# Studies on Dithio-*o*-toluate Copper(I) Complexes with Bis(diphenylphosphino)-methane. Crystal Structures of {Di-μ₃-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*

## 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, $\beta = 96.81(3)°$, $Z = 2$; 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 tetra-nuclear complexes in which two pairs of Cu atoms are triply bridged by a dppm ligand and two dithio-carboxylate 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 ortho-gonal 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 com-pounds 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 com-plexes, we have undertaken the structure determina-tions of both *o*-tolyl derivatives.

## Experimental

### Synthesis

Compounds $[(CuS_2CT)_2dppm]_2$ (**I**) and $[CuS_2CTdppm]_2$ (**II**) were prepared as previously de-scribed [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 pro-cedure applied to the $\theta$ values of 24 (**I**) and 27 (**II**) reflections carefully measured on a Siemens AED single-crystal diffractometer.

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, $\beta$ = 96.81(3)°, $V$ = 3793(2) Å$^3$, $Z$ = 2, $D_c$ = 1.48 g cm$^{-3}$, $F(000)$ = 1736, Cu-K$\alpha$ radiation, $\bar{\lambda}$ = 1.54178 Å; $\mu$(Cu-K$\alpha$) = 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, CuK$\alpha$ radiation, $\lambda$ = 1.54178 Å, $\mu$(Cu-K$\alpha$) = 33.18 cm$^{-1}$. Space group $Pccn$ from systematic absences.

Intensities were collected at room temperature using the Ni-filtered Cu-K$\alpha$ 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 Diffrat-

tometrica 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$_3$I*

0.5 g of I were dissolved in 10 ml of CS$_2$ and reacted at reflux with 1 ml CH$_3$I. After three hours

TABLE I. Fractional Atomic Coordinates of the Non-Hydrogen Atoms ($\times 10^4$) 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 ($\times 10^4$) 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)$_2$dppm]$_2$ [15] were obtained by extraction with CH$_2$Cl$_2$, concentration and ether addition. The red pentane solution when evaporated gave TCS$_2$CH$_3$, as an orange-red oil of 98.7% purity (CFG).

*Reaction of II with CH$_3$I*

1 ml of CH$_3$I 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$_2$Cl$_2$ plus ether, gave [CuI-dppm]$_n$ [15] as a crystalline white powder.

## Results and Discussion

The crystal structure of **I** consists of centrosymmetric tetranuclear [(CuS$_2$CT)$_2$dppm]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-$\mu$-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
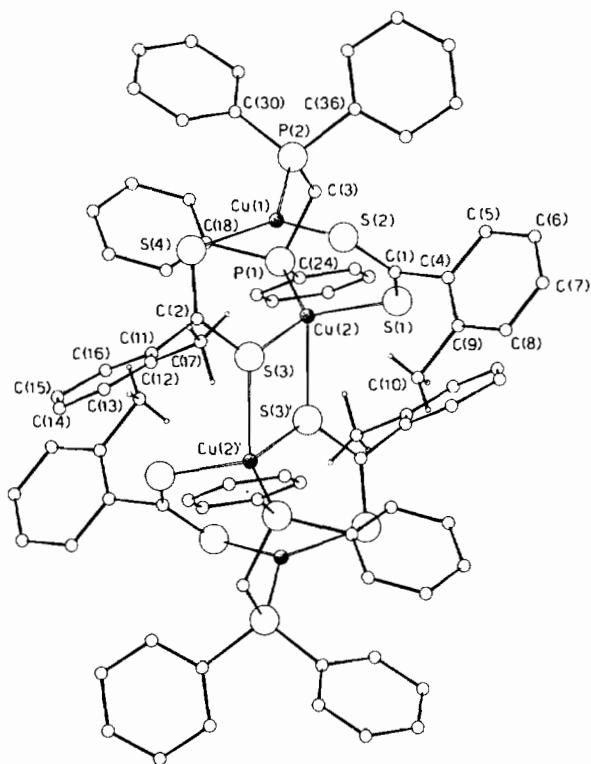
Fig. 1. Perspective view of the tetranuclear [(CuS$_2$CT)$_2$dppm]$_2$ complex.

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$_2$CAr(dppm)]$_2$ complexes, on the basis of the $\nu_{CS_2}$ 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 (A) 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 (A) 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 $S_2$C-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 $S_2$C-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 ${}^1$H NMR spectra of these complexes [9]. The width of the $\nu_{CS_2}$ peaks of **II**, larger than in the triphenyl derivatives (where the sulphur atoms of the chelating $CS_2$ groups are
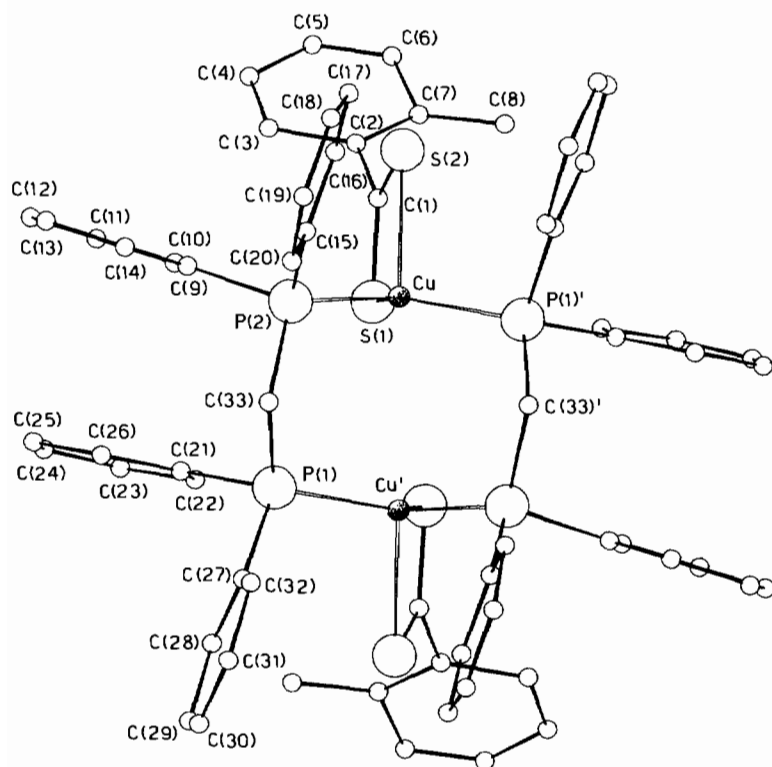


Fig. 2. Perspective view of the dinuclear [CuS$_2$CTdppm]$_2$ complex along the two-fold axis.

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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*Analogous reactions have been reported for organocopper compounds [22].

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