DALTON

Copper complexes of 1,3-bis(2-pyridyl)-1-thiapropane (bpt) and pyridine-2(1*H*)-thione. Crystal structure of $[\{Cu(\mu\text{-}O_2CMe)_2(bpt)\}_2]$ and metal-promoted cleavage of bpt†

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The reactivity of the asymmetric thioether 1,3-bis(2-pyridyl)-1-thiapropane [1-(2-pyridyl)-2-(2-pyridylsulfanyl)ethane] (bpt) with copper-(I) and -(II) starting materials has been investigated. Reaction with $[Cu(NCMe)_4]PF_6$ in MeCN gave a cluster formulated as $[Cu_4(bpt)_6][PF_6]_4$, whilst reaction in tetrahydrofuran resulted in partial cleavage of bpt to give the mixed thionato–thioether complex $[Cu_2(SC_5H_4N)(bpt)]PF_6$ [SC_5H_4NH = pyridine-2(1*H*)-thione]. Reaction with $[Cu_2(\mu\text{-}O_2CMe)_4]$ in MeOH gave the dimer $[\{Cu(\mu\text{-}O_2CMe)_2\text{-}(bpt)\}_2]$, whose crystal structure shows that the bpt ligands are monodentate and co-ordinated *via* the N atom remote from the thioether. The compound bpt undergoes cleavage with other copper(II) salts such as $Cu(BF_4)_2$, ultimately giving the hexameric copper(I) complex $[Cu_6(SC_5H_4N)_6]$. The details of this reaction have been investigated. Reaction of SC_5H_4NH with $Cu(NO_3)_2$ in the presence of HNO_3 gave $[Cu(NO_3)(SC_5H_4NH)_2]$, which in turn reacted progressively with PPh_3 to give $[Cu(NO_3)(SC_5H_4NH)_2(PPh_3)]$ and the known complex $[Cu(SC_5H_4NH)_2(PPh_3)_2]NO_3$, whose crystal structure has been determined. Other complexes of SC_5H_4NH with copper(I) and a range of anions have been prepared, and the crystal structure of the dimer $[Cu_2(SC_5H_4NH)_6]\text{-}[MeC_6H_4SO_3]_2$ is reported.

Type 1 copper centres are found in a variety of copper metalloproteins, including blue copper oxidases,[1] plastocyanins[2] and nitrite reductases.[3] Their roles as electron-transfer agents are associated with the distinctive properties of the copper atom, which is generally co-ordinated by two histidine, one cysteinate and one methionine ligand in a highly distorted tetrahedral or trigonal-pyramidal environment.[4] Model studies using simple copper complexes to mimic this arrangement have highlighted the remarkably flexible nature of the copper with regard to its co-ordination geometry, a phenomenon termed plasticity.[5,6] We have previously reported the crystal structure of a molybdenum(0) complex of the asymmetric thioether 1,3-bis(2-pyridyl)-1-thiapropane [1-(2-pyridyl)-2-(2-pyridylsulfanyl)ethane] (bpt),[7] in which the four- and six-membered chelate rings formed by the tridentate N_2S-donor bpt ligand result in a highly distorted octahedral geometry around the metal centre. In the hope of preparing structurally distorted copper complexes of bpt, we have now investigated the chemistry of this thioether with a number of copper-(I) and -(II) starting materials.

Results and Discussion

Reactions of bpt with copper(II)

The preparation and spectroscopic properties of bpt have been described previously.[7] Reaction of bpt with copper(II) acetate gave the dimeric adduct $[\{Cu(\mu\text{-}O_2CMe)_2(bpt)\}_2]$ **1**. Its molecular structure, determined by X-ray crystallography, is shown in Fig. 1, and selected bond lengths and angles are given in Table 1. In this complex the bpt ligand is monodentate, behaving as a simple pyridine; the structure is a classic example of a carboxylate-bridged dinuclear copper(II) adduct,[8] closely related to that of $[\{Cu(\mu\text{-}O_2CMe)_2(py)\}_2]$ (py = pyridine).[9] The molecule lies about a centre of symmetry; the geometry around the copper atoms is essentially five-co-ordinate square pyramidal, and the geometrical properties of the complex are in good agreement with the literature values for related complexes.[8–10] It is noteworthy that in complex **1** copper(II) prefers to co-ordinate the harder pyridine nitrogen donor over the thioether sulfur. Furthermore, the pyridine ring remote from the sulfur is preferred for co-ordination. This is evidently due primarily to electronic rather than steric effects, since molecular models show that the steric difference between the two possible isomers is minimal. It has been argued[11] that since the pyridine rings in this type of complex are staggered with respect to the orthogonal planes of the carboxylate ligands, pyridine is acting essentially as a pure σ donor; in this case the inductively electron-withdrawing properties of the thioether compared to the alkyl group could account for the choice of pyridine donor in complex **1**.

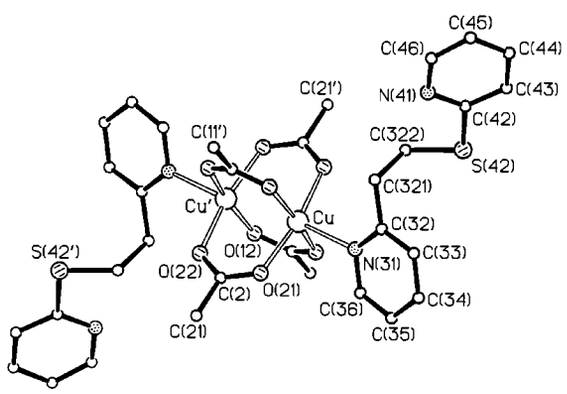


Fig. 1 Crystal structure of $[\{Cu(\mu\text{-}O_2CMe)_2(bpt)\}_2]$ **1**

The room-temperature magnetic moment of complex **1** was measured as 1.35 μ_B, typical for complexes of this type.[11] Even though the copper centres in **1** are paramagnetic, it was possible to observe the non-co-ordinated ends of the bpt ligands by NMR spectroscopy (Tables 4 and 5). Together with the low

† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

Table 1 Selected dimensions (bond lengths in Å, angles in °) in $[\{Cu(\mu\text{-}O_2CMe)_2(bpt)\}_2]$ **1** with estimated standard deviations (e.s.d.s) in parentheses *

(*a*) About the Cu atom

Cu···Cu′	2.651(1)	Cu–O(21)	1.979(3)
Cu–O(11)	1.974(3)	Cu–O(22′)	1.960(3)
Cu–O(12′)	1.958(3)	Cu–N(31)	2.217(3)
O(11)–Cu–O(12′)	167.5(1)	O(12′)–Cu–O(22′)	90.9(1)
O(11)–Cu–O(21)	90.6(1)	O(12′)–Cu–N(31)	99.7(1)
O(11)–Cu–O(22′)	87.3(1)	O(21)–Cu–O(22′)	167.6(1)
O(11)–Cu–N(31)	92.8(1)	O(21)–Cu–N(31)	91.4(1)
O(12′)–Cu–O(21)	88.5(1)	O(22′)–Cu–N(31)	100.9(1)

(*b*) In the acetate ligands

O(11)–C(1)	1.246(5)	O(21)–C(2)	1.255(5)
C(1)–O(12)	1.253(5)	C(2)–O(22)	1.254(5)
C(1)–C(11)	1.515(7)	C(2)–C(21)	1.495(7)
Cu–O(11)–C(1)	122.1(3)	Cu–O(21)–C(2)	124.8(3)
O(11)–C(1)–O(12)	125.8(4)	O(21)–C(2)–O(22)	125.0(4)
Cu′–O(12)–C(1)	124.5(3)	Cu′–O(22)–C(2)	122.2(3)

(*c*) In the bpt ligand

C(32)–C(321)	1.501(6)	C(322)–S(42)	1.799(5)
C(321)–C(322)	1.528(6)	S(42)–C(42)	1.769(5)
Cu–N(31)–C(32)	129.6(3)	C(321)–C(322)–S(42)	116.1(3)
Cu–N(31)–C(36)	112.2(3)	C(322)–S(42)–C(42)	102.7(2)
N(31)–C(32)–C(321)	117.5(4)	S(42)–C(42)–N(41)	119.3(3)
C(33)–C(32)–C(321)	122.0(4)	S(42)–C(42)–C(43)	117.2(4)
C(32)–C(321)–C(322)	113.6(4)		

(*d*) Torsion angles in the bpt ligand

N(31)–C(32)–C(321)–C(322)	−94.2(4)
C(33)–C(32)–C(321)–C(322)	85.8(5)
C(32)–C(321)–C(322)–S(42)	−71.7(4)
C(321)–C(322)–S(42)–C(42)	−89.3(4)
C(322)–S(42)–C(42)–N(41)	18.8(4)
C(322)–S(42)–C(42)–C(43)	−160.5(4)

* Primed atoms are related by the operation: $1 - x$, $1 - y$, $1 - z$.

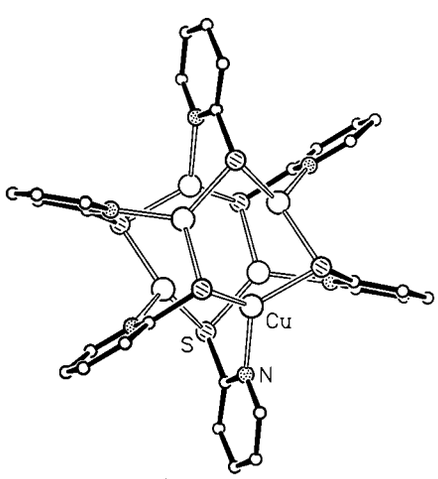
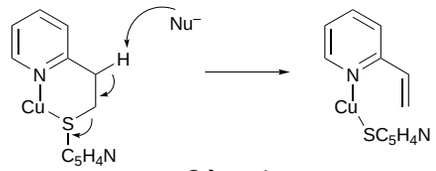


Fig. 2 Crystal structure of $[Cu_6(SC_5H_4N)_6]$ **2**

solution conductivity[12] of **1** (Table 3), these observations suggest that the solid-state structure is retained in solution.

