On some Copper(I) Perthiocarboxylates and their Reactions with Tertiary Phosphines. Crystal Structure of Tetra(*p*-tolyldithiocarboxylato)tetracopper(I), $[CuS_2C\text{-}p\text{-tolyl}]_4$, and of [Bis(triphenylphosphine)(*p*-tolyldithiocarboxylato)copper(I)] Triphenylphosphine Sulfide, $[CuS_2C\text{-}p\text{-tolyl}(PPh_3)_2]\cdot PPh_3S$

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(Received November 4, 1988; revised January 19, 1989)

Abstract

Some copper(I) perthiocarboxylates $[CuS_3CAr]_4$ (I) (Ia, Ar = Ph; Ib, Ar = *p*-tolyl) were prepared in high yields from the corresponding aldehydes and ammonium polysulfide in basic medium. By reacting them with triphenylphosphine in different ratios, formation of PPh_3S occurred and the following series of products could be isolated: $[(CuS_3CAr)_2(CuS_2CAr)_2]py_2$ (II); $[CuS_2CAr]_4$ (III); $[(CuS_2CAr)_4(PPh_3)_2]$ (IV); $[CuS_2CAr(PPh_3)_2]$ (V). In the case of *p*-tolyl the complex $[CuS_2CAr(PPh_3)_2]\cdot PPh_3S$ (VIb) was also obtained. Some significant IR and NMR (^{13}C, ^{31}P) data of the above compounds are reported. The crystal structures of compounds **IIIb** and **VIb** were established by single crystal X-ray diffraction methods. Crystals of **IIIb** are triclinic, space group $P\bar{1}$, with a = 13.879(4), b = 10.324(3), c = 13.479(4) Å, α = 99.04(2), β = 113.31(3), γ = 92.34(2)° and Z = 2. Crystals of **VIb** are also triclinic, space group $P\bar{1}$, with a = 15.833(5), b = 10.999(3), c = 15.690(5) Å, α = 103.12(3), β = 90.88(2), γ = 94.05(2)° and Z = 2. The structures have been solved by direct and Fourier (**IIIb**) and by Patterson and Fourier (**VIb**) methods and refined by blocked full-matrix least-squares to R = 0.059 for **IIIb** and R = 0.051 for **VIb**. The structure of **IIIb** consists of discrete units of four copper atoms bound to sulfur atoms from four *p*-tolyldithiocarboxylate groups acting as tridentate ligands. A sulfur atom of each ligand coordinates to one only copper atom and the other bridges two adjacent metals so that each metal is pseudo-trigonally surrounded by three sulfur atoms. In the structure of **VIb** monomeric complexes are present in which the metal atom is pseudo-tetrahedrally coordinated by two phosphorous atoms from triphenylphosphine ligands and by two sulfur atoms from one chelating *p*-tolyldithiocarboxylate group. Triphenylphosphine sulfide molecules are also present in the crystals of **VIb**.

The complex autoxidative reactions of some dithiocarboxylates in pyridine, which cause a partial transformation of the sulfur atoms in coordinated 'SO_4' groups, were also investigated.

Introduction

Recently, we synthesized the tetranuclear copper(I)-*o*-tolylperthiocarboxylate, $[CuS_3C\text{-}o\text{-}T]_4$ (T = tolyl) and its X-ray structure was also established [1]. Here we report the synthesis of the corresponding phenyl and *p*-tolyl derivatives which were then employed for the preparation of a series of dithiocarboxylates, in part new, in part, like the copper(I)-perthiodithiobenzoate $[(CuS_3CPh)_2(CuS_2CPh)_2]$, already known [2] and obtained by less easy methods. The structures of the new kinds of compounds were also determined by X-ray diffraction.

Experimental

Materials

When not otherwise specified the reagents employed were commercial products.

Preparation of the Perthiocarboxylates, $[CuS_3CAr]_4$

The perthiocarboxylates, $[CuS_3CAr]_4$ (I) (Ia, Ar = Ph; Ib, Ar = *p*-T), were prepared in high yield following the procedure of Fackler *et al.* [3] for the Zn(II) perthiotoluates. The compounds precipitated as amorphous powders, which, among common solvents, could be recrystallized only from pyridine.

Copper(I)phenylperthiocarboxylate, $[CuS_3CPh]_4$ (Ia)

The compound was prepared following the literature [1, method B]. Recrystallized from pyridine–ether the solvate $[(CuS_3CPh)_2py]$ was obtained, from which pyridine could be completely removed by heating under vacuum at 100 °C for 2 h. Yield 87.5%.

0020-1693/89/$3.50

*Copper(I)-p-tolylperthiocarboxylate, $[CuS_3C\text{-}pT]_4$ (**Ib**)*

This compound was also prepared by the above method and recrystallized from pyridine–ether. Yield 81.9%. Red–violet crystals of $(p\text{-}TCS_2)_2$ (melting point (m.p.) 147–148 °C, from MeOH; correct elemental analysis and molecular weight) were recovered as the main by-product from the mother liquors and washing solutions, after evaporation of the solvents, followed by extraction with n-pentane.

Reactions of $[CuS_3CAr]_4$ with Triphenylphosphine

The reactions are described for **Ib**, which gave the most complete series of products. The phenyl derivatives were obtained by corresponding methods. The *o*-tolylperthiocarboxylate gave products corresponding to those of the phenyl derivative, except for the perthiodithiocarboxylate, which could not be prepared.

*$[(CuS_3C\text{-}p\text{-}T)_2(CuS_2C\text{-}p\text{-}T)_2]py_2$ (**IIb**)*

0.25 g (0.95 mmol) of PPh_3 were added under stirring to a suspension of 0.5 g (0.47 mmol) of **Ib** in 10 ml of pyridine. The red–brown solution was filtered clear. Needles were formed by treatment with EtOH to incipient crystallization and standing. They were washed thoroughly with ether and dried in vacuum. Yield 72.7%.

*$[CuS_2C\text{-}p\text{-}T]_4$ (**IIIb**)*

From the red–brown solution, slowly formed by addition of 0.5 g (1.9 mmol) of PPh_3 to a suspension of 0.5 g (0.47 mmol) of **Ib** in 20 ml of toluene, microcrystals began to precipitate after 10 min. They filtered off after 2 h and washed at first with a little toluene, then repeatedly with ether. Yield almost quantitative (97%).

