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THE DIRECT ELECTROCHEMICAL SYNTHESIS OF ADDUCTS OF BIS(DIPHENYLPHOSPHINO)METHANE (dppm) WITH COPPER(I) THIOLATES AND THE X-RAY CRYSTAL STRUCTURE OF $Cu_4(\mu\text{-}SC_5H_{11})_4(dppm)_2$

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Abstract—Adducts of bis(diphenylphosphino)methane (dppm) with copper(I) thiolates can be prepared by oxidizing anodic copper into an acetonitrile solution of dppm and RSH ($R = n\text{-}C_4H_9$, C_5H_{11}, C_6H_5, *o,m,p*-$CH_3C_6H_4$, 2-naphthyl). The products are $(CuSR)_2 \cdot dppm$ for $R = n\text{-}C_4H_9$, C_5H_{11} or C_6H_5, and $CuSR \cdot 1.5dppm$ for $R = o\text{-}CH_3C_6H_4$ or 2-naphthyl. No adducts were obtained for $R = m\text{-}$ or $p\text{-}CH_3C_6H_4$. Reaction between $(CuSC_5H_{11})_2 \cdot dppm$ ($C_5H_{11} = C_2H_5C(CH_3)_2\text{-}$) and CS_2 gives the insertion product $CuS_2CSC_5H_{11} \cdot dppm$. An X-ray crystallographic study of $(CuSC_5H_{11})_2 \cdot dppm$ reveals the presence of a novel Cu_4S_4 ring, in which sulphur atoms are below a Cu_4 plane; this Cu_4S_4 ring is capped by two six-membered Cu_2SCP_2 rings in the boat form.

The direct electrochemical synthesis of thiolato complexes of zinc,[1,2] cadmium,[1,2] mercury,[1] tin,[3] lead[3] and indium[4] has been the subject of recent papers from this laboratory. As in the other applications of this technique, which involves the anodic oxidation of a metal in a non-aqueous solution of the ligand precursor, the most important advantages are the simplicity of the technique and the high product yield. In the case of copper or silver, solutions of either alkyl or aryl thiols give rise to the MSR compounds in a one-step synthesis and adducts of CuSR with donors such as 1,10-phenanthroline are also accessible by the electrochemical route.[5,6] The reaction of $CuSC_5H_{11}$ with carbon disulphide gave the unusual copper(I)–thiolato–thioxanthato cage complex $Cu_8(SC_5H_{11})_4(S_2CSC_5H_{11})_4$.[5]

We now report an extension of this work to the preparation of adducts of various copper(I) thiolates with the bidentate phosphorus donor bis(diphenylphosphino)methane(dppm). The crystal structure of the adduct formed with $CuSC_5H_{11}$ reveals the presence of a central Cu_4S_4 ring, capped by Cu_2SCP_2 boat-form rings. The reaction between this compound and carbon disulphide results in the insertion of CS_2 into the Cu—S bond.

EXPERIMENTAL

General

Solvents were distilled from calcium hydride and stored over molecular sieves. Copper was used as foils, 0.25 mm thick, which were washed successively with conc. nitric acid and distilled water then dried before use. Thiols and dppm (Aldrich) were used as supplied.

Copper analysis was by atomic absorption spectrophotometry then microanalyses were carried out by Guelph Chemical Laboratories Ltd. Infrared spectra were recorded on a Nicolet 5DX instrument. Proton NMR spectra were obtained with a Bruker WP-80, and ^{31}P spectra with a Bruker 90 spectrometer. Mass spectra were recorded on a Varian MAT CH-5 spectrometer operating in the E.I. mode.

Electrochemical procedures

The general method was that described in previous papers,[1–3,6,7] using a cell of the form:

$$Pt_{(-)}/CH_3CN + RSH + dppm/Cu_{(+)}.$$

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Table 1. Experimental conditions for the electrochemical synthesis of dppm (= L) adducts of copper(I) thiolates

Thiol	Quantity[a] (cm^3)	dppm[a] (g)	Initial[b] voltage (v)	Time of electrolysis (h)	Metal dissolved (g)	Product
n-C_4H_9SH	1.5	0.9	25	4.3	0.32	$(CuSR)_2 \cdot L$
$C_5H_{11}SH$[c]	1	0.8	5	2.5	0.18	$(CuSR)_2 \cdot L$
C_6H_5SH	1	1.0	10	3	0.22	$(CuSR)_2 \cdot L$
o-$CH_3C_6H_4SH$	1	1.0	10	4	0.29	$CuSR \cdot 1.5L$
m-$CH_3C_6H_4SH$	1.5	0.8	20	3.3	0.26	CuSR
p-$CH_3C_6H_4SH$	0.5	0.9	5	5	0.36	See text
2-$C_{10}H_7SH$	0.5(g)	0.7	10	2.5	0.19	$CuSR \cdot 1.5L$

[a] In 50 cm^3 acetonitrile, plus *ca* 25 mg Et_4NClO_4.