Reaction of bpt with other copper(II) starting materials such as $CuSO_4$ and $Cu(BF_4)_2$ in alcohol–water mixtures initially gave green solutions, but no copper(II) complexes could be isolated. In time the solutions precipitated an orange solid, insoluble in all organic solvents tested. When the reaction was carried out in dimethyl sulfoxide (dmso) solution crystals suitable for X-ray crystallography were obtained and found to be a known complex of pyridine-2(1*H*)-thione (SC_5H_4NH), namely $[Cu_6(SC_5H_4N)_6]$ **2** (Fig. 2). The structure of this complex was originally obtained by Kitagawa *et al.*,[13] who prepared it by the reaction of the copper(I) salt $[Cu(NCMe)_4]PF_6$ with SC_5H_4NH in acetone.



Scheme 1

In order to explain the formation of complex **2** from copper(II) plus bpt, we examined the reaction of $CuSO_4$ with bpt in more detail. Upon boiling an equimolar mixture of the reactants in methanol–water solution for 4 h, $[Cu_6(SC_5H_4N)_6]$ was obtained in 50% yield. The green colour of the reaction solution suggested that the remaining copper(II) had not reacted; the solution was acidic, and contained 2-vinylpyridine as shown by ^{1}H NMR spectroscopy and its characteristic odour. The overall reaction can therefore be written as in equation (1) where dpds is bis(2-pyridyl) disulfide and vpy is

$$CuSO_4 + 2bpt \longrightarrow \tfrac{1}{6}[Cu_6(SC_5H_4N)_6] + \tfrac{1}{2}dpds + 2vpy + H_2SO_4 \quad (1)$$

2-vinylpyridine. The cleavage of bpt to SC_5H_4NH and vpy is the reverse of the reaction used for its preparation, and is evidently promoted by both copper-(II) and -(I) (see below). The reaction is reminiscent of the metal-promoted cleavage of $RSCH_2CH_2SR$ groups to give a thiolate plus vinyl thioether;[14] it might involve the formation of a chelate ring incorporating the pyridine nitrogen and the thioether sulfur, which would render the protons of the ethylene linkage susceptible to nucleophilic attack as shown in Scheme 1.

These observations led us to consider the co-ordination chemistry of copper with SC_5H_4NH in more detail.

Reactions of pyridine-2(1*H*)-thione with copper

The co-ordination chemistry of SC_5H_4NH and other heterocyclic thioamides with copper is an active research area which has recently been reviewed in detail.[15] Although the reaction of SC_5H_4NH with $Cu(O_2CMe)_2$ was investigated as long ago as 1900,[16] the exact nature of the product has proved elusive, being successively formulated as $[Cu_2(SC_5H_4N)_2]$,[16] $[\{Cu(SC_5H_4N)\}_n]$[17] and $[Cu_4(SC_5H_4N)_4]$.[18] The last formulation was based primarily on the mass spectrum of the complex, which showed $[Cu_4(SC_5H_4N)_4]^+$ as the highest mass ion, with the correct $^{63/65}$Cu isotopic ratio for a Cu_4 species. Further support for a tetrameric structure has been deduced from the observation that the complex can be prepared from the crystallographically characterised species $[Cu_2(SC_5H_4NH)_6]Cl_2$.[19] The cation of this complex is a dimer with a Cu_2S_2 core, which could serve as a basis for formation of a Cu_4S_4 heterocubane. The cation of the bromide analogue is isostructural,[20] and that of the toluene-*p*-sulfonate $[Cu_2(SC_5H_4NH)_6][MeC_6H_4SO_3]_2$, characterised by X-ray crystallography during the course of the present study (complex **3**, see Fig. 3 and Table 2), is basically the same (see below). Notwithstanding these observations, we now identify $[\{Cu(SC_5H_4N)\}_n]$ as the hexamer $[Cu_6(SC_5H_4N)_6]$, as confirmed by its crystal structure. Although we were able to observe the molecular ion in the mass spectrum of authentic $[Cu_6(SC_5H_4N)_6]$, this peak had only 0.24% of the intensity of the largest peak {that of $[Cu_2(SC_5H_4N)_2]^+$} and 0.44% of the intensity of the $[Cu_4(SC_5H_4N)_4]^+$ peak; the largest peak above *m/z* 700 was that of $[Cu_5(SC_5H_4N)_4]^+$, with an intensity of 0.51% of that of the $[Cu_2(SC_5H_4N)_2]^+$ peak. It would appear that under the fairly severe conditions required to observe the mass spectrum

Table 2 Selected dimensions (bond lengths in Å, angles in °) in $[Cu_2(SC_5H_4NH)_6][MeC_6H_4SO_3]_2$ **3** with e.s.d.s in parentheses[a]

(*a*) About the copper atom

Cu···Cu′	2.744(1)	Cu–S(2)	2.307(1)
Cu–S(1)	2.406(1)	Cu–S(3)	2.304(1)
Cu–S(1′)	2.403(1)		
S(1)–Cu–S(1′)	110.4[b]	S(1′)–Cu–S(2)	107.8[b]
S(1)–Cu–S(2)	118.3[b]	S(1′)–Cu–S(3)	118.5[b]
S(1)–Cu–S(3)	97.0[b]	S(2)–Cu–S(3)	105.0[b]

(*b*) In the ligands

S(1)–C(11)	1.717(3)	Cu–S(1)–Cu′	69.6[b]
		Cu–S(1)–C(11)	109.6(1)
		Cu′–S(1)–C(11)	113.9(1)
S(2)–C(21)	1.710(3)	Cu–S(2)–C(21)	116.0(1)
S(3)–C(31)	1.698(4)	Cu–S(3)–C(31)	109.1(1)

(*c*) In proposed hydrogen bonds

N(12)···O(41″)	2.765(3)	H(12)···O(41″)	1.80
N(22)···O(42)	2.731(4)	H(22)···O(42)	1.83
N(32)···S(1′)	3.689(3)	H(32)···S(1′)	2.79
N(12)–H(12)···O(41″)	165.8	N(32)–H(32)···S(1′)	152.8
N(22)–H(22)···O(42)	151.8		

[a] The primes indicate the symmetry relations: ′ $1 - x, 1 - y, -z$; ″ $1 - x, -y, -z$. [b] E.s.d. is less than 0.05°.

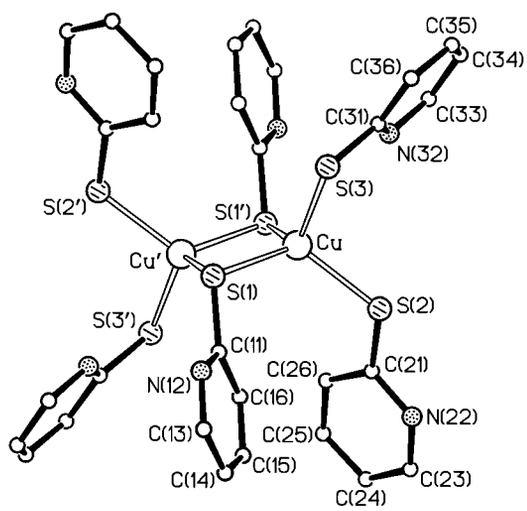


Fig. 3 Crystal structure of the cation of $[Cu_2(SC_5H_4N)_6][MeC_6H_4SO_3]_2$ **3**

of this complex (370 °C) it suffers extensive degradation; indeed, the same mass spectrum is also observed for quite unrelated complexes (see below).

It is noteworthy that although the crystal structure of complex **3** shows it to be a centrosymmetric dimer with four terminal and two bridging SC_5H_4NH ligands, its ^1H and ^{13}C NMR spectra show only one type of SC_5H_4NH ligand, even in weakly co-ordinating solvents such as dichloromethane. This suggests that in solution, either $[Cu_2(SC_5H_4NH)_6]^{2+}$ dissociates to the known[21] $[Cu(SC_5H_4NH)_3]^+$ cation, or that the terminal and bridging SC_5H_4NH ligands exchange rapidly. Either way, the bridging thione bonds must be readily broken in solution. In the crystal we note that there are significant variations in the geometries of the cations of the halide salts (which are essentially identical[19,20]) and of complex **3**. In our complex the four $Cu–S_{bridging}$ bonds are equal at 2.405(1) Å (Table 2). The $Cu–S_{terminal}$ distances are also the same, at 2.305(1) Å. The Cu···Cu′ distance, at 2.744(1) Å, is considerably shorter than in the chloride, 2.907(2)[19] or 2.950(2)[20] Å, and bromide, 2.907(2) Å,[20] and correspondingly the Cu–S–Cu′ angles are quite different, 69.6° in **3** *versus* 74.3(1) or 74.6(1)° in the chloride, 73.8(1)° in the bromide. The principal differences, however, are in the orientations of the pyridine rings, a consequence of the different hydrogen-bonding schemes and packing of the anions, halide *versus* toluene-*p*-sulfonate, with respect to the cations. Two N–H···X hydrogen bonds and an intramolecular hydrogen bond are recorded for the halide structures; similarly, all three crystallographically independent N–H groups in **3** are involved in hydrogen bonds, two to oxygen atoms of neighbouring anions (in quite different directions from the halide structures) and the third a rather longer, intramolecular N–H···S contact, involving different groups from those in the halides. The hydrogen bonding connects the ions in sheets in the halides, but in **3** the linking is in chains (Fig. 4).