*$[Cu_4(S_2C\text{-}p\text{-}T)_4)(PPh_3)_2]$ (**IVb**)*

This was prepared as already reported [4].

*$[CuS_2C\text{-}p\text{-}T(PPh_3)_2]$ (**Vb**)*

This was previously prepared like **Va** [5]. While the last compound could also be obtained by reaction of the corresponding perthiocarboxylate with PPh_3 in Ph/Cu = 3 ratio, under these conditions the *p*-tolyl derivative gave only **VI**.

*$[CuS_2C\text{-}p\text{-}T(PPh_3)_2]\cdot PPh_3S$ (**VIb**)*

Addition of 1.5 g (5.7 mmol) of PPh_3 to a suspension of 0.5 g (0.47 mmol) of **Ib** in 20 ml of toluene gave a green–brown solution, from which crystals of the same colour precipitated after many hours. They were washed with ether and dried in vacuum. Yield 70%.

In all these reactions, but the latter, PPh_3S was recovered in consistent amounts from the mother liquors and identified by comparison with a commercial sample.

*Autoxidation of **IIIb** in Pyridine*

A total of 0.37 g (1.60 mmol Cu) of **IIIb** was dissolved in dry pyridine and the red–brown solution was stirred in dry oxygen at atmospheric pressure and room temperature, following the gas uptake. After 10 h this had practically ceased (2.21 mmol) and, without significant changes in the colour of the solution, a pale blue precipitate was obtained. After concentration and filtration of the solid ($[Cu(py)_3SO_4]$; $\geqslant$0.7 mmol Cu) under nitrogen, the mother liquor was evaporated to dryness. The brown residue, extracted with CH_2Cl_2, left an orange–brown solid ($CuS_3C\text{-}p\text{-}T$; $\geqslant$0.6 mmol Cu). The yellow–green extract, again evaporated to dryness and treated with benzene left a green–blue solid ($(p\text{-}TCOO)_2Cu\cdot H_2O$; $\approx$0.2 mmol Cu). Some *p*-toluic acid and free sulfur were further recovered from the benzene solution.

Alternatively pyridine was at first completely removed from the oxidized solution and the residue extracted with dry ether under nitrogen. The extract evaporated in the air left a cream powder, which was a mixture of *p*-toluic anhydride, *p*-toluic acid and elemental sulfur. The residue was a mixture of $[Cu(py)_3SO_4]$ and $[CuS_3C\text{-}p\text{-}T]_4$.

$Cu(py)_3SO_4$: Found: Cu, 15.8; O, 16.3; S, 7.9; py (GLC in MeOH plus NH_3) 58.8. Calc. for $C_{15}H_{15}CuN_3O_4S$: Cu, 16.00; O, 16.12; S, 8.08; py, 59.80%.

The other reaction products were identified by comparison of their IR spectra with those of authentic samples. Satisfactory elemental analyses were also obtained.

For the determination of the stoichiometry of the reaction, in another two runs the residue was extracted thoroughly with hot water, acidulated with HCl. The extract contained SO_4^{2-} ions, which, determined as $BaSO_4$, corresponded exactly to the formation of one sulfate group for two copper atoms.

*Autoxidation of **VIb** in Pyridine*

The reaction and the separation of the products of the autoxidation were conducted as previously described, on 0.4 g (0.275 mmol) of complex **IVb**. The uptake of oxygen (2.23 mmol), was practically complete after 8 h, with the formation of 2.8 sulfate groups for four copper atoms. The other products of the reaction were the same as above; furthermore some PPh_3S (0.15 g, 5.1 mmol) was recovered.

*X-ray Data Collection and Refinement of **IIIb** and **VIb***

A red–brown irregularly shaped crystal of **IIIb** (dimensions *c.* 0.22 × 0.30 × 0.35 mm) and a green–brown irregularly shaped crystal of **VIb** (dimensions *c.* 0.20 × 0.34 × 0.38 mm) were used for the X-ray analyses. Unit cell parameters were obtained by least-squares refinement of the θ values of 30 (**IIIb**) and 29 (**VIb**) reflections, carefully measured on a Siemens AED single crystal diffractometer.

Complex **IIIb**: $C_{32}H_{28}Cu_4S_8$, $M = 923.24$, triclinic, $a = 13.879(4)$, $b = 10.324(3)$, $c = 13.479(4)$ Å, $\alpha = 99.04(2)$, $\beta = 113.31(3)$, $\gamma = 92.34(2)°$, $V = 1740(1)$ Å^3, $Z = 2$, $D_c = 1.761$ g cm^{-3}, $F(000) = 928$, Cu Kα radiation, $\bar{\lambda} = 1.54178$ Å; μ(Cu Kα) = 73.40 cm^{-1}. Space group $P\bar{1}$ from structure determination.

Complex **VIb**: $C_{62}H_{52}CuP_3S_3$, $M = 1049.74$, triclinic, $a = 15.833(5)$, $b = 10.999(3)$, $c = 15.690(5)$ Å, $\alpha = 103.12(3)$, $\beta = 90.88(2)$, $\gamma = 94.05(2)°$, $V = 2653(1)$ Å^3, $Z = 2$, $D_c = 1.314$ g cm^{-3}, $F(000) = 1092$, Cu Kα radiation, $\bar{\lambda} = 1.54178$ Å; μ(Cu Kα) = 28.19 cm^{-1}. Space group $P\bar{1}$ from structure determination.

Intensities were collected at room temperature using Ni-filtered Cu Kα radiation for both compounds with θ–2θ scan technique. All the reflections in the range $3 \leqslant \theta \leqslant 70°$ for **IIIb** and $3 \leqslant \theta \leqslant 70°$ for **VIb** were measured. Of 6443 (**IIIb**) and 9849 (**VIb**) independent reflections, 5233 (**IIIb**) and 6670 (**VIb**), having $I \geqslant 2\sigma(I)$, were considered observed and used in the analyses. Correction for absorption effects [6] were applied for both compounds using the program ABSORB [7] (max. and min. values for the transmission factors were: 1.250 and 0.820 for **IIIb** and 1.165 and 0.872 for **VIb**).

