Structure and Magnetism of Analogous *O*-Bridged (Phenolato) and *S*-Bridged (Thiophenolato) Binuclear Copper(II) Complexes. Crystal Structure of the Binuclear *S*-Bridged Complex μ-[2,6-Bis(4′-cyclohexyl-4′-hydroxy-2′,3′-diazabuta-1′,3′-dien-1′-yl)-4-methylthiophenolato(3−)-*S*,N^2,*O*($Cu^{1,2}$)]-methanol-μ-(pyrazolyl-*N*,*N*′)-dicopper(II)†

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Magnetostructural correlations have been made on a matched pair of *O*-bridged (phenolato) and *S*-bridged (thiophenolato) binuclear copper(II) complexes of type [Cu_2(L-*X*)(pz)], where L-*O* and L-*S* are 2,6-bis(4′-cyclohexyl-4′-hydroxy-2′,3′-diazabuta-1′,3′-dien-1′-yl)-4-methyl-phenolate(3−) and -thiophenolate(3−) respectively and pz is an exogenous bridging pyrazolyl ligand. The crystal structure of [Cu_2(L-*S*)(pz)(CH_3OH)] is the first structure reported for a binuclear copper(II) complex containing a thiophenolato bridging group within a binucleating ligand framework. Crystals are monoclinic, space group $P2_1/c$, with a = 15.887(5), b = 12.714(4), c = 29.178(6) Å, β = 91.81(2)°, T = 23 ± 1 °C, and Z = 8. Crystals were generally of poor quality and it was only with difficulty that a suitable crystal for intensity data collection was obtained. Automatic diffractometry provided Bragg intensities for 4 594 independent reflections and the structure has been refined by least-squares methods to R 0.163 (all data) and 0.086 [$I > 2\sigma(I)$]. The structure consists of two crystallographically unique but chemically similar binuclear molecules in the asymmetric unit, each with one four-co-ordinate and one five-co-ordinate copper atom bridged by a thiophenolate-sulphur atom of the binucleating ligand and by a pyrazolyl group. The Cu ••• Cu separations are 3.474(3) and 3.424(3) Å in the two molecules, with Cu–S–Cu angles of 101.5(2) and 99.5(2)° respectively. The angles around the S atom are compatible with a pyramidal (sp^3) disposition of bonds which contrasts with the (presumed) trigonal-planar (sp^2) bonding of the phenolato O atom in [Cu_2(L-*O*)(pz)]. Variable-temperature magnetic susceptibility measurements have shown that the antiferromagnetic coupling in [Cu_2(L-*S*)(pz)] is much weaker ($2J = -5.2$ cm^{-1}) than in [Cu_2(L-*O*)(pz)] ($2J = -382$ cm^{-1}). In a related *S*-bridged complex possessing different side groups attached to the thiophenolate ring, the coupling is weakly ferromagnetic. These differences in exchange coupling can be related to geometric differences in the Cu_2(L-*X*) bridging moiety.

The dependence of magnetic exchange within binuclear copper(II) complexes upon stereochemical factors and the nature of the bridging species has been the subject of many recent studies.[1–4] The way in which a thiolate sulphur centre might mediate in magnetic exchange would be of considerable interest but binuclear complexes with bridging thiolates are very scarce, possibly because of the tendency of copper(II) to oxidise thiols to disulphides. To the best of our knowledge, the first such systems to be reported [5,6] were those of (**1**) and (**2**), the former showing Curie behaviour over the temperature range 120—296 K, indicating very weak coupling between adjacent copper(II) centres in marked contrast to the behaviour of related complexes of binucleating ligands containing a bridging phenolate unit. More recently the crystal structure of another thiolate-bridged dicopper(II) complex has been described, namely, [$Cu_2(L^1)_2(SC_6H_4Me$-*p*)]ClO_4 [L^1 = difluoro{3,3′-trimethylenedinitrilobis[butan-2-one oximato(2−)]}borate(1−)] in which each copper is bound by a macrocyclic N_4 ligand, L^1, and the two metals are bridged by a single thiophenolate; however, no magnetic properties were reported.[7,8]

It seemed to us important to examine the magnetic properties of matched pairs of dicopper(II) complexes derived from two closely related binucleating ligands, identical except that one contained a bridging phenolate moiety and the other a bridging thiophenolate. The present paper deals with the matched pair of (**3a**) and (**3b**). The phenolate-based binucleating ligand in (**3a**) will be referred to as L-O^{3-} and the thiophenolate-based ligand in (**3b**) as L-S^{3-} so that [Cu_2(L-*O*)(pz)] is (**3a**) and [Cu_2(L-*S*)(pz)] is (**3b**) (pz = pyrazolyl).

The magnetic susceptibilities of (**3a**) and (**3b**) and of a related *S*-bridged complex [Cu_2(L′-*S*)(pz)] (**4**), have been measured on a Faraday balance over the temperature range 4.2—300 K. Differences in the sign and magnitude of the exchange coupling constant, J, are discussed in relation to the geometry of the bridging S or O atom.

Experimental

Synthesis.—[Cu_2(L-*S*)(pz)]. A solution of the dimethylcarbamoyl-sulphur-protected ligand, H_2L-*S*·C(O)N(CH_3)$_2$[6] (0.50 g, 1 mmol) in dimethylformamide (dmf) (15 cm^3) at *ca.*

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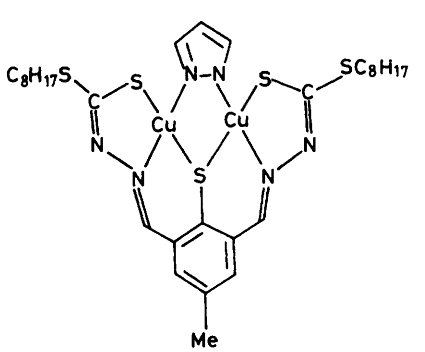
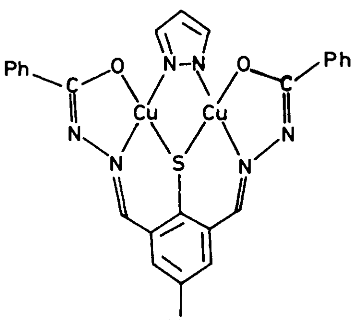
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

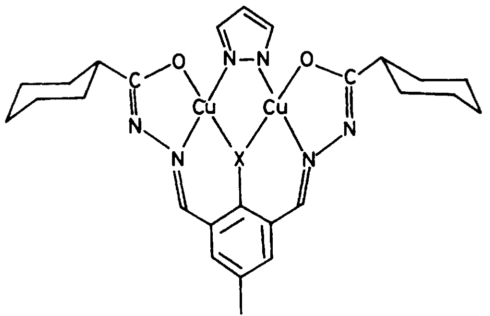
Non-S.I. unit employed: B.M. = 0.927 × 10^{-23} A m^2.



