Studies on Dithio-*o*-toluate Copper(I) Complexes with Bis(diphenylphosphino)-methane. Crystal Structures of {Di-μ_3-dithio-*o*-toluato-S,S',S'-bis[μ-bis-(diphenylphosphino)methane-μ-dithio-*o*-toluato-S,S']}tetracopper(I) and {Di[μ-bis(diphenylphosphino)methane]bis(dithio-*o*-toluato-S,S')}dicopper(I)

ANNA MARIA MANOTTI LANFREDI, FRANCO UGOZZOLI

Istituti di Chimica Generale ed Inorganica e di Strutturistica Chimica della Università, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via M. D'Azeglio 85, 43100 Parma, Italy

ANNAMARIA CAMUS and NAZARIO MARSICH

Istituto di Chimica, Università di Trieste, Piazzale Europa 1, 34127 Trieste, Italy

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Abstract

The structures of $[(CuS_2CT)_2dppm]_2$ (**I**) (T = *o*-tolyl; dppm = bis(diphenylphosphino)methane) and $[CuS_2CTdppm]_2$ (**II**) have been determined by X-ray methods. Crystals of **I** are monoclinic, space group $P2_1/n$, with a = 15.163(4), b = 18.691(5), c = 13.478(4) Å, β = 96.81(3)°, Z = 2; crystals of **II** are orthorhombic, space group *Pccn*, with a = 23.267(4), b = 13.016(3), c = 20.731(5) Å, Z = 4. The structures of **I** and **II** have been solved by Patterson and Fourier methods and refined by full-matrix least-squares to R = 0.082 for **I** and 0.092 for **II**. The structure of **I** consists of centrosymmetric tetranuclear complexes in which two pairs of Cu atoms are triply bridged by a dppm ligand and two dithiocarboxylate groups from the dithio-*o*-toluate ligands. These last behave differently: one of them through a sulphur atom is also bonded to a Cu atom of the other pair so forming a tetranuclear complex. The Cu atoms of each pair show different coordination: Cu(1) displays a distorted trigonal and Cu(2) a distorted trigonal pyramidal geometry. The structure of **II** consists of dimers, in which each copper atom, doubly bridged by two dppm ligands, completes a distorted trigonal pyramidal coordination through two sulphur atoms from dithio-*o*-toluate anions acting as chelating ligands. In both compounds the phenyl group of the dithio-*o*-toluate anions is orthogonal to the corresponding CS_2 group. Both complexes give methyldithio-*o*-toluate in high yields by reaction with methyl iodide.

Introduction

There is increasing interest in binuclear or cluster complexes of transition metals as models for compounds of biological and catalytic interest. Bis(diphenylphosphino)methane (dppm) is one of the diphosphine ligands most suitable to lock together two metal atoms in close proximity [1]. Some complexes of this ligand with copper(I) compounds and their X-ray structures are already known [2–8]. The complexes studied in this paper were obtained by CS_2 insertion into the copper–carbon bond of arylcopper(I) compounds followed by dppm addition [9]. Stable $[CuS_2CAr(dppm)]_2$ complexes (with Cu/dppm ratio 1:1) were obtained with Ar = phenyl and *o*-, *m*- or *p*-tolyl, while complexes $[(CuS_2CAr)_2dppm]_2$ (with Cu/dppm ratio 2:1) were obtained only with Ar = *o*-tolyl.

In order to elucidate the structures of these complexes, we have undertaken the structure determinations of both *o*-tolyl derivatives.

Experimental

Synthesis

Compounds $[(CuS_2CT)_2dppm]_2$ (**I**) and $[CuS_2CTdppm]_2$ (**II**) were prepared as previously described [9] and recrystallized from toluene (T = *o*-tolyl and dppm = bis(diphenylphosphino)methane).

Crystal Structure Determination of I and II

A flattened orange crystal of **I** (of dimensions *ca.* 0.15 × 0.20 × 0.30 mm) and a prismatic red crystal of **II** (of dimensions *ca.* 0.16 × 0.32 × 0.60 mm) were used for the X-ray analyses. The unit cell parameters were refined by a least squares procedure applied to the θ values of 24 (**I**) and 27 (**II**) reflections carefully measured on a Siemens AED single-crystal diffractometer.

