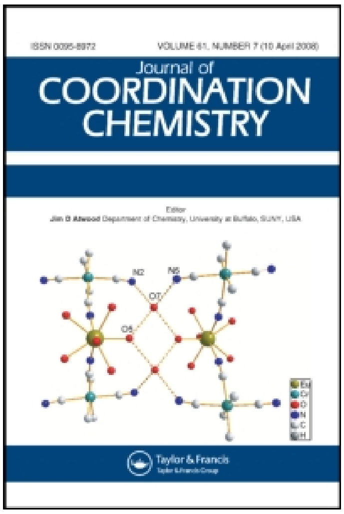

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and Structure of two I(Arylperthiocarboxylato) (Aryldithiocarboxylato) (pyridine)$_2$dicopper(I)] complexes

Xianglin Jin[a]; Kaluo Tang[a]; Yuzhen Han[a]; Annamaria Camus[b]; Nazario Marsich[b]
[a] Institute of Physical Chemistry, Peking University, Beijing, PR of China [b] Diparlimento di Scienze Chimiche, Universitá degli Studi di Trieste, Trieste, Italy

To cite this Article Jin, Xianglin , Tang, Kaluo , Han, Yuzhen , Camus, Annamaria and Marsich, Nazario(1990) 'Synthesis and Structure of two I(Arylperthiocarboxylato) (Aryldithiocarboxylato) (pyridine)$_2$dicopper(I)] complexes', Journal of Coordination Chemistry, 22: 1, 1 — 6

To link to this Article: DOI: 10.1080/00958979009408202

URL: http://dx.doi.org/10.1080/00958979009408202

J. Coord. Chem. 1990, Vol. 22, pp. 1-6
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND STRUCTURE OF TWO [(ARYLPERTHIOCARBOXYLATO) (ARYLDITHIOCARBOXYLATO) (PYRIDINE)$_2$DICOPPER(I)] COMPLEXES

XIANGLIN JIN, KALUO TANG, YUZHEN HAN
Institute of Physical Chemistry, Peking University, Beijing 100871, P.R. of China

ANNAMARIA CAMUS* and NAZARIO MARSICH
Dipartimento di Scienze Chimiche, Università degli Studi di Trieste, 34127 Trieste, Italy

(Received February 7, 1990)

The structures of $[Cu_2(S_3CC_6H_5)(S_2CC_6H_5)py_2]$ (I) and $[Cu_2(S_3C\text{-}p\text{-}C_6H_4CH_3)(S_2C\text{-}p\text{-}C_6H_4CH_3)py_2]$ (II) have been determined by X-ray methods. Crystals of I are monoclinic, space group $P2_1/c$, with $a = 9.718(4)$, $b = 10.698(4)$, $c = 24.995(9)$ Å, $\beta = 92.77(3)°$, $Z = 4$; crystals of II are triclinic, space group $P\bar{1}$, with $a = 7.802(6)$, $b = 11.990(7)$, $c = 14.630(7)$ Å, $\alpha = 91.76(4)$, $\beta = 95.76(4)$, $\gamma = 93.25(5)°$, $Z = 2$. The structures have been solved by direct and Fourier methods and refined to $R = 0.058$ for I and $R = 0.090$ for II. Both complexes show a dimeric configuration in which the geometries around the two copper atoms are different. The dithio group acts as bridging planar ligand between the two metal atoms; the perthio group acts as a chelate for the first copper atom, while its terminal sulfur atom also bridges the two metal atoms. Two pyridine molecules complete the coordination of the second copper atom to form a distorted tetrahedron.

Keywords: Copper(I), arylperthio- and aryldithio-carboxylates, synthesis, X-ray structure

INTRODUCTION

Over the last few years numerous oligomeric arylperthio-, dithio- and mixed perthio-dithiocarboxylates of copper(I) have been studied.[1-9] Among them, the tetrameric complex $[Cu_4(S_3CC_6H_5)(S_2CC_6H_5)_2py_2]$ (py = pyridine) was the first mixed perthio-dithio-carboxylate complex of copper(I) to be structurally investigated.[3] Recently, however, we have obtained a complex with the same ligands, but with a different Cu:py ratio, and which is dimeric. We report here the synthesis and X-ray structure of this new product and of the analogous *p*-tolyl derivative.

