Structures and Spectroscopic Properties of Chain Polymeric Complexes of Copper(II) Halides with 2,3,5,6-Tetrafluoro-1,4-bis(2-pyridylsulfenyl)benzene and Its 4-Pyridylsulfenyl Analogue

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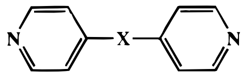
The syntheses are reported of the “extended reach” ligand 2,3,5,6-tetrafluoro-1,4-bis(2-pyridylsulfenyl)benzene (L^1), its 4-pyridylsulfenyl analogue (L^2), and their copper(II) complexes $CuLX_2$ (X = Cl or Br). X-ray studies have been carried out on L^1, L^2, and the complexes $Cu(L^1)Cl_2{\cdot}2CHCl_3$ (**1**) and $[Cu(L^2)(DMF)Br_2]{\cdot}DMF$ (**2**). Complex **1** has a chain polymeric structure with a *trans*-planar $CuCl_2N_2$ coordination geometry. Complex **2** is also a chain polymer structure, but in this case a DMF molecule is bonded in the apical position above a *trans*-$CuBr_2N_2$ unit, producing a slightly distorted square pyramidal geometry at the copper centers. The transition energies obtained from the single-crystal electronic spectrum of $Cu(L^1)Cl_2{\cdot}2CHCl_3$ and the *g*-values from its EPR spectrum are used to derive bonding parameters, and these are compared with those of other planar CuL_2Cl_2 complexes with amine ligands. The electronic reflectance spectrum of $[Cu(L^2)(DMF)Br_2]{\cdot}DMF$ implies broadly similar amine bonding parameters. This compound exhibits an unusual **g**-tensor with $g_{||} < g_{\perp}$, which is interpreted in terms of exchange-averaging of the molecular **g**-tensors of the two molecules in the unit cell.

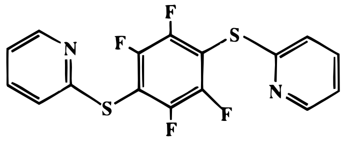
Introduction

The use of 4,4′-bipyridine as a bridging ligand between metal centers has been a popular way of generating macrocyclic squares[1] or more extended polymeric structures.[2] A related strategy is the use of two 4-pyridyl units linked by a spacer unit, X, as depicted in **I** (Chart 1), and a variety of linking X groups have been employed.[2g,3] Because of our interest in the polymer-forming ability of extended reach ligands involving “end” groups containing both N and S atoms[4] and also the use of linking groups with the potential for permitting electronic communication between metal centers,[5] we are studying metal complexes with ligands of type **I** with 1,4-bis(thiophenyl) units as the linker group X.

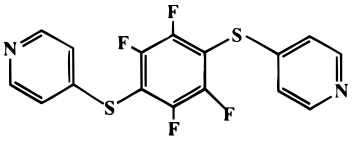
Chart 1



I



L^1



L^2

We report here the preparation and structures of 2,3,5,6-tetrafluoro-1,4-bis(2-pyridylsulfenyl)benzene (L^1) and its 4-pyridylsulfenyl analogue (L^2) and also the structures and spec-

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Table 1. Crystallographic Data for L^1, L^2, Cu(L^1)Cl$_2$·2CHCl$_3$ (**1**), and [Cu(L^2)(DMF)Br$_2$]·DMF (2)

	L^1	L^2	**1**	**2**
formula	$C_{16}H_8N_2F_4S_2$	$C_{16}H_8N_2F_4S_2$	$C_{18}H_{10}Cl_8CuF_4N_2S_2$	$C_{22}H_{22}Br_2CuF_4N_4O_2S_2$
fw	368.4	368.4	741.5	737.9
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a, Å	5.757(1)	5.573(1)	7.553(1)	20.476(2)
b, Å	7.619(1)	7.683(1)	9.030(1)	9.494(1)
c, Å	17.317(2)	17.692(1)	11.106(3)	15.026(2)
α, deg			102.01(1)	
β, deg	91.47(1)	95.41(1)	108.74(2)	107.73(1)
γ, deg			102.89(2)	
V, Å^3	759.3(2)	754.1(1)	666.3(2)	2782.1(6)
Z	2^a	2^a	1^a	4
ρ_{calcd}, g cm^{-3}	1.611	1.622	1.848	1.762
λ, Å	1.541 78	1.541 78	0.710 73	1.541 78
μ, cm^{-1}	36.1	36.4	18.2	63.7
T, °C	20	20	20	−70
$R_1{}^b$	0.045	0.075	0.036	0.056
$wR_2{}^c$	0.124	0.191	0.091	0.129

^{a} The molecule has crystallographic C_i symmetry. ^{b} $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{c} $wR_2 = [\sum(w\ |F_o{}^2 - F_c{}^2\ |^2)/\sum w|F_o{}^2|^2]^{1/2}$.

troscopic properties of some chain polymeric complexes they form with copper(II).