The structures were solved by direct and Fourier methods for **IIIb** and by Patterson and Fourier methods for **VIb**; the refinements of both structures were carried out by blocked full-matrix least squares using the SHELX system of computer programs [8]. First isotropic and then anisotropic thermal parameters were estimated for all the non-hydrogen atoms of both compounds. All the hydrogen atoms of **IIIb** and **VIb** were located from ΔF syntheses and refined isotropically.

The weighting scheme used in the last cycles of refinement was $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ with $g = 0.0084$ for **IIIb** and $g = 0.0112$ for **VIb**. Final R and R_w were respectively 0.059 and 0.080 for **IIIb** and 0.051 and 0.069 for **VIb**. Atomic scattering factors, corrected for the anomalous dispersion of Cu, P and S, were taken from ref. 9. Final atomic coordinates for the non-hydrogen atoms are given in Tables 1 and 2 for **IIIb** and **VIb** respectively.

The calculations were carried out on the CRAY X-MP/12 computer of the 'Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale' (CINECA, Casalecchio, Bologna).

TABLE 1. Fractional atomic coordinates ($\times 10^4$) for the non-hydrogen atoms with e.s.d.s in parentheses for IIIb

Atom	*x/a*	*y/b*	*z/c*
Cu(1)	4194(1)	2478(1)	2281(1)
Cu(2)	4075(1)	3431(1)	4298(1)
Cu(3)	4644(1)	1081(1)	4157(1)
Cu(4)	2694(1)	1389(1)	2716(1)
S(1)	5336(1)	3977(1)	3720(1)
S(2)	6352(1)	1617(1)	4550(1)
S(3)	2456(1)	2825(1)	1559(1)
S(4)	2789(1)	4700(2)	3627(1)
S(5)	3572(1)	−440(1)	2686(1)
S(6)	4527(1)	738(1)	1315(1)
S(7)	4007(1)	2009(1)	5403(1)
S(8)	1774(1)	1193(2)	3735(1)
C(1)	6379(4)	2997(4)	4065(4)
C(2)	7319(4)	3442(5)	3899(4)
C(3)	7531(4)	4767(5)	3828(5)
C(4)	8394(5)	5159(7)	3652(5)
C(5)	9104(5)	4268(7)	3564(5)
C(6)	8893(5)	2986(7)	3618(6)
C(7)	8032(5)	2571(6)	3805(5)
C(8)	10063(6)	4750(10)	3381(7)
C(9)	2318(4)	4325(5)	2263(4)
C(10)	1761(4)	5278(6)	1609(5)
C(11)	1580(5)	6486(6)	2120(7)
C(12)	1168(6)	7439(8)	1519(8)
C(13)	897(5)	7254(10)	437(9)
C(14)	1032(6)	6056(10)	−116(7)
C(15)	1450(5)	5058(10)	466(6)
C(16)	472(9)	8364(14)	−196(13)
C(17)	4023(4)	−541(4)	1646(4)
C(18)	3925(4)	−1885(5)	1026(4)
C(19)	4037(4)	−2982(5)	1520(5)
C(20)	3926(5)	−4219(5)	932(5)
C(21)	3674(5)	−4434(5)	−198(5)
C(22)	3583(5)	−3340(6)	−688(5)
C(23)	3734(5)	−2077(6)	−93(5)
C(24)	3478(7)	−5840(6)	−843(7)
C(25)	2678(3)	1476(4)	5019(4)
C(26)	2370(4)	1289(4)	5926(4)
C(27)	3129(4)	1210(5)	6968(4)
C(28)	2829(5)	1009(5)	7807(5)
C(29)	1782(5)	911(6)	7638(5)
C(30)	1029(5)	1008(6)	6614(5)
C(31)	1301(4)	1169(5)	5758(5)
C(32)	1459(7)	735(11)	8569(7)

Results

Only very few Cu(I) perthiocarboxylates so far have been prepared: the *o*-tolyl derivative mentioned above [1] and two α-naphthyl derivatives $[CuS_3CC_{10}H_7]_n$ (n = 2, 4) [10, 11]. The preparative methods reported in "Experimental' allow one to obtain compounds of this class easily, so that they can be advantageously used as precursors for the preparation of some dithiocarboxylates, by reaction with tertiary phosphines.

With triphenylphosphine the following products, with or without phosphine ligands according to the Cu/P ratio used, have been isolated from **Ia** and **Ib** (eqns. (1)–(3))

TABLE 2. Fractional atomic coordinates ($\times 10^4$) for the non-hydrogen atoms with e.s.d.s in parentheses for **VIb**

