Crystal Structure of a Novel Tetranuclear Dithiocarboxylato Copper(I) Complex, $[\{Cu(S_2CC_6H_4Me\text{-}p)\}_4(PPh_3)_2]$ *

Anna Maria Manotti Lanfredi and Antonio Tiripicchio
Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, 43100 Parma, Italy
Annamaria Camus and Nazario Marsich
Dipartimento di Scienze Chimiche, Università di Trieste, Piazzale Europa 1, 34127 Trieste, Italy

---

The complex $[\{Cu(S_2CC_6H_4Me\text{-}p)\}_4(PPh_3)_2]$ (**1**) was obtained by reaction of $[\{Cu(S_3CC_6H_4Me\text{-}p)\}_4]$ with PPh_3 in toluene in a ratio Cu : P = 1 : 1.5. Its structure, determined by *X*-ray diffraction methods, shows a distorted trigonal-pyramidal arrangement of four copper atoms, with four surrounding dithiocarboxylate groups acting as triply bridging ligands. Three of the ligands bridge the apical and two basal metal atoms, the fourth bridges the three basal copper atoms. Crystals of (**1**) are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions $a = 12.995(3)$, $b = 15.783(4)$, $c = 16.002(5)$ Å, $\alpha = 83.66(2)$, $\beta = 102.97(3)$, and $\gamma = 93.38(2)°$. The structure has been solved by direct and Fourier methods and refined by block-matrix least squares to $R = 0.073$ for 3 978 observed reflections.

By investigating the reactivity of carbon disulphide with aryl organocopper compounds, we have recently isolated some copper(I) perthio- and dithio-carboxylates and some derivatives with tertiary phosphines.[1-5] In these products the functional group acts as a chelating ligand[1,3] or as a doubly or triply bridging ligand,[3] in the last case one of the sulphur atoms being bound to two metal atoms. In the complex reported here, $[\{Cu(S_2CC_6H_4Me\text{-}p)\}_4(PPh_3)_2]$ (**1**), the four dithio groups behave as triply bridging ligands and are involved in an intricate network of bonds with four copper atoms.

Results and Discussion

Complex (**1**) was prepared in high yield by adding triphenylphosphine to a toluene suspension of copper(I) trithioperoxy-*p*-toluate[5] in a ratio Cu : P = 1 : 1.5; the formation of one triphenylphosphine sulphide from each perthio group occurred, as indicated in equation (1). The product is stable in

$$[\{Cu(S_3CC_6H_4Me\text{-}p)\}_4] + 6PPh_3 \longrightarrow [\{Cu(S_2CC_6H_4Me\text{-}p)\}_4(PPh_3)_2] + 4PPh_3S \quad (1)$$

air and moderately soluble in common solvents.

Description of the Crystal Structure of $[\{Cu(S_2CC_6H_4Me\text{-}p)\}_4(PPh_3)_2]$ (**1**).—The structure of complex (**1**) is represented in the Figure; selected bond distances and angles are given in Table 1. Four dithiocarboxylate ligands are bound to four copper atoms through an intricate bonding system, as each ligand is tridentate with one sulphur bound to one metal and the other to two metals, so that each copper atom is bound to three sulphurs and is involved in three bridges. The four copper atoms are in a trigonal-pyramidal arrangement with Cu(2) in the apical position and the other three occupying the basal positions. Two of the three basal Cu atoms, Cu(1) and Cu(3), are also bound to a P atom from a PPh_3 ligand. The Cu–Cu distances can be divided in two groups: the three involving the apical Cu(2) with the three basal atoms Cu(1), Cu(3), and Cu(4) are rather short [Cu(2)–Cu(1) 2.766(2), Cu(2)–Cu(3) 2.653(2), and Cu(2)–Cu(4) 2.574(4) Å] and the three involving the basal copper atoms are much longer [Cu(1)–Cu(3) 3.500(3), Cu(3)–Cu(4) 3.253(4), and Cu(1)–Cu(4) 3.971(4) Å]. Even if the short Cu–Cu distances are close to that found in copper metal (2.556),[6] it has already been pointed out that short metal–metal separations in copper(I) complexes are not a sign of direct metal–metal bonding, especially when bridging atoms are present.[7] In the present compound the short distances could be imposed by the stereochemical requirements of the triply bridging ligands and be indicative of only soft attractive interactions. If the Cu–Cu bonding is neglected, two copper atoms, Cu(2) and Cu(4), display distorted trigonal co-ordination and the other two, Cu(1) and Cu(3), involved also in bonds with the PPh_3 ligands, distorted tetrahedral co-ordination. The co-ordination distortions could be determined either by the steric demands of the ligands or by attractive Cu–Cu interactions.