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The crystal data are as follows:

Complex **I**: $C_{82}H_{72}Cu_4P_4S_8$, M = 1692.0, monoclinic, a = 15.163(4), b = 18.691(5), c = 13.478(4) Å, β = 96.81(3)°, V = 3793(2) Å^3, Z = 2, D_c = 1.48 g cm^{-3}, $F(000)$ = 1736, Cu-Kα radiation, $\bar{\lambda}$ = 1.54178 Å; μ(Cu-Kα) = 44.30 cm^{-1}. Space group $P2_1/n$ from systematic absences.

Complex **II**: $C_{66}H_{58}Cu_2P_4S_4$, M = 1230.4, orthorhombic, a = 23.267(4), b = 13.016(3), c = 20.731(5) Å, V = 6278(2) Å^3, Z = 4, D_c = 1.30 g cm^{-3}, $F(000)$ = 2544, CuKα radiation, λ = 1.54178 Å, μ(Cu-Kα) = 33.18 cm^{-1}. Space group $Pccn$ from systematic absences.

Intensities were collected at room temperature using the Ni-filtered Cu-Kα radiation for both compounds with $\theta-2\theta$ scan technique. All the reflections in the range of $3 < \theta < 60°$ for both compounds were measured. Of 5613 (**I**) and 5188 (**II**) independent reflections, 2819 (**I**) and 1602 (**II**), having $I > 2\sigma(I)$, were considered observed and used in the analyses.

The intensities were corrected for the usual Lorentz and polarization factors; no absorption correction was applied for **I** while for **II** correction for absorption was applied using the method of Walker and Stuart [10] (min. and max. transmission factors 0.760 and 1.264).

Both structures were solved by Patterson and Fourier methods and the refinements were carried out by least-squares full-matrix cycles, using the SHELX system of computer programs [11] with first isotropic and then anisotropic thermal parameters for the Cu, S and P atoms only for both compounds. Only the hydrogen atoms of the methyl group of the dithiotoluate ligand of **I** were directly localized from a difference synthesis; the other hydrogen atoms of **I** and all the H-atoms of **II** were placed in their geometrically calculated positions and included in the final structure factor calculations with isotropic thermal parameters. The final conventional R values were 0.082 for **I** and 0.092 for **II** (observed reflections only). Unit weights were used in each stage of the refinement of both compounds, by analyzing the variations of $|\Delta F|$ as a function of $|F_o|$. Final atomic coordinates for the non-hydrogen atoms are given in Tables I and II for **I** and **II** respectively. Atomic coordinates of the hydrogen atoms, atomic thermal parameters and a list of calculated and observed structure factors for both compounds are available from the authors on request.

The calculations were carried out on the Cyber 76 computer of the 'Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale' (CINECA, Casalecchio, Bologna) and on the GOULD-SEL 32/77 computer of the 'Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma)'. In addition to the quoted program, PARST [12], ASSORB [13] and PLUTO [14] programs have been used.

Reaction of I with CH_3I

0.5 g of **I** were dissolved in 10 ml of CS_2 and reacted at reflux with 1 ml CH_3I. After three hours

TABLE I. Fractional Atomic Coordinates of the Non-Hydrogen Atoms (×10^4) for **I** with e.s.d.s in Parentheses.