(1)

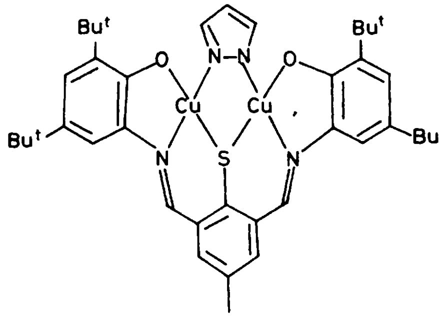


(2)



(3a); X = O

(3b); X = S



(4)

90 °C was added to a solution of copper(II) acetate monohydrate (0.40 g, 2 mmol) and pyrazole (0.076 g, 1.1 mmol) in a mixture of methanol (5 cm^3) and dmf (5 cm^3) heated on a steam-bath. Boiling methanol (25 cm^3) was added to the dark brown solution so formed which was then filtered whilst hot. Upon being allowed to cool to room temperature the filtrate deposited dark brown needles of $[Cu_2(L\text{-}S)(pz)(CH_3OH)]$ which were collected, and washed with dmf–methanol (1:1) and then methanol. A sample for magnetic measurements was dried in a stream of dinitrogen containing methanol vapour. Samples of solvent-free $[Cu_2(L\text{-}S)(pz)]$ for analysis and magnetic measurements were dried at 80 °C *in vacuo*. Yield: 0.35 g, 57% (Found: C, 50.3; H, 5.3; Cu, 20.6; N, 13.6; S, 5.4. $C_{26}H_{32}Cu_2N_6O_2S$ requires C, 50.4; H, 5.2; Cu, 20.5; N, 13.6; S, 5.2%).

$[Cu_2(L\text{-}O)(pz)]$. Cyclohexanecarbohydrazide, $C_6H_{11}C(O)NHNH_2$ (0.673 g, 4.74 mmol) dissolved in boiling ethanol (5 cm^3) was added to a boiling solution of 2-hydroxy-5-methylisophthalaldehyde (0.388 g, 2.37 mmol) in ethanol (15 cm^3) and the resulting yellow solution was heated at the boiling point for *ca.* 5 min. This hot solution was added to a suspension of copper(II) acetate monohydrate (0.947 g, 4.74 mmol) in boiling ethanol (60 cm^3) and the resulting mixture heated at the boiling point for 15 min. After the mixture had been allowed to cool to room temperature the suspended fine crystalline, pea green solid was collected, washed with ethanol, and dried at 80 °C *in vacuo*. Yield: 0.73 g. This solid was intended and is presumed to be $[Cu_2(L\text{-}O)(OC_2H_5)]$ but was used in the next stage of the preparation without full characterisation. Thus $[Cu_2(L\text{-}O)(OC_2H_5)]$ was heated in boiling chloroform (200 cm^3) and the hot mixture filtered to remove a small quantity of dirty grey amorphous material. Pyrazole (0.25 g, 3.7 mmol) in boiling ethanol (200 cm^3) was added to the hot dark green filtrate and the resulting solution was allowed to cool to room temperature. A small quantity of flocculent grey-blue solid was removed by filtration and the filtrate evaporated at atmospheric pressure to *ca.* one third its initial volume during which fine needles separated. The crystals were collected from the hot mixture, washed with ethanol, and dried at 80 °C *in vacuo*. Yield: 0.25 g (Found: C, 51.8; H, 5.7; Cu, 20.7; N, 13.9. $C_{26}H_{32}Cu_2N_6O_3$ requires C, 51.7; H, 5.3; Cu, 21.0; N, 13.9%).

$[Cu_2(L'\text{-}S)(pz)]$. To a solution of 2-amino-4,6-di-t-butylphenol (2.63 g, 11.9 mmol) in methanol (45 cm^3) was added 2-(*N,N*-dimethylthiocarbamato-*S*)-5-methylisophthalaldehyde (1.36 g, 5.4 mmol) in boiling methanol (50 cm^3). The resulting orange solution was heated under reflux for 10 min and then allowed to cool to room temperature. The fine yellow needles of the dimethylcarbamoyl-sulphur-protected ligand were collected, washed with methanol, and dried *in vacuo*. Yield: 2.63 g, 74%. A mixture of this sulphur-protected ligand (1.00 g, 1.5 mmol) and pyrazole (0.11 g, 1.75 mmol) dissolved in boiling chloroform (4 cm^3) was added to a solution of copper(II) acetate monohydrate (0.62 g, 3.12 mmol) in boiling methanol (70 cm^3). The mixture was heated under reflux for 30 min and then allowed to cool to room temperature. The brown-purple crystalline solid which separated was collected, washed with methanol, and dried at 80 °C *in vacuo*. Yield: 86% (Found: C, 61.6; H, 6.9; N, 7.2. $C_{40}H_{50}Cu_2N_4O_2S$ requires C, 61.7; H, 6.5; N, 7.2%).

Magnetic Measurements.—These were obtained using a Faraday balance as described previously.[9] Measurements were made on both the methanol and solvent-free forms of (**3b**).