The copper–sulphur bond distances seem to be influenced by the different co-ordination of the metals. Although some differences can be observed in these distances within each copper environment, the ones involving Cu(1) and Cu(3) atoms are longer than those involving Cu(2) and Cu(4).

In each ligand, where the aromatic ring is normal and the carbon atoms are within at least 0.03(2) Å of being coplanar, the C–S bonds involving the unidentate sulphur [average 1.662(7) Å] are shorter than those involving the bridging sulphur atom [average 1.722(6) Å]. The CS_2 groups are tilted with respect to the aromatic rings by 29.7(3), 29.3(4), 50.3(4), and 1.4(7)° for the rings involving C(2), C(10), C(18), and C(26) respectively, showing planarity only for the $S_2CC_6H_4Me$-*p* moiety identified by C(26).

Experimental

Preparation of $[\{Cu(S_2CC_6H_4Me\text{-}p)\}_4(PPh_3)_2]$ (**1**).—Triphenylphosphine (1.2 g, 4.6 mmol) was added to a suspension of $[\{Cu(S_2CC_6H_4Me\text{-}p)\}_4]$[5] (0.8 g, 0.76 mmol) in toluene (20 cm^3). A gradual dissolution occurred, followed by precipitation of a brown powder when the solution was treated with light petroleum (b.p. 30—50 °C). (Crystals of PPh_3S coprecipitated upon standing were washed away with a little diethyl ether.) Yield 95%. Recrystallization from CS_2 and ether gave dark

---

* 1,2,3;1,2,4;1,3,4;2,3,4-Tetrakis(μ_3-dithio-*p*-toluato-*S*, μ-*S′*)-1,2-bis(triphenylphosphine)tetracopper(I).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Relevant bond distances (Å) and angles (°) in complex (**1**)