[b] Voltage required to produce an initial current of 30 mA.

[c] $C_5H_{11}SH$ = 2-methyl-2-butanethiol.

Details of solution composition, etc. are given in Table 1. All operations were carried out under a flow of dry nitrogen, which bubbled through the solution thereby mixing the contents of the cell. As the experiment proceeded, hydrogen was evolved at the cathode and the solution became yellow as soluble products formed. Yellow solids eventually precipitated as the nitrogen flow continued and were collected, washed with n-pentane and dried *in vacuo*. In the case of $(CuSR)_2 \cdot$dppm, with R = n-C_4H_9, C_5H_{11} (= $C_2H_5C(CH_3)_2$-) and 2-$C_{10}H_7$, precipitation continued over a period of 12 h after the end of electrolysis, whereas for $(CuSC_6H_4CH_3$-$o) \cdot 1.5$ dppm and $(CuSC_6H_5)_2 \cdot$dppm, precipitation was essentially complete at the end of the electrolysis. No adducts were obtained with R = m- or p-$CH_3C_6H_4$. In the former case, the product was CuSR (Found: Cu, 33.8%, Calc. for $CuSC_6H_4CH_3$: Cu, 34.0%); with the *para* compound, the infrared spectrum showed the presence of dppm in the product, but copper analysis (Found: Cu, 28.5%) suggested that the product was a mixture of CuSR and a dppm adduct. These systems were not investigated further. Yields were generally better than 90%, based on the quantity of metal dissolved from the anode.

These dppm addition compounds are soluble in benzene and chlorinated hydrocarbons, and in some cases react with carbon disulphide (see below). The products were characterized by elemental analysis (Table 2), and by infrared and ^1H NMR spectroscopy (Table 3) which established the presence of the RS^- and dppm ligands. The spectra reported in Table 3 refer to freshly prepared solutions; in the case of the arylthiolato derivatives slow decomposition occurred, as evidenced by the appearance of the blue–green colour of copper(II) in the solution.

Reaction with carbon disulphide

$(CuSC_5H_{11})_2 \cdot$dppm (0.5 g, 0.70 mmol) was dissolved in CS_2 (40 cm^3), giving a red–brown solution which was stirred for 2 h, during which time an orange solid began to precipitate. The mixture was stirred for 3 days at ambient temperature, after which the solid was collected, washed with CS_2 and then n-pentane, and dried *in vacuo*. Found: Cu, 9.5. Calc. for $CuS_2CSC_5H_{11} \cdot$dppm, $C_{31}H_{33}CuP_2S_3$, Cu, 10.1%. The mass spectrum showed prominent peaks at m/e = 666 $(CuSC_5H_{11})_4^+$: 595 $Cu_4(SC_5H_{11})_3S^+$: 524 $(CuSC_5H_{11} \cdot CuS)_2^+$: 453

Table 2. Analytical results for dppm adducts of copper(I) thiolates

Compound	Found (%) Cu	Found (%) C	Found (%) H	Found (%) N	Calc. (%) Cu	Calc. (%) C	Calc. (%) H	Calc. (%) N
$(CuSC_4H_9$-$n)_2 \cdot$dppm	18.8				18.4			
$(CuSC_5H_{11})_2 \cdot$dppm	18.1	58.8	6.47		17.7	58.6	6.14	
$(CuSC_6H_5)_2 \cdot$dppm	17.2	61.5	4.88		17.4	60.9	4.39	
$(CuSC_6H_4CH_3$-$o) \cdot 1.5$dppm	8.2	70.2	5.70		8.4	70.0	5.24	
$CuSC_{10}H_7 \cdot 1.5$dppm	7.4	71.4	5.10		8.0	71.1	5.41	

Table 3. ^{1}H and ^{31}P NMR spectra of dppm adducts of copper(I) thiolates[a]