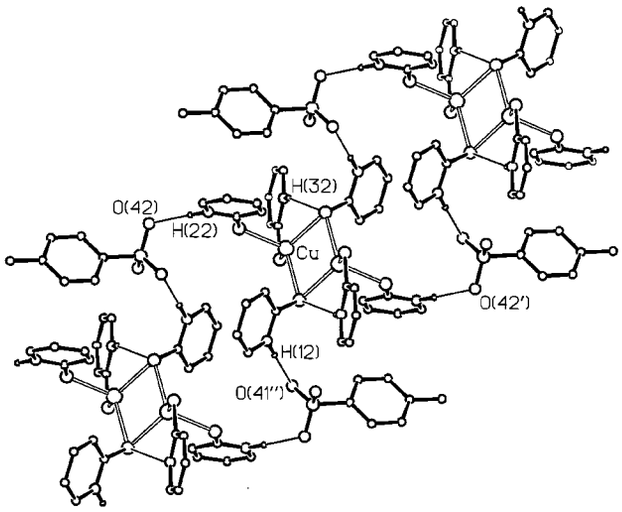


Fig. 4 View of the hydrogen-bonding scheme in complex **3**. The H···O and H···S hydrogen bonds are shown with the thinner lines. The scheme continues in double-linked chains through the crystal

The *in situ* reduction of copper(II) with an excess of SC_5H_4NH is a useful method for the preparation of SC_5H_4NH complexes of copper(I), which can give different products from those obtained by the direct reaction of the analogous copper(I) salt. For example, reaction of $CuCl_2$ and $CuBr_2$ with SC_5H_4NH was reported to give $[CuCl(SC_5H_4NH)]$ and $[CuBr_2(SC_5H_4NH)_2]$ respectively,[17,19] whereas the analogous reactions with CuCl and CuBr gave $[CuCl(SC_5H_4NH)_3]$ and $[CuBr(SC_5H_4NH)_2]$ respectively.[17] In contrast to these results, we found that reaction of $CuBr_2$ and SC_5H_4NH gives $[CuBr(SC_5H_4NH)]$ **4**. The low conductivity of complex **4** in dimethylformamide (dmf) solution suggests that the bromine atoms are co-ordinated; the complex is probably polymeric in the solid state, with bridging through both sulfur and bromine atoms to give a copper co-ordination number of four. The choice of anion is critical to the stoichiometry of the product, thus reaction of $CuSO_4$ with 3 equivalents of SC_5H_4NH gives $[Cu_2(SC_5H_4NH)_4]SO_4$ **5**, or alternatively $[Cu(SC_5H_4NH)_2]BPh_4$ **6** if $NaBPh_4$ is added to the reaction solution. These complexes are all air-stable, diamagnetic solids; $[Cu_2(SC_5H_4NH)_4]SO_4$ is readily soluble in water, but the solution soon precipitates $[Cu_6(SC_5H_4N)_6]$ with concomitant liberation of acid. Addition of a trace of sulfuric acid to solutions of **5** significantly retards the decomposition process; the ^1H NMR spectrum of **5** was not significantly affected by this measure. Similarly, the tetraphenylborate complex **6** rapidly starts to decompose upon dissolution in organic solvents such as dmso; $[Cu_6(SC_5H_4N)_6]$ is precipitated and the solution becomes acidic. Further evidence of decomposition is observed in the ^1H and ^{13}C NMR spectra of **6**, which show the formation of a species which we identify as $HSC_5H_4NH^+BPh_4^-$. This is itself unstable, reacting further to give benzene and (presumably) a $SC_5H_4NH·BPh_3$ adduct. Although the initial decomposition of **6** is rapid, as the acidity

Table 3 Colours, melting points, conductivities and analytical[a] data for the complexes

	Complex	Colour	M.p./°C	Λ_M[b]/S cm^2 mol^{-1}	Analysis (%) C	H	N	X[c]
1	$[\{Cu(\mu\text{-}O_2CMe)_2(bpt)\}_2]$	Green	162[d,e]	8	48.4 (48.3)	4.4 (4.6)	6.9 (7.0)	—
2	$[Cu_6(SC_5H_4N)_6]$	Orange	305[d]	—[f]	34.6 (34.6)	2.3 (2.3)	7.8 (8.1)	—
3	$[Cu_2(SC_5H_4NH)_6][MeC_6H_4SO_3]_2$	Orange	152	100	46.2 (46.5)	3.8 (3.9)	7.1 (7.4)	10.6[g] (11.2)
4	$[CuBr(SC_5H_4NH)]$	Orange	184[d,e]	25	23.6 (23.6)	1.9 (2.0)	5.4 (5.5)	—
5	$[Cu_2(SC_5H_4NH)_4]SO_4\cdot 2H_2O$	Yellow	159[e]	71	34.4 (34.1)	3.0 (3.4)	7.8 (8.0)	17.5[g] (18.1)
6	$[Cu(SC_5H_4NH)_2]BPh_4\cdot H_2O$	Yellow	74[d]	45[h]	65.9 (65.5)	5.0 (5.2)	4.5 (4.5)	11.1 (10.3)
7	$[Cu_2(SO_4)(SC_5H_4NH)_2]$	Yellow	142[d]	37	27.4 (27.0)	2.3 (2.3)	6.4 (6.3)	21.5 (21.6)
8	$[Cu(NO_3)(SC_5H_4NH)_2]$	Yellow	146[d]	41	34.5 (34.5)	2.8 (2.9)	12.1 (12.1)	17.8 (18.4)
9	$[Cu(SC_5H_4NH)_2]PF_6$	Yellow	175[d]	64	28.4 (27.9)	2.1 (2.3)	6.4 (6.5)	31[i,j] (34)
10	$[Cu(NO_3)(SC_5H_4NH)(py)]$	Orange	126[k]	49[l]	38.8 (38.0)	3.2 (3.2)	13.1 (13.3)	10.2 (10.2)
11	$[Cu(NO_3)(SC_5H_4NH)_2(PPh_3)]$	Yellow	118	49	54.9 (55.1)	4.1 (4.1)	6.4 (6.9)	10.5 (10.5)
12	$[Cu(SC_5H_4NH)_2(PPh_3)_2]NO_3$	Yellow	127	69	—	—	—	—
13	$[Cu_2(bpt)_3][PF_6]_2\cdot C_3H_6O$	Yellow	140	141	41.6 (41.7)	3.7 (3.8)	7.4 (7.5)	25.9[i] (25.8)
14	$[Cu_2(SC_5H_4N)(bpt)]PF_6\cdot 0.25C_3H_6O$	Orange	146	73	35.1 (34.8)	2.7 (2.9)	6.7 (6.9)	24.0[i] (23.6)
15	$[Cu(py)_4]PF_6$	Pale green	169[d]	71	46.0 (45.8)	3.7 (3.8)	10.6 (10.7)	27.9[i] (27.6)

[a] Calculated values in parentheses. [b] In dmf; accepted ranges[12] for 1:1 and 1:2 electrolytes are 65–90 and 130–170 S cm^2 mol^{-1} respectively. [c] X = S unless stated otherwise. [d] Decomposes. [e] Shows signs of decomposition below this temperature. [f] Insufficient solubility for measurement. [g] Copper analysis. [h] Λ_M for $NaBPh_4$ measured under the same conditions = 47 S cm^2 mol^{-1}. [i] PF_6 analysis. [j] The poor solubility of this complex limited the precision of the determination. [k] Melts with decomposition. [l] Sample dissolved by heating to 100 °C then allowing to cool to room temperature before measurement.

of the solution increases the rate decreases, allowing observation of its $^{13}C\text{-}\{^1H\}$ NMR spectrum.

During the course of these studies we noted that although $[Cu_6(SC_5H_4N)_6]$ is often readily precipitated, some of the copper(I)–SC_5H_4NH products evidently stay in solution in these reactions. Speculating that this may be associated with the formation of the acid by-product, we investigated these reactions in the presence of the conjugate acid. Reaction of $CuSO_4$ with SC_5H_4NH in the presence of H_2SO_4 gave a new complex formulated as $[Cu_2(SO_4)(SC_5H_4NH)_2]$ **7**. This compound has a different stoichiometry from that of **5**, $[Cu_2(SC_5H_4NH)_4]SO_4$; moreover whilst complex **5** is a 1:1 electrolyte in dmf, **7** is non-conducting. Only a relatively small excess of acid is required for the isolation of complex **7**; use of more than 2 equivalents leads to the formation of an orange tar rather than a yellow powder. Reaction of $Cu(NO_3)_2$ with SC_5H_4NH in the presence of HNO_3 gave the new complex $[Cu(NO_3)(SC_5H_4NH)_2]$ **8**. This material exhibits an unusual stability pattern. The freshly prepared complex is bright yellow and indefinitely stable if stored in a sealed ampoule. It also shows no deterioration if left in air for several weeks, and is unaffected by light and atmospheric moisture. However, if a sample of the complex, whether freshly prepared or not, is transferred to a stoppered tube, it turns green overnight. The decomposition may not be as advanced as it appears, since the microanalysis and IR spectrum of the green material were only marginally different from those of the undecomposed compound. Upon removing the stopper the characteristic odour of NO_2 was noted. This suggests that the reaction may be autocatalytic; if the compound is left in air any NO_x formed is free to escape, whereas in a stoppered tube it would be more likely to attack the complex.