Crystallography.—Attempts to grow single crystals of $[Cu_2(L\text{-}S)(pz)(CH_3OH)]$ by slow evaporation from a number of combinations of mixed solvents invariably resulted in clusters of fine fluffy needles unsuitable for *X*-ray diffraction studies. Single crystals marginally suitable for such studies were obtained directly from the dmf–methanol mother-liquor. Oscillation and Weissenberg photographs showed that some crystals decomposed in the *X*-ray beam and others, sealed in Lindemann glass tubes with mother-liquor present, were either disordered or twinned. Eventually a single crystal, sealed in a thin-walled Lindemann glass tube with a trace of mother-liquor, was obtained which was neither disordered nor twinned. The diffraction spots on Weissenberg photographs from this crystal were sharp and well defined, although intensities were generally weak and data did not extend much beyond (sin θ)/λ *ca.* 0.4 Å^{-1}. Photographic examination of a large number of crystals did not yield a better one, so this crystal, a needle of dimensions 0.04 × 0.12 × 0.5 mm, was used for intensity data collection. No decomposition of this crystal was apparent over a period of one year.

Oscillation and Weissenberg photographs showed the crystals to be monoclinic, and the space group was determined as $P2_1/c$ from the systematic absences. Unit-cell parameters, together with their estimated standard deviations (e.s.d.s), were derived by a least-squares analysis[10] of the setting angles, determined on a diffractometer at 22 °C with Cu-K_α radiation (λ = 1.541 8 Å), for 12 angularly well separated reflections each with $16 < 2\theta < 54°$.

Crystal data. $C_{27}H_{36}Cu_2N_6O_3S$, M = 651.78, monoclinic, a = 15.887(5), b = 12.714(4), c = 29.178(6) Å, β = 91.81(2)°, U = 5 890.6 Å^3, Z = 8, D_c = 1.47 Mg m^{-3}, $F(000)$ = 5 408, space group $P2_1/c$, μ(Cu-K_α) = 2.573 mm^{-1}.[11]

Intensity data were recorded at 23 ± 1°C on an automatic Siemens AED diffractometer with nickel-filtered Cu-K_α radiation. The crystal had well developed (100), (010), and (001) faces with perpendicular distances between parallel faces of 0.04, 0.5, and 0.12 mm respectively. The crystal was sealed in a thin-walled Lindemann glass tube and aligned with the b axis approximately parallel to the diffractometer 0 axis. Intensities were measured by a background–peak–background θ/2θ scan procedure, with a 2θ scan rate of 5° min^{-1}, a scan range of 1.4 + 0.4 tan θ, and stationary background counts each of half the scan time. Three reference reflections, monitored every 50 reflections, showed no significant variations in intensities during data collection.

A unique quadrant of data was collected within the limit (sin θ)/λ < 0.417 Å^{-1}. In addition, the observable data within the range 0.417 < (sin θ)/λ < 0.562 Å^{-1} were collected by the use of a preliminary point-count limit chosen to skip the very large amount of data with essentially zero intensities at higher angles. A total of 4 804 reflections were measured, of which 4 594 were unique. The R value[12] for the merging of equivalent data was 0.025. The integrated intensities were corrected for Lorentz and polarisation effects, and for absorption.[11]

Structure determination and refinement. The positions of the four copper atoms in the asymmetric unit were obtained by direct methods,[13] and subsequent difference Fourier syntheses

Table 1. Atomic positional co-ordinates, with e.s.d.s in parentheses, for $[Cu_2(L\text{-}S)(pz)(CH_3OH)]$*