Experimental Section

Preparation of Compounds. 2,3,5,6-Tetrafluoro-1,4-bis(2-pyridylsulfenyl)benzene (L^1). A solution of 2-mercaptopyridine (5.55 g, 0.05 mol) in dry DMF (50 mL) was added to a suspension of NaH (2.0 g of 60% oil dispersion) also in DMF (50 mL). After ca. 20 min the resulting clear solution was added very slowly, via a dropping funnel, to a solution of hexafluorobenzene (4.65 g, 0.025 mol) in DMF (10 mL). A slightly exothermic reaction was observed, and the solution became orange and cloudy. The mixture was allowed to react at room temperature for 2 h. Addition of water (600 mL) led to precipitation of an off-white solid which was collected and air-dried. The crude product was dissolved in chloroform and filtered through a pad of silica. The filtrate was concentrated on a rotary evaporator and treated with diethyl ether (20 mL), affording colorless crystals (50% yield), mp 154−158 °C (dec to a dark red liquid). Anal. Calcd for $C_{16}H_8F_4N_2S_2$: C, 52.2; H, 2.2; N, 7.6. Found: C, 51.9; H, 2.2; N, 7.6. EI-MS: m/z 368 [M$^+$]. ^{1}H NMR (270 MHz, CDCl$_3$): δ 7.08 (2 H, m), 7.20 (2 H, d), 7.55 (2 H, m), 8.34 (2 H, s). The constitution of this ligand was also confirmed by single-crystal X-ray diffraction methods (see below).

2,3,5,6-Tetrafluoro-1,4-bis(4-pyridylsulfenyl)benzene (L^2). This was obtained from 4-mercaptopyridine by the same method as for L^1: colorless crystals (38% yield), mp 182−184 °C (dec). Anal. Calcd for $C_{16}H_8F_4N_2S_2$: C, 52.2; H, 2.2; N, 7.6. Found: C, 52.0; H, 2.4; N, 7.6. EI-MS: m/z 368 [M$^+$]. ^{1}H NMR (270 MHz, CDCl$_3$): δ 7.06 (4 H, m), 8.34 (4 H, m). The constitution of this ligand was also confirmed by single-crystal X-ray diffraction methods (see below).

Metal Complexes. Cu(L^1)Cl$_2$. A solution of CuCl$_2$·2H$_2$O (0.085 g, 0.5 mmol) in ethanol (15 mL) was added to one of L^1 (0.184 g, 0.5 mmol) in chloroform (15 mL). After ca. 1 h blue/violet dichroic crystals started to form. After 2 d the solid was filtered off and washed with a little chloroform and air-dried (44% yield). Anal. Calcd for $C_{16}H_8Cl_2CuF_4N_2S_2$: C, 38.2; H, 1.6; N, 5.6. Found: C, 38.2; H, 1.8; N, 5.4.

Cu(L^1)Br$_2$·0.5CHCl$_3$. This was obtained as for the previous compound but using anhydrous copper(II) bromide: dark green crystals (80% yield). Anal. Calcd for $C_{16}H_8Br_2CuF_4N_2S_2$·0·5CHCl$_3$: C, 30.4; H, 1.3; N, 4.3. Found: C, 30.9; H, 1.5; N, 4.4.

Cu(L^2)Cl$_2$. Addition of a solution of CuCl$_2$·2H$_2$O (0.085 g, 0.5 mmol) in ethanol (10 mL) to one of L^2 (0.184 g, 0.5 mmol) in ethanol (10 mL) gave an immediate precipitate of a pale blue solid (71% yield). Anal. Calcd for $C_{16}H_8Cl_2CuF_4N_2S_2$: C, 38.2; H, 1.6; N, 5.6. Found: C, 38.0; H, 1.7; N, 5.8.

Cu(L^2)Br$_2$·2DMF. Addition of a solution of CuBr$_2$ (0.111 g, 0.5 mmol) in ethanol (10 mL) to one of L^2 (0.184 g, 0.5 mmol) in chloroform (10 mL) gave an immediate precipitate of a bright green powder (70% yield). This solid was suspended in a hot mixture of ethanol (10 mL) and chloroform (10 mL) and DMF added dropwise to the boiling solution until all the solid had dissolved. Storage at room temperature yielded dark green crystals. Anal. Calcd for $C_{16}H_8Br_2CuF_4N_2S_2$·2DMF: C, 35.8; H, 3.0; N,7.6. Found: C, 35.6; H, 3.2; N, 7.4.

Microanalyses and Spectroscopy. Elemental analyses were performed by the Microanalytical Laboratory, Imperial College. NMR spectra were recorded on a JEOL JNM-EX270 spectrometer. Mass spectra were measured on a VG Autospec Q spectrometer at the Mass Spectrometry service, Department of Chemistry, Imperial College.

The single-crystal electronic spectrum of Cu(L^1)Cl$_2$·2CHCl$_3$ was measured using a Cary 5A spectrophotometer with the sample cooled by a Cryodyne model 21 cryostat. To prevent the sample losing solvent, it was cooled to ca. 250 K before being subjected to a vacuum. The electronic spectra of the powdered sample and of the other complexes were obtained by the diffuse reflectance method, at room temperature, using a Beckmann DK2 spectrophotometer.