Complexes **7** and **8** were investigated as starting materials for further synthesis. The sulfato complex **7** reacts with HX (X = Br or Cl) to give $[CuBr(SC_5H_4NH)]$ and the known complex[19] $[CuCl(SC_5H_4NH)]$ respectively; however reaction with HPF_6 gives a product with different stoichiometry, $[Cu(SC_5H_4NH)_2]PF_6$ **9**. This species is presumably formed *via* a disproportionation reaction. Although solutions of complex **7** in water are stable for up to 1 h, treatment with salts such as $NaBF_4$ or $Na(SC_6H_2Pr^i_3\text{-}2,4,6)$ led to the immediate precipitation of $[Cu_6(SC_5H_4N)_6]$. The nitrato-complex **8** reacts with an excess of pyridine to give $[Cu(NO_3)(SC_5H_4NH)(py)]$ **10** and

Table 4 Proton NMR data[a]

Compound	δ(*J*/Hz)
SC_5H_4NH[b]	12.10 (s, 1 H, H^1), 7.52 ('d', 1 H, H^6), 7.37 (m, 2 H, $H^{3,4}$), 6.72 ('t', 1 H, H^5)
$HSC_5H_4NH^+$[b,c]	8.44 (m, 1 H, H^6), 8.25 ('t', 1 H, H^4), 7.87 ('d', 1 H, H^3), 7.66 ('t', 1 H, H^5)
bpt[d]	8.54 ('d', 1 H, H^6), 8.43 ('d', 1 H, H^6), 7.59 ('t', 1 H, H^4), 7.47 ('t', 1 H, H^4), 7.20 ('d', 1 H, H^3), 7.18 ('d', 1 H, H^3), 7.13 ('t', 1 H, H^5), 6.97 ('t', 1 H, H^5), 3.58 (t, J_{HH} = 7.4, $CH_2C_5H_4N$), 3.18 (t, J_{HH} = 7.4, CH_2S)
1[e]	8.47 (br, 1 H, H^6), 7.58 ('t', 1 H, H^4), 7.25 ('d', 1 H, H^3), 7.07 ('t', 1 H, H^5), 3.86 (br, 2 H, CH_2)
3[f]	14.22 (br s, 3 H, H^1), 7.97 ('d', 3 H, H^6), 7.64 (m, 6 H, $H^{3,4}$), 7.47 (d, 2 H, $O_3SC_6H_4Me$), 7.10 (d, 2 H, $O_3SC_6H_4Me$), 7.07 ('t', 3 H, H^5), 2.27 (s, 3 H, $O_3SC_6H_4Me$)
4[g]	14.46[h] (br s, 1 H, H^1), 8.27 ('d', 1 H, H^6), 7.86 (m, 2 H, $H^{3,4}$), 7.26 ('t', 1 H, H^5)
5[i]	14.42[h] (br s, 1 H, H^1), 8.08 ('d', 1 H, H^6), 7.70 (m, 2 H, $H^{3,4}$), 7.15 ('t', 1 H, H^5)
6[f,j]	14.23[h] (br s, 1 H, H^1), 7.99 ('d', 2 H, H^6), 7.61 (m, 4 H, $H^{3,4}$), 7.17 (m, 8 H, BPh_4), 7.04 ('t', 2 H, H^5), 6.91 (t, 8 H, BPh_4), 6.78 (t, 4 H, BPh_4)
7[i]	14.70 (br s, 1 H, H^1), 8.14 (br, 1 H, H^6), 7.71 (br, 1 H, H^4), 7.54 (br, 1 H, H^3), 7.17 (br, 1 H, H^5)
8[f]	14.27 (br s, 1 H, H^1), 8.01 (br, 1 H, H^6), 7.64 (br m, 1 H, H^4), 7.58 (br m, 1 H, H^3), 7.06 ('t', 1 H, H^5)
9[e,k]	8.28 (br, 1 H, H^6), 7.77 (br, 2 H, $H^{3,4}$), 7.33 (br, 1 H, H^5)
11[b]	13.00 (br s, 2 H, H^1), 7.76 ('d', 2 H, H^6), 7.31–7.46 (m, 19 H, $H^{3,4}$, PPh_3), 6.87 (m, 2 H, H^5)
12[f]	14.00 (br s, 2 H, H^1), 7.82 ('d', 2 H, H^6), 7.46–7.24 (m, 34 H, $H^{3,4}$, PPh_3), 6.89 ('t', 2 H, H^5)
13[b,l]	8.48 (m, 1 H, H^6), 8.41 (m, 1 H, H^6), 7.70 (m, 1 H, H^4), 7.58 (m, 1 H, H^4), 7.25 (m, 3 H, $H^{3,5}$), 7.08 (m, 1 H, H^5), 3.52 (t, J_{HH} = 7.1, 2 H, $CH_2C_5H_4N$), 3.15 (t, J_{HH} = 7.1, 2 H, CH_2S)
14[f,l]	8.73–8.01 (br m, 3 H, H^6), 7.85 ('t', 1 H, H^4), 7.66 ('t', 1 H, H^4), 7.52–6.75 (br m, 7 H, $H^{4,3,5}$), 3.49 (br, 2 H, $CH_2C_5H_4N$), 3.17 (br, 2 H, CH_2S)
15[b]	8.53 (br, 2 H, H^2), 7.82 (m, 1 H, H^4), 7.42 (br, 2 H, H^3)

[a] br = Broad, s = singlet, d = doublet, t = triplet, m = multiplet; multiplicities in inverted commas are pseudo-multiplicities, generally showing second-order couplings also, but valuable for peak assignments. [b] In CD_3CN. [c] Acidified with $MeSO_3H$. [d] In CD_2Cl_2. [e] In $(CD_3)_2CO$; spectrum of complex **1** shows other very broad features above δ 8. [f] In $(CD_3)_2SO$. [g] In $(CD_3)_2NCDO$. [h] Shown to exchange with D_2O. [i] In $(CD_3)_2SO$ plus a little concentrated H_2SO_4. [j] Spectrum also contains a minor component at δ 8.47, 7.80 and 7.27, possibly $HSC_5H_4NH^+BPh_4^-$ (see text). [k] H^1 will be exchanged in this solvent. [l] Spectrum also shows solvent of crystallisation.

Table 5 ^{13}C-{^1H} NMR data[a]

Compound	δ(*J*/Hz)
SC_5H_4NH	179.2 (C^2), 138.6 (C^6), 138.0 (C^4), 134.1 (C^3), 113.8 (C^5)
$HSC_5H_4NH^+$	154.5 (C^2), 146.9 (C^6), 142.8 (C^4), 129.0 (C^3), 123.8 (C^5)
bpt	159.9 (C^2), 158.8 (C^2), 149.3 (C^6), 149.2 (C^6), 136.0 (C^4), 135.8 (C^4), 123.0 (C^3), 121.9 (C^3), 121.3 (C^5), 119.2 (C^5), 37.8 ($CH_2C_5H_4N$), 29.1 (CH_2S)
1	159.8 (C^2), 150.3 (C^6), 137.0 (C^4), 122.8 (C^3), 120.3 (C^5)
3	171.0 (C^2), 145.6 (C^6), 140.2 ($O_3SC_6H_4Me$), 139.3 ($O_3SC_6H_4Me$), 137.7 (C^4), 131.7 (C^3), 128.1 ($O_3SC_6H_4Me$), 125.5 ($O_3SC_6H_4Me$), 116.4 (C^5), 20.8 ($O_3SC_6H_4Me$)
4[b]	146.4 (C^6), 144.9 (C^4), 137.5 (C^3), 123.1 (C^5)
5	167.9 (C^2), 141.1 (C^6), 139.9 (C^4), 131.4 (C^3), 117.9 (C^5)
6	171.4 (C^2), 163.4 (q, J_{CB} = 49, BPh_4), 140.1 (C^6), 139.2 (C^4), 135.6 (BPh_4), 131.8 (C^3), 125.3 (br, BPh_4), 121.5 (BPh_4), 116.2 (C^5)
7	162.0 (C^2), 139.7 (C^6), 138.5 (C^4), 128.9 (C^3), 117.2 (C^5)
8	171.0 (C^2), 140.2 (C^6), 139.3 (C^4), 131.7 (C^3), 116.4 (C^5)
9	164.8 (C^2), 143.8 (C^6), 141.8 (C^4), 132.4 (C^3), 121.1 (C^5)
11	171.5 (C^2), 139.8 (C^6), 139.1 (C^4), 133.3 (d, J_{CP} = 16, PPh_3), 132.7 (d, J_{CP} = 28, PPh_3), 131.9 (C^3), 130.2 (PPh_3), 128.9 (d, J_{CP} = 9, PPh_3), 116.1 (C^5)
12	173.0 (C^2), 139.1 (C^6), 138.8 (C^4), 133.3 (d, J_{CP} = 16, PPh_3), 133.0 (d, J_{CP} = 22, PPh_3), 131.2 (C^3), 130.1 (PPh_3), 128.8 (d, J_{CP} = 9, PPh_3), 115.3 (C^5)
13[c]	160.9 (C^2), 158.9 (C^2), 150.5 (C^6), 150.2 (C^6), 137.9 (C^4), 137.5 (C^4), 124.7 (C^3), 123.3 (C^3), 122.9 (C^5), 120.9 (C^5), 38.1 ($CH_2C_5H_4N$), 30.2 (CH_2S)
14[c,d]	36.9 ($CH_2C_5H_4N$), 30.3 (CH_2S)
15	150.5 (C^2), 137.8 (C^4), 125.7 (C^3)

[a] All resonances are singlets unless stated otherwise; solvents as in Table 4. [b] C^2 is probably obscured by the solvent. [c] Spectrum also shows solvent of crystallisation. [d] Spectrum also shows a set of aromatic signals at δ 160–120, but the sample was not sufficiently stable to allow for detailed analysis.