Atom	*x/a*	*y/b*	*z/c*
Cu	2938(1)	1083(1)	2232(1)
S(1)	3126(1)	2589(1)	3624(1)
S(2)	4163(1)	522(1)	2955(1)
S(3)	666(1)	4213(1)	7566(1)
P(1)	3269(1)	2132(1)	1187(1)
P(2)	1909(1)	−482(1)	2075(1)
P(3)	1472(1)	3970(1)	6625(1)
C(1)	3991(2)	1804(4)	3739(3)
C(2)	4576(2)	2234(4)	4510(3)
C(3)	5157(3)	1448(4)	4728(3)
C(4)	5677(3)	1833(5)	5468(3)
C(5)	5649(3)	3002(5)	6012(3)
C(6)	5079(3)	3795(5)	5793(3)
C(7)	4554(3)	3428(4)	5055(3)
C(8)	6223(6)	3399(10)	6818(5)
C(9)	3586(3)	1163(4)	150(3)
C(10)	4347(3)	1388(5)	−233(3)
C(11)	4569(4)	571(6)	−1000(4)
C(12)	4046(4)	−450(5)	−1385(4)
C(13)	3291(4)	−688(5)	−1006(4)
C(14)	3073(4)	102(4)	−236(3)
C(15)	2368(3)	2931(4)	908(3)
C(16)	2021(3)	2784(5)	81(4)
C(17)	1300(4)	3367(6)	−54(4)
C(18)	908(4)	4088(6)	638(5)
C(19)	1257(4)	4238(5)	1464(4)
C(20)	1969(4)	3661(5)	1615(4)
C(21)	4122(3)	3370(4)	1419(3)
C(22)	4793(3)	3238(5)	1962(3)
C(23)	5506(3)	4087(6)	2085(4)
C(24)	5533(4)	5065(6)	1685(4)
C(25)	4871(4)	5229(6)	1160(5)
C(26)	4162(4)	4367(5)	1021(4)
C(27)	818(2)	−135(4)	1887(3)
C(28)	693(3)	723(5)	1405(4)
C(29)	−119(3)	996(6)	1188(4)
C(30)	−803(3)	425(6)	1479(4)
C(31)	−689(3)	−440(5)	1973(4)
C(32)	120(3)	−734(5)	2178(3)
C(33)	2071(2)	−1759(4)	1136(3)
C(34)	1460(3)	−2289(4)	495(3)
C(35)	1644(4)	−3196(5)	−241(4)
C(36)	2454(4)	−3576(5)	−337(4)
C(37)	3070(4)	−3083(5)	288(4)
C(38)	2897(3)	−2178(5)	1018(4)
C(39)	1831(2)	−1254(4)	2986(3)
C(40)	1569(3)	−2509(5)	2879(4)
C(41)	1479(4)	3037(5)	3595(4)
C(42)	1666(4)	−2331(6)	4423(4)
C(43)	1943(4)	−1096(5)	4533(3)
C(44)	2028(3)	−555(5)	3831(3)
C(45)	2069(2)	5418(3)	6550(2)
C(46)	2777(3)	5386(4)	6039(3)
C(47)	3218(3)	6485(4)	5973(4)
C(48)	2959(3)	7611(4)	6398(3)
C(49)	2253(4)	7649(4)	6892(3)
C(50)	1812(3)	6563(4)	6974(3)
C(51)	2258(2)	2898(3)	6759(2)
C(52)	2452(3)	2740(4)	7593(3)
C(53)	3066(3)	1947(4)	7707(3)
C(54)	3499(3)	1334(4)	7010(3)
C(55)	3312(3)	1475(4)	6182(3)
C(56)	2692(3)	2258(4)	6055(3)
C(57)	1000(2)	3333(4)	5537(3)
C(58)	932(4)	4025(6)	4933(4)
C(59)	567(5)	3499(7)	4107(4)
C(60)	256(4)	2302(6)	3893(4)
C(61)	307(4)	1596(6)	4496(4)
C(62)	677(4)	2109(5)	5326(4)

(continued)

TABLE 2. *(continued)*

$$[\mathrm{CuS_3CAr}]_4 + 2\mathrm{PPh_3} \longrightarrow [(\mathrm{CuS_3CAr})_2(\mathrm{CuS_2CAr})_2]\ (\mathbf{II}) + 2\mathrm{PPh_3S} \qquad (1)$$

$$[\mathrm{CuS_3CAr}]_4 + 4\mathrm{PPh_3} \longrightarrow [\mathrm{CuS_2CAr}]_4\ (\mathbf{III}) + 4\mathrm{PPh_3S} \qquad (2)$$

$$[\mathrm{CuS_3CAr}]_4 + 6\mathrm{PPh_3} \longrightarrow [(\mathrm{CuS_2CAr})_4(\mathrm{PPh_3})_2]\ (\mathbf{IV}) + 4\mathrm{PPh_3S} \qquad (3)$$

When the solvent was carbon disulfide an equivalent more of triphenylphosphine was required to obtain the same products.

The perthiodithiocarboxylates could be recrystallized without disproportionating only from pyridine.

Noteworthy is the formation of **IIIa** and **IIIb**, which we were unable to prepare by CS_2 insertion in the parent organocopper(I) compounds, like the *o*-tolyl derivative [5].

Pyridine solutions of compounds **III** and **IV**, underwent autoxidation with formation, in the absence of moisture, of a Cu(II) complex, of rough formula $[\mathrm{Cu(py)_3SO_4}]$, Cu(I) perthiocarboxylate and aryl anhydride. On the basis of oxygen uptake, the number of SO_4 groups produced and amounts of perthiocarboxylate and triphenyl sulfide recovered, the proposed stoichiometries of these oxidations (Ar = *p*-tolyl) are respectively

$$[\mathrm{CuS_2CAr}]_4 \xrightarrow[\mathrm{py}]{5.5\mathrm{O_2}} 2[\mathrm{Cu(py)_3SO_4}] + \frac{2}{n}[\mathrm{CuS_3CAr}]_n + (\mathrm{ArCO})_2\mathrm{O} \qquad (4)$$

$$[(\mathrm{CuS_2CAr})_4(\mathrm{PPh_3})_2] \xrightarrow[\mathrm{py}]{8.25\mathrm{O_2}} 3[\mathrm{Cu(py)_3SO_4}] + \frac{1}{n}[\mathrm{CuS_3CAr}]_n + 2\mathrm{PPh_3S} + \frac{3}{2}(\mathrm{ArCO})_2\mathrm{O} \qquad (5)$$

$(ArCOO)_2Cu$, ArCOOH, and sulfur, which were also isolated during the working up of the mother liquors in air, are produced by subsequent reactions.

The formation of a copper(II) sulfate complex with just three pyridine ligands, though pyridine was in large excess as reaction solvent, indicated that the SO_4 group was coordinated to copper, rather than in the ionic form. By the way the product is a non-electrolyte in methanol and its IR spectrum reflects a low symmetry for the SO_4 group, showing also (in nujol) a strong broad peak at 878 cm^{-1}, i.e. in a region where strong absorptions are reported for the coordinated sulfates [12]. The transformation of part of the sulfur of the dithiocarboxylate groups to sulfate, at room temperature and atmospheric pressure, is to our knowledge unprecedented. Normally coordinated sulfates are obtained by reaction of SO_2 with η^2-dioxygen complexes $L_nM(O_2)$ [12], so that intermediates of this kind could be considered in the mechanism of these autoxidations.

The reaction between compounds **I** and triphenylphosphine with a PPh_3:Cu ratio = 3 gave the known **Va** complex [5] with the phenyl group, but with the *p*-tolyl group the **VIb** compound was obtained. This last compound could in effect be obtained by reacting $[CuS_2C\text{-}p\text{-}T]_4$ with PPh_3 and PPh_3S in the above stoichiometric ratios. The triphenylphosphine sulfide molecule dissociates in solution, as demonstrated by the molecular weight of the complex, which, measured both in dichloroethane and toluene, was half the theoretical one.

Analytical data for the above compounds, together with colours and melting points are given in Table 3. Table 4 collects some relevant IR and NMR data.