	x/a	y/b	z/c
Cu_1	2217(2)	5484(1)	2009(2)
Cu_2	691(2)	4670(1)	1200(2)
S_1	76(3)	5026(2)	2621(3)
S_2	1387(3)	6260(3)	2797(3)
S_3	670(3)	5614(2)	56(3)
S_4	2588(3)	6000(2)	591(3)
P_1	1644(3)	3729(2)	1367(3)
P_2	2887(3)	4577(2)	2867(3)
C_1	480(11)	5832(9)	3029(12)
C_2	1640(10)	6026(8)	−145(11)
C_3	2243(11)	3737(9)	2647(11)
C_4	−74(11)	6247(9)	3720(12)
C_5	190(12)	6191(10)	4754(12)
C_6	−311(13)	6599(10)	5405(14)
C_7	−982(13)	7044(10)	5022(14)
C_8	−1269(14)	7087(11)	3972(15)
C_9	−791(12)	6645(9)	3323(12)
C_{10}	−1103(15)	6686(12)	2188(16)
C_{11}	1596(10)	6467(8)	−1102(11)
C_{12}	1487(12)	7182(9)	−1132(13)
C_{13}	1543(12)	7586(10)	−2032(13)
C_{14}	1700(14)	7195(11)	−2885(15)
C_{15}	1860(13)	6464(10)	−2874(14)
C_{16}	1780(11)	6075(9)	−1970(12)
C_{17}	1307(14)	7612(11)	−175(15)
C_{18}	2552(10)	3690(8)	582(11)
C_{19}	2551(12)	4168(9)	−202(12)
C_{20}	3270(13)	4165(10)	−782(14)
C_{21}	3965(13)	3703(11)	−548(14)
C_{22}	3977(13)	3196(10)	233(14)
C_{23}	3262(11)	3201(9)	813(12)
C_{24}	1260(10)	2806(8)	1324(11)
C_{25}	876(12)	2512(10)	2126(13)
C_{26}	647(14)	1793(12)	2136(16)
C_{27}	805(13)	1323(10)	1348(14)
C_{28}	1193(13)	1629(11)	541(14)
C_{29}	1415(12)	2346(10)	496(13)
C_{30}	3987(10)	4335(8)	2597(11)
C_{31}	4352(11)	4731(9)	1848(11)
C_{32}	5196(13)	4522(10)	1546(13)
C_{33}	5649(14)	3941(11)	2005(15)
C_{34}	5298(14)	3554(11)	2759(15)
C_{35}	4478(12)	3742(10)	3040(12)
C_{36}	2955(10)	4656(8)	4265(10)
C_{37}	3779(11)	4678(9)	4862(12)
C_{38}	3759(12)	4765(10)	5921(13)
C_{39}	2940(12)	4802(9)	6295(12)
C_{40}	2127(12)	4785(9)	5695(12)
C_{41}	2143(12)	4702(9)	4628(12)

TABLE II. Fractional Atomic Coordinates of the Non-Hydrogen Atoms (×10^4) for **II** with e.s.d.s in Parentheses.

	x/a	*y/b*	*z/c*
Cu	1966(1)	1594(2)	318(1)
S_1	2115(2)	1399(4)	1452(3)
S_2	1214(2)	381(4)	730(3)
P_1	3512(2)	2104(4)	−142(3)
P_2	2502(2)	661(3)	−369(3)
C_1	1571(8)	571(15)	1426(10)
C_2	1400(10)	−93(17)	2008(11)
C_3	1739(12)	−998(23)	2080(14)
C_4	1571(15)	−1616(27)	2645(18)
C_5	1112(12)	−1321(21)	2984(13)
C_6	790(12)	−515(23)	2933(14)
C_7	954(14)	221(24)	2375(15)
C_8	591(14)	1068(26)	2239(16)
C_9	2814(8)	−557(15)	−101(9)
C_{10}	2857(8)	−694(15)	567(9)
C_{11}	3109(9)	−1594(18)	807(11)
C_{12}	3317(9)	−2361(18)	357(12)
C_{13}	3260(8)	−2199(15)	−284(11)
C_{14}	3016(9)	−1269(16)	−539(10)
C_{15}	2079(9)	210(15)	−1068(10)
C_{16}	1543(9)	−206(15)	−940(10)
C_{17}	1183(10)	−587(18)	−1446(12)
C_{18}	1390(11)	−529(19)	−2064(12)
C_{19}	1915(13)	−109(22)	−2201(13)
C_{20}	2293(12)	337(22)	−1713(14)
C_{21}	3870(8)	1125(15)	382(10)
C_{22}	3846(10)	1328(18)	1040(12)
C_{23}	4143(11)	562(22)	1430(13)
C_{24}	4410(11)	−275(21)	1149(13)
C_{25}	4425(10)	−436(18)	516(12)
C_{26}	4168(8)	287(16)	88(10)
C_{27}	4122(8)	2610(16)	−610(10)
C_{28}	4592(9)	2888(16)	−252(11)
C_{29}	5091(10)	3346(19)	−552(12)
C_{30}	5060(10)	3459(19)	−1231(13)
C_{31}	4599(11)	3173(18)	−1609(12)
C_{32}	4104(9)	2714(17)	−1279(11)
C_{33}	3112(7)	1328(13)	−747(8)