with PPh_3 to give $[Cu(NO_3)(SC_5H_4NH)_2(PPh_3)]$ **11**. Both of these complexes have only limited stability in solution; on standing, a solution of $[Cu(NO_3)(SC_5H_4NH)(py)]$ in pyridine precipitated a mixture of $[Cu_6(SC_5H_4N)_6]$ and pyridinium nitrate, whilst attempted crystallisation of $[Cu(NO_3)(SC_5H_4NH)_2(PPh_3)]$ from ethanol gave, as the isolated product in low yield, the known complex $[Cu(SC_5H_4NH)_2(PPh_3)_2]NO_3$ **12**, originally prepared by the reaction of $Cu(PPh_3)_2NO_3$ with SC_5H_4NH.[22] The crystal structure of complex **12** is shown in Fig. 5, and selected dimensions are given in Table 6. The structure of the analogous perchlorate complex, $[Cu(SC_5H_4NH)_2(PPh_3)_2]ClO_4\cdot 2CHCl_3$,[23] shows very similar tetrahedral co-ordination and dimensions about the copper atom. Whereas the $\{Cu(PPh_3)_2(S)_2\}$ fragments of the cations of the two complexes can be reasonably well superimposed, the orientations of the SC_5H_4NH ligands are quite different and, as in complex **3** and its analogues, these appear to be determined by hydrogen-bonding contacts. In complex **12** dimeric units are formed by the linking of pairs of cations through pairs of anions by hydrogen bonding about a centre of symmetry (Table 6). The links to both cations are made through one oxygen atom, O(51), of the nitrate ion; the other two O atoms are not involved. In the perchlorate one of the SC_5H_4NH ligands is hydrogen bonded to an anion; the other is intramolecularly bonded to the sulfur atom of the first SC_5H_4NH ligand. The intermolecular hydrogen bonding scheme is thus limited to single cation–anion units.

The higher conductivity of the ionic nitrate complex **12** compared to the other nitrato complexes **8**, **10** and **11** (Table 3) suggests that the nitrate is probably co-ordinated in these last three. Reaction of SC_5H_4NH with copper(II) nitrite in nitrous acid gave only $[Cu_6(SC_5H_4N)_6]$, as did the equivalent reaction with copper(II) methanesulfonate in methanesulfonic acid.

Table 6 Selected dimensions (bond lengths in Å, angles in °) in $[Cu(SC_5H_4NH)_2(PPh_3)_2]NO_3$ **12** with e.s.d.s in parentheses *

(*a*) About the copper atom

Cu–S(1)	2.397(2)	Cu–P(3)	2.308(2)
Cu–S(2)	2.358(2)	Cu–P(4)	2.294(2)
S(1)–Cu–S(2)	100.3(1)	S(1)–Cu–P(4)	106.7(1)
S(1)–Cu–P(3)	101.3(1)	S(2)–Cu–P(4)	120.6(1)
S(2)–Cu–P(3)	104.1(1)	P(3)–Cu–P(4)	120.4(1)

(*b*) In the SC_5H_4NH ligands

S(1)–C(11)	1.703(6)	Cu–S(1)–C(11)	108.0(2)
S(2)–C(21)	1.708(7)	Cu–S(2)–C(21)	110.2(2)

(*c*) In the phosphine ligands

P(3)–C(31a)	1.831(6)	P(4)–C(41a)	1.832(6)
P(3)–C(31b)	1.840(6)	P(4)–C(41b)	1.823(6)
P(3)–C(31c)	1.829(6)	P(4)–C(41c)	1.827(6)
Cu–P(3)–C(31a)	112.6(2)	Cu–P(4)–C(41a)	112.4(2)
Cu–P(3)–C(31b)	115.3(2)	Cu–P(4)–C(41b)	112.6(2)
C(31a)–P(3)–C(31b)	102.8(3)	C(41a)–P(4)–C(41b)	103.7(3)
Cu–P(3)–C(31c)	115.9(2)	Cu–P(4)–C(41c)	122.1(2)
C(31a)–P(3)–C(31c)	104.9(3)	C(41a)–P(4)–C(41c)	101.2(3)
C(31b)–P(3)–C(31c)	103.8(3)	C(41b)–P(4)–C(41c)	102.7(3)

(*d*) Proposed hydrogen-bonding contacts

N(12)···O(51)	2.872(8)	N(22)···O(51′)	2.800(8)
H(12)···O(51)	2.26(7)	H(22)···O(51′)	2.05(6)
N(12)–H(12)···O(51)	132(6)	N(22)–H(22)···O(51′)	167(6)
H(12)···O(51)···H(22′)	136(2)		

* The prime indicates the symmetry relation: $1 - x$, $1 - y$, $1 - z$.

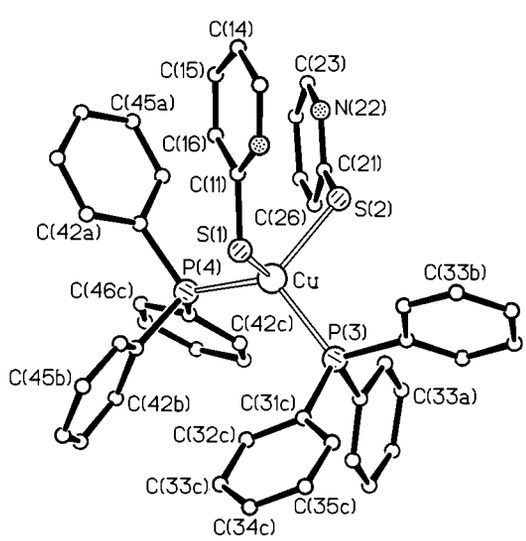


Fig. 5 Crystal structure of the cation of $[Cu(SC_5H_4NH)_2(PPh_3)_2]NO_3$ **12**

Reactions of bpt with copper(I)

The products obtained from the reaction of bpt with $[Cu(NCMe)_4]PF_6$ depend on the reaction solvent. When equimolar amounts of bpt and the copper salt were allowed to react in acetonitrile no identifiable products were obtained; however, the use of an excess of bpt afforded a pale yellow material formulated empirically as $[Cu_2(bpt)_3][PF_6]_2$ **13**. The ^{1}H and ^{13}C-{^{1}H} NMR spectra showed only one set of bpt resonances, suggesting a symmetrical structure in solution, whilst the mass spectrum again showed only $[Cu_4(SC_5H_4N)_4]^+$ as the highest molecular weight ion, presumably due to the necessarily high inlet temperature of 370 °C. The stoichiometry of complex **13** recalls the well known class of thiolate-bridged clusters $[Cu_4(SR)_6]^{2-}$ (R = alkyl or aryl).[24] Molecular models derived from the crystallographically established $\{Cu_4(SPh)_6\}$ moiety suggest that a $[Cu_4(bpt)_6]^{4+}$ cluster is feasible in steric terms. Well characterised examples of thioether-bridged copper(I) species, although rare, are not unknown; the clusters $[Cu_4Br_4(ddtp)_2]$ [ddtp = 1,5-bis(3′,5′-dimethylpyrazolyl)-3-thiapentane][25] and $[\{Cu^I_3Cu^{II}Cl_5(tht)_3\}_n]$ (tht = tetrahydrothiophene)[26] are examples.

The reaction of bpt with $[Cu(NCMe)_4]PF_6$ in tetrahydrofuran (thf) resulted in the precipitation of an orange product formulated empirically as $[Cu_2(SC_5H_4N)(bpt)]PF_6$ **14**, in which half of the bpt reagent has evidently undergone metal-promoted cleavage to give a pyridine-2-thionate ligand (see above). This was confirmed by the identification of 2-vinylpyridinium hexafluorophosphate in the supernatant by ^{1}H, ^{13}C-{^{1}H} and ^{31}P NMR spectroscopy, hence the overall reaction can be written as in equation (2). The ^{1}H NMR spectrum of

$$2[Cu(NCMe)_4]PF_6 + 2bpt \longrightarrow [Cu_2(SC_5H_4N)(bpt)]PF_6 + vpy + HPF_6 \quad (2)$$

complex **14** confirms the presence of the SC_5H_4N ligand in that the ratio of aromatic to aliphatic protons is 3 : 1 rather than the 2 : 1 expected for bpt alone. As with complex **13**, the mass spectrum of **14** showed $[Cu_4(SC_5H_4N)_4]^+$ as the highest mass ion. In the absence of X-ray structural information no firm conclusions can be drawn about the structure of this complex, although one possibility is a modification of the $[Cu_6(SC_5H_4N)_6]$ cluster **2** in which three of the SC_5H_4N ligands are replaced by bpt ligands.