Cu(1)–Cu(2)	2.766(2)	Cu(2)–S(6)	2.227(4)	Cu(4)–S(8)	2.188(6)	S(8)–C(25)	1.669(13)
Cu(2)–Cu(3)	2.653(2)	Cu(2)–S(7)	2.271(4)	S(1)–C(1)	1.720(11)	P(1)–C(33)	1.808(13)
Cu(2)–Cu(4)	2.574(4)	Cu(3)–S(2)	2.351(5)	S(2)–C(1)	1.671(13)	P(1)–C(39)	1.841(14)
Cu(1)–S(1)	2.392(4)	Cu(3)–S(3)	2.339(5)	S(3)–C(9)	1.739(13)	P(1)–C(45)	1.853(13)
Cu(1)–S(3)	2.389(4)	Cu(3)–S(7)	2.404(4)	S(4)–C(9)	1.657(14)	P(2)–C(51)	1.825(14)
Cu(1)–S(5)	2.278(4)	Cu(3)–P(2)	2.277(4)	S(5)–C(17)	1.652(13)	P(2)–C(57)	1.794(14)
Cu(1)–P(1)	2.299(4)	Cu(4)–S(4)	2.190(5)	S(6)–C(17)	1.702(13)	P(2)–C(63)	1.817(15)
Cu(2)–S(1)	2.236(5)	Cu(4)–S(6)	2.346(4)	S(7)–C(25)	1.727(15)		
S(5)–Cu(1)–P(1)	110.5(1)	Cu(4)–Cu(2)–S(7)	86.4(1)	Cu(2)–Cu(4)–S(8)	100.7(2)	Cu(2)–S(6)–C(17)	109.2(4)
S(3)–Cu(1)–P(1)	103.0(2)	Cu(4)–Cu(2)–S(6)	57.9(1)	Cu(2)–Cu(4)–S(6)	53.6(1)	Cu(2)–S(7)–Cu(3)	69.1(1)
S(3)–Cu(1)–S(5)	112.4(2)	Cu(4)–Cu(2)–S(1)	151.9(1)	Cu(2)–Cu(4)–S(4)	121.9(2)	Cu(3)–S(7)–C(25)	114.4(5)
S(1)–Cu(1)–P(1)	105.2(2)	Cu(3)–Cu(2)–S(7)	57.8(1)	S(6)–Cu(4)–S(8)	108.9(2)	Cu(2)–S(7)–C(25)	111.4(5)
S(1)–Cu(1)–S(5)	110.8(1)	Cu(3)–Cu(2)–S(6)	134.3(1)	S(4)–Cu(4)–S(8)	131.4(2)	Cu(4)–S(8)–C(25)	106.9(5)
S(1)–Cu(1)–S(3)	114.4(1)	Cu(3)–Cu(2)–S(1)	95.2(1)	S(4)–Cu(4)–S(6)	114.7(2)	S(1)–C(1)–S(2)	124.8(8)
Cu(2)–Cu(1)–P(1)	153.9(2)	Cu(3)–Cu(2)–Cu(4)	76.9(1)	Cu(1)–S(1)–Cu(2)	73.3(1)	S(2)–C(1)–C(2)	119.1(9)
Cu(2)–Cu(1)–S(5)	90.2(1)	Cu(2)–Cu(3)–P(2)	154.4(2)	Cu(1)–S(1)–C(1)	111.0(5)	S(1)–C(1)–C(2)	116.0(9)
Cu(2)–Cu(1)–S(3)	82.4(1)	Cu(2)–Cu(3)–S(7)	53.1(1)	Cu(2)–S(1)–C(1)	106.6(5)	S(3)–C(9)–S(4)	124.8(9)
Cu(2)–Cu(1)–S(1)	50.7(1)	Cu(2)–Cu(3)–S(3)	85.9(1)	Cu(3)–S(2)–C(1)	111.6(5)	S(4)–C(9)–C(10)	117.8(9)
Cu(1)–Cu(2)–S(7)	136.6(1)	Cu(2)–Cu(3)–S(2)	90.1(1)	Cu(1)–S(3)–Cu(3)	95.5(2)	S(3)–C(9)–C(10)	117.3(9)
Cu(1)–Cu(2)–S(6)	96.5(1)	S(7)–Cu(3)–P(2)	105.3(1)	Cu(1)–S(3)–C(9)	107.9(5)	S(5)–C(17)–S(6)	129.6(7)
Cu(1)–Cu(2)–S(1)	55.9(1)	S(3)–Cu(3)–P(2)	109.5(2)	Cu(3)–S(3)–C(9)	124.0(5)	S(6)–C(17)–C(18)	114.1(9)
Cu(1)–Cu(2)–Cu(4)	96.0(1)	S(3)–Cu(3)–S(7)	136.6(2)	Cu(4)–S(4)–C(9)	108.1(5)	S(5)–C(17)–C(18)	116.3(9)
Cu(1)–Cu(2)–Cu(3)	80.4(1)	S(2)–Cu(3)–P(2)	104.9(2)	Cu(1)–S(5)–C(17)	114.0(5)	S(7)–C(25)–S(8)	122.9(9)
S(6)–Cu(2)–S(7)	120.4(2)	S(2)–Cu(3)–S(7)	90.3(2)	Cu(2)–S(6)–Cu(4)	68.5(2)	S(8)–C(25)–C(26)	119.9(9)
S(1)–Cu(2)–S(7)	112.5(2)	S(2)–Cu(3)–S(3)	104.7(2)	Cu(4)–S(6)–C(17)	105.4(5)	S(7)–C(25)–C(26)	117.0(9)
S(1)–Cu(2)–S(6)	120.7(2)						