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	0.263 4(1)	0.016 8(2)	0.462 5(1)	Cu(3)	−0.113 7(2)	0.484 2(2)	0.640 3(1)
Cu(2)	0.250 6(1)	0.238 1(2)	0.531 8(1)	Cu(4)	0.028 0(2)	0.282 2(2)	0.652 0(1)
S(1)	0.167 9(3)	0.119 6(4)	0.494 3(1)	S(2)	−0.026 4(3)	0.390 4(3)	0.597 7(1)
O(1)	0.328 1(6)	−0.093 2(9)	0.434 9(4)	O(4)	−0.182 8(7)	0.591 5(9)	0.665 8(4)
O(2)	0.291 7(7)	0.334 2(9)	0.579 2(3)	O(5)	0.112 2(8)	0.203 9(10)	0.685 6(4)
O(3)	0.334 4(7)	0.317 3(11)	0.474 4(4)	O(6)	−0.104 2(7)	0.209 9(9)	0.674 3(4)
N(1)	0.186 9(7)	−0.017 0(11)	0.411 2(4)	N(7)	−0.194 3(8)	0.503 8(11)	0.589 2(4)
N(2)	0.212 5(8)	−0.107 8(10)	0.386 8(4)	N(8)	−0.247 9(9)	0.588 0(11)	0.594 3(5)
N(3)	0.342 7(8)	0.044 2(10)	0.511 1(4)	N(9)	−0.039 7(8)	0.467 6(12)	0.693 8(4)
N(4)	0.333 2(8)	0.129 3(12)	0.540 3(4)	N(10)	0.017 1(8)	0.392 1(12)	0.697 0(4)
N(5)	0.178 2(8)	0.434 7(10)	0.552 1(4)	N(11)	0.109 0(10)	0.098 4(12)	0.621 5(6)
N(6)	0.165 4(8)	0.347 3(10)	0.523 3(4)	N(12)	0.047 1(8)	0.173 0(10)	0.607 1(5)
C(1)	0.106 7(9)	0.181 7(12)	0.450 4(5)	C(28)	−0.088 3(9)	0.316 7(12)	0.558 6(5)
C(2)	0.074 7(8)	0.284 0(12)	0.459 5(5)	C(29)	−0.061 1(9)	0.210 2(13)	0.546 0(5)
C(3)	0.014 4(9)	0.323 4(12)	0.426 9(5)	C(30)	−0.099 6(10)	0.163 2(13)	0.506 9(5)
C(4)	−0.014 8(9)	0.270 0(13)	0.388 0(5)	C(31)	−0.169 2(10)	0.206 0(13)	0.483 7(5)
C(5)	0.021 7(9)	0.174 5(13)	0.380 2(5)	C(32)	−0.199 3(10)	0.302 9(13)	0.499 9(5)
C(6)	0.083 8(9)	0.127 4(12)	0.410 3(5)	C(33)	−0.159 9(9)	0.357 1(12)	0.536 9(5)
C(7)	0.120 7(9)	0.026 3(12)	0.395 3(5)	C(34)	−0.207 0(9)	0.449 4(12)	0.550 8(5)
C(8)	0.286 5(11)	−0.137 4(14)	0.402 2(6)	C(35)	−0.236 5(12)	0.627 8(16)	0.636 2(7)
C(9)	0.326 1(10)	−0.228 5(13)	0.375 4(5)	C(36)	−0.291 1(13)	0.723 8(17)	0.645 9(7)
C(10)	0.382 1(10)	−0.295 4(13)	0.407 9(5)	C(37)	−0.240 7(15)	0.794 9(19)	0.677 5(8)
C(11)	0.417 1(11)	−0.386 6(15)	0.377 9(6)	C(38)	−0.294 9(16)	0.895 5(21)	0.690 1(9)
C(12)	0.467 6(12)	−0.341 7(15)	0.338 3(6)	C(39)	−0.373 5(15)	0.866 1(20)	0.707 8(8)
C(13)	0.413 4(12)	−0.271 6(16)	0.308 6(6)	C(40)	−0.418 6(18)	0.804 3(22)	0.679 7(10)
C(14)	0.377 1(11)	−0.181 1(14)	0.338 6(5)	C(41)	−0.368 5(15)	0.692 6(19)	0.667 0(8)
C(15)	0.410 0(10)	−0.015 0(14)	0.525 0(5)	C(42)	−0.035 4(11)	0.532 5(14)	0.732 0(6)
C(16)	0.446 6(10)	0.035 1(14)	0.562 7(5)	C(43)	0.027 8(11)	0.489 2(15)	0.760 1(7)
C(17)	0.400 0(10)	0.122 8(13)	0.571 1(5)	C(44)	0.059 6(13)	0.407 7(16)	0.736 6(7)
C(18)	0.245 9(11)	0.417 3(14)	0.578 1(6)	C(45)	0.138 2(14)	0.132 2(20)	0.659 6(8)
C(19)	0.272 9(9)	0.507 6(13)	0.610 4(5)	C(46)	0.211 8(18)	0.065 0(23)	0.681 5(10)
C(20)	0.263 0(11)	0.469 6(15)	0.659 2(6)	C(47)	0.288 8(13)	0.119 7(18)	0.679 0(7)
C(21)	0.294 5(12)	0.562 5(16)	0.692 5(7)	C(48)	0.369 9(14)	0.055 7(17)	0.699 9(8)
C(22)	0.375 9(12)	0.604 1(16)	0.681 3(6)	C(49)	0.355 3(18)	−0.058 1(22)	0.697 9(10)
C(23)	0.385 1(13)	0.635 9(17)	0.634 0(7)	C(50)	0.282 2(13)	−0.103 4(16)	0.700 0(7)
C(24)	0.360 8(10)	0.540 7(14)	0.601 2(6)	C(51)	0.202 4(13)	−0.043 0(17)	0.682 4(7)
C(25)	0.101 3(11)	0.355 3(13)	0.496 3(5)	C(52)	0.008 8(10)	0.151 1(14)	0.570 2(6)
C(26)	−0.080 6(10)	0.316 5(13)	0.355 6(5)	C(53)	−0.208 2(10)	0.152 3(14)	0.442 0(6)
C(27)	0.421 0(15)	0.338 6(18)	0.480 8(7)	C(54)	−0.142 7(11)	0.231 3(14)	0.716 6(6)

* Co-ordinates for molecule 2 beginning with Cu(3) follow those for molecule 1. In subsequent Tables and in Figure 1 atoms in molecule 2 are given the same number as the corresponding atoms in molecule 1 and the two molecules are defined by the labels molecule 1 and molecule 2.

Table 2. Interatomic distances (Å) in the two independent molecules of [Cu_2(L-*S*)(pz)(CH_3OH)]

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Cu(1)–S(1)	2.227(5)	2.236(5)	Cu(2)–S(1)	2.258(5)	2.251(5)
Cu(1)–O(1)	1.93(1)	1.92(1)	Cu(2)–O(2)	1.94(1)	1.91(1)
Cu(1)–N(1)	1.95(1)	1.95(1)	Cu(2)–N(4)	1.92(1)	1.93(1)
Cu(1)–N(3)	1.90(1)	1.94(1)	Cu(2)–N(6)	1.95(1)	1.94(1)
S(1)–C(1)	1.77(1)	1.75(1)	Cu(2)–O(3)	2.39(1)	2.40(1)
O(1)–C(8)	1.27(2)	1.28(2)	O(2)–C(18)	1.28(2)	1.27(3)
N(1)–N(2)	1.42(2)	1.38(2)	N(5)–N(6)	1.41(2)	1.42(2)
N(1)–C(7)	1.26(2)	1.33(2)	N(6)–C(25)	1.27(2)	1.25(2)
N(2)–C(8)	1.30(2)	1.33(2)	N(5)–C(18)	1.32(2)	1.27(3)
N(3)–N(4)	1.39(2)	1.32(2)	O(3)–C(27)	1.41(3)	1.42(2)
N(3)–C(15)	1.36(2)	1.39(2)	N(4)–C(17)	1.37(2)	1.33(2)
C(1)–C(2)	1.42(2)	1.47(2)	C(1)–C(6)	1.40(2)	1.38(2)
C(2)–C(3)	1.42(2)	1.41(2)	C(5)–C(6)	1.43(2)	1.41(2)
C(3)–C(4)	1.39(2)	1.39(2)	C(4)–C(5)	1.37(2)	1.41(2)
C(6)–C(7)	1.49(2)	1.46(2)	C(2)–C(25)	1.46(2)	1.50(2)
C(8)–C(9)	1.54(2)	1.53(3)	C(18)–C(19)	1.54(2)	1.57(4)
C(9)–C(10)	1.54(2)	1.51(3)	C(19)–C(20)	1.52(2)	1.41(4)
C(9)–C(14)	1.49(2)	1.45(3)	C(19)–C(24)	1.49(2)	1.38(4)
C(10)–C(11)	1.57(2)	1.59(4)	C(20)–C(21)	1.60(3)	1.63(3)
C(11)–C(12)	1.54(2)	1.42(3)	C(21)–C(22)	1.44(3)	1.47(3)
C(12)–C(13)	1.50(3)	1.33(4)	C(22)–C(23)	1.45(3)	1.30(4)
C(13)–C(14)	1.57(3)	1.67(4)	C(23)–C(24)	1.58(3)	1.56(3)
C(15)–C(16)	1.39(2)	1.39(2)	C(16)–C(17)	1.36(2)	1.35(3)
C(4)–C(26)	1.51(2)	1.51(2)			