^{1}H NMR, ^{13}C NMR and IR Spectra

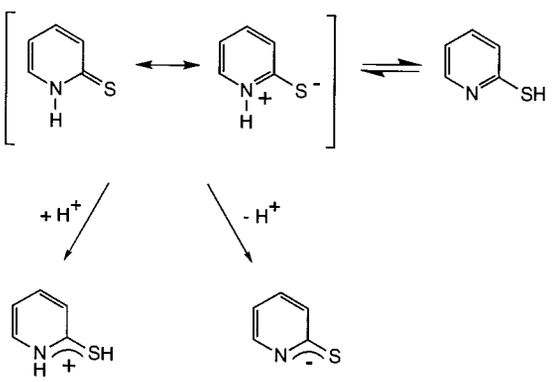
As an aid to interpretation of the spectra of the SC_5H_4NH complexes, we also prepared and characterised the simple tetrakis(pyridine)copper(I) species $[Cu(py)_4]PF_6$ **15**. Although the potentially hazardous perchlorate analogue, $[Cu(py)_4]ClO_4$, is known and has been characterised by X-ray crystallography,[27] equilibrium and enthalpy measurements[28] and ^{63}Cu NMR spectroscopy,[29] to the best of our knowledge the ^{1}H and ^{13}C NMR and IR properties of the $[Cu(py)_4]^+$ cation have not previously been described. In complex **15**, where the ligands are necessarily co-ordinated through nitrogen, the pyridine $H^{3/5}$ and H^4 protons exhibit chemical shifts intermediate between those of free pyridine, which are relatively shielded, and those of the pyridinium salt $C_5H_5NH^+Cl^-$, which are relatively deshielded.[30] In contrast, the chemical shift of the pyridine $H^{2/6}$ protons in **15** is not intermediate between those for free py and $C_5H_5NH^+Cl^-$, but rather is very close to the value for free py; this additional shielding is presumably a consequence of the proximity of these protons to the metal. Turning to the complexes of SC_5H_4NH, **3**–**9**, **11** and **12**, in each case the chemical shifts of all four aryl protons are intermediate between those of free SC_5H_4NH and $HSC_5H_4NH^+O_3SMe^-$ (Table 4); the observation that, unlike the $H^{2/6}$ protons of compound **15**, the H^6 protons do not show an additional shielding, is consistent with co-ordination of SC_5H_4NH through sulfur rather than through nitrogen in these complexes. The ^{13}C NMR spectra of the py and SC_5H_4NH complexes (Table 4) show very similar effects.

The infrared spectra of the complexes of both bpt and SC_5H_4NH give little by way of diagnostic information, beyond confirmation of the presence of pyridine groups and the various anions. No ν(SH) band was observed, consistent with the co-ordination of SC_5H_4NH through S in the thione tautomer rather than through N in the pyridinethiol tautomer (see below). Clearly, given the possibility of protonation of the pyridine N, even if ν(C=N) of the pyridine ring could be unambiguously assigned, a shift in frequency between the complexes and free SC_5H_4NH could not be taken as evidence for co-ordination of this atom.

Table 7 Nitrogen-14 NMR data for selected compounds and related species[a]

Compound	δ^b
SC_5H_4NH	−182 (170)[c]
$HSC_5H_4NH^+O_3SMe^-$	−184 (140)[d]
$Na^+SC_5H_4N^-$	−94 (2400)[d]
3	−177 (770)
6	−180 (1050)
8	−10 (55), −182 (830)
11	−4 (40), −192 (800)

[a] Referenced to external $MeNO_2$. Data obtained on Me_2SO–$(CD_3)_2SO$ solutions unless stated otherwise. [b] Linewidth at half maximum (Hz) in parentheses. [c] In CCl_4. [d] In EtOH–CD_3OD.



Scheme 2

^{14}N NMR Spectra of pyridine-2(1*H*)-thione and its complexes

It has long been recognised that SC_5H_4NH exists in tautomeric equilibrium with pyridine-2-thiol (HSC_5H_4N).[31,32] The substantially higher dipole moment of the thione compared to the thiol tautomer[33] is readily explained in terms of a resonance hybrid for SC_5H_4NH involving a contribution from the zwitterionic form;[34] these are illustrated in Scheme 2, along with the thionium cation and thionate anion formed by protonation and deprotonation respectively of SC_5H_4NH. It should be noted that, with all these species, valence-bond representations are only approximate descriptions. The $SC_5H_4NH \rightleftharpoons HSC_5H_4N$ equilibrium has been probed by a variety of techniques, including ^{14}N and ^{15}N NMR spectroscopies.[35,36] Comparison of the ^{14}N chemical shifts of SC_5H_4NH in acetone and methanol solutions (δ *ca.* −187) with those of its N- and S-methylated derivatives 1-methylpyridine-2-thione (δ *ca.* −189) and 1-(2-pyridyl)-1-thiaethane [2-(methylsulfanyl)pyridine] (NC_5H_4SMe, δ −79 and −88 in acetone and methanol respectively) allowed Stefaniak[35] to deduce that SC_5H_4NH is 95 ± 5% in the SC_5H_4NH form in these solvents. We have obtained data for the species shown in Scheme 2 and also for selected complexes (Table 7). It is important to note here that dissolved dinitrogen gives an ^{14}N peak at δ −71 ppm, exactly in the region where substituted pyridines are expected to appear. For compounds which have moderate solubilities or large linewidths, the dinitrogen peak can have comparable intensity, hence samples were prepared under argon or sealed under vacuum.

The ^{14}N chemical shift of the thionium cation is virtually unchanged compared to that of SC_5H_4NH, and close to that of the pyridinium cation (δ −172 in dmso). In contrast, the thionate anion exhibits substantial deshielding compared to SC_5H_4NH, with a chemical shift similar to those of substituted pyridines such as NC_5H_4SMe (see above). The severe line broadening of this signal may be associated with the high non-bonding electron density at N as well as the presence of the sodium cation.[37]

For all the complexes of SC_5H_4NH in Table 7, in which the pyridine nitrogen is not co-ordinated but is protonated, very broad lines were observed, with linewidth at half maximum values in the range of 750–1050 Hz. The chemical shifts of the SC_5H_4NH ligands lie in the range of δ −177 to −192, consistent with retention of the thione tautomer upon co-ordination. In the case of the nitrato-complexes **8** and **11** the large difference in linewidths between the nitrato- and SC_5H_4NH peaks was reflected in disparate peak heights; for some of the other complexes, such as the sulfato salt **5**, the SC_5H_4NH peak was probably too broad to observe at all. For complex **15**, in which the pyridine ligands are of necessity N-bonded to the metal, no signals were observed in the ^{14}N NMR spectrum, even when recorded at 100 °C. The linewidth probably exceeds 2500 Hz in this case. We were likewise unable to observe any ^{14}N signals for the bpt complexes **13** and **14**.

Conclusion

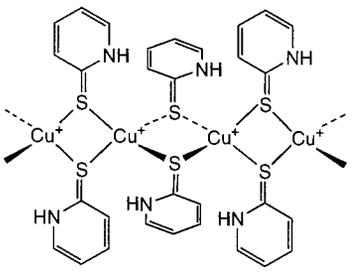
The chemistry of copper with SC_5H_4NH and related heterocyclic thiones is known for its very high degree of product variability depending on kinetic factors such as solvent, pH, anion, stoichiometry, *etc.*[15] This versatility is associated with the ready formation of a variety of Cu–S–Cu bridging modes, together with the plasticity of copper co-ordination geometries and the high substitution lability of both bridging and terminal SC_5H_4NH ligands. These considerations appear to apply equally to the thioether ligand bpt, with the added complication of the possibility of cleavage by both copper-(I) and -(II); for complex **14** this leads to a product in which half of the bpt is cleaved but the other half remains intact. The source of this remarkable specificity is probably the low solubility of the product in the reaction solvent, thf.

The tosylate salt **3** provides a basis for consideration of the structures of the other SC_5H_4NH complexes in this study. Thus removal of two terminal SC_5H_4NH ligands from the $[Cu_2(\mu\text{-}SC_5H_4NH)_2(SC_5H_4NH)_4]^{2+}$ core of **3** would allow all the SC_5H_4NH ligands to become bridging, giving a cationic polymer as shown in Scheme 3, **A**; this is probably the structure of the complexes of stoichiometry $[Cu(SC_5H_4NH)_2]^+$ in which the SO_4^{2-}, BPh_4^- and PF_6^- anions are non-co-ordinating, **5**, **6** and **9** respectively. If the anion is also able to act as a bridging ligand, as in the bromide complex **4** and the sulfato-complex **7**, the Cu:SC_5H_4NH stoichiometry can be reduced further to 1:1 whilst retaining an approximately tetrahedral geometry at copper, as shown for complex **4** in Scheme 3. Complexes **8** and **10**, in which the nitrate groups appear to be co-ordinated, might involve a single bridging SC_5H_4NH ligand, as in Scheme 3, **B**, whilst the introduction of triphenylphosphine co-ligands evidently gives monomeric complexes **11** and **12**, perhaps due to steric factors.

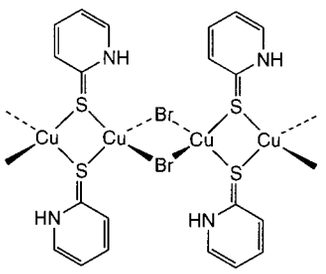
Finally, the stabilities of many of the complexes of SC_5H_4NH in solution depend critically on pH. In acid conditions the nitrogen atoms of the S-co-ordinated SC_5H_4NH ligands are protonated, preventing involvement of the nitrogen atom in co-ordination. Once the proton is removed to give the anion, Cu–N bonds can readily be formed due to the facile displacement of other SC_5H_4NH ligands and the highly insoluble S,N-co-ordinated hexamer $[Cu_6(SC_5H_4N)_6]$ **2** is readily precipitated from solution; as a result, this complex acts as a thermodynamic sink into which the other complexes tend to fall.

Experimental

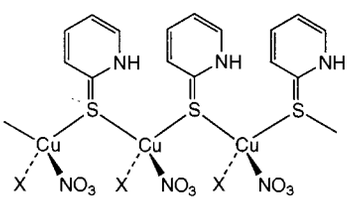
The compounds bpt[7] and $[Cu(NCMe)_4]PF_6$[38] were prepared by the literature procedures. All other chemicals were obtained from commercial sources. Pyridine was distilled from NaOH under a nitrogen atmosphere before use. Reactions were carried out in air unless noted otherwise.