a precipitate began to form, while the orange-brown colour of the solution changed gradually to red. After 6 h the reaction was interrupted and the solvent evaporated. The residue was extracted repeatedly with pentane, leaving a pale violet powder from which white crystals of $[(CuI)_2dppm]_2$ [15] were obtained by extraction with CH_2Cl_2, concentration and ether addition. The red pentane solution when evaporated gave TCS_2CH_3, as an orange-red oil of 98.7% purity (CFG).

Reaction of II with CH_3I

1 ml of CH_3I was added to a solution of 0.5 g of **II** in 10 ml of CS_2. In a few minutes the deep orange colour of the solution changed to pale orange. The solution was evaporated to dryness and the residue extracted with pentane. Evaporation of the pentane gave 0.136 g (92% yield) of TCS_2-CH_3 of 99.0% purity (CFG). The orange residue, recrystallized from CH_2Cl_2 plus ether, gave $[CuI\text{-}dppm]_n$ [15] as a crystalline white powder.

Results and Discussion

The crystal structure of **I** consists of centrosymmetric tetranuclear $[(CuS_2CT)_2dppm]2$ complexes. Their perspective view is represented in Fig. 1. Selected bond distances and angles are given in Table III. Two pairs of Cu atoms are triply bridged by a dppm ligand and two dithiocarboxylate groups from the dithio-*o*-toluate ligands. One of the two sulphur atoms of one dithio-*o*-toluate anion is also bonded to a Cu atom of the other pair, so forming a tetranuclear complex; in the same way as the two independent dithio-*o*-toluate anions, one acts as a double and the other as a triple bridging ligand, confirming the presence of two different kinds of dithio-*o*-toluate groups as suggested by IR spectra. The Cu atoms of each pair show different coordination: Cu(1) displays a distorted trigonal geometry [the P(2), S(2), S(4), Cu(1) atoms are displaced from the mean plane through them by −0.110(4), −0.112(5), −0.099(4), 0.134(3) Å respectively]; Cu(2) shows a distorted trigonal pyramidal coordination with the axial position occupied by the sulphur atom from the centrosymmetric moiety at a rather long distance [Cu(2)–S(3′) = 2.565(5) Å] [the displacements of the basal P(1), S(1), S(3) and Cu(2) atoms from the mean plane through them are −0.139(5), −0.113(5), −0.127(5) and 0.173(3) respectively, with the Cu(2) atom displaced towards the apex of the pyramid]. The Cu–P and Cu–S bond lengths around Cu(1) are significantly shorter than the corresponding distances in the basal coordination plane around Cu(2), as expected from the different coordination of the two Cu atoms. The planes passing through S(2)S(4)P(2) and S(1)S(3)P(2) are nearly parallel, the dihedral angle between them being ~3°.

Both trigonal planar and trigonal pyramidal arrangements around Cu^I atoms have also been found in di-μ-chlorotris(*trans*-cyclooctene)dicopper(I) [16]. In this last compound the apical positions of the Cu atom trigonally coordinated are completely free, while in **I** an apical position of the trigonally coordinated Cu(1) atom is occupied by the Cu(2) atom at a distance of 2.874(4) Å. This last distance falls within the lowest values of the observed Cu(I)–Cu(I) distances in complexes bridged by dppm [3, 4] or sulphur containing ligands [17]. As previously pointed by Mehrotra and Hoffmann [18] on bonding relationships in d^{10}–d^{10} systems, it is not easy to distinguish if this short distance corresponds to metal–metal interaction