revealed the positions of all 78 non-hydrogen atoms. Least-squares refinement in two blocks (one binuclear molecule in each block), with data uncorrected for absorption and with anisotropic thermal parameters assigned to all non-carbon atoms [433 variables, 2 674 data with $I > 2\sigma(I)$], converged with a reliability index R, defined as $\Delta F/\Sigma|F_o|$ where $\Delta F = ||F_o| - |F_c||$, of 0.100. The function minimised was $\Sigma w(\Delta F)^2$, where w is the weight assigned to the $|F_o|$ values. Of the 36 hydrogen atoms in each molecule, 29 were included in the scattering model at idealised positions (C–H = 1.08 Å) and with a variable overall thermal parameter. The methyl hydrogens and those of the co-ordinated methanol molecule were omitted. Refinement converged (434 variables, 2 674 data) with R 0.092. After absorption corrections were applied to the intensity data,[11] with transmission factors ranging between 0.90 and 0.71, the same refinement converged with R 0.086 and R' 0.078 {defined as $[\Sigma w(\Delta F)^2/wF_o]^{\frac{1}{2}}$ with $w = [\sigma^2(F_o) + 0.000\,4F_o^2]^{-1}$}.

Use of all 4 594 data at this final stage of refinement, with negative intensities set to zero, gave convergence with R 0.163 and R' 0.086. Despite the higher R values, the refinement employing all data gave lower e.s.d. values for the structural parameters (*e.g.* e.s.d.s of 0.005 Å for Cu–S bonds rather than 0.006 Å from the 2σ refinement) and is therefore considered the better refinement of the structure.[14] All data presented below and in the tables refer to the refinement employing all reflections. The maximum parameter shift-to-error ratio at convergence was 0.10:1. The largest peaks on a final difference synthesis were of heights 1.01 and -0.90 e Å^{-3}, with most of the large peaks lying close to atoms of the cyclohexyl groups. Final atomic positional co-ordinates, with e.s.d.s in parentheses, are listed in Table 1.

Neutral-atom scattering factor curves for C, N, O, and S were taken from ref. 15, that for neutral Cu was from ref. 16, and that for H was from ref. 17. Real and imaginary anomalous dispersion corrections were applied to the non-hydrogen atoms.[11] Structure determination and refinement were performed with the SHELX 76 program system[12] on the Commonwealth Department of Health IBM 3083J computer.

Table 3. Selected bond angles (°) in the two independent molecules of [Cu_2(L-*S*)(pz)(CH_3OH)]

	Molecule 1	Molecule 2
Cu(1)–S(1)–Cu(2)	101.5(2)	99.5(2)
Cu(1)–S(1)–C(1)	109.1(5)	107.5(5)
Cu(2)–S(1)–C(1)	110.6(5)	109.1(5)
S(1)–Cu(1)–O(1)	168.4(4)	165.6(4)
S(1)–Cu(1)–N(1)	91.9(4)	92.7(4)
S(1)–Cu(1)–N(3)	91.5(4)	91.1(4)
O(1)–Cu(1)–N(1)	81.1(5)	80.5(5)
O(1)–Cu(1)–N(3)	95.5(5)	96.0(5)
N(1)–Cu(1)–N(3)	176.6(5)	176.0(6)
S(1)–Cu(2)–O(2)	160.3(4)	157.8(4)
S(1)–Cu(2)–N(4)	88.1(4)	89.8(4)
S(1)–Cu(2)–N(6)	91.3(4)	91.4(4)
O(2)–Cu(2)–N(4)	98.5(5)	96.0(6)
O(2)–Cu(2)–N(6)	81.9(5)	81.5(5)
N(4)–Cu(2)–N(6)	179.2(6)	176.1(5)
S(1)–Cu(2)–O(3)	105.6(3)	96.0(3)
O(2)–Cu(2)–O(3)	93.0(4)	105.4(5)
N(4)–Cu(2)–O(3)	90.0(5)	89.8(5)
N(6)–Cu(2)–O(3)	90.7(5)	93.7(5)

Results and Discussion

Structure of [Cu_2(L-*S*)(pz)(CH_3OH)].—The crystal structure of [Cu_2(L-*S*)(pz)(CH_3OH)] consists of two discrete crystallographically independent but chemically similar binuclear molecules. The molecular geometry and atom numbering of one of the chemically similar [Cu_2(L-*S*)(pz)(CH_3OH)] molecules is shown in Figure 1. Interatomic bond distances and selected angles, with e.s.d.s derived from the refinement, are given in Tables 2 and 3. There are no intermolecular contacts of significance involving copper atoms.

Each chemically similar molecule of [Cu_2(L-*S*)(pz)(CH_3OH)] has the anticipated binuclear arrangement, with copper(II) atoms bridged by a thiolate-sulphur atom and by a pyrazolate group. One of the copper atoms is four-co-ordinate, with approximately square-planar geometry, whereas the other is in an approximately square-pyramidal environment with a

