)		
Cl–Cu–S	88.75(5)	86.13(3)		
Cu–N–C(1)	114.5(4)	116.9(2)		
Cu–N–C(5)	126.2(4)	124.4(2)		
C(1)–N–C(5)	119.0(5)	118.4(3)	118.1(5)	116.5(5)
N–C(1)–C(2)	123.3(6)	122.9(3)	122.5(6)	123.9(6)
C(1)–C(2)–C(3)	118.6(7)	118.7(3)	119.6(7)	120.4(7)
C(2)–C(3)–C(4)	118.7(7)	119.7(4)	119.8(8)	117.1(7)
C(3)–C(4)–C(5)	120.9(7)	118.8(3)	117.5(6)	119.6(6)
C(4)–C(5)–N	119.4(6)	121.3(3)	122.5(5)	122.5(5)
C(4)–C(5)–C(6)	120.8(5)	120.2(3)	121.9(6)	120.7(5)
N–C(5)–C(6)	119.7(5)	118.4(3)	115.7(5)	116.8(5)
C(5)–C(6)–S	122.9(4)	120.9(2)	119.2(4)	120.1(4)
C(5)–C(6)–C(7)	127.4(6)	126.8(3)	129.2(5)	128.7(5)
S–C(6)–C(7)	109.6(5)	112.3(2)	111.7(4)	111.2(4)
Cu–S–C(6)	84.8(2)	84.2(1)		
Cu–S–C(9)	151.3(3)	140.7(1)		
C(6)–S–C(9)	92.2(3)	91.3(2)	91.6(3)	91.3(3)
C(6)–C(7)–C(8)	113.3(6)	111.5(3)	112.3(6)	113.2(6)
C(7)–C(8)–C(9)	112.8(7)	113.2(3)	113.5(6)	112.8(5)
C(8)–C(9)–S	112.2(6)	111.6(2)	111.0(4)	111.5(4)
S–C(9)–C(10)		117.6(2)	118.9(4)	118.5(5)
C(8)–C(9)–C(10)		130.8(3)	130.1(6)	130.0(5)
C(9)–C(10)–O		119.3(3)	120.9(6)	121.5(6)
C(9)–C(10)–C(11)		118.4(3)	118.0(6)	115.9(6)
O–C(10)–C(11)		122.3(3)	121.2(6)	122.5(7)

[a] See Table 5.

Moreover, by virtue of the geometric constraints imposed by the coordination, the two individually planar portions of the ligand are twisted out of coplanarity, the dihedral angle between the two planes being 26.2(2)° in **I** and 30.3(1)° in **II**. The five-membered chelate ring is substantially puckered (puckering amplitude, $Q = 0.455(5)$ (**I**) and 0.544(2) Å (**II**); phase angle $\varphi(2) = -24.9(7)$ (**I**) and $-25.6(3)°$ (**II**)). By contrast, in the two independent molecules of the free ligand the two planar moieties are practically coplanar, their planes making an angle of 3.0(2)° in A and of 2.4(2)° in B. Therefore the ligand molecule (Fig. 3; the drawing refers to molecule A) as a whole can be considered approximately planar, the largest deviation from the plane of best fit for any contributing atom being 0.13 Å in A and 0.07 Å in B.

As regards the 2,2′-bipyridyl (bipy) ligand, it is well known that the copper(II) ion can give numerous complexes of general formula $Cu(bipy)_2X_2$ [5–9]. In these complexes, if the two bipyridyl molecules should take a coplanar arrangement around the Cu atom there would be a severe steric interference between the hydrogen on the 6- and 6′-carbon atoms. Actually, no coplanar disposition of bipyridyl ligands has been found for the bis-bipyridyl Cu^{2+} complexes. The two bipyridyl molecules are forced to slant against one another, giving rise to a flattened tetrahedral arrangement of their nitrogen atoms as in $[Cu(bipy)_2ClO_4]ClO_4$ [6] or to a quasi-trigonal bipyramidal coordination as in $[Cu(bipy)_2Cl]Cl$ [8]. As a consequence of these geometrical arrangements, the second anion does not participate in coordinative bonding, as it does for **I** and **II**. Again in contrast to the behaviour of the 2,2′-pyridylthiophene ligands, in the coordinated 2,2′-bipyridyl molecules the two heteroaromatic rings remain practically coplanar and all the Cu–N vectors lie on the same planes of the rings.