EXPERIMENTAL

Preparations

Both complexes were prepared by stirring 0.5 mmol of Cu(I)arylperthiocarboxylate with the same amount of Cu(I)aryldithiocarboxylate (aryl = C_6H_5, $p\text{-}C_6H_4CH_3$;

---

* Author for correspondence.

reagents prepared by reported methods[8]) in 20 cm^3 of pyridine for 1 hour. The solution was then diluted with petroleum ether (b.p. 50–70°C) to incipient crystallization. Crystals formed on standing overnight.

[$Cu_2(S_3CC_6H_5)(S_2CC_6H_5)py_2$] (I): orange-brown crystals of indefinite m.p. (lost solvent and decomposed at 90–100°C; the black residue melted at about 230°C). *Anal.*, Calcd. for $C_{24}H_{20}Cu_2N_2S_5$: C, 46.35; H, 3.22; Cu, 20.32; N, 4.48; S, 25.63%. Found: C, 45.5, H, 3.7; Cu, 20.3; N, 4.4; S, 25.3%.

[$Cu_2(S_3C$-p-$C_6H_4CH_3)(S_2C$-p-$C_6H_4CH_3)py_2$] (II): brown-black crystals, m.p. 250–251°C. *Anal.*, Calcd. for $C_{26}H_{24}Cu_2N_2S_5$: C, 47.90; H, 3.71; Cu, 19.50; N, 4.30; S, 24.59%. Found: C, 47.7, H, 3.6; Cu, 19.6; N, 4.0; S, 24.5%.

Crystal Structure Determinations of I and II

Flattened crystals of I (of *ca* 0.08 × 0.20 × 0.25 mm) and II (of *ca* 0.05 × 0.15 × 0.12 mm) were used for the X-ray analyses. Intensities were collected on a Syntex-R3 four-circle diffractometer at room temperature using MoKα radiation with θ–2θ (for II) and ω (for I) scan techniques. All the reflections in the range of $0 < 2\theta < 45°$ were measured for both compounds. Of 3859 (I) and 3845 (II) independent reflections collected, 2509 (I) and 1991 (II), having $I > 3\sigma(I)$, were used in the analyses. The intensities were corrected for Lorentz and polarization factors; corrections for absorption were not applied.

Crystal Data

Complex I: $C_{24}H_{20}Cu_2N_2S_5$, $M = 625.49$, monoclinic, $P2_1/c$, $a = 9.718(4)$, $b = 10.698(4)$, $c = 24.995(9)$ Å, $\beta = 92.77(3)°$, $V = 2596(2)$ Å^3, $Z = 4$, $D_c = 1.60$ gcm^{-3}, $F(000) = 1264$, $\mu(MoK\alpha) = 19.69$ cm^{-1}.

Complex II: $C_{26}H_{24}Cu_2N_2S_5$, $M = 651.86$, triclinic, $P\bar{1}$, $a = 7.802(6)$, $b = 11.990(7)$, $c = 14.630(7)$ Å, $\alpha = 91.76(4)$, $\beta = 95.70(5)$, $\gamma = 93.23(5)°$, $V = 1359(2)$ Å^3, $Z = 2$, $D_c = 1.59$ gcm^{-3}, $F(000) = 664$, $\mu(MoK\alpha) = 18.82$ cm^{-1}.

All calculations were performed on a PANAFACOM U-1500 computer, using the SHELX-76 crystallographic package.[10] Both structures were solved by direct and Fourier methods; direct methods, yielded the Cu and S atom positions and all the remaining non-hydrogen atoms were located by standard Fourier techniques. The hydrogen atoms were placed in their geometrically calculated positions and included in the final structure factor calculations with isotropic thermal parameters. The refinement with anisotropic temperature factors for non-hydrogen atoms gave the final values $R = 0.058$ for I and 0.090 for II (observed reflections only). Final atomic coordinates of the non-hydrogen atoms are given in Tables I and II, respectively.