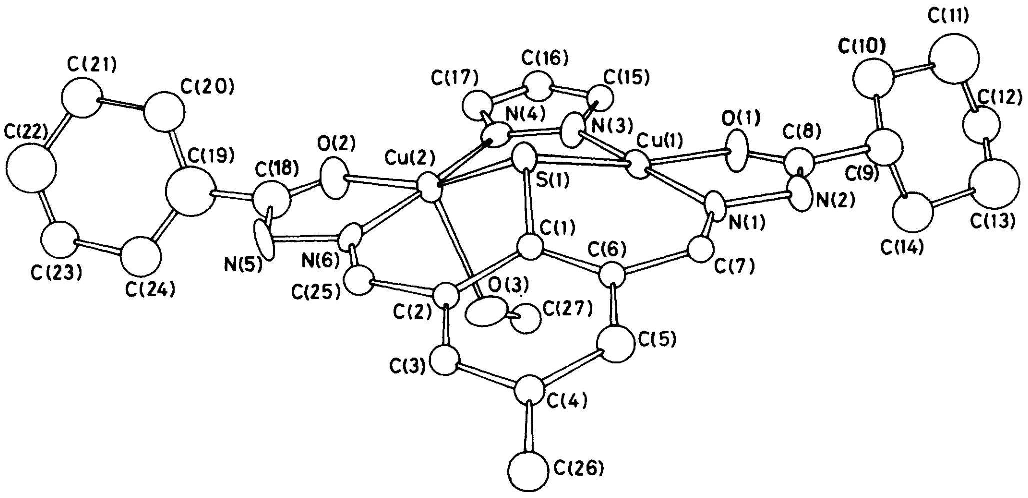


Figure 1. A view of molecule 2 of $[Cu_2(L\text{-}S)(pz)(CH_3OH)]$. The pyramidal nature of the bridging thiolate-sulphur atom, S(1), can be clearly seen in this perspective. The thermal ellipsoids are drawn at the 20% probability level

Table 4. Deviations (Å) of selected atoms from some mean planes in $[Cu_2(L\text{-}S)(pz)(CH_3OH)]$

Atoms in plane		Molecule 1	Molecule 2
N(1),N(3),O(1)	Cu(1)	−0.007(2)	0.034(2)
	S(1)	−0.374(4)	0.562(4)
N(4),N(6),O(2)	Cu(2)	0.012(2)	−0.051(2)
	S(1)	−0.695(4)	0.711(4)
N(1),N(3),O(1),S(1)	N(1)	0.09(1)	−0.13(1)
	N(3)	0.08(1)	−0.12(1)
	O(1)	−0.09(1)	0.14(1)
	S(1)	−0.075(4)	0.111(4)
	Cu(1)	0.082(2)	−0.100(2)
N(4),N(6),O(2),S(1)	N(4)	0.15(1)	−0.15(1)
	N(6)	0.17(1)	−0.17(1)
	O(2)	−0.17(1)	0.18(1)
	S(1)	−0.149(4)	0.144(4)
	Cu(2)	0.172(2)	−0.219(2)

methanol molecule co-ordinated in the apical position (Figure 1). The in-plane Cu^{II}–O and Cu^{II}–N bond distances [1.91(1)—1.95(1) Å] are normal, whereas the apical Cu–O(methanol) bond of the square-pyramidal copper atom is long [2.40(1) Å].

Interest in the structure of $[Cu_2(L\text{-}S)(pz)(CH_3OH)]$ naturally focusses on the Cu–S–Cu bonding. The sulphur atom in $[Cu_2(L\text{-}S)(pz)(CH_3OH)]$ has an approximately pyramidal configuration, as seen in Figure 1 and from the Cu–S–Cu and Cu–S–C angles which lie in the ranges 99.5(2)—101.5(2) and 107.5(5)—110.6(5)°, respectively. The Cu–S–C angles are a little larger than the values found recently in a mononuclear pseudo-tetrahedral 'CuN_2S_2' complex [105.3(1)°] [18] and in the 'blue' protein, plastocyanin (107°).[19] The Cu^{II}–S distances in the two unique molecules of $[Cu_2(L\text{-}S)(pz)(CH_3OH)]$ [2.227(5)—2.258(5) Å] are considerably shorter than those of 2.436(7) and 2.506(7) Å in $[Cu_2(L^1)_2(SC_6H_4Me\text{-}p)]^+$,[7,8] and the Cu–S–Cu angles of 101.5(2) and 99.5(2)° are significantly less than that of 128.6(3)° in the same cation. In $[Cu_2(L\text{-}S)(pz)(CH_3OH)]$ the bridging thiolate-sulphur atom forms part of the strongly bound co-ordination plane of each copper atom, whereas in the $[Cu_2(L^1)_2(SC_6H_4Me\text{-}p)]^+$ cation the bridging thiolate-sulphur atom plays the role of an axial ligand, interacting more weakly with copper atoms already well accommodated by strongly bound N_4 basal sets.

Deviations of copper and thiolate-sulphur atoms from the N,N,O co-ordination planes are given in Table 4. It is seen that the copper atoms are essentially in the appropriate N,N,O planes, even in the square-pyramidal [Cu(2)] cases, and that the sulphur atoms deviate from these co-ordination planes by distances ranging from 0.374(4) to 0.711(4) Å. The molecules are folded about the C–S axis (Figure 1) with angles between adjacent N,N,O co-ordination planes of 16.0° in molecule 1 and 11.8° in molecule 2. The apically-co-ordinated methanol molecule lies within the fold of the ligand (Figure 1), a geometry which effectively precludes the co-ordination of a second methanol to the adjacent (square-planar) copper atom. If mean co-ordination planes are calculated through the S,N,N,O atoms, the copper atoms are found to deviate from these planes so as to lie within the fold of the ligand (Table 4).

The Cu ··· Cu separations are 3.474(3) Å in molecule 1 and 3.424(3) Å in molecule 2, significantly shorter than that of 4.453(5) Å in the $[Cu_2(L^1)_2(SC_6H_4Me\text{-}p)]^+$ cation,[7,8] and they are also significantly less than the Pd ··· Pd internuclear distances of 3.605—3.699(1) Å observed in some palladium complexes of the same binucleating ligand.[20,21]

The geometries of the binucleating ligand in both molecules of the asymmetric unit of $[Cu_2(L\text{-}S)(pz)(CH_3OH)]$ are similar to those of the same ligand in related palladium complexes.[20,21] The bridging thiolate-sulphur atom in all of these complexes has the same approximately pyramidal configuration. The only other difference between ligand conformations is in the relative orientations of the cyclohexyl substituents. In $[Cu_2(L\text{-}S)(pz)(CH_3OH)]$ the cyclohexyl groups, all of which have the chair conformation, are poorly resolved due to some small disorder of these groups within the crystal lattice.