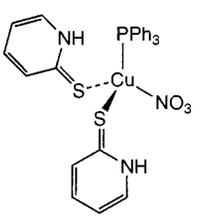
A



4



B



11

Scheme 3 **B**, X = SC_5H_4NH or py

Infrared spectra were recorded on Nujol mulls using KBr plates in the range 4600–400 cm^{-1} and a Shimadzu FTIR-8101M spectrophotometer, ^1H, ^{13}C, ^{14}N and ^{31}P NMR spectra at 270.17, 67.94, 19.52 and 109.38 MHz respectively on a JEOL GSX270 spectrometer. The ^1H and ^{13}C chemical shifts are quoted relative to external $SiMe_4$, ^{14}N shifts relative to external $MeNO_2$. Magnetic susceptibilities were obtained in solution by ^1H NMR spectroscopy using the Evans method.[39] Fast atom bombardment (FAB) mass spectra were kindly provided by Dr. Ali Abdulsadda of the School of Chemistry and Molecular Science, University of Sussex. Conductivities and melting points were obtained using a Portland Electronic conductivity meter and an Electrothermal melting-point apparatus respectively.

Microanalyses (C, H, N and S) were determined by Mr. C. J. Macdonald (Nitrogen Fixation Laboratory) or Mr. A. Saunders (University of East Anglia). Copper analyses were obtained from Southern Science Ltd. on samples dissolved in concentrated HNO_3. Quantitative ^{31}P NMR measurements were carried out on samples dissolved in dmso containing a constant amount of PBu_4Br as reference and calibrated using a set of NBu_4PF_6 standards prepared using the same solvent.

Preparations

[{Cu(μ-O_2CMe)$_2$(bpt)}$_2$] 1. The compound bpt (1.25 g, 5.8 mmol) was added to a solution of $Cu(O_2CMe)_2·H_2O$ (1.10 g, 5.5 mmol) in MeOH (75 cm^3) and the solution was boiled under reflux for 2 h. The hot solution was filtered and concentrated *in vacuo* to *ca.* 10 cm^3. Addition of an excess of Et_2O gave a precipitate; this was filtered off, washed with Et_2O and dried *in vacuo*. The crude product was dissolved in hot acetone; the resulting solution was filtered and left to evaporate, giving crystals of [{Cu(μ-O_2CMe)$_2$(bpt)}$_2$] (1.2 g, 55%). IR: 1618s, 1573s, 1557m, 1283m, 1128m, 771m, 756w, 681m, 627w, 593w, 506w and 484w cm^{-1}.

[{Cu(SC_5H_4NH)$_2$}$_2$(μ-SC_5H_4NH)$_2$][$MeC_6H_4SO_3$]$_2$ 3. Copper(II) oxide (0.17 g, 2.1 mmol) was dissolved in a solution of toluene-*p*-sulfonic acid hydrate (0.40 g, 2.1 mmol) in water (10 cm^3). The solution was filtered, and added to a solution of SC_5H_4NH (1.05 g, 9.4 mmol) in EtOH (20 cm^3). The resulting solution was stirred for 30 min, then the solvent was removed *in vacuo*, giving a red tar. This was stirred thoroughly with acetone, then allowed to settle and the solvent was decanted off; the procedure was repeated, giving an orange solid. This was filtered off and washed with acetone followed by Et_2O. Recrystallisation from EtOH gave analytically pure [Cu_2(SC_5H_4NH)$_6$][$MeC_6H_4SO_3$]$_2$ **3** (0.82 g, 69%). IR: 1565m, 1210m, 1167m, 1129m, 1030m, 1009m, 990m, 752m, 683m, 569m and 486m cm^{-1}.

[CuBr(SC_5H_4NH)] 4. A solution of SC_5H_4NH (1.00 g, 9.0 mmol) in MeOH (20 cm^3) was added to a solution of $CuBr_2$ (1.00 g, 4.5 mmol) in water (35 cm^3), giving immediate precipitation. The mixture was stirred for 3 h, then filtered. The solid was washed with water, then MeOH and finally Et_2O, and dried *in vacuo* as [CuBr(SC_5H_4NH)] **4** (1.06 g, 93%). The product is soluble only in strongly co-ordinating solvents such as dmso and dmf. IR: 1603m, 1586s, 1510m, 1266m, 1159w, 1130s, 1034w, 1001w, 741s, 621w and 477m cm^{-1}.

Complex **4** was also prepared by the addition of concentrated hydrobromic acid (1.0 cm^3) to a freshly prepared solution of **7** (0.1 g, 0.24 mmol) in water (20 cm^3). The resulting mixture was stirred for 30 min, and the precipitate was isolated as above (0.081 g, 71%).

[Cu_2(SC_5H_4NH)$_4$]SO_4·2H_2O 5. A solution of SC_5H_4NH (2.80 g, 25.2 mmol) in MeOH (50 cm^3) was added portionwise over 5 min to a solution of $CuSO_4·5H_2O$ (2.0 g, 8.0 mmol) in water (30 cm^3). The orange solution was stirred for 5 h, giving a thick yellow suspension. This was filtered, and the solid was dried to constant weight *in vacuo* as [Cu_2(SC_5H_4NH)$_4$]-$SO_4·2H_2O$ **5** (2.22 g, 79%). IR: 1602m, 1578s, 1255m, 1166m, 1136s (br), 1081m, 1031m, 991w, 879m, 750s, 595w and 483w cm^{-1}.

[Cu(SC_5H_4NH)$_2$]BPh_4·H_2O 6. A solution of SC_5H_4NH (2.80 g, 25.2 mmol) in MeOH (30 cm^3) was added to a solution of $CuSO_4·5H_2O$ (2.0 g, 8.0 mmol) in water (30 cm^3), giving a clear, deep orange solution. This was stirred for 5 min, then filtered, and a solution of $NaBPh_4$ (2.74 g, 8.0 mmol) in water (50 cm^3) was added. The resulting suspension was stirred for 10 min, then filtered. The solid was washed with water, dried by vacuum aspiration, then stirred with Et_2O (100 cm^3). The mixture was filtered and the Et_2O extraction repeated twice. The solid was then dried to constant weight *in vacuo* as [Cu(SC_5H_4NH)$_2$]-$BPh_4·H_2O$ **6** (4.99 g, 100%). IR: 1603m, 1575s, 1504m, 1262m, 1131s, 1031w, 997w, 849w, 733s, 705s, 604m and 482w cm^{-1}.

[Cu_2(SO_4)(SC_5H_4NH)$_2$] 7. The salt $CuSO_4·5H_2O$ (1.12 g, 4.49 mmol) was dissolved in 2.24 mol dm^{-3} H_2SO_4 (1.0 cm^3, 2.24 mmol) plus the minimum amount of water. A solution of SC_5H_4NH (1.0 g, 8.99 mmol) in MeOH (35 cm^3) was added in one portion, giving an orange solution. This was stirred for 5 h, to no visible effect, then filtered, and added to acetone (200 cm^3); the resulting precipitate was immediately filtered off, washed with acetone and dried *in vacuo* as [Cu_2(SO_4)-(SC_5H_4NH)$_2$] **7** (0.94 g, 94%). IR: 1593s, 1516w, 1264w, 1129s (br), 1036m, 858m, 760m, 577m, 486w and 438w cm^{-1}.

[Cu(NO_3)(SC_5H_4NH)$_2$] 8. A solution of $Cu(NO_3)_2·2.5H_2O$ (3.31 g, 14.2 mmol) in water (5 cm^3) plus concentrated HNO_3 (0.5 cm^3, 7.7 mmol) was added to a solution of SC_5H_4NH (5.0 g, 45 mmol) in EtOH (100 cm^3). The resulting suspension was stirred for 10 min, then filtered, and the bright yellow solid was washed with EtOH followed by Et_2O and dried *in vacuo* as

$[Cu(NO_3)(SC_5H_4NH)_2]$ **8** (4.81 g, 97%). The complex can be recrystallised as very fine needles from dmf acidified with HNO_3. IR: 1593s, 1507w, 1314s, 1260m, 1132m, 1084w, 1034w, 826w, 750s, 617m, 482m and 442w cm^{-1}.

$[Cu(SC_5H_4NH)_2]PF_6$ 9. Aqueous HPF_6 (1.0 cm^3 of 60% w/w) was added dropwise to a rapidly stirred, filtered solution of $[Cu_2(SO_4)(SC_5H_4NH)_2]$ (0.10 g, 0.22 mmol) in water (20 cm^3). The resulting suspension was stirred for 10 min, then filtered. The solid was washed with water, dried by vacuum aspiration, then extracted with several portions of Et_2O. The product was then dried to constant weight *in vacuo* as $[Cu(SC_5H_4NH)_2]PF_6$ **9** (0.078g, 81%). The complex is soluble in acetone, but only moderately soluble in dmso. IR: 1582m, 1512w, 1265w, 1161w, 1129m, 1084w, 845s, 756m, 722m, 559m and 484w cm^{-1}.

$[Cu(NO_3)(SC_5H_4NH)(py)]$ 10. This preparation was carried out under a nitrogen atmosphere. A suspension of $[Cu(NO_3)(SC_5H_4NH)_2]$ (0.36 g, 1.03 mmol) in pyridine (25 cm^3) was boiled under reflux for 1 h. The resulting suspension was filtered to remove $[Cu_6(SC_5H_4N)_6]$ (*ca.* 0.14 g, 78%) and the filtrate was concentrated to *ca.* 5 cm^3 *in vacuo*. Addition of an excess of Et_2O precipitated a red tar. The solvent was decanted off and the residue dried *in vacuo* for several hours, then stirred with Et_2O for 1 h. The mixture was filtered to give a yellow powder, which was dried *in vacuo.* The crude product was dissolved in hot pyridine, and an excess of Et_2O was added; the precipitate was filtered off, washed with Et_2O and dried *in vacuo* as $[Cu(NO_3)(SC_5H_4NH)(py)]$ **10** (0.043 g, 13%). IR: 1578m, 1547m, 1414m, 1313(sh), 1267m, 1125m, 1084w, 1038w, 1003w, 822w, 754s, 681m, 608w, 490w and 442w cm^{-1}.