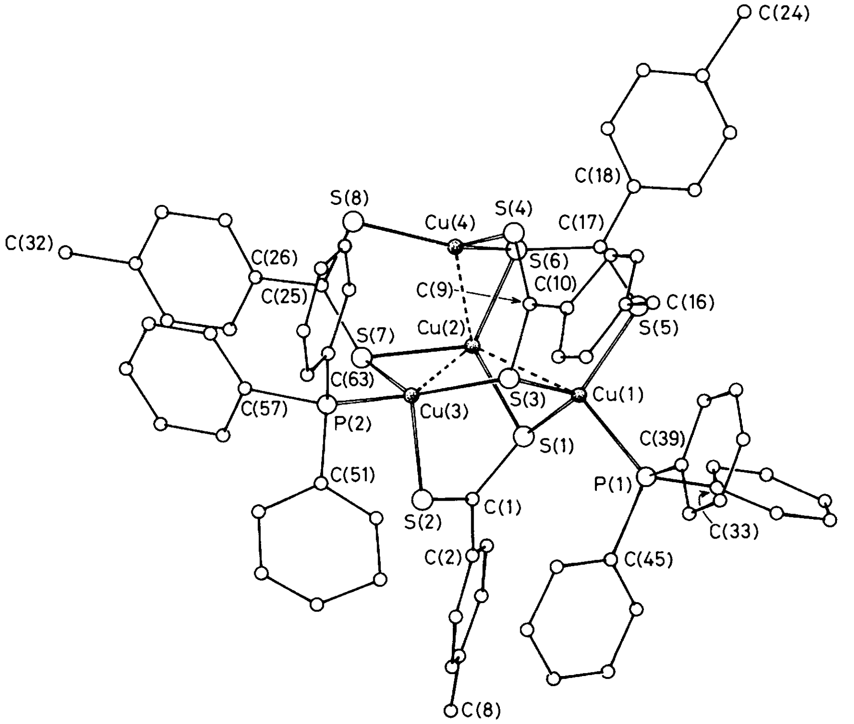

Figure. Perspective view of the tetranuclear complex $[\{Cu(S_2CC_6H_4Me\text{-}p)\}_4(PPh_3)_2]$ with the atomic numbering scheme

brown crystals, m.p. 180—182 °C (Found: C, 56.3; H, 3.8; Cu, 17.5; P, 4.35; S, 17.9. $C_{68}H_{58}Cu_4P_2S_8$ requires C, 56.4; H, 4.05; Cu, 17.55; P, 4.30; S, 17.7%).

Crystal Structure Determination of Complex (**1**).—An irregularly shaped dark brown crystal, of approximate dimensions 0.20 × 0.35 × 0.37 mm, was used for the *X*-ray analysis.

Crystal data. $C_{68}H_{58}Cu_4P_2S_8$, $M = 1\,447.82$, triclinic, $a = 12.995(3)$, $b = 15.783(4)$, $c = 16.002(5)$ Å, $\alpha = 83.66(2)$, $\beta = 102.97(3)$, $\gamma = 93.38(2)°$, $U = 3\,177(2)$ Å^3 (by least-squares refinement from the values of 30 accurately measured