The μ-*N*,*N*′-bridging pyrazolate groups are planar, with a maximum deviation of any atom from the appropriate mean plane of 0.02(2) Å. The average dihedral angle between the mean planes of the pyrazolate group and the benzene ring of each of the two molecules of the asymmetric unit is 12.8°.

An examination of the molecular structure of $[Cu_2(L\text{-}S)(pz)(CH_3OH)]$ indicates that the two major problems encountered in the crystallography arose from ready loss of the weakly co-ordinated methanol with consequent loss of crystallinity, and disorder in the cyclohexyl groups. This disorder is manifested by the presence of some large peaks of

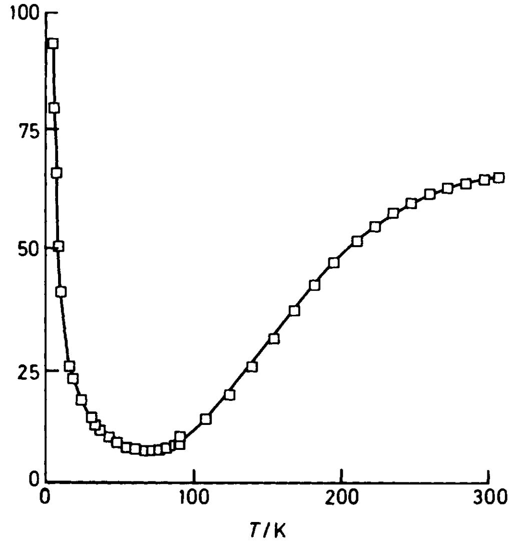


Figure 2. Temperature dependence of χ_{Cu} for [Cu_2(L-*O*)(pz)]. The solid line is that calculated using the parameters given in the text

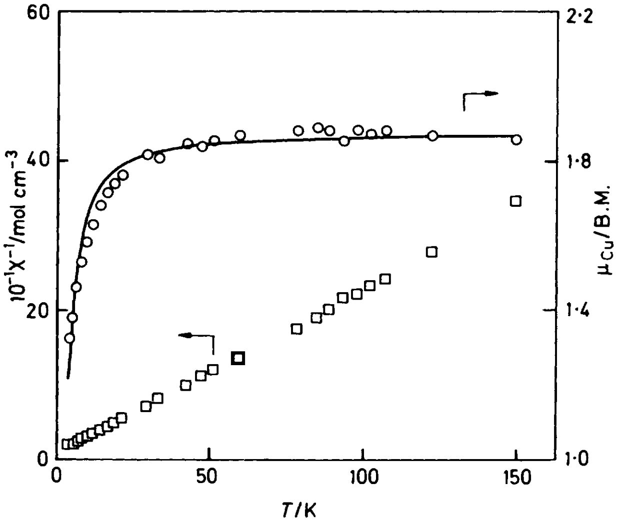


Figure 3. Temperature dependence of χ_{Cu}^{-1} and μ_{Cu} for [Cu_2(L-*S*)(pz)]. The solid line is that calculated using the parameters given in the text

residual electron density in the final difference Fourier analysis close to the cyclohexyl groups, and by the large variation in C–C distances in these groups (Table 2).

The disorder present in the crystal used for data collection meant that very few high-angle data were observable. The result of this limitation in the data is low resolution of the atomic positions and, ultimately, low precision (high e.s.d.s) in bond distances and angles. Fortunately the presence of two chemically similar but crystallographically unique molecules in the asymmetric unit provides an internal check on the overall integrity of the structure solution. The agreement between analogous bond distances and angles in the two molecules is in general excellent, and well within the limits suggested by the e.s.d. values. For this reason, we believe the small differences between certain features of the two molecules are real effects and not merely artefacts arising from inadequacies in the reflection data.

Magnetic Properties.—The magnetic moments at room temperature of [Cu_2(L-*S*)(pz)(CH_3OH)] and of solvent-free [Cu_2(L-*S*)(pz)] are both 1.85 B.M. (per Cu). The variable-temperature data are also very similar, thus indicating that the co-ordinated methanol does not significantly influence the exchange coupling between the Cu atoms. A μ_{Cu} value of 1.85 B.M. for complex (**4**), and an earlier reported value of 1.76 for (**1**),[6] are compatible with generally weak coupling in these thiophenolate-bridged complexes.

In contrast, the *O*-bridged derivative, [Cu_2(L-*O*)(pz)], displays a room-temperature moment of 1.25 B.M. (per Cu) with a χ_{Cu} *versus* *T* plot which is typical of that expected for strongly antiferromagnetically coupled copper(II) complexes.[1–4] As seen in Figure 2, the susceptibilities decrease gradually towards zero as the temperature decreases from 300 to 100 K and then increases rapidly at the lowest temperatures due to the effect of trace quantities of a monomeric impurity. The data can be fitted well to the Bleaney–Bowers expression[22] for a spin-coupled $S_1 = S_2 = \frac{1}{2}$ system yielding the best-fit parameters $g = 2.19 \pm 0.02$ and $2J = -382 \pm 2$ cm^{-1} (% of monomer = 1.56).

The susceptibilities of [Cu_2(L-*S*)(pz)] show a Curie-like dependence on temperature with a corresponding temperature independent μ_{Cu} value of 1.85 B.M. in the range 300—25 K. Below 25 K the moment decreases quite rapidly to a value of 1.32 B.M. at 4.2 K (Figure 3). These data can be fitted reasonably well to the Bleaney–Bowers expression with a small negative 2*J* value of -5.2 ± 0.2 cm^{-1} and $g = 2.1 \pm 0.02$. In view of the similar μ_{Cu} *versus* *T* data for the sample [Cu_2(L-*S*)(pz)(CH_3OH)], which has been shown (see above) to possess two structurally slightly different binuclear molecules in the asymmetric unit, it is possible that the small divergencies from the Bleaney–Bowers model could come from an 'averaging' of two slightly different *J* (and *g*) values. Fitting of the magnetic data for [Cu_2(L-*S*)(pz)(CH_3OH)] gave a similar quality of fit with parameter values close to those obtained for the anhydrous material, *viz.* $g = 2.03 \pm 0.01$, $2J = -3.6 \pm 0.1$ cm^{-1}.