The EPR measurements on powdered samples of Cu(L^1)Cl$_2$·2CHCl$_3$ and Cu(L^1)Br$_2$·0.5CHCl$_3$ were made at the EPSRC c.w. EPR Service Centre, Department of Chemistry, University of Manchester, at room temperature at both X- and Q-band frequencies on a Bruker ESP300E spectrometer fitted with an ER4102ST or an ER5106QT resonator, respectively. Magnetic fields and microwave frequencies were calibrated with a Bruker ER035M NMR gaussmeter and an EIP model 588C microwave pulse counter, respectively. The simulations of the spectra were also carried out in the EPR Service Centre using in-house software.[6] The EPR measurements on Cu(L^2)Cl$_2$ and Cu(L^2)Br$_2$·2DMF were made at room temperature on powdered samples at X-band frequency using a Varian E12 spectrometer at Imperial College.

Crystallographic Analyses. Crystal data for L^1, L^2, and the complexes Cu(L^1)Cl$_2$·2CHCl$_3$ (**1**) and Cu(L^2)Br$_2$·2DMF (**2**) and summaries of the crystallographic analyses are given in Table 1. The data were collected on Siemens P4 diffractometers, using ω scans and graphite-monochromated Cu Kα radiation for L^1, L^2, and compound **2** and Mo Kα radiation for **1.** The data were corrected for Lorentz and polarization factors and, for **L^1**, **1**, and **2**, for absorption. The structures were solved by direct methods, and all the major occupancy non-hydrogen atoms were refined anisotropically by full-matrix least squares based on F^2. For **2** the hydrogen atoms of the methyl groups were located from ΔF maps, assigned isotropic thermal parameters, U(H) $= 1.5U_{eq}$(C), and allowed to ride on their parent atoms. The remaining hydrogen atoms in all four structures were placed in calculated positions,

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **1**

Cu−N(1)	2.011(2)	Cu−C	2.255(1)
S−C(7)	1.770(3)	S−C(6)	1.781(3)
N(1)−Cu−N(1′)	180.0	N(1)−Cu−Cl′	90.1(1)
N(1)−Cu−Cl	89.9(1)	Cl−Cu−Cl′	180.0
C(7)−S−C(6)	100.9(1)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex **2**

Cu−N(1)	1.993(5)	Cu−N(11)	2.000(5)
Cu−O(20)	2.248(5)	Cu−Br(1)	2.451(1)
Cu−Br(2)	2.467(1)	S(1)−C(4)	1.761(7)
S(1)−C(7)	1.772(8)	S(2)−C(17)	1.759(7)
S(2)−C(14)	1.776(7)		
N(1)−Cu−N(11)	172.9(2)	N(1)−Cu−O(20)	96.6(2)
N(11)−Cu−O(20)	90.5(2)	N(1)−Cu−Br(1)	89.8(2)
N(11)−Cu−Br(1)	89.9(2)	O(20)−Cu−Br(1)	96.4(2)
N(1)−Cu−Br(2)	89.2(2)	N(11)−Cu−Br(2)	89.3(2)
O(20)−Cu−Br(2)	98.2(2)	Br(1)−Cu−Br(2)	165.3(1)
C(4)−S(1)−C(7)	103.3(4)	C(17)−S(2)−C(14)	101.4(3)

assigned isotropic thermal parameters, $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ [$U(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C\text{-}Me})$], and allowed to ride on their parent atoms. Computations were carried out using the SHELXTL PC program system.[7]

Selected bond lengths and angles for the structures of **1** and **2** are listed in Tables 2 and 3, respectively.

Results and Discussion

Ligands L^1 and L^2 were readily obtained from the reaction between hexafluorobenzene and deprotonated 2- or 4-mercaptopyridine in DMF, but the yields were only moderate.

Structures of L^1 and L^2. The structure of L^1 is centrosymmetric, with the pyridine rings being steeply inclined to the central $C_6F_4S_2$ unit. The torsional twists about the S−py and S−C_6F_4 bonds are 11 and 66°, respectively. The molecules pack to form parquet-like sheets which are dominated principally by edge-to-face C−H⋯π interactions (denoted *a* in Figure 1) between the pyridyl rings (H⋯π =2.78 Å, C−H⋯π angle 152°) and with secondary, weaker F⋯π interactions[8] into the opposite face of each pyridyl ring (denoted *b* in Figure 1); the F⋯π distance is 3.31 Å, with a C−F⋯π angle of 146°. The shortest intermolecular S⋯S separation is 5.75 Å.

The solid-state structure of L^2 is very similar to that of L^1; it is also centrosymmetric, and the pyridyl and $C_6F_4S_2$ rings are steeply inclined. The torsional twists about the S−py and S−C_6F_4 bonds are 12 and 64°, respectively. The pattern of bonding does not differ significantly from that seen in L^1. Despite the change from *ortho* to *para* position of the pyridine, the similarity between the two structures also extends to the packing of the molecules, there being the same pyridyl−pyridyl C−H⋯π interactions (H⋯π = 2.87 Å, C−H⋯π angle 153°). The only noticeable difference is a marked increase in the equivalent F⋯π separation which in L^2 is increased to 3.65 Å. The shortest S⋯S approach is slightly reduced to 5.40 Å.