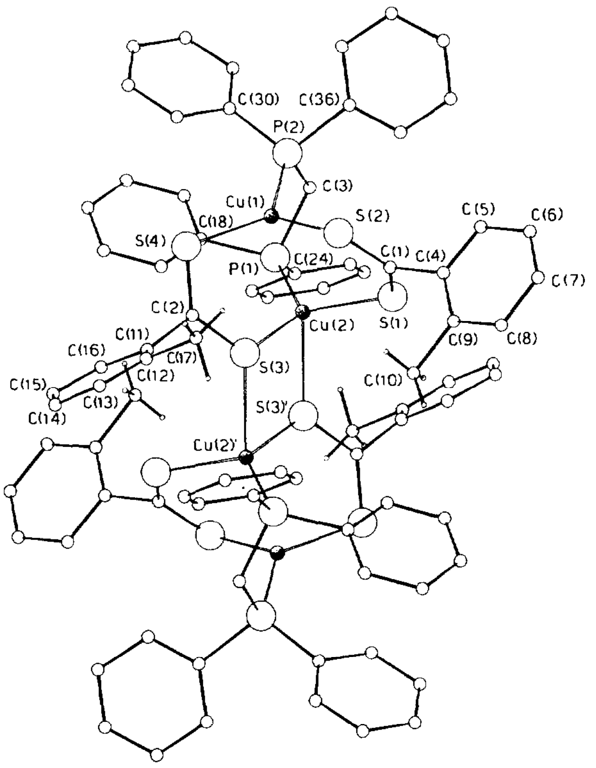

Fig. 1. Perspective view of the tetranuclear $[(CuS_2CT)_2dppm]_2$ complex.

or to a request of the bridging ligands. The Cu(2)–Cu(2′) distance, between copper atoms doubly bridged by two sulphur atoms from centrosymmetric pairs, is 3.843(4) Å.

For the $[CuS_2CAr(dppm)]_2$ complexes, on the basis of the ν_{CS_2} stretching frequencies [9], structures with both bridging or chelating dithiocarboxylate groups were possible, the last suggested by the similarity of the IR patterns of **II** with those of the corresponding triphenyl derivative [19]. The X-ray analysis of **II** has demonstrated the presence of dimers (with imposed C_2 symmetry) whose perspective view is represented in Fig. 2. Bond distances and angles are given in Table IV. Two copper atoms are doubly bridged by two dppm ligands, tetracoordination being achieved by each Cu atom through two sulphur atoms from dithio-*o*-toluate anions acting as chelating ligands. The two sulphur atoms are unsymmetrically bonded to the copper atom [the distances Cu–S(1) and Cu–S(2) are 2.390(6) and 2.507(6) respectively] and the S(1), P(1′) and P(2) are nearly coplanar with the Cu atom [the deviations of the S(1), P(2), P(1′) and Cu atoms from the mean plane through them are –0.101(5), –0.078(4), –0.104(5) and 0.078(3) Å, respectively] so the coordination around Cu may be considered as trigonal pyramidal with the sulphur atom, S(2), at the vertix of the pyramid

TABLE III. Seclected Bond Distances (Å) and Angles (°) in I.