Furthermore, Cu–N bond lengths in **I** and **II** (2.025(5) and 2.021(2) Å) are intermediate between the corresponding axial (1.98 Å) and equatorial (2.08 Å) bond lengths found in $[Cu(bipy)_2Cl]Cl$, whereas the Cu–Cl bond distances (2.265(2) and 2.264(1) Å) are slightly

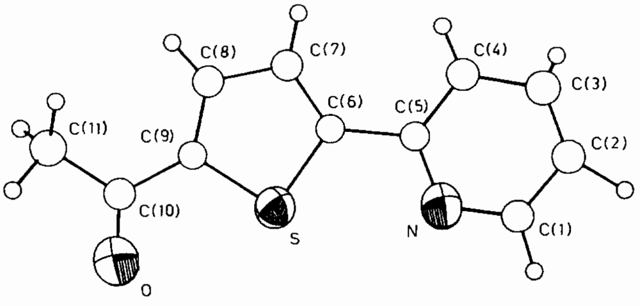

Fig. 3. ORTEP drawing of molecule A of compound **III** with thermal ellipsoids at the 50% probability level.

shorter than that observed in the mentioned bipyridyl compound (2.36 Å).

The Cu–S bonds in **I** and **II**, which are significantly different (that in the apyth complex being shorter), warrant a brief comment. Both these values, 2.968(2) and 2.904(1) Å, are well outside the range of values for which Cu–S bonding has been postulated, the normal Cu–S single bond being 2.39 Å. It is interesting to note that a search of the Cambridge crystallographic database yielded only three examples of six-coordinate copper(II) compounds having in the coordination sphere two N, two Cl and two S and that in all of them similar semicoordinating Cu–S distances have been found, e.g. 2.886(1) and 2.970(1) Å in [1,7-bis(5-methylimidazol-4-yl)-2,6-dithiaheptane]dichlorocopper [26], 2.623(3) and 2.805(3) Å in dichloro-[1,6-bis(5-methyl-4-imidazolyl)-2,5-dithiahexane]copper [27] and 3.001(2) Å in bis[2-(ethylthiomethyl)benzimidazole]dichlorocopper [28]. Incidentally it can be added that the Cu–N and Cu–Cl distances in these compounds vary between 1.949 and 2.000 Å and between 2.322 and 2.562 Å, respectively. Similar long metal–sulfur bonds also occur in all the above mentioned η^1,S-thiophene complexes (M–S 2.96–3.15 Å) except the Ru and Cu(II) derivatives where the M–S bond (2.28–2.41 Å) is clearly a bonding distance.

The molecular packing in all the three compounds indicates only normal van der Waals interactions between the molecules. Excluding the hydrogen atoms, there are no intermolecular close contacts less than 3.5 Å in **I**, 3.2 Å in **II** and 3.4 Å in **III**, the shortest contacts being:

I	C(7)···C(9)	$(x, -y-\frac{1}{2}, z+\frac{1}{2})$	3.517(9) Å
	S···C(1)	$(1+x, y, z)$	3.583(7)
	Cl···C(9)	$(1-x, -y, -z)$	3.592(8)
II	O···O	$(-1-x, -y, 1-z)$	3.327(5)
	O···C(4)	$(-x-\frac{1}{2}, y-\frac{1}{2}, \frac{1}{2}-z)$	3.230(5)
	C(3)···C(8)	$(1+x, y, z)$	3.326(5)
III	C(2)···O(1)	$(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3.401(9)
	C(4)···C(16)	$(x, y+1, z-1)$	3.473(9)
	S(2)···C(18)	$(x, y, z+1)$	3.538(7)

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