Copper Complexes. Reaction of L^1 and L^2 with copper(II) chloride or bromide in the solvent systems given in the Experimental Section readily afforded complexes of stoichiometry $CuLX_2$ (where X = Cl or Br). The crystal structure of one of each pair of compounds was determined both to explore the long-range geometry and also to provide a firm basis for the analysis of their spectra and comparison of the derived parameters with those of related copper(II) systems.[9−11]

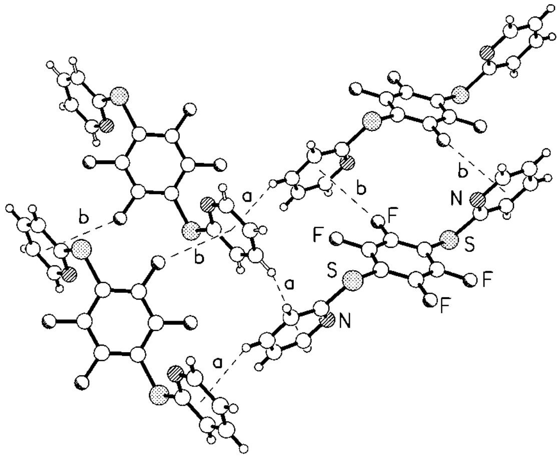

Figure 1. Molecular packing in the crystals of L^1 showing the edge-to-face C−H⋯π interactions, *a* = 2.78 Å, and the secondary F⋯π interactions, *b* = 3.31 Å.

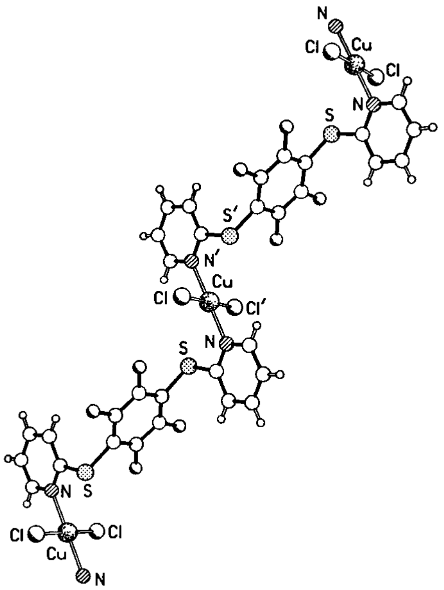

Figure 2. Part of the chain polymeric structure of compound **1**.

Structure of $Cu(L^1)Cl_2{\cdot}2CHCl_3$ (1). The X-ray analysis of the complex obtained from L^1 and copper(II) chloride in a mixture of ethanol and chloroform reveals the formation of a chain polymer structure (Figure 2). The copper atoms and the C_6F_4 rings are positioned on independent inversion centers. The most noticeable change in the conformation of the organic ligand upon complexation is in the position of the nitrogen atom with respect to the C_6F_4 ring center. In the free ligand the two nitrogen atoms are directed toward the ring center whereas in the copper complex they are directed away. The pyridyl rings are still steeply inclined to the C_6F_4 ring, with torsional twists about the S−C(C_6F_4) and S−C(py) bonds of 75 and 134°, respectively.

The Cu−N and Cu−Cl bond lengths are 2.011(2) and 2.255(1) Å, respectively, and there are no significant departures from

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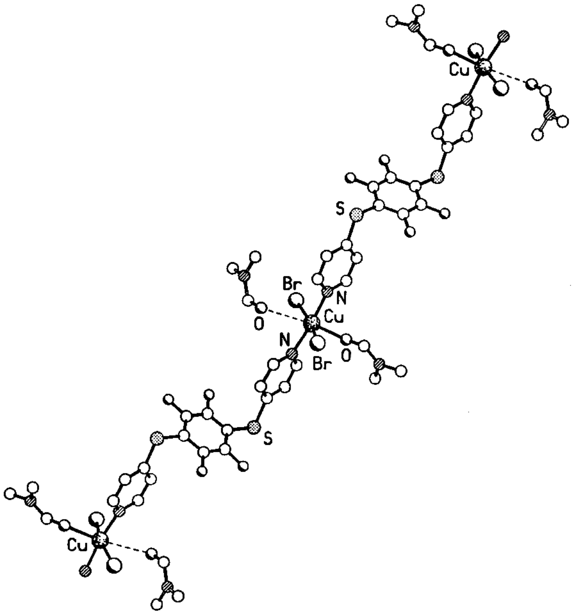

Figure 3. Part of the chain polymeric structure of compound **2**.

planar coordination geometry within the CuN_2Cl_2 unit. The two pyridyl rings are inclined by 72° to the copper coordination plane, and this results in an approach to the copper atom by the sulfur atoms above and below that plane. The Cu···S distances are 3.12 Å, but the angle of their approach to the coordination plane is fairly shallow at 52°.

There are no interchain interactions of any note, the parallel chains being interleaved by included chloroform solvent molecules. These solvent molecules, however, are oriented with their C−H bonds directed toward the coordinated Cl atoms with a C···Cl distance of 3.4 Å and an associated H···Cl contact of 2.70 Å, indicating a possible weak C−H···Cl hydrogen bond. The chloroform molecules are quite readily lost from the crystals, and "dried" samples had microanalytical results consistent with the solvent-free stoichiometry.