Crystal Structures of IIIb and VIb

Structures of compounds **Ic** ($[CuS_3CAr]_4$, Ar = *o*-T) [1], **IIa** [2], **IVb** [4] and **Va** [5] have already been reported, and we have now determined by X-ray diffraction the structures of complexes **IIIb**

TABLE 3. General properties and elemental analyses of the compounds

No.	Compound[a] Colour	Melting point (°C)[b] Crystallized from[e]	Analyses (%)[c] C	H	Cu	N	P	S	Solvent[d]
Ia	CuS_3CPh black	253 dec.	33.5 (33.8)	2.3 (2.0)	25.4 (25.5)			38.8 (38.65)	
	$[CuS_3CPh]_2py$[f] black	260–261 dec. py + ether	38.7 (39.6)	2.4 (2.6)	22.0 (22.0)	2.15 (2.4)		33.7 (33.35)	13.3 (13.7)
Ib	$CuS_3C\text{-}p\text{-}T$ orange–brown	255–257 dec. py + ether	36.6 (36.5)	2.6 (2.7)	23.9 (24.2)			36.8 (36.6)	
IIa	$[(CuS_3CPh)_2(CuS_2CPh)_2]py_2$[f, g] black	248–250 dec.[h] py + MeOH	41.0 (41.9)	2.4 (2.8)	22.9 (23.3)	2.4 (2.6)		29.7 (29.4)	14.2 (14.5)
IIb	$(CuS_3C\text{-}p\text{-}T)(CuS_2C\text{-}p\text{-}T)py_2$[f] brown–black	253–255 dec.[h] py + EtOH	44.7 (47.9)	3.6 (3.7)	19.3 (19.5)	3.7 (4.3)		24.5 (24.6)	24.2 (24.3)
IIIa	CuS_2CPh brown–black	199–200 dec. CS_2 + n-heptane	38.6 (38.8)	2.1 (2.3)	28.9 (29.3)			29.4 (29.6)	
IIIb	$[CuS_2C\text{-}p\text{-}T]_4$ brown–black	202–205 dec. CS_2 + n-heptane	41.3 (41.6)	2.9 (3.0)	27.4 (27.5)			27.6 (27.8)	
IVa	$(CuS_2CPh)_2PPh_3$ dark brown	175–176 CH_2Cl_2 + EtOH	54.8 (55.2)	3.6 (3.6)	18.2 (18.3)		4.3 (4.4)	18.2 (18.4)	
IVb	$[(CuS_2C\text{-}p\text{-}T)_4(PPh_3)_2]$ dark brown	181–183 hot toluene	56.3 (56.4)	3.8 (4.0)	17.5 (17.5)		4.3 (4.3)	17.9 (17.7)	
VIb	$[CuS_2C\text{-}p\text{-}T(PPh_3)_2]PPh_3S$ green–brown (dicroic)	181–182.5 toluene + ether	70.8 (70.9)	5.1 (5.0)	6.1 (6.0)		8.6 (8.8)	9.2 (9.2)	

[a] Minimal formulae are given for compounds, whose structures were not confirmed by X-ray diffraction methods. [b] Samples introduced in the m.p. apparatus at a temperature near to final one. [c] Calculated values in parentheses. [d] Determined by GLC with internal standard benzene. The complete dissolution of the samples was achieved by addition of PPh_3. [e] All the products are soluble in pyridine (py) and, except pyridine solvates, practically insoluble in aliphatic hydrocarbons, methanol, ether, acetone, CCl_4, CH_3CN, DMSO. [f] C, H, N were determined by a gas chromatographic analyzer, which required a pretreatment of the sample involving a partial loss of solvent, particularly relevant in the case of the IIb compound. [g] Ref. 2. [h] When the sample was introduced at $t \geqslant 120$ °C it melted immediately with gas evolution; afterwards it resolidificated and the solid melted again at the reported temperature. When the sample was introduced at room temperature a gradual loss of solvent occurred and only the final m.p. was observed.

TABLE 4. Some spectroscopic data of Cu(I) perthiocarboxylates and related compounds

Compound	IR[a]		^{13}C NMR[b]		^{31}P NMR[c]	
	$\nu_{asym}CS_3$ or CS_2[d]	$\nu_{sym}CS_3$ or CS_2[d]	δCS_3 or CS_2	solvent	δ_P	$\delta_{P(5)}$
Ia	1031sh					
	1020s,br	894mw	228	e		
	1016sh					
Ib	1031s,br	889mw	229?	e		
	1016					
IIIa	1030sh	895sh				
	1005s,br	887s,br	234.1	e		
	997sh					
IIIb	1013s,br	891s,br	234.0	e		
	980sh					
IVa	1030sh					
	1011s,br	899/890(d) m,br	238.2	e	0.3	
	998s,br					
IVb	1024w					
	1020/1013(d) s,br	894m,br	238.4	e	−0.9	
	(982sh,w)	887sh				
Va	1026w					
	1013s	927w	248.5	f		
	(?997m)					
Vb	1027sh					
	1018s	927w	248.8	e	≈1	
	988/981w		248.0	f		
VI	1028sh					
	1015s	927w	248.8	e	0.5	43.3
	999sh		247.9	f		
	979m					

[a] In KBr; s = strong; m = medium; w = weak; br = broad; sh = shoulder; d = doublet. [b] Room temperature spectra; chemical shifts in ppm from TMS. [c] Chemical shifts in ppm from H_3PO_4 10% in D_2O; solvent $CDCl_3$. [d] We have maintained the notation used for compounds V, where CS_2 acts as symmetric chelating ligand, also if this is not strictly correct for the perthiocarboxylates and other compounds on the basis of the established structures. [e] Solvent = d_5-pyridine. [f] Solvent = $CDCl_3$.

and **VIb**, so that the whole series of products is structurally characterized. Some differences, however, could be present, due to different steric requirements of the various aryl moieties.