$[Cu(NO_3)(SC_5H_4NH)_2(PPh_3)]$ 11. This preparation was done under a nitrogen atmosphere. Methanol (25 cm^3) was added to a solid mixture of $[Cu(NO_3)(SC_5H_4NH)_2]$ (0.50 g, 1.44 mmol) and PPh_3 (0.40 g, 1.52 mmol) and the mixture was boiled under reflux for 10 min, giving an orange solution. This was allowed to cool, then filtered. The filtrate was concentrated to *ca.* 2 cm^3 *in vacuo*, and Et_2O was added, causing separation of a yellow tar. The supernatant was decanted off and the solid dried *in vacuo* for several hours, then stirred with Et_2O (20 cm^3). This gave a powder, which was filtered off, washed with Et_2O and dried *in vacuo* as $[Cu(NO_3)(SC_5H_4NH)_2(PPh_3)]$ **11** (0.54 g, 61%). IR: 1565s, 1306m, 1130s, 1024w, 754s, 695m, 617m, 517m, 484m and 446w cm^{-1}.

Recrystallisation of $[Cu(NO_3)(SC_5H_4NH)_2(PPh_3)]$ by slow diffusion of Et_2O into an EtOH solution gave, in low yield, crystals of $[Cu(SC_5H_4NH)_2(PPh_3)_2]NO_3$ **12**, whose IR spectrum was virtually identical to that of the starting complex.

$[Cu_2(bpt)_3][PF_6]_2\cdot C_3H_6O$ 13. The compound bpt (1.25 g, 5.78 mmol) was added to a solution of $[Cu(NCMe)_4]PF_6$ (1.0 g, 2.68 mmol) in MeCN (40 cm^3). The mixture was stirred under a nitrogen atmosphere for 24 h, then filtered to remove $[Cu_6(SC_5H_4N)_6]$. The filtrate was concentrated *in vacuo* to *ca.* 5 cm^3 and an excess of Et_2O was added, causing precipitation of a yellow oil. The mixture was kept at −20 °C overnight, whereupon the oil solidified; the solid was filtered off, washed with Et_2O and dried *in vacuo*. The crude product apparently contained some HPF_6; it was purified by repeatedly dissolving in acetone and precipitating with Et_2O as $[Cu_2(bpt)_3][PF_6]_2\cdot C_3H_6O$ **13** (0.42 g, 28%). IR: 1709m (acetone), 1605m, 1586m, 1428m, 1279w, 1225m, 1167m, 1136w, 941w, 882m, 839s, 768m, 727m, 558s and 484w cm^{-1}.

$[Cu_2(SC_5H_4N)(bpt)]PF_6\cdot 0.25C_3H_6O$ 14. The compound bpt (1.25 g, 5.78 mmol) was added to a solution of $[Cu(NCMe)_4]PF_6$ (1.0 g, 2.68 mmol) in thf (40 cm^3) under a nitrogen atmosphere and the mixture was boiled under reflux for 4 h. The orange precipitate was filtered off, washed with thf and dried *in vacuo*. The filtrate was concentrated to near dryness *in vacuo* and taken up in $[^2H_6]$acetone for NMR studies (see Results and Discussion). The orange precipitate was dissolved in acetone; the solution was filtered, and Et_2O was added to the filtrate; the resulting precipitate was filtered off, washed with Et_2O and dried *in vacuo* as $[Cu_2(SC_5H_4N)(bpt)]PF_6\cdot 0.25C_3H_6O$ **14** (0.67 g, 82%). IR: 1710w (acetone), 1606w, 1585m, 1556w, 1422m, 1278w, 1160w, 1128m, 840s, 759m, 721m, 557m and 483w cm^{-1}.

$[Cu(py)_4]PF_6$ 15. Pyridine (30 cm^3) was added to solid $[Cu(NCMe)_4]PF_6$ (1.0 g, 2.68 mmol) under a nitrogen atmosphere. The solution was stirred for 20 min, then filtered, and the filtrate was concentrated *in vacuo* to *ca.* 10 cm^3, then kept at −20 °C overnight. The microcrystalline precipitate was filtered off, washed with Et_2O and dried *in vacuo* as $[Cu(py)_4]PF_6$ **15** (0.97 g, 69%). IR: 1575s, 1482m, 1443m, 1215m, 1154w, 1067m, 1038m, 1005w, 885m, 845s, 750s, 700s, 623w, 558s and 415m cm^{-1}. The solid complex is reasonably stable to air, but solutions are rapidly oxidised, turning green within seconds.

Crystallography

The crystal structure analysis of $[Cu_2(SC_5H_4NH)_6][MeC_6H_4SO_3]_2$ **3** is described in detail here. The analyses of the other samples followed similar procedures; major variations for complexes **1** and **12** are given with their crystal data below.

Crystal data. $C_{30}H_{30}Cu_2N_6S_6\cdot 2C_7H_7O_3S$, $M = 1136.4$, monoclinic, space group $P2_1/n$ (equivalent to no. 14), $a = 16.881(1)$, $b = 9.9724(8)$, $c = 14.887(1)$ Å, $\beta = 97.604(6)°$, $U = 2484.0(4)$ Å^3, $Z = 2$, $D_c = 1.519$ g cm^{-3}, $F(000) = 1168$, $\mu(Mo\text{-}K\alpha) = 12.3$ cm^{-1}, $\lambda(Mo\text{-}K\alpha) = 0.710\,69$ Å.

Crystals are deep yellow, rectangular plates. One, *ca.* 0.11 × 0.20 × 0.48 mm, was mounted on a glass fibre and, after preliminary photographic examination, transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell parameters (from the settings of 25 reflections, $\theta = 12$–$13°$, each centred in four orientations) and for measurement of diffraction intensities to $\theta_{max} = 25°$. There were 4364 unique reflections, 2982 of which were 'observed' with $I > 2\sigma_I$.

During processing, corrections were applied for Lorentz-polarisation effects, slight crystal deterioration (5.0% overall), absorption (by semiempirical ψ-scan methods) and to eliminate negative net intensities (by Bayesian statistical methods). The structure was determined by the heavy-atom method using the SHELX program[40] and refined (on F) by full-matrix least-squares methods. Hydrogen atoms were included in idealised positions; those on pyridine and phenyl rings were set to ride on their parent C or N atoms, and those in the methyl groups were refined with geometrical constraints. The isotropic thermal parameters of all the H atoms were allowed to refine freely, and the non-H atoms were refined with anisotropic thermal parameters. Refinement was smooth and rapid, converging with $R = 0.062$ and $R_g = 0.044$[40] for all 4364 reflections weighted $w = \sigma_F^{-2}$. In the final difference map the highest peaks were between the anion and cation (*ca.* 0.55 e Å^{-3}) and within the anion (*ca.* 0.37 e Å^{-3}).

Scattering factor curves for neutral atoms were taken from ref. 41. Computer programs used in this analysis have been noted above and in Table 4 of ref. 42, and were run on a MicroVAX 3600 machine in the Nitrogen Fixation Laboratory, University of Sussex, Brighton.

$[\{Cu(\mu\text{-}O_2CMe)_2(bpt)\}_2]$ 1. *Crystal data*. $C_{32}H_{36}Cu_2N_4O_8S_2$, $M = 795.9$, monoclinic, space group $P2_1/n$ (equivalent to no. 14), $a = 27.330(3)$, $b = 7.8772(6)$, $c = 8.0866(7)$ Å, $\beta = 93.480(8)°$, $U = 1737.7(3)$ Å^3, $Z = 2$, $D_c = 1.521$ g cm^{-3}, $F(000) = 820$, $\mu(Mo\text{-}K\alpha) = 14.0$ cm^{-1}.

Crystals are well defined, green plates; sample selected was

0.04 × 0.21 × 0.26 mm. Total number of unique reflections = 3061, 'observed' reflections ($I > 2\sigma_I$) 2080. No crystal deterioration. Structure determined by the heavy-atom method using SHELX. Refinement of F using SHELXN; final R and R_g values were 0.071 and 0.056 for all 3601 reflections weighted $w = (\sigma_F^2 + 0.00043F^2)^{-1}$. The final difference map showed peaks of *ca.* 0.5 e Å^{-3}, close to Cu and O in an acetate ligand.

$[Cu(SC_5H_4NH)_2(PPh_3)_2]NO_3$ 12. *Crystal data*. $C_{46}H_{40}CuN_3O_3P_2S_2$, $M = 872.5$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.156(2)$, $b = 13.060(1)$, $c = 16.038(2)$ Å, $\alpha = 97.500(8)$, $\beta = 94.269(12)$, $\gamma = 90.861(11)°$, $U = 2102.6(5)$ Å^3, $Z = 2$, $D_c = 1.378$ g cm^{-3}, $F(000) = 940$, μ(Mo-Kα) = 7.3 cm^{-1}.

Beautiful, yellow triangular prisms, crystal size 0.14 × 0.30 × 0.33 mm. Total number of unique reflections = 7381, 'observed' reflections ($I > 2\sigma_I$) 3930. No crystal deterioration. Structure determined by automated Patterson methods using SHELXS;[43] refinement on F using SHELXN; final R and R_g values were 0.086 and 0.089 for 5750 reflections (with $I > \sigma_I$) weighted $w = (\sigma_F^2 + 0.00250F^2)^{-1}$. The final difference map showed peaks at *ca.* 0.55 e Å^{-3} close to both cation and anion.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/535.

Acknowledgements

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