Structure of $[Cu(L^2)(DMF)Br_2]\cdot DMF$ (2). The solid-state structure of **2** is again polymeric (Figure 3), though in this case only the C_6F_4 rings are positioned on inversion centers. The structure contains two independent L^2 ligands, each with conformations very similar to that of the free ligand. The torsional twists about the S(1)−C(4) and S(1)−C(7) bonds are 6 and 78°, respectively, while those about S(2)−C(14) and S(2)−C(17) are 15 and 66°. Accompanying the approximately orthogonal orientation of the pyridyl and C_6F_4 ring systems there is a characteristic enlargement of the "internal" angles[12] at C(4) and C(14) [S(1)−C(4)−C(5) 126.5(6)° and S(2)−C(14)−C(15) 123.7(6)°].

As in **1**, the halide ions and pyridine nitrogen atoms are coordinated to copper in a *trans*-disposition, but in **2** the coordination geometry at Cu is slightly distorted square pyramidal with the apical coordination site being additionally occupied by the oxygen atom of a DMF molecule from the solvent mixture used to recrystallize the complex (Figure 4). The copper atom lies 0.22 Å out of the $CuBr_2N_2$ plane in the direction of the coordinated DMF molecule. The Cu−N distances (Table 3) are the same and do not differ significantly from that observed in **1**; the Cu−O distance, 2.248(5) Å, as expected, is slightly longer. In addition to the coordinated DMF molecule, there is a longer approach (3.27 Å) by the oxygen atom of a further, but disordered, DMF molecule in the vacant "octahedral" coordination site on the copper atom.

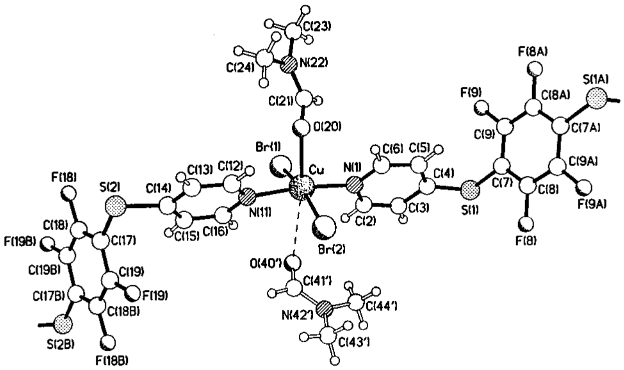

Figure 4. Square pyramidal copper coordination environment in compound **2**, showing also the approach (broken bond) of a second DMF molecule to the "vacant" coordination site.

In **2** the planes of the pyridine rings are slightly less steeply inclined to the basal coordination plane, with the ring containing N(1) being inclined by 64° while that containing N(11) is inclined by 54°. The polymer chains are arranged, in one direction, parallel to each other to form sheets, adjacent sheets having their chain axes inclined by ca. 34°. There are no $\pi-\pi$ stacking interactions between either adjacent planes or adjacent sheets.

Spectroscopic Studies and Bonding Parameters. The electronic spectra of several crystals of **1** were measured in the visible/near-infrared region, at 290 and 15 K, with the electric vector of polarized light along the two extinction directions. The peaks decreased somewhat in intensity and sharpened on cooling, as expected for a centrosymmetric complex where the absorption intensity is induced by coupling with ligand vibrations.[13] At low temperature four bands are clearly resolved, centered at 15 200, 16 400, 17 800, and 20 200 cm^{-1} (Figure 5). The much weaker peaks at lower energy are assigned to infrared overtones. The index of the crystal face was not identified, so the molecular projections associated with the polarization directions are unknown. However, because of the low formal symmetry of the complex, quantitative interpretation of the relative intensities of the bands is not warranted.

The peak positions are very similar to those observed for planar 4-coordinate complexes of the type *trans*-CuL_2Cl_2, where L is a substituted pyridine.[9] For instance, at 15 K the complex with L = 2,6-lutidine exhibits bands centered at 14 720, 16 630, 18 330, and 19 670 cm^{-1}. This implies that in **1** the copper(II) ion is also effectively 4-coordinate and that the sulfur atoms (3.12 Å from the metal center) have little influence upon the energies of the d-orbitals and so may be neglected in the interpretation of the "d-d" spectrum.

Two assignments have been advanced for the electronic spectra of the compounds *trans*-CuL_2Cl_2. That by McDonald and Hitchman,[9] labeled I in Table 4, proposes the following sequence of transition energies:

$$^2A_g(x^2-y^2) \rightarrow {}^2B_{1g}(xy) < {}^2B_{3g}(yz) < {}^2B_{2g}(xz) < {}^2A_g(z^2)$$

Here, the d-orbitals are defined using a coordinate system with

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[12] The deformations observed are analogous to those present in diphenyl ethers and reported in: Colquhoun, H. M.; O'Mahoney, C. J.; Williams, D. J. *Polymer* **1993**, *34*, 218.