Cu(1)–S(2)	2.265(6)	S(3)–C(2)	1.71(2)
Cu(1)–S(4)	2.270(5)	S(4)–C(2)	1.65(1)
Cu(1)–P(2)	2.228(4)	C(2)–C(11)	1.52(2)
Cu(2)–S(1)	2.325(5)	P(1)–C(3)	1.85(1)
Cu(2)–S(3)	2.341(4)	P(1)–C(18)	1.83(2)
Cu(2)–S(3^i)	2.565(5)	P(1)–C(24)	1.82(1)
Cu(2)–P(1)	2.270(5)	P(2)–C(3)	1.85(2)
S(1)–C(1)	1.69(2)	P(2)–C(30)	1.81(2)
S(2)–C(1)	1.65(2)	P(2)–C(36)	1.88(1)
C(1)–C(4)	1.54(2)		
S(2)–Cu(1)–P(2)	119.2(2)	S(1)–C(1)–C(4)	116.3(12)
S(2)–Cu(1)–S(4)	109.2(2)	S(2)–C(1)–C(4)	113.4(12)
S(4)–Cu(1)–P(2)	128.1(2)	Cu(1)–S(4)–C(2)	103.5(6)
S(1)–Cu(2)–P(1)	116.9(2)	Cu(2)–S(3)–C(2)	119.9(5)
S(1)–Cu(2)–S(3)	110.6(2)	S(3)–C(2)–S(4)	126.6(9)
S(3)–Cu(2)–P(1)	127.4(2)	S(3)–C(2)–C(11)	115.2(9)
S(3^i)–Cu(2)–S(1)	103.5(2)	S(4)–C(2)–C(11)	118.2(10)
S(3^i)–Cu(2)–S(3)	76.9(2)	Cu(1)–P(2)–C(3)	111.2(5)
S(3^i)–Cu(2)–P(1)	111.0(2)	P(2)–C(3)–P(1)	110.3(8)
Cu(1)–S(2)–C(1)	107.4(6)	Cu(2)–P(1)–C(3)	108.8(5)
Cu(2)–S(1)–C(1)	110.9(6)	Cu(2)–S(3)–Cu(2^i)	103.0(2)
S(1)–C(1)–S(2)	130.3(10)	C(2)–S(3)–Cu(2^i)	128.9(5)
Cu(2)–P(1)–C(18)	119.1(5)	Cu(1)–P(2)–C(30)	117.5(5)
Cu(2)–P(1)–C(24)	122.3(5)	Cu(1)–P(2)–C(36)	115.3(5)

i: $-x, 1-y, -z$

TABLE IV. Selected Bond Distances (Å) and Angles (°) in **II**.

Cu–S(1)	2.390(6)	P(1)–C(21)	1.87(2)
Cu–S(2)	2.507(6)	P(1)–C(27)	1.84(2)
Cu–P(1^i)	2.240(6)	P(1)–C(33)	1.86(2)
Cu–P(2)	2.249(6)	S(1)–C(1)	1.66(2)
P(2)–C(9)	1.83(2)	S(2)–C(1)	1.68(2)
P(2)–C(15)	1.85(2)	C(1)–C(2)	1.54(3)
P(2)–C(33)	1.84(2)		
S(1)–Cu–S(2)	72.5(2)	Cu–P(2)–C(9)	119.7(7)
S(1)–Cu–P(1^i)	124.8(2)	Cu–P(2)–C(15)	111.9(7)
S(1)–Cu–P(2)	119.0(2)	Cu–P(2)–C(33)	116.3(6)
S(2)–Cu–P(1^i)	106.0(2)	C(9)–P(2)–C(15)	100.0(9)
S(2)–Cu–P(2)	105.2(2)	C(9)–P(2)–C(33)	103.4(8)
P(2)–Cu–P(1^i)	114.4(2)	C(15)–P(2)–C(33)	103.1(9)
Cu^i–P(1)–C(21)	119.3(7)	Cu–S(1)–C(1)	85.8(7)
Cu^i–P(1)–C(27)	109.7(7)	S(1)–C(1)–S(2)	119.9(11)
Cu^i–P(1)–C(33)	116.7(6)	C(1)–S(2)–Cu	81.7(7)
C(21)–P(1)–C(27)	101.9(9)	S(1)–C(1)–C(2)	122.4(15)
C(21)–P(1)–C(33)	104.2(8)	S(2)–C(1)–C(2)	117.6(15)
C(27)–P(1)–C(33)	103.0(9)	P(1)–C(33)–P(2)	110.8(9)

i: $1/2 - x, 1/2 - y, z$

at a longer distance. The narrow bite of the S_2C-fragment [the S(1)–Cu–S(2) bond angle is 72.5(2)°] is responsible for the distortion from the idealized trigonal pyramidal geometry. In the eight-membered $Cu_2P_4C_2$ ring, having a pseudo D_{2d} symmetry (or saddle conformation), the Cu–Cu distance is 3.426(3) Å.

The coordination of Cu in **II** is different from that usually found in related copper(I) complexes containing the $Cu(I)P_2S_2$ chromophore and in which the S_2C-chelating fragment [19, 20] is symmetrically bonded to the metal atom in a tetrahedral arrangement. Also the face-to-face dimeric structure, although easily predictable and well known for rhodium, platinum and other metals [1], is new for copper(I) complexes of dppm and trigonal pyramidal metal centres disposed face-to-face are also a novelty [the P–Cu–P angle is 114.4(2)°]. In bimetallic complexes two bridging dppm ligands are generally *trans* and rarely *cis* coordinated [21] to the metal in square-planar arrangements.