Table 2. Fractional atomic co-ordinates ($\times 10^4$) for non-hydrogen atoms with estimated standard deviations in parentheses for complex (**1**)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Cu(1)	2 614(1)	7 618(1)	8 880(1)	C(28)	2 118(13)	3 473(13)	5 285(12)
Cu(2)	2 907(2)	6 155(1)	8 169(1)	C(29)	2 912(15)	3 214(11)	4 958(10)
Cu(3)	2 118(2)	7 137(1)	6 740(1)	C(30)	3 870(16)	3 652(13)	5 123(13)
Cu(4)	4 565(2)	6 721(1)	7 630(2)	C(31)	4 007(18)	4 359(12)	5 617(12)
S(1)	1 576(3)	6 315(2)	8 808(2)	C(32)	2 759(22)	2 474(15)	4 399(15)
S(2)	415(3)	6 900(3)	7 011(2)	C(33)	1 571(10)	8 357(9)	10 441(8)
S(3)	2 839(3)	8 285(3)	7 515(2)	C(34)	1 747(13)	7 564(11)	10 833(10)
S(4)	5 169(3)	8 039(3)	7 737(3)	C(35)	1 717(14)	7 365(14)	11 704(13)
S(5)	4 180(3)	7 436(2)	9 851(2)	C(36)	1 549(13)	7 997(14)	12 173(12)
S(6)	4 531(3)	5 920(2)	8 949(2)	C(37)	1 403(13)	8 801(14)	11 798(12)
S(7)	2 350(3)	5 624(2)	6 874(2)	C(38)	1 441(13)	9 011(11)	10 948(10)
S(8)	4 575(3)	5 849(3)	6 660(3)	C(39)	2 086(12)	9 688(9)	9 217(9)
P(1)	1 612(3)	8 567(2)	9 314(2)	C(40)	3 154(15)	9 814(12)	9 445(12)
P(2)	1 848(3)	7 555(3)	5 301(2)	C(41)	3 575(17)	10 632(13)	9 448(14)
C(1)	453(9)	6 420(8)	8 002(8)	C(42)	2 949(19)	11 316(15)	9 182(12)
C(2)	−529(10)	6 024(9)	8 214(8)	C(43)	1 897(19)	11 186(11)	8 934(12)
C(3)	−476(11)	5 308(9)	8 807(10)	C(44)	1 441(15)	10 360(10)	8 946(10)
C(4)	−1 376(12)	4 870(11)	8 950(11)	C(45)	191(10)	8 606(9)	8 784(9)
C(5)	−2 387(10)	5 122(10)	8 503(10)	C(46)	−52(13)	8 827(11)	7 889(11)
C(6)	−2 437(13)	5 855(11)	7 967(12)	C(47)	−1 105(14)	8 839(12)	7 465(12)
C(7)	−1 509(11)	6 295(10)	7 820(10)	C(48)	−1 906(13)	8 663(12)	7 896(14)
C(8)	−3 335(14)	4 620(13)	8 639(16)	C(49)	−1 652(12)	8 453(12)	8 768(15)
C(9)	4 148(10)	8 652(9)	7 635(9)	C(50)	−591(12)	8 407(13)	9 202(12)
C(10)	4 359(11)	9 582(10)	7 645(9)	C(51)	610(11)	8 104(9)	4 900(9)
C(11)	3 641(15)	10 165(12)	7 211(12)	C(52)	34(12)	8 054(12)	4 039(11)
C(12)	3 866(15)	11 023(14)	7 117(13)	C(53)	−874(15)	8 578(14)	3 747(16)
C(13)	4 840(15)	11 346(11)	7 523(12)	C(54)	−1 158(18)	9 034(17)	4 330(18)
C(14)	5 533(13)	10 770(11)	7 992(12)	C(55)	−580(16)	9 107(13)	5 156(16)
C(15)	5 344(12)	9 902(12)	8 084(11)	C(56)	319(13)	8 631(10)	5 440(14)
C(16)	5 117(22)	12 267(13)	7 389(20)	C(57)	1 758(10)	6 706(8)	4 627(8)
C(17)	4 848(8)	6 627(8)	9 704(8)	C(58)	2 510(14)	6 532(11)	4 197(10)
C(18)	5 919(9)	6 503(8)	10 303(8)	C(59)	2 382(18)	5 838(13)	3 711(11)
C(19)	6 035(11)	6 470(9)	11 187(10)	C(60)	1 525(17)	5 280(14)	3 685(11)
C(20)	7 020(11)	6 402(10)	11 725(11)	C(61)	746(15)	5 446(12)	4 110(11)
C(21)	7 907(12)	6 358(10)	11 414(11)	C(62)	868(14)	6 141(11)	4 570(11)
C(22)	7 799(11)	6 357(11)	10 541(12)	C(63)	2 814(11)	8 294(9)	4 926(9)
C(23)	6 807(11)	6 413(10)	9 992(11)	C(64)	2 550(17)	8 929(10)	4 239(10)
C(24)	8 998(14)	6 297(15)	11 993(15)	C(65)	3 309(17)	9 436(13)	3 947(13)
C(25)	3 400(10)	5 331(9)	6 487(9)	C(66)	4 353(18)	9 323(13)	4 290(14)
C(26)	3 209(11)	4 607(10)	5 944(10)	C(67)	4 666(16)	8 704(14)	4 995(17)
C(27)	2 279(12)	4 143(11)	5 798(11)	C(68)	3 854(13)	8 184(13)	5 315(12)