[13] For a recent discussion of the polarized spectra of transition metal complexes see: Hitchman, M. A.; Riley, M. J. Polarized Absorption Spectroscopy. In *Inorganic Electronic Structure and Spectroscopy*; Lever, A. B. P., Ed.; Solomon, E. I., Eds.; Wiley: New York, in press; Vol. 1.

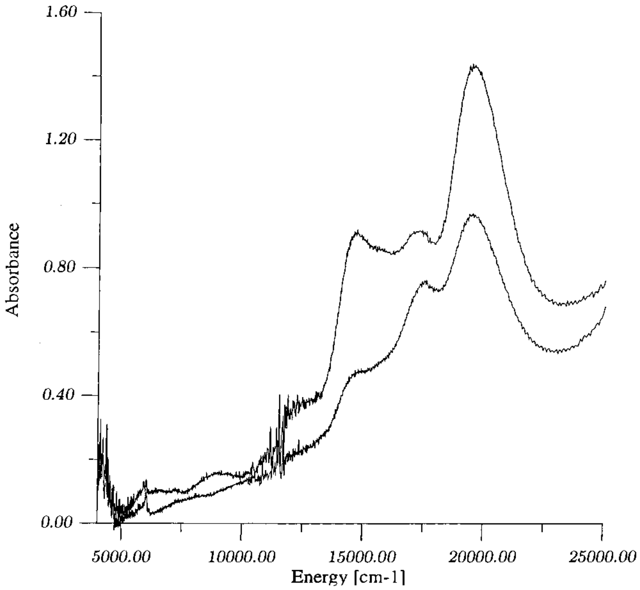

Figure 5. Electronic spectra of a crystal of compound **1** at 15 K with the electric vector of polarized light along the two extinction directions. The morphology of the crystal is unknown.

Table 4. Metal−Ligand Bonding Parameters (cm^{-1}) and *g*-Values for the Two Possible Assignments of the Electronic Spectrum of $Cu(L^1)Cl_2{\cdot}2CHCl_3$

assgnt I			assgnt II		
excited state	*E*(obsd)	E(calcd)	excited state	*E*(obsd)	*E*(calcd)
$^2B_{1g}(xy)$	15 200	15 125	$^2B_{1g}(xy)$	15 200	15 155
$^2B_{3g}(yz)$	16 400	16 430	$^2B_{3g}(yz)$	16 400	16 310
$^2B_{2g}(xz)$	17 800	17 790	$^2A_g(z^2)$	17 800	17 930
$^2A_g(z^2)$	20 200	20 430	$^2B_{2g}(xz)$	20 200	20 395

bonding parameters

assgnt I	assgnt II
$e_\sigma(av) = 5940$, $e_\pi(Cl) = 735$ $e_{\pi y}(N) = 635$, $e_{ds} = 2055$	$e_\sigma(ave) = 6675$, $e_\pi(Cl) = 1950$ $e_{\pi y}(N) = 650$, $e_{ds} = 975$

calcd *g*-values

assgnt I	assgnt II
$g_x = 2.043$, $g_y = 2.057$, $g_z = 2.206$	$g_x = 2.030$, $g_y = 2.063$, $g_z = 2.204$

x lying along the Cu−N bond directions, *y* approximately parallel to the Cu−Cl bonds, and *z* orthogonal to *x* and *y*. On the basis of a detailed analysis of the band intensities, Bridgeman et al. have recently proposed a slightly different assignment (II in Table 4) in which the energies of the two highest energy states are interchanged.[14] Either assignment seems possible for the spectrum of **1**. Both were therefore used to estimate a set of metal−ligand bonding parameters via the computer program CAMMAG developed by Gerloch and co-workers,[15] which calculates the transition energies of a complex within the framework of the angular overlap model (AOM) using the geometry defined by the crystal structure. In the calculations, the π-interaction of the chloride, $e_\pi(Cl)$, is assumed to be isotropic about the Cu−Cl bond axis, and $e_{\pi y}(N)$ defines the π-interaction of the amine normal to the plane of the ligand; the π-interaction in the plane of this ligand is assumed to be negligible, as found in other studies of aromatic amines.[16] A further parameter, e_{ds}, describes the influence of the configuration interaction between the $A_g(z^2)$ and $A_g(4s)$ states, which is quite pronounced for planar complexes of this kind.[17] An effective spin−orbit coupling constant of 620 cm^{-1} was used in the calculations. As pointed out by Bridgeman et al.,[14] the transition energies of a complex of this kind are insensitive to the individual σ-bonding parameters of the chloride and the amine ligands. Hence, only the *average* of these, $e_\sigma(av)$, could be deduced from the spectra. On the other hand, because the planes of the amines are approximately at right angles to the plane formed by the metal ligand bonds (Figure 2), the excited states are quite sensitive to the individual metal−ligand π-bonding parameters, which may be deduced accurately.