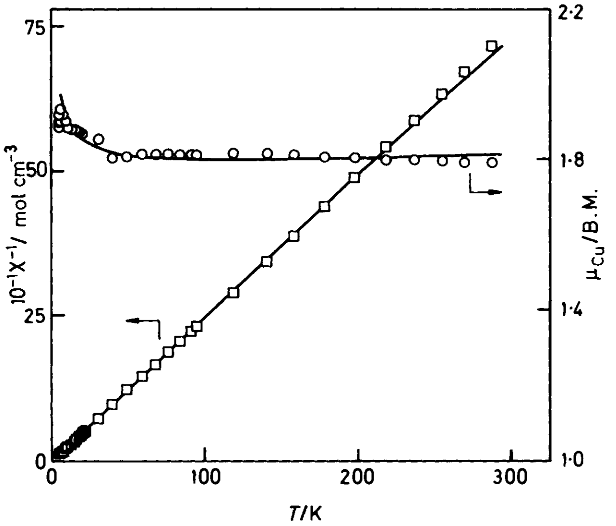


Figure 4. Temperature dependence of χ_{Cu}^{-1} and μ_{Cu} for [Cu_2(L′-*S*)(pz)] (**4**). The solid line is that calculated using the parameters given in the text

Interestingly, while the susceptibilities for (**4**) are also Curie-like, the corresponding μ_{Cu} values show a small gradual *increase* from 1.80 to 1.93 B.M. as the temperature decreases from 40 to 6 K. This is then followed by a small decrease in μ_{Cu} on further cooling to 4.2 K (Figure 4). Such behaviour has been noted recently in related *O*-bridged systems[3,4,9] and is due to nett intramolecular ferromagnetic coupling. The decrease in μ_{Cu} at very low temperatures is due either to zero-field splitting of the $S' = 1$ ground state or to weak *inter*molecular antiferromagnetic coupling. The data in the range 6—300 K could be fitted quite well using $g = 2.04 \pm 0.02$, and $2J = +6 \pm 1$ cm^{-1}, although the fitting errors are characteristically large for positive J situations.[3,4]

Since J values are made up of an antiferromagnetic and a ferromagnetic contribution,[2,4] it is clear from the present data on (**3b**) (both with and without CH_3OH) and (**4**) that the antiferromagnetic contribution is very small, leading to an overall small negative value in (**3b**) and an overall small positive value in (**4**). Such observations are consistent with the interpretation given recently for similarly weakly coupled *O*-bridged (phenolato or alcoholato) copper(II) complexes containing one- or two-atom exogenous bridging groups.[3,4,9] The exogenous superexchange pathway plays a minimal role in these kinds of systems, the endogenous pathway being most important and extremely dependent on both the geometry of the bridging O or S atom and on the relative dispositions of the Cu–ligand planes. Detailed arguments have been given elsewhere.[3,4] In essence, a trigonal planar (sp^2) geometry of the bridging atom, together with coplanarity of the adjacent Cu–ligand planes, leads to overall strong antiferromagnetic coupling and a correspondingly medium to large negative J value. This is due to good overlap between the $d_{x^2-y^2}$ magnetic orbitals on Cu and the sp^2 orbitals on the bridging atom. As the geometry of the bridging atom approaches pyramidal (sp^3), usually with a dihedral angle concomitantly developing between the adjacent Cu–ligand planes, the J value approaches zero or becomes overall positive. Any deviation of the bridging atom from the Cu–ligand best-plane will also lead to poor overlap with the Cu $d_{x^2-y^2}$ magnetic orbital, thus reducing the antiferromagnetic contribution. From the crystal structure of $[Cu_2(L\text{-}S)(pz)(CH_3OH)]$ we see that the pyramidally disposed S atom of the thiophenolate bridge renders this interpretation of the J values applicable. Likewise, by comparison with many recent studies on related *O*-bridged complexes,[3,4,9] it is possible (in the absence of a crystal structure) confidently to predict that in $[Cu_2(L\text{-}O)(pz)]$ (*i*) the phenolate oxygen atom will have a trigonal-planar geometry, (*ii*) the binuclear species will be overall coplanar, and (*iii*) *r*(Cu–Cu) will be *ca.* 3.4 Å and the Cu–O–Cu angle *ca.* 130°.

Further indirect confirmation of such geometric features within Cu–(SR)–Cu and Cu–(OR)–Cu moieties being primarily responsible for the observed differences in exchange coupling is offered on consideration of the expected ordering of J values if co-ordination geometry, bridge angle, and all else were kept constant. As Holm and co-workers[23] have recently pointed out {in comparing $[\{Fe(salen)\}_2S]$ with $[\{Fe(salen)\}_2O]$ (H_2salen = *NN'*-ethylenebis(salicylideneimine) and on the basis of the theory of Hoffmann and co-workers[24]}, the J value for an *S*-bridge would be expected to be more negative than for an *O*-bridge. Likewise, Br bridging in Cu^{II} dimers should lead to stronger antiferromagnetism than Cl bridging.[25] While it is known[4,9] that many subtle features in the ligand framework of binucleated complexes of the present types can influence J values, it does appear that geometric differences at the endogenous bridging atom are paramount.* There is, however, a dearth of available matched pairs of M(OR)M and M(SR)M species (of M = Cu^{II} or any other metal ions) and further examples are required in order to test out the generality of the present ideas.

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* A referee has pointed out that the local copper environments in complexes of the present type may be different on account of crystal-packing effects associated with the plasticity effect of the copper(II) ion. These effects may also influence the magnetic exchange (see, for example, B. J. Hathaway, Proc. 9th Conf. Coord. Chem., 1983, p. 93 and J. Gazo, I. B. Bersuker, J. Garas, M. Kabesova, J. Kohout, H. Langfelderova, M. Melnik, M. Serator, and F. Valach, *Coord. Chem. Rev.*, 1976, **19**, 253).