The structure of **IIIb** reveals discrete units of four copper atoms, disposed almost at the vertices of a tetrahedron, bound to four *p*-tolyldithiocarboxylate groups acting as tridentate ligands (Fig. 1). A sulfur atom of each ligand coordinates to only one copper atom and the other bridges two adjacent copper atoms so that each metal is in an approximately trigonal and almost planar arrangement of three sulfur atoms. Relevant bond distances and angles are given in Table 5. The Cu–Cu distances associated with the copper atoms bridged by the two sulfur atoms from a CS_2 moiety and one sulfur atom from a neighbouring CS_2 group range from 2.584(1) to 2.814(2) Å [Cu(2)–Cu(3) = 2.584(1), Cu(1)–Cu(4) = 2.631(2), Cu(3)–Cu(4) = 2.703(2), Cu(1)–Cu(2) = 2.814(2) Å]; the remaining Cu(2)–Cu(4) and Cu(1)–Cu(3) distances, associated with metal atoms doubly bridged by the sulfur atoms from two CS_2 moieties, are 2.773(2) and 2.973(1) Å respectively.

Copper tetranuclear units are present in the structure of **Ic** [1], where four *o*-tolyl-perthiocarboxylate –C(S)SS groups coordinate to the metals as tridentate bridging ligands so that five membered CuSSCS chelate rings are formed and the shortest Cu–Cu distances [ranging from 2.757(2) to 2.872(2) Å] are observed for the metals bridged by the terminal perthio atom from the ligands.

Tridentate *p*-tolyldithiocarboxylate groups, comparable to those observed in the present compound, have been found in **IV**, where, however, four copper atoms, each engaged in three bridges, are in a distorted trigonal-pyramidal arrangement.

Common features of the structures of **Ic**, **IIIb** and **IVb** are the trigonal arrangements of the three sulfur atoms bonded to each copper atom. In partic-

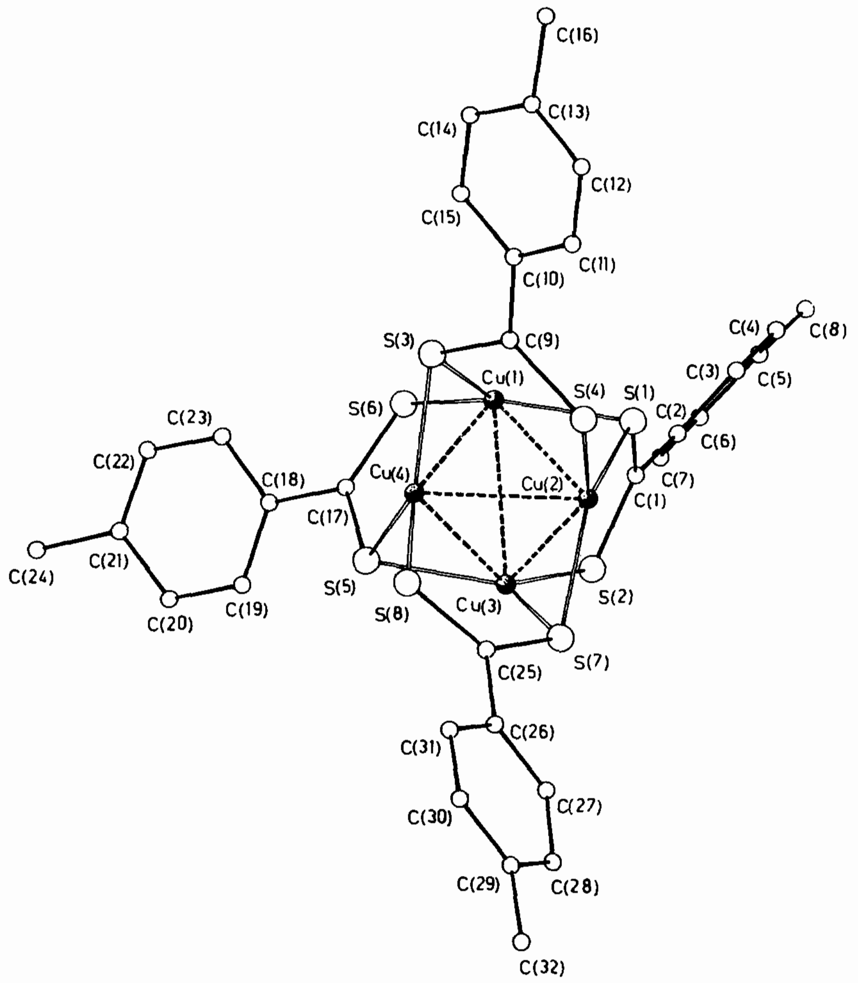

Fig. 1. Perspective view of the tetranuclear IIIb complex with the atomic numbering scheme.

TABLE 5. Relevant bond distances (Å) and angles (°) in IIIb

Cu(1)–Cu(2)	2.814(2)	Cu(3)–S(5)	2.260(2)
Cu(1)–Cu(3)	2.973(1)	Cu(3)–S(7)	2.294(2)
Cu(1)–Cu(4)	2.631(2)	Cu(4)–S(3)	2.257(2)
Cu(2)–Cu(3)	2.584(1)	Cu(4)–S(5)	2.293(2)
Cu(2)–Cu(4)	2.773(2)	Cu(4)–S(8)	2.238(2)
Cu(3)–Cu(4)	2.703(2)	S(1)–C(1)	1.751(5)
Cu(1)–S(1)	2.257(2)	S(2)–C(1)	1.664(5)
Cu(1)–S(3)	2.283(2)	S(3)–C(9)	1.745(6)
Cu(1)–S(6)	2.225(2)	S(4)–C(9)	1.662(5)
Cu(2)–S(1)	2.265(2)	S(5)–C(17)	1.739(6)
Cu(2)–S(4)	2.238(2)	S(6)–C(17)	1.669(6)
Cu(2)–S(7)	2.274(2)	S(7)–C(25)	1.744(5)
Cu(3)–S(2)	2.239(2)	S(8)–C(25)	1.658(4)
Cu(3)–Cu(1)–Cu(4)	57.3(1)	S(2)–Cu(3)–S(5)	123.4(1)
Cu(2)–Cu(1)–Cu(4)	61.1(1)	S(5)–Cu(4)–S(8)	108.1(1)
Cu(2)–Cu(1)–Cu(3)	53.0(1)	S(3)–Cu(4)–S(8)	125.4(1)
Cu(1)–Cu(2)–Cu(4)	56.2(1)	S(3)–Cu(4)–S(5)	124.7(1)
Cu(1)–Cu(2)–Cu(3)	66.7(1)	Cu(1)–S(1)–Cu(2)	76.9(1)
Cu(3)–Cu(2)–Cu(4)	60.5(1)	Cu(1)–S(3)–Cu(4)	70.8(1)