Compound	^{1}H Aromatic[b]	CH$_2$(dppm)	Alkyl Thiolate[c]	^{31}P
dppm	7.25 m(10)	2.76 t(1)	—	−22.93[d]
$(\text{CuSC}_4\text{H}_9\text{-}n)_2\cdot$dppm	7.15 m(10)	3.25 t(1)	2.42 t, 1.16m, 0.65 t(10)	−14.73
$(\text{CuSC}_5\text{H}_{11})_2\cdot$dppm	7.22 m(10)	2.95 t(1)	1.49 q, 1.30 s, 0.88 t(11)	−17.23
$(\text{CuSC}_6\text{H}_5)_2\cdot$dppm	6.98 m,br	2.73 s,br[e]	—	−14.17
$(\text{CuSC}_6\text{H}_4\text{CH}_3\text{-}o)\cdot 1.5$dppm	7.01 m,br(11.5)	2.66 s,br(1)	2.38 s(1)(*o*-CH$_3$)	−18.93
$\text{CuSC}_{10}\text{H}_7\cdot 1.5$dppm	7.38 m,br	2.48 s,br[e]	—	−18.76
$\text{CuS}_2\text{CSC}_5\text{H}_{11}\cdot$dppm	—	—	—	−36.86

[a] In CD$_2$Cl$_2$ solution. Frequencies for ^{1}H, ppm from Me$_4$Si and for ^{31}P, ppm for 85% H$_3$PO$_4$. Integrated relative intensities in parentheses. m = multiple, q = quartet, t = triplet, s = singlet, br = broad.

[b] Frequency at most intense peak.

[c] Total relative intensity of alkyl hydrogens.

[d] Lit. value −23.00 ppm (T. G. Appleton, M. A. Bannett and I. B. Tomkins, *J. Chem. Soc., Dalton Trans.* 1976, 439).

[e] Poor integration: see text.

$\text{CuSC}_5\text{H}_{11}$ $(\text{CuS})_3$: 421 $\text{Cu}_4\text{SC}_5\text{H}_{11}\text{S}_2^+$: 382 $(\text{C}_6\text{H}_5)_4\text{P}_2\text{CH}_2^+$: 262 Ph_3P^+: 199 $(\text{C}_6\text{H}_5)_2\text{PCH}_2^+$. When these experiments were repeated with $(\text{CuSC}_6\text{H}_4\text{CH}_3\text{-}o)\cdot 1.5$dppm (0.24 g, 0.31 mmol) and excess CS$_2$ using similar procedures, identical colour changes were observed and a precipitate was obtained. This was dissolved in benzene (10 cm^3), ethanol (30 cm^3) added to this solution and the mixture left overnight. The yellow solid which then appeared was shown to be the starting material (Found: Cu, 8.1. Calc. Cu, 8.3%) recovered in 70% yield.

Decomposition of $\text{CuS}_2\text{CSC}_5\text{H}_{11}\cdot$dppm

(i) $\text{CuS}_2\text{CSC}_5\text{H}_{11}\cdot$dppm (0.25 g, 0.40 mmol) was added to benzene (20 cm^3) and the solvent brought to reflux, to give a dark red–brown solution. After about 15 min, the colour changed to pale yellow. After a further 2 h reflux, the solution was taken to dryness, yielding a yellow gummy solid; addition of *n*-pentane (15 cm^3) caused this material to decompose, with traces of a green solid being formed. We were unable to characterize the yellow solid obtained.

(ii) A similar treatment of a suspension of $\text{CuS}_2\text{CSC}_5\text{H}_{11}\cdot$dppm (0.29 g) in refluxing *n*-hexane (30 cm^3) underwent a colour change within the first hour to give a deep red–brown mixture. On further refluxing, much of the red suspended solid dissolved. After 18 h, the mixture was filtered and the filtrate taken to dryness *in vacuo*; the resultant red–brown residue was dissolved in acetonitrile (3 cm^3) and reprecipitated by the addition of methanol (20 cm^3) followed by slow evaporation. The final solid consisted of a mixture of colourless and red crystals. The former melted at 118–122°C (c.f. dppm, M.p. 121°C), and the latter at 135–142°C (c.f. $\text{CuS}_2\text{CSC}_5\text{H}_{11}\cdot$dppm, m.p. 140°C). The ^{1}H NMR spectrum of the red crystals confirmed the presence of dppm.