RESULTS AND DISCUSSION

The dimeric copper(I) complexes I and II with mixed arylperthio- and aryldithiocarboxylato ligands show a similar molecular configuration (Figures 1 and 2). The molecules do not possess a symmetry centre, unlike the dimeric copper(I) complexes [$Cu_2(S_3C$–α$C_{10}H_7)_2py_2$][2] and [$Cu_2(S_3C$–o–$C_6H_4CH_3)_2py_2$][4] (with only perthiocarboxylato and pyridine ligands). In complexes I and II the dithio group acts as bridging planar ligand between the two copper atoms, while the perthio group acts as a chelate on one of the metal atoms and also as a bridging ligand for the two coppers through its terminal sulfur atom. The coordination mode of the perthio group is hence as in other copper(I)perthiocarboxylates.[1-6] The copper atom bonded to only two sulfur atoms coordinates a further two molecules of pyridine, so that the coordination geometries around the two copper atoms are different; one forms a distorted tetrahedron with two sulfur and two nitrogen atoms, the other a trigonal plane with three sulfur atoms. Selected bond lengths and bond angles for the complexes are listed in Tables III and IV.

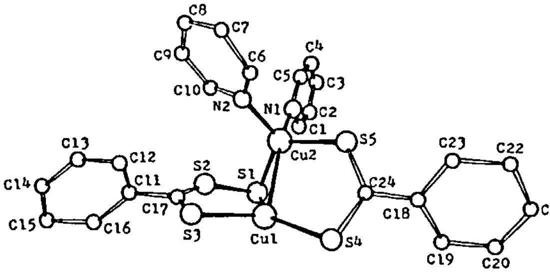

FIGURE 1 Structure of the $[Cu_2(S_3CC_6H_5)(S_2CC_6H_5)py_2]$ complex.

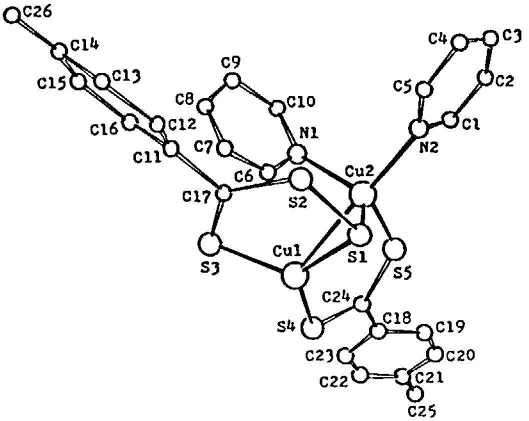

FIGURE 2 Structure of the $[Cu_2(S_3C\text{-}p\text{-}C_6H_4CH_3)(S_2C\text{-}p\text{-}C_6H_4CH_3)py_2]$ complex.

In comparison with I, the tetrameric $[Cu_4(S_3CC_6H_5)_2(S_2CC_6H_5)_2py_2]$ complex (III),[3] containing the same ligands, shows a zigzag chain configuration, in which the Cu–Cu distances are slightly longer (III, 2.701(1) and 2.764(2) Å; I, 2.660(2) Å), but the coordination mode of the perthiobenzoate to two copper atoms is maintained. In both complexes the Cu–S distances involving the bridging sulfur atom are significantly different (III, 2.386(2) and 2.231(2) Å; I, 2.307(3) and 2.243(3) Å) and longer than the non-bridging ones, which show values close to each other (III, 2.220(2); I, 2.215(3) Å). The dithiobenzoate acts differently in III and I, being terdentate in the tetrameric complex. Again, the Cu–S distances to the bridging sulfur atom are different (2.468(2) and 2.283(2) Å) and longer than the non-bridging ones, similar in turn to the analogous values for the perthio group (III, 2.179(2); I, *av.* 2.228(8) Å).