(continued)

TABLE 5. *(continued)*

Cu(1)–Cu(3)–Cu(2)	60.4(1)	Cu(3)–S(5)–Cu(4)	72.8(1)
Cu(2)–Cu(3)–Cu(4)	63.2(1)	Cu(2)–S(7)–Cu(3)	68.9(1)
Cu(1)–Cu(3)–Cu(4)	55.0(1)	S(1)–C(1)–S(2)	123.7(4)
Cu(2)–Cu(4)–Cu(3)	56.3(1)	S(2)–C(1)–C(2)	119.5(4)
Cu(1)–Cu(4)–Cu(3)	67.7(1)	S(1)–C(1)–C(2)	116.8(4)
Cu(1)–Cu(4)–Cu(2)	62.7(1)	S(3)–C(9)–S(4)	122.8(4)
S(3)–Cu(1)–S(6)	112.5(1)	S(4)–C(9)–C(10)	119.5(4)
S(1)–Cu(1)–S(6)	129.0(1)	S(3)–C(9)–C(10)	117.7(4)
S(1)–Cu(1)–S(3)	118.3(1)	S(5)–C(17)–S(6)	125.3(3)
S(4)–Cu(2)–S(7)	122.1(1)	S(6)–C(17)–C(18)	119.9(4)
S(1)–Cu(2)–S(7)	131.6(1)	S(5)–C(17)–C(18)	114.8(4)
S(1)–Cu(2)–S(4)	106.2(1)	S(7)–C(25)–S(8)	124.2(3)
S(5)–Cu(3)–S(7)	119.0(1)	S(8)–C(25)–C(26)	119.8(4)
S(2)–Cu(3)–S(7)	117.5(1)	S(7)–C(25)–C(26)	116.0(4)

ular in **IIIb** the displacements of the metal atoms from the plane through the sulfur atoms are 0.068(2), 0.035(2), 0.060(2) and 0.179(2) Å for Cu(1), Cu(2), Cu(3) and Cu(4) atoms respectively.

In the present compound, as observed in **IV**, the C–S bonds from each *p*-tolyldithiocarboxylate ligand, are significantly different, the C–S distance involving the monodentate sulfur (av. 1.662(2) Å) being shorter than that involving the bridging sulfur atom (av. 1.745(3) Å).

The dihedral angles the CS_2 groups form with the associated aromatic ring are 20.6(2), 7.5(3), 33.5(3) and 15.7(3)° for the rings identified by C(2), C(10), C(18) and C(26) carbon atoms respectively: these values, very different with respect to the values of ~90° found for the corresponding angles in the *o*-tolylderivative (**Ic**) are only partially in good agreement with the corresponding ones found in **IVb** [29.7(3), 29.3(4), 50.3(4) and 1.47(3)°]; the smaller range of the mentioned dihedral angles in **IIIb** [7.5(3)–33.5(3)° versus 1.47(3)–50.3(3)°] seems to be attributable to the more symmetrical metal atoms arrangement in **IIIb** with respect to that observed in **IVb** with the consequent more similar steric requirement for the ligands.

The structure of **VIb** consists of monomeric $[Cu(PPh_3)_2(S_2C\text{-}p\text{-tolyl})]$ complexes with triphenylphosphine sulfide molecules interposed in the lattice. Figure 2 shows a perspective view of the structure of the complex whose relevant bond distances and angles are given in Table 6. The metal atom is pseudotetrahedrally coordinated by two phosphorous atoms from triphenylphosphine ligands and two sulfur atoms from a *p*-tolyldithiocarboxylate anion acting as a chelating ligand. The values of the S(1)–C(1)–S(2) and P(1)–Cu–P(2) angles, [73.9(1) and 124.2(1)°], are imposed by the bidentate CS_2 group requirement and triphenylphosphine molecules steric demand respectively; the other angles range from 106.6(1) to 119.0(1)°. The small distortion of the complex is not restricted to the bond angles but also appears in the bond distances. Indeed, the Cu–P bond lengths are equivalent [Cu–P(1) = 2.258(2) and Cu–P(2) = 2.254(1) Å] and the Cu–S bond distances, very similar each to other [Cu–S(1) = 2.423(2) and Cu–S(2) = 2.418(2) Å], support symmetrical bonding of the sulfur ligands.

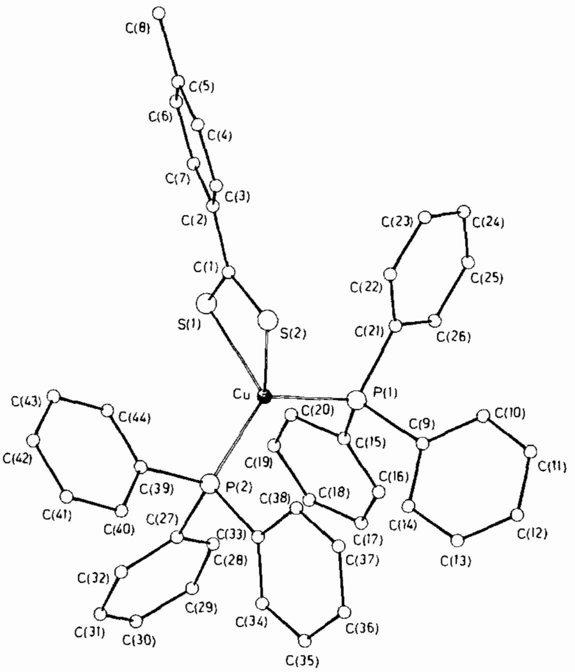

Fig. 2. Perpective view of the mononuclear $[Cu(PPh_3)_2(S_2C\text{-}p\text{-tolyl})]$ complex from **VIb** with the atomic numbering scheme.