Crystallography

A pale yellow crystal of $(\text{CuSC}_5\text{H}_{11})_2\cdot$dppm (1), dimensions 0.15 × 0.15 × 0.20 mm, was mounted in a Syntex P2$_1$ diffractometer, and data collected by the methods normally used in this laboratory.[8] The results were corrected for Lorentz and polarization effects; absorption was judged to be negligible, and no such corrections were made. Table 4 gives the appropriate experimental details.

The intensity statistics suggested a centric space group and the space group $P\bar{1}$ was assumed and subsequently confirmed by the successful refinement. The structure was solved by direct methods (SHELX-76)[9] and refined by a least-squares method, minimizing the function $\Sigma w(|F_o|-|F_c|)^2$, where $w = [\sigma^2(F_o)+0.0001F_o^2]^{-1}$. When the positional and anisotropic parameters of the non-hydrogen atoms were refined in two blocks, the carbon atoms of the thiolato ligands, and especially C(9) and C(10), showed large thermal parameters, suggesting a significant disorder for these atoms. In the final cycles of refinement, hydrogen atoms were only included on the phenyl and C(01) methylene carbon atoms; an idealized geometry, with $r(\text{C—H}) = 0.95$ Å, was assumed and individual iso-

Table 4. Summary of crystal data, intensity collection and structural refinement for **1**

Formula, *fw*	$C_{70}H_{88}Cu_4P_4S_4$, 1435.81
Cell constants[a] at 22°C	a, 12.350(2) Å; α, 63.97(1)° b, 14.143(3) Å; β, 102.71(2)° c, 12.430(3) Å; γ, 113.21(1)°
Cell volume (Å^3)	1790 (1)
Space group	$P\bar{1}$
Z	1
d(calc.), (exp.) (g cm^{-3})	1.332, 1.35[b]
Absorption coefficient (cm^{-1})	13.5
Radiation	MoK_α (λ = 0.71069 Å)
2θ (max) for data collection	45°
Scan width	Kα_1−0.8° to Kα_2+0.8°
Total reflections measured ($-h$, $\pm k$, $\pm l$)	4764
Unique "observed" reflections ($I \geqslant 2\Sigma(I)$)	3108
$R = (\Sigma \lVert F_o\rvert - \lvert F_c\rVert/\Sigma \lvert F_o\rvert)$	0.056
$R_w = (\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2)^{1/2}$	0.058
$S = [\Sigma(w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(m-n)]^{1/2}$	1.6
Shift/e.s.d. (max) in the final cycle	0.4
Max (e Å^{-3}) in the final dimap	0.7

[a] Cell constants were derived by least-squares analysis of the diffractometer angular setting of 28 well-centred reflections (2θ range = 20–26°).

[b] Measured in a mixture of cyclohexane and CCl_4.

tropic temperature factors were refined for each of these hydrogen atoms. The final R value was 0.056, with R_w = 0.058.

The source of atomic scattering factors and the computer programmes used in the calculations, were those used previously.[10] Selected bond distances and angles are given in Table 5, and Fig. 1 shows the molecular structure with the atomic numbering scheme. Tables of atom coordinates, anisotropic thermal parameters, bond lengths and angles in the phenyl and thiolato groups, and observed and calculated structure factors, are available as supplementary material from the Editor.

RESULTS AND DISCUSSION

Preparative and spectroscopic

The results show that the preparation of dppm adducts of various copper(I) thiolates is readily achieved by the one-step high yield syntheses described. The stoichiometry clearly depends on the nature of the organic group attached to the thiolato sulphur atom, since both 1 : 1 and 1 : 1.5 adducts

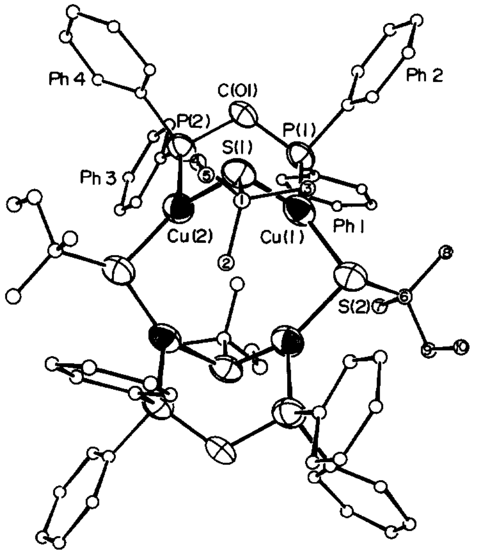

Fig. 1. Structure of the centrosymmetric molecule of **1**. For clarity, hydrogen atoms are omitted and the carbon atoms of the phenyl and thiol groups are plotted as spheres of arbitrary size. All the other atoms are plotted as 50% probability thermal ellipsoids. The numbering scheme for the phenyl carbon atoms follows that for the corresponding rings (C11, C12, . . . etc.).