TABLE I
Atomic coordinates (× 10^4) for the $[Cu_2(S_3CC_6H_5)(S_2CC_6H_5)py_2]$ complex.

atom	*x/a*	*y/b*	*z/c*
Cu1	8733(1)	120(1)	3048(1)
Cu2	7164(1)	1978(1)	3377(1)
S1	9301(3)	2150(3)	3020(1)
S2	8998(3)	2545(3)	2227(1)
S3	8174(3)	−156(3)	2186(1)
S4	8928(3)	−1049(3)	3769(1)
S5	6931(3)	866(3)	4137(1)
N1	6828(8)	3805(8)	3657(4)
N2	5397(8)	1750(9)	2880(3)
C1	7849(11)	4588(11)	3785(5)
C2	7727(14)	5685(12)	4057(6)
C3	6478(16)	6007(13)	4220(7)
C4	5378(13)	5241(14)	4094(7)
C5	5582(12)	4146(12)	3816(6)
C6	4408(13)	980(13)	3002(5)
C7	3150(13)	963(14)	2717(7)
C8	2917(13)	1704(16)	2297(6)
C9	3926(15)	2485(17)	2161(5)
C10	5154(13)	2519(14)	2471(5)
C11	8129(10)	1395(11)	1322(4)
C12	7565(12)	2507(12)	1105(5)
C13	7341(13)	2625(13)	554(6)
C14	7672(14)	1694(17)	219(5)
C15	8235(13)	588(15)	427(5)
C16	8439(11)	464(13)	970(4)
C17	8403(9)	1231(10)	1905(4)
C18	7952(9)	−993(9)	4763(4)
C19	9174(10)	−1479(10)	5005(4)
C20	9198(11)	−1928(12)	5515(5)
C21	8028(13)	−1992(12)	5800(5)
C22	6822(12)	−1558(12)	5561(5)
C23	6775(10)	−1065(11)	5059(4)
C24	7930(9)	−419(9)	4232(4)

Each of the central copper atoms in III also coordinates one pyridine ligand. The coordination geometry is a distorted tetrahedron formed by three sulfur and one nitrogen atoms, while that around the two terminal copper atoms is a trigonal plane. The Cu–N distances are very similar in complexes I and III.

The unexpected formation of two kinds of complexes (I and III) with different configurations, notwithstanding that both were obtained from pyridine and contained the same other ligands in the same ratio, is evidently due to the different preparative conditions. The dimeric complex was formed in a "one pot" reaction between copper(I) perthio- and dithiobenzoates, which in pyridine are present mainly as mono- or dinuclear forms, as indicated by molecular weight measurements. The other complex was prepared by a redox reaction between copper(II) and dithiobenzoate and the pyridine was introduced during the recrystallization. Presumably, in the second step of reaction, the pyridine coordinates to a preformed tetrameric structure, stable enough not to be dissociated by the solvent.

TABLE II

Atomic coordinates (× 10^4) for the $[Cu_2(S_3C\text{-}p\text{-}C_6H_4CH_3)(S_2C\text{-}p\text{-}C_6H_4CH_3)py_2]$ complex.

atom	*x/a*	*y/b*	*z/c*
Cu1	6232(4)	3295(2)	2486(2)
Cu2	3177(4)	2475(2)	1746(2)
S1	4798(8)	4002(5)	1239(3)
S2	3985(8)	5427(5)	1792(3)
S3	6038(8)	4693(5)	3486(3)
S4	7583(8)	1745(5)	2626(4)
S5	4302(7)	814(5)	1541(4)
N1	819(23)	2415(15)	924(11)
N2	2326(20)	2790(14)	3011(12)
C1	−14(33)	1518(21)	636(15)
C2	−1632(29)	1454(22)	92(16)
C3	−2313(32)	2455(30)	−117(16)
C4	−1464(28)	3389(22)	178(14)
C5	126(33)	3393(20)	667(14)
C6	2925(31)	2226(20)	3760(16)
C7	2456(35)	2476(23)	4617(16)
C8	1410(42)	3318(23)	4741(16)
C9	712(34)	3893(21)	4011(15)
C10	1307(32)	3560(20)	3156(15)
C11	4148(28)	6572(16)	3367(13)
C12	4103(31)	7588(16)	2992(14)
C13	3616(34)	8507(18)	3432(16)
C14	2956(29)	8398(17)	4300(14)
C15	3041(29)	7377(19)	4690(14)
C16	3606(26)	6474(16)	4245(13)
C17	4824(25)	5588(16)	2907(13)
C18	7074(28)	−380(16)	2004(13)
C19	6672(28)	−1115(17)	1231(14)
C20	7297(30)	−2146(18)	1211(14)
C21	8431(29)	−2512(18)	1940(15)
C22	8793(34)	−1799(19)	2682(15)
C23	8204(29)	−720(18)	2716(14)
C24	6322(29)	764(16)	2049(12)
C25	9052(37)	−3693(21)	1918(20)
C26	2383(40)	9401(21)	4792(18)

TABLE III

Selected bond lengths (Å) for the complexes.