In each dithio-*o*-toluate ligand of both compounds the dihedral angle between the mean planes through the phenyl ring and the CS_2 group is nearly 90° probably according to the steric demand of the methyl-phenyl moiety of the dithio-*o*-toluate ligand: hence the possibility of resonance is lost and this fact explains the absence of specially deshielded aromatic protons in the ^1H NMR spectra of these complexes [9]. The width of the ν_{CS_2} peaks of **II**, larger than in the triphenyl derivatives (where the sulphur atoms of the chelating CS_2 groups are

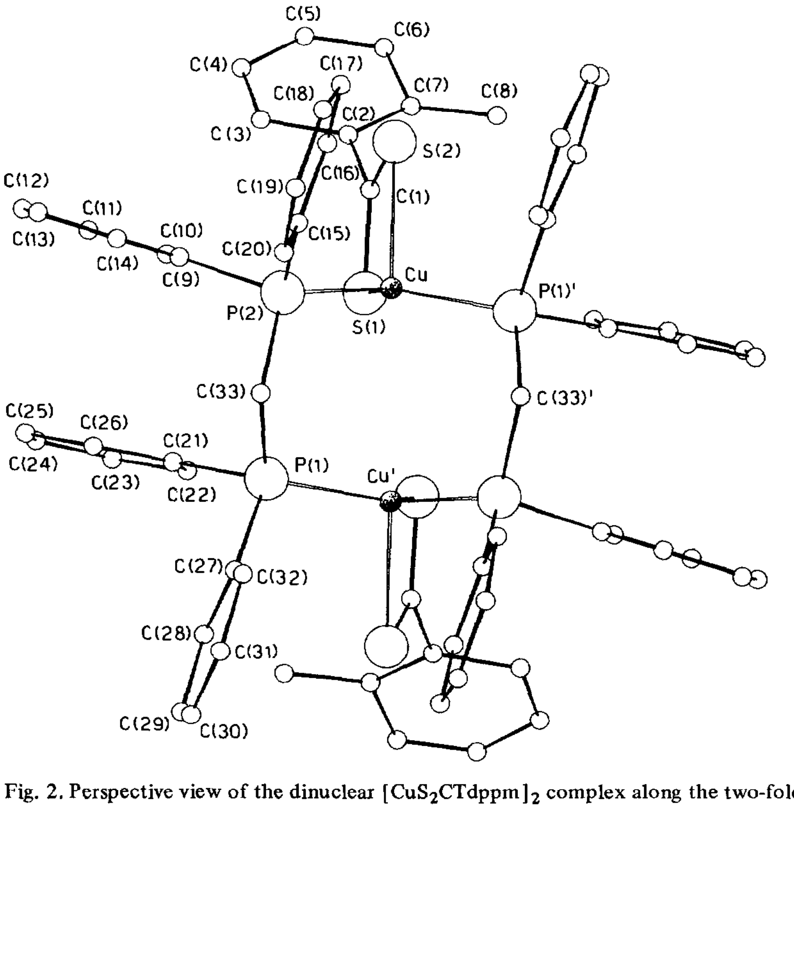

Fig. 2. Perspective view of the dinuclear $[CuS_2CTdppm]_2$ complex along the two-fold axis.

symmetrically bonded to the copper atom), are attributable to the unsymmetrical Cu–S bonds in the chelating CS_2 groups.

The structural differences between **I** and **II** are reflected in the very different rate of their reactivity with methyl iodide. The reaction, practically immediate at room temperature for **II**, requires a prolonged treatment at reflux for **I**. The reactions gave in both cases methyldithio-*o*-toluate of high purity in excellent yields, as already found with the $CuS_2CR(PPh_3)_2$ and $(CuS_2CR)_n(diphos)_m$ complexes [19]*. The main products of the phosphine moieties were $[CuI)_2dppm]_2$ and $[CuIdppm]_n$ respectively.

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