Table 5. Selected bond lengths (Å) and angles (°) for **1**

(a) Bond lengths			
Cu(1)—S(1)	2.268(2)	S(2)—C(6)	1.884(10)
Cu(1)—S(2)	2.221(2)	P(1)—C(01)	1.861(7)
Cu(1)—P(1)	2.246(1)	P(1)—C(11)	1.825(9)
Cu(2)—S(1)	2.241(3)	P(1)—C(21)	1.834(10)
Cu(2)—S(2)[a]	2.253(3)	P(2)—C(01)	1.862(8)
Cu(2)—P(2)	2.301(2)	P(2)—C(31)	1.821(10)
S(1)—C(1)	1.876(8)	P(2)—C(41)	1.844(10)
(b) Angles			
S(1)—Cu(1)—S(2)	119.5(1)	Cu(1)—P(1)—C(11)	123.2(3)
S(1)—Cu(1)—P(1)	103.3(1)	Cu(1)—P(1)—C(21)	110.5(2)
S(2)—Cu(1)—P(1)	135.8(1)	C(01)—P(1)—C(11)	105.9(4)
S(2)[a]—Cu(2)—S(1)	141.8(1)	C(01)—P(1)—C(21)	97.8(4)
S(1)—Cu(2)—P(2)	100.5(1)	C(11)—P(1)—C(21)	102.3(4)
S(2)[a]—Cu(2)—P(2)	117.2(1)	Cu(2)—P(2)—C(01)	113.5(2)
Cu(1)—S(1)—Cu(2)	85.9(1)	Cu(2)—P(2)—C(31)	124.7(3)
Cu(1)—S(1)—C(1)	113.3(3)	Cu(2)—P(2)—P(41)	106.2(2)
Cu(2)—S(1)—C(1)	119.0(4)	C(01)—P(2)—C(31)	105.3(4)
Cu(2)[a]—S(2)—Cu(1)	98.5(1)	C(01)—P(2)—C(41)	100.9(4)
Cu(1)—S(2)—C(6)	118.0(3)	C(31)—P(2)—C(41)	103.1(4)
Cu(2)[a]—S(2)—C(6)	106.8(4)	P(1)—C(01)—P(2)	116.7(4)
Cu(1)—P(1)—C(01)	113.7(2)		

[a] Symmetry equivalent position is $2-x$, $1-y$, $-z$.

were obtained (see Table 2), but these differences are not the result of any electrochemical effect, since in each of the preparations reported in Table 1, the electrochemical efficiency, defined as moles metal dissolved per Faraday of charge, is 1.04 ± 0.03 mol F^{-1}. As in similar studies of the synthesis of metal thiolates,[1-6] the mechanism can be written as

$$\text{cathode:}\quad RSH + e \rightarrow RS^- + 1/2H_2(g)$$

$$\text{anode:}\quad RS^- + Cu \rightarrow CuSR + e$$

and this clearly is also valid for $R = m\text{-}CH_3C_6H_4$, where only CuSR was recovered, and $R = p\text{-}CH_3C_6H_4$ where the product was apparently a mixture of CuSR and CuSR · xdppm. The relative stability of crystalline CuSR · xdppm complexes ($x = 0$, 0.5, 1.5) must therefore be a function of the properties of R and not of the method of preparation. Given the variety of structures found for adducts and anionic complexes of the copper(I) thiolates, it would be premature to attempt any discussion of the nature of the relationship between R and the stoichiometry of the adducts.

While the infrared and ^1H NMR results confirm the presence of both R and dppm in the products, the most useful structural information is found in the ^{31}P NMR spectra (Table 3). Each of the adducts shows a ^{31}P resonance in the region +4 to +7 ppm from that in dppm itself. A number of previous studies[11-13] have established that the ^{31}P resonance frequency can be used diagnostically to distinguish bridging dppm from the chelated ligand, with the former all showing shifts to more positive frequencies compared to the free ligand. By this criterion, we conclude that all the CuSR adducts prepared involve bridging dppm and this has been formed by X-ray crystallography in the case of $(CuSC_5H_{11})_2 \cdot$dppm.