	Complex I	Complex II
Cu(1)-Cu(2)	2.660(2)	2.642(4)
Cu(1)-S(1)	2.243(3)	2.257(6)
Cu(1)-S(3)	2.215(3)	2.213(6)
Cu(1)-S(4)	2.196(3)	2.192(7)
Cu(2)-S(1)	2.307(3)	2.347(6)
Cu(2)-S(5)	2.261(3)	2.245(7)
Cu(2)-N(1)	2.107(9)	2.091(17)
Cu(2)-N(2)	2.085(8)	2.059(18)
S(1)-S(2)	2.035(4)	2.029(8)

TABLE IV
Selected bond angles (°) for the complexes.

	Complex I	Complex II
S(1)-Cu(1)-S(3)	98.5(1)	98.9(2)
S(1)-Cu(1)-S(4)	124.5(1)	130.1(2)
S(3)-Cu(1)-S(4)	136.8(1)	130.8(2)
S(1)-Cu(2)-S(5)	119.7(1)	114.5(2)
S(1)-Cu(2)-N(1)	102.2(2)	105.3(5)
S(1)-Cu(2)-N(2)	120.6(3)	112.6(5)
S(5)-Cu(2)-N(1)	100.7(3)	106.6(5)
S(5)-Cu(2)-N(2)	109.1(3)	116.3(5)
N(1)-Cu(2)-N(2)	99.8(3)	99.6(6)
Cu(1)-S(1)-Cu(2)	71.5(1)	70.0(2)

We have found that the molecular configurations of Cu(I)–1,1-dithiolate complexes are affected by ligand bulkiness. The similar structures of Cu(I) α-perthionaphthoate[1,2] and perthio-*o*-toluate[4−6] and of Cu(I) perthiodithiobenzoate and perthiodithio-*p*-toluate reflect the similar steric requirements of these groups. It seems that the steric cone angle of the *p*-toluate species is smaller than that of the *o*-toluate case and similar to that of benzoate.

SUPPLEMENTARY MATERIAL

Atomic coordinates for the hydrogen atoms, full lists of bond lengths and angles, atomic thermal parameters and a list of calculated and observed structure factors for both compounds are available from the authors on request.

ACKNOWLEDGEMENTS

This work was supported in part by China's National Natural Science Foundation and in part by the Italian MPI, both of which are gratefully acknowledged.

REFERENCES

1. Tang Kaluo, Gan Hong, Xu Xiaojie, Zhou Gongdu and Tang Youqi, *Sci. Sin., Ser. B, (Engl. Ed.)*, 456 (1984).
2. Jin Xianglin, Jin Yiyan and Tang Youqi, *Acta Chim. Sin., (Engl. Ed.)*, 4, 343 (1986).
3. Jin Xianglin, Jin Yiyan, Tang Kaluo and Tang Youqi, *Sci. Sin., Ser. B.*, 225 (1987).
4. Tang Kaluo, Jin Xianglin, Xiao Qunong, Sun Jiangquan and Tang Youqi, *J. Struct. Chem.*, **7**, 247 (1988).
5. A.M. Manotti Lanfredi, A. Tiripicchio, A. Camus and N. Marsich. *Inorg. Chim. Acta*, **142**, 269 (1988).
6. J.A. Scheuerman, F.R. Fronczek and J. Selbin, *Inorg. Chim. Acta*, **148**, 177 (1988).
7. A.M. Manotti Lanfredi, A. Tiripicchio, A. Camus and M. Marsich, *J. Chem, Soc., Dalton Trans.*, 753 (1989).
8. A. Camus, N. Marsich, A.M. Manotti Lanfredi and F. Ugozzoli, *Inorg. Chim. Acta*, **61**, 87 (1989).
9. Tang Kaluo, Jin Xianglin, Hu Yonglin and Tang Youqi, to be published.
10. G.M. Sheldrick, SHELX-76 Program for Crystal Structure Determination (Univ. of Cambridge, U.K., 1976).