The bonding parameters $e_\sigma(ave)$, $e_\pi(Cl)$, $e_{\pi y}(N)$, and e_{ds} were deduced from the four observed transition energies; it may be noted that the parameter e_{ds} is influenced largely by the transition to the $^2A_g(z^2)$ level. The parameters giving optimum agreement with the two spectral assignments are listed in Table 4. These may be compared with the bonding parameters $e_\sigma(Cl) = 5030$, $e_\pi(Cl) = 700$, and $e_{ds} = 1320$ cm^{-1} deduced[9,18] for planar $CuCl_4{}^{2-}$ in a range of compounds with Cu−Cl bond distances very similar to that in **1** [e.g. Cu−Cl = 2.268 Å in $(methadonium)_2CuCl_4$[19]]. Assignment I for the spectrum of compound **1** gives a chloride π-bonding parameter quite similar to that in the tetrachlorocuprate ion, whereas assignment II gives a significantly higher value. Both assignments imply that the pyridine group acts as a weak π-donor toward copper(II), as also found in other complexes involving this type of ligand.[10,20] If it is assumed that the chloride σ-bonding parameter in **1** is similar to that in planar $CuCl_4{}^{2-}$, assignment I suggests the value $e_\sigma(N) = 6850$ cm^{-1} for the amine ligand, whereas assignment II implies the value $e_\sigma(N) = 8320$ cm^{-1}. These may be compared with bonding parameters derived for pyridine groups in several polydentate ligands bound to copper(II)[10,11,20] which range from 5750 to 6590 cm^{-1} for $e_\sigma(N)$ and 875 to 1300 cm^{-1} for $e_{\pi y}(N)$. The Cu−N distances in these lie between 1.986 and 2.04 Å and are therefore similar to that in the present complex (2.011 Å). For a planar complex configuration interaction between the d_{z^2} and metal 4s orbitals lowers the energy of the former orbital by $4e_{ds}$. Assignment I implies a depression of 8220 cm^{-1}, and assignment II, one of 3900 cm^{-1}. Either value is of the same order of magnitude as the estimate of ~6000 cm^{-1} for a complex without axial ligation, obtained by analyzing the transition energies of a range of copper(II) complexes with varying degrees of tetragonal distortion.[21]

The *g*-values calculated for the two assignments using orbital reduction parameters $k_{\|} = 0.65$ and $k_\perp = 0.75$ are also listed in Table 4. The powder EPR spectrum measured for the complex

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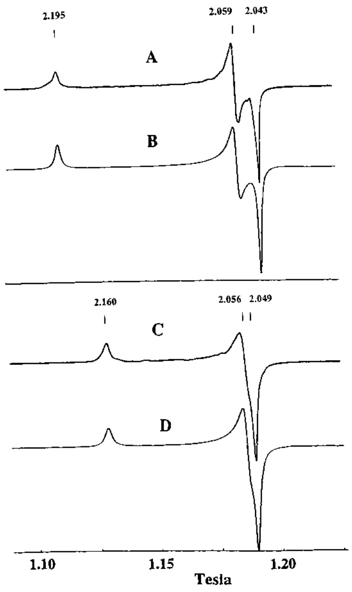

Figure 6. Q-band (34.117 GHz) EPR spectra of powdered samples: A, compound **1**; B, simulated spectrum of (A) with *g*-values of 2.043, 2.059, and 2.195; C, compound Cu(L^1)Br_2; D, simulated spectrum of (C) with *g* values of 2.049, 2.056, and 2.160.

at Q-band (Figure 6) is characteristic of an axially symmetric **g**-tensor with a slight orthorhombic distortion. The observed *g*-values, $g_x = 2.043$, $g_y = 2.059$, and $g_z = 2.195$, are in excellent agreement with those calculated using assignment I (Table 4). Because of the larger difference in the ligand σ-bonding parameters, and greater splitting between the ${}^2B_{3g}(yz)$, ${}^2B_{2g}(xz)$ excited states, assignment II gives a somewhat larger in-plane *g*-anisotropy than is observed experimentally. It should be noted that, as this compound has only one molecule in the unit cell, the powder EPR spectrum corresponds directly to the molecular **g**-tensor.

The electronic reflectance spectrum of Cu(L^1)Br_2 is very similar to that of **1**, as is its powder EPR spectrum (Figure 6), though with a smaller orthorhombic distortion ($g_x = 2.049$, $g_y = 2.056$, $g_z = 2.160$). It is likely that this compound has essentially the same structure as that of **1,** but we were unable to obtain X-ray quality crystals to confirm this.