The amylthiolate complex undergoes an easy insertion reaction with carbon disulphide to give the corresponding thioxanthate complex. Similar *in situ* formation of the $RSCS_2^-$ derivative has been found in the case of $CuSC_5H_{11}$ itself[5] and with $Cd(SR)_2$ ($R = n\text{-}C_4H_9$, C_6H_5).[14] The obvious contrast between $CuSC_5H_{11}$ and its dppm adduct lies in the formation of $Cu_8(SR)_4(S_2CSR)_4$ in the first case as against $CuS_2CSR \cdot$dppm in the second, again implying different structures. With the 1 : 1.5 adduct of $CuSC_6H_4CH_3\text{-}o$, no insertion product was obtained on working up the CS_2 reaction mixture and to this extent the behaviour of CuSR species appears to parallel that of $Cd(SR)_2$ ($R = n\text{-}C_4H_9$, C_6H_5). The colour changes observed with $CuSC_6H_4CH_3\text{-}o$ suggest that an unstable intermediate is formed when this molecule is in contact with CS_2. With the thioxanthato derivatives then, as with the dppm adducts of CuSR, changes in the properties of the R group produce significant changes in the stability and structure of the molecules concerned.

We have not been able to elucidate the structure of $CuS_2CSC_5H_{11}\cdot$dppm, but the ^{31}P NMR spectrum (CH_2Cl_2) shows a broad singlet at -36.86 ppm from 85% H_3PO_4, which establishes that in this compound dppm is acting as a chelating ligand;[11–13] further work on this structure is planned. The mass spectra of this compound and of $CuSC_5H_{11}$, are essentially identical, as is the spectrum of $Cu_8(SC_5H_{11})_4(S_2CSC_5H_{11})_4$, indicating that the processes in the ion source involve loss of CS_2 and dppm, leaving CuSR which then gives rise to a series of low intensity ions.

The structure of $(CuSC_5H_{11})_2\cdot$dppm, $Cu_4(\mu\text{-}SC_5H_{11})_4(dppm)_2$ (**1**)

The structures of copper(I) thiolate derivatives provide one of the most intriguing problems of stereochemistry amongst the derivatives of the d^{10} metal ions. The present results identify a novel arrangement involving a Cu_4S_4 ring capped with two six-membered Cu_2SCP_2 rings. The four copper atoms of the central Cu_4S_4 ring are in a crystallographically imposed plane and sufficiently far apart as to exclude Cu—Cu bonding $Cu(1)\cdots Cu(2) = 3.071(1)$ Å, $Cu(1)\cdots Cu(2)^* = 3.389(1)$ Å (c.f. ref. 6). The sulphur atoms S(1) and S(1)* are -1.52 Å from this Cu_4 plane, and S(2) and S(2)* -0.42 Å from it. Each copper atom has a CuS_2P coordination kernel and is almost trigonally planar, with a deviation of 0.11 Å for Cu(1) from the Cu(1), P(1), S(1), S(2) plane, and 0.07 Å from Cu(2), P(2), S(1), S(2)* in the case of Cu(2). The sum of the bond angles at copper is 358.6° [Cu(1)] and 359.5° [Cu(2)] respectively. The Cu—S bond distances of 2.268(2) and 2.221(2) Å at Cu(1), and 2.253(3) and 2.241(3) Å at Cu(2), are in the range reported for the $Cu(SPh)_3^-$ anion, which has Cu—S bond lengths of 2.274(4)–2.335(4) Å in the PPh_4^+ salt[15] and 2.239(2)–2.258(2) Å with the Et_4N^+ cation.[16] In the octacopper cage structure[5] $Cu_8(SC_5H_{11})_4(S_2CSC_5H_{11})_4$, there is a wide variety of Cu—S interactions, with mono-, bi- and tridentate sulphur ligands and as a result a direct comparison with the present values is difficult, especially since the thiolato sulphur atoms in that compound are all triply bridging. Nevertheless, the range of Cu—S(thiolate) distances in this cage is 2.237(5)–2.301(5) Å, in good agreement with the values reported above. There seems to be no benefit at this point in further comparisons with the Cu—S distances in other cage structures of different stereochemistry.