The structural parameters of this complex are in close agreement with those observed in the previously reported structure of **Va** [5, 13] containing an identical donor atom set in a tetrahedral environment. The only differences are envisaged in the rotations of the aryl groups with respect to the corresponding planar CuSSC ring: the dihedral angles that the last moiety forms with the aryl group are

TABLE 6. Relevant bond distances (Å) and angles (°) in **VIb**

Cu–S(1)	2.423(2)	P(2)–C(33)	1.826(4)
Cu–S(2)	2.418(2)	P(2)–C(39)	1.822(5)
Cu–P(1)	2.258(2)	C(1)–C(2)	1.479(5)
Cu–P(2)	2.254(1)	C(2)–C(3)	1.396(6)
S(1)–C(1)	1.698(4)	C(2)–C(7)	1.398(6)
S(2)–C(1)	1.689(4)	C(3)–C(4)	1.379(6)
P(1)–C(9)	1.830(4)	C(4)–C(5)	1.377(7)
P(1)–C(15)	1.826(5)	C(5)–C(6)	1.390(8)
P(1)–C(21)	1.819(4)	C(5)–C(8)	1.508(9)
P(2)–C(27)	1.829(4)	C(6)–C(7)	1.381(7)
P(1)–Cu–P(2)	124.2(1)	C(9)–P(1)–C(21)	102.0(2)
S(2)–Cu–P(2)	108.9(1)	C(9)–P(1)–C(15)	105.5(2)
S(2)–Cu–P(1)	113.5(1)	C(39)–P(2)–Cu	115.1(2)
S(1)–Cu–P(2)	119.0(1)	C(33)–P(2)–Cu	112.0(2)
S(1)–Cu–P(1)	106.6(1)	C(27)–P(2)–Cu	118.3(2)
S(1)–Cu–S(2)	73.9(1)	C(33)–P(2)–C(39)	103.6(2)
C(1)–S(1)–Cu	83.6(2)	C(27)–P(2)–C(39)	103.5(2)
C(1)–S(2)–Cu	83.9(2)	C(27)–P(2)–C(33)	102.5(2)
C(21)–P(1)–Cu	118.6(2)	S(1)–C(1)–S(2)	118.4(3)
C(15)–P(1)–Cu	111.0(2)	S(2)–C(1)–C(2)	121.0(3)
C(9)–P(1)–Cu	115.2(2)	S(1)–C(1)–C(2)	120.6(3)
C(15)–P(1)–C(21)	103.2(2)		

29.2(3) and 3.5(1)° in the **Va** orthorhombic [5] and triclinic [13] form respectively, while in the present compound the angle is 15.5(1)°.

The bond distances and angles in the triphenylphosphine sulfide molecule are as expected.

Van der Waals contacts in both **IIIb** and **VIb** are quite normal.

Infrared Spectra

Although the patterns of the IR spectra of the **I** and **III** (with Ar = Ph, *p*-T) compounds are similar, some significant differences can also be observed. Like in the *o*-tolyl derivatives [1] the values of $\nu(\mathrm{CS})_{\mathrm{asym}}$ of the dithiocarboxylates are shifted about 15 cm^{-1} towards lower frequencies in comparison with those of the perthiocarboxylates; furthermore in the spectra of the perthio compounds a peak near 500 cm^{-1} (Ph, 514 w; *p*-T, 503 w cm^{-1}) is again present, which was previously attributed to the S–S stretching vibration. The absorption associated with this vibration is weak, as expected owing to the low polarity of the S–S bond.

The $\nu(\mathrm{CS}_2)_{\mathrm{sym}}$ is broader and stronger in the spectra of **III** and the absorptions bands in the 1250–1200 (Ph, 1216; *p*-T, 1220) and 600–550 (Ph, 646; *p*-T, 580) cm^{-1} region are stronger. These differences can be appreciated by accurate comparison of the spectra of compounds **I** and **III**, but it is difficult to decide whether group CS_3 or CS_2 is present when only one spectrum of the couple is available. An almost intermediate pattern is shown by the spectra of perthiodithiocarboxylates, but it becomes more and more similar to those of compounds **I** by repeated crystallizations.

In the spectra of the **IV** complexes, both the bands at about 1000 and 900 cm^{-1} are split, suggesting the presence of non-equivalent CS_2 chelating groups, which was then confirmed by the X-ray structure [4].

The comparison of the spectra of compounds **IV** with those of the **V** complexes [5] shows a substantial reduction of intensity of the peak at 1100 cm^{-1} in the new complexes and a shift of about 30 cm^{-1} to higher frequencies of the $\nu(\mathrm{CS}_2)_{\mathrm{sym}}$ absorption, which loses also its doublet character (Ph, 890, 899 → 926; *o*-T, 898, 900 → 930; *p*-T, 988, 990 → 927 cm^{-1}).

The spectrum of compound **VIb** is practically the overlap of those of **Vb** and $\mathrm{PPh_3S}$, in agreement with the structure of the complex, where the triphenylphosphine sulfide is not coordinated to copper, but acts as the solvent of crystallization.

NMR Spectra

NMR spectra of $^{1}\mathrm{H}$, $^{13}\mathrm{C}$, and $^{31}\mathrm{P}$ were investigated.

The spectra were in agreement with the given formulae and confirmed some phenomena already observed for similar compounds, like the width of the peak of the methyl group and of $^{31}\mathrm{P}$ in the complexes with PPh_3 [14], but the low solubility of the products hindered the comparison of the patterns for the whole series in the same solvent.

$^{1}\mathrm{H}$ NMR spectra are not very useful for distinguishing between the presence of CS_3 or CS_2 groups and to infer the different modes of binding of the latter. Indications of this kind are available instead from the $^{13}\mathrm{C}$ spectra, which have been discussed elsewhere [15]. From the δ values of the functional groups (Table 4), it can be seen that the range of resonances is different for CS_3 and CS_2 and that it is also possible to distinguish between chelated and bridging CS_2 groups, resonating more than 10 ppm apart.

$^{31}\mathrm{P}$, in the complexes with phosphine, resonates close to the frequency of the standard (Table 4). This absorption in d_5-pyridine solutions of complexes **IV**, changed gradually to a new signal, at about 42 ppm, as a consequence of the reported formation of $\mathrm{PPh_3S}$ ($\delta_{\mathrm{P(S)}}$ = 42.1 ppm) by reaction with oxygen.

Supplementary Material

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.

Acknowledgements

We are grateful to the Italian MPI for support of this work. We thank Dr E. Cebulec for C, H and S analyses and Mr P. de Baseggio for assistance in recording the IR spectra.

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Note Added in Proof

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