reflections), $\lambda = 1.541\ 78$ Å, space group $P\bar{1}$, $Z = 2$, $D_c = 1.514$ g cm^{-3}, $F(000) = 1\ 480$, $\mu(\text{Cu-}K_\alpha) = 47.14$ cm^{-1}.

Data collection and processing. Siemens AED diffractometer, θ—2θ mode, using nickel-filtered Cu-K_α radiation. All the reflections in the range $3 \leqslant \theta \leqslant 60°$ were measured. Of 9 379 independent reflections, 3 978, having $I \geqslant 2\sigma(I)$, were considered observed and used in the analysis. A correction for absorption effects[8] was applied using the program ABSORB[9] (maximum and minimum values of the transmission factors: 1.2729 and 0.7340).

Structure analysis and refinement. Direct and Fourier methods, block-matrix least-squares refinement with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms; hydrogens clearly located in a Fourier difference map and refined isotropically. Weighting scheme used in the last cycles: $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ with $K = 0.2973$ and $g = 0.0218$. Final R and R' values 0.073 and 0.094. The SHELX system of computer programs was used.[10] Atomic scattering factors, corrected for anomalous dispersion of Cu, S, and P, are given in ref. 11. All calculations were performed 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). Final atomic co-ordinates for the non-hydrogen atoms are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

We are grateful to the Italian Ministero della Pubblica Istruzione for support of this work.

References

1 A. Camus, N. Marsich, and G. Nardin, *J. Organomet. Chem.*, 1980, **188**, 389.
2 A. Camus, N. Marsich, and G. Pellizer, *J. Organomet. Chem.*, 1983, **259**, 367.
3 A. M. Manotti Lanfredi, F. Ugozzoli, A. Camus, and N. Marsich, *Inorg. Chim. Acta*, 1985, **99**, 111.
4 A. M. Manotti Lanfredi, A. Tiripicchio, N. Marsich, and A. Camus, *Inorg. Chim. Acta*, 1988, **142**, 269.
5 N. Marsich, A. Camus, and A. M. Manotti Lanfredi, Proc. XX Ital. Congr. Inorg. Chem., Pavia, September, 1987.

6 L. E. Sutton (ed.), *Chem. Soc., Spec. Publ.*, 1958, No. 11, 95.

7 P. K. Mehrotra and R. Hoffmann, *Inorg. Chem.*, 1978, **17**, 2187.

8 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

9 F. Ugozzoli, ABSORB, A computer program for correcting observed structure factors from absorption effects in crystal structure analysis, *Comput. Chem.*, 1987, **11**, 109.

10 G. M. Sheldrick, SHELX program for crystal structure determination, University of Cambridge, 1976.

11 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

Received 8th April 1988; *Paper* 8/01383G