Copper–phosphorus bond lengths have been reported for a number of compounds. With triphenylphosphine acting as a terminal ligand to the $(Cu\text{—}\mu\text{-}SPh)_2$ ring, the Cu—P distances are 2.308(2) and 2.304(2) Å,[17] while in $(\mu_2\text{-}SPh)_2(\mu\text{-}SPh)_2(CuPPh_3)_4\cdot$toluene, the corresponding values are 2.238(2) and 2.217(2) Å.[18] The Cu—P distances in **1** are 2.301(2) and 2.246(2) Å, in reasonable agreement with the results quoted. The only example of a dppm complex is the cage structure $Cu_4(dppm)(CS_3)_2$,[19] where the Cu—P bond lengths are 2.272(7), 2.277(8), 2.286(7) and 2.347(8) Å, again in agreement with the bond distances in **1**. As with the Cu—S bonds, it is not helpful to attempt any detailed analysis in view of the different structural types involved.

The unique feature of the molecule is the eight-membered ring, for which there is apparently no analogue in other copper(I)–thiolate complexes. Cubanoid copper(I) structures are known, as is the step or chair version of the cube (c.f. ref. 18). The molecule $(\mu\text{-}SBu^t)_4Cu_4(PPh_3)_2$ is quoted as an example of the open eight-membered ring,[18] but no details are yet available. Several examples of six-membered Cu_2SCP_2 rings in the boat form are to be found among copper(I) thiolate cage structures and especially in $Cu_4(dppm)_2(CS_3)_2$, where the identical sub-unit occurs, albeit with small differences in the bond distances and angles.[19] Finally we note that there is only one tetrameric molecule per unit cell, with Van der Waals interactions between units.

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REFERENCES

1. F. F. Said and D. G. Tuck, *Inorg. Chim. Acta* 1982, **59**, 1.
2. J. L. Hencher, M. A. Khan, F. F. Said and D. G. Tuck, *Polyhedron* 1985, **4**, 1263.
3. J. L. Hencher, M. A. Khan, F. F. Said, R. Sieler and D. G. Tuck, *Inorg. Chem.* 1982, **21**, 2787.
4. J. H. Green, R. Kumar and D. G. Tuck, unpublished results.
5. R. K. Chadha, R. Kumar and D. G. Tuck, *J. Chem. Soc., Chem. Commun.* 1986, 188.
6. R. K. Chadha, R. Kumar and D. G. Tuck, *Can. J. Chem.* 1987, **65**, 1336.
7. C. Oldham and D. G. Tuck, *J. Chem. Ed.* 1982, **59**, 420.
8. M. A. Khan, R. S. Steevensz, D. G. Tuck, J. G. Noltes and P. W. R. Corfield, *Inorg. Chem.* 1980, **19**, 3407.
9. G. M. Sheldrick, *Computing in Crystallography*

(Edited by G. Schlenk), pp. 34–42. Delft University Press (1978).

10. M. A. Khan, C. Peppe and D. G. Tuck, *Acta Cryst.* 1983, **C39**, 1339.
11. G. K. Anderson, H. C. Clark and J. A. Davies, *J. Organomet. Chem.* 1981, **210**, 135.
12. S. J. Cooper, M. P. Brown and R. J. Puddephatt, *Inorg. Chem.* 1981, **20**, 1374.
13. A. R. Sanger, *J. Chem. Soc., Dalton Trans.* 1981, 228.
14. S. J. Black, F. W. B. Einstein, P. C. Hayes, R. Kumar and D. G. Tuck, *Inorg. Chem.* 1986, **25**, 4181.
15. D. Coucouvanis, C. N. Murphy and S. K. Karodia, *Inorg. Chem.* 1980, **19**, 2993.
16. C. D. Garner, J. R. Nicholson and W. Clegg, *Inorg. Chem.* 1984, **23**, 2148.
17. I. G. Dance, P. J. Guerney, A. D. Rae and M. L. Scudder, *Inorg. Chem.* 1983, **22**, 2883.
18. I. G. Dance, M. L. Scudder and L. J. Fitzpatrick, *Inorg. Chem.* 1985, **24**, 2547.
19. A. M. M. Lanfredi, A. Tiripicchio, A. Camus and N. Marsich, *J. Chem. Soc., Chem. Comm.* 1983, 1126.