The electronic reflectance spectrum of [Cu(L^2)(DMF)Br_2]·DMF (**2**) measured at room temperature consists of a single broad band, centered at ~14100 cm^{-1}, which is slightly asymmetric to lower energy. The absorption intensity was too high to allow single-crystal measurements to be made. The intense absorption is consistent with the noncentrosymmetric nature of this 5-coordinate complex.[13] Presumably, all four d−d transitions contribute to the broad band centered at ~14 100 cm^{-1} and the low resolution of the spectrum means that in this case the bonding interactions may only be investigated within broad limits. It was assumed that the coordinated bromide has similar parameters to those derived[11] for this ligand in the complex Cu(ppo)$_2$Br$_2$, $e_\sigma(\text{Br}) = 4250$ and $e_\pi(\text{Br}) = 675$ cm^{-1}, where ppo is a 4-substituted pyridine. For the axially coordinated DMF group a value of e_σ similar to that derived for the axial ligand in the Cu(NH$_3$)$_5^{2+}$ ion was assumed, $e_\sigma(\text{ax}) =$ ca. -750 cm^{-1}. The two complexes have a similar, square-based pyramidal geometry, and the bond length of the axial ligand in **2** (2.248 Å) is not too different from that in the Cu(NH$_3$)$_5^{2+}$ ion (2.193 Å).[22] The negative value reflects the fact that the parameter includes the influence of d−s mixing.[17] The e_π parameter of the axial DMF ligand was set at 200 cm^{-1}. With these constraints, reasonable agreement with the transition energies observed for **2** was obtained using σ-bonding parameters for the amine in the range $e_\sigma(\text{N}) = 6000 \pm 500$ cm^{-1}; the fit was relatively insensitive to the π-bonding parameter which affects only the energy of the ${}^2B_{2g}(xz)$ state. Thus, $e_\sigma(\text{N}) = 5500$ and $e_{\pi y}(\text{N}) = 550$ cm^{-1} yield the excited-state energies 10 560, 12 040, 12 980, and 14 290 cm^{-1}, while $e_\sigma(\text{N}) = 6500$ and $e_{\pi y}(\text{N}) = 650$ cm^{-1} give 12 010, 13 600, 14 640, and 15 960 cm^{-1}. It therefore appears that the bonding parameters of the amine in **2** are broadly similar to those suggested by assignment I of the spectrum of **1** and to those of substituted pyridine groups in other similar complexes.[10,11,20]

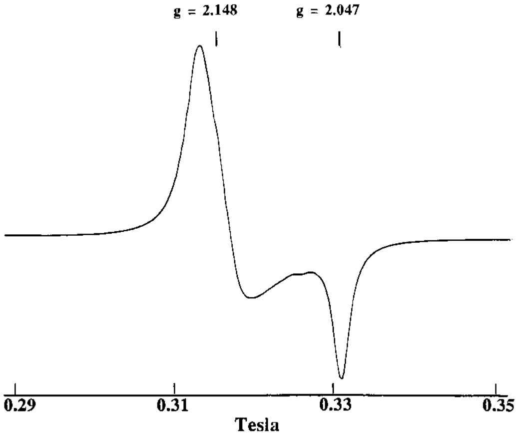

Figure 7. X-band (9.499 GHz) EPR spectrum of a powdered sample of compound **2**.

The EPR spectrum of **2** differs drastically from that of **1** in that it shows a line shape characteristic of an axially symmetric **g**-tensor but with the two *higher* **g**-values approximately equal (Figure 7). When observed for a molecule, such a **g**-tensor implies a ${}^2A_g(z^2)$ ground state, which is clearly incompatible[23] with the geometry of the present complex. However **2** has two molecules in the unit cell, so if the rate of electron exchange between these is faster than the EPR time scale, the observed **g**-tensor will be that of the *crystal* rather than the *molecule*, with principal values which depend on the relative orientations of the two molecules.[24] The molecular **g**-values of **2** calculated by CAMMAG using bonding parameters lying within the above range, and an isotropic orbital reduction parameter $k = 0.65$, are highly anisotropic, $g_x = 2.03 \pm 0.01$, $g_y = 2.08 \pm 0.01$, and $g_z = 2.23 \pm 0.02$. However, the *crystal* *g*-values, calculated assuming exchange-averaging as described previously[24] ($g_1 = 2.04 \pm 0.01$, $g_2 = 2.15 \pm 0.01$, $g_3 = 2.16 \pm 0.01$) show approximate axial symmetry and are in excellent agreement with the observed spectrum, where $g_{||} = 2.047$ and $g_\perp = 2.148$.

Conclusions. The crystallographic studies show that L^1 and L^2 are effective ligands for linking metal ions into polymeric arrays, which, in the specific cases of the copper(II) halides, results in chain polymer formation with long-range separation between the metal centers.

Although there are examples of complexes in which N-heterocyclic ligands with exocyclic sulfur atoms *ortho*-disposed to the ring nitrogen use both atoms to chelate to metal ions,[25]

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the close similarity of the single-crystal “d-d” spectrum of compound **1** to those of analogous planar, 4-coordinate copper(II) complexes having two trans pyridine groups and two trans chloride ions as ligands implies that the sulfur atom at 3.12 Å from the copper centers does not interact significantly with the metal d-orbitals.

Although the optical spectra of compounds **1** and **2** could not be assigned completely unambiguously, the transition energies and g-values imply that the pyridine groups have bonding parameters similar to those in analogous complexes and act as weak π-donors. While the EPR spectrum of compound **2** is unusual in having $g_{||}$ smaller than $g_{\perp}$, this is simply due to the molecular packing in the crystal lattice of this compound rather than an anomalous ground state.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of 2,3,5,6-tetrafluoro-1,4-bis(2-pyridylsulfenyl)benzene (L^1) and its 4-pyridylsulfenyl analogue (L^2) and of $Cu(L^1)Cl_2 \cdot 2CHCl_3$ and $[Cu(L^2)(DMF)Br_2] \cdot DMF$ are available on the Internet only. Access information is given on any current masthead page.

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