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Perthiocarboxylate Complex. Synthesis, Structure and Spectroscopic Characterization of the Tetrameric Copper(I) *o*-Tolylperthiocarboxylate, $[Cu(S)SSCC_7H_7]_4$

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Abstract

The $[CuS_3C–o\text{-tolyl}]_4$ complex has been prepared through different routes. Its crystal structure has been determined by X-ray diffraction methods. Crystals are triclinic, space group $P\bar{1}$, with a = 12.810(5), b = 13.051(6), c = 12.789(5) Å, α = 94.88(2), β = 98.61(2), γ = 104.11(3)°, and Z = 2. The structure has been solved from diffractometer data by direct and Fourier methods and refined by block-matrix least-squares to R = 0.058 for 4674 observed reflections. The structure consists of discrete tetramers, in which a tetrahedron of copper atoms is bonded to four *o*-tolylperthiocarboxylato ligands: each of these ligands bridges two metal atoms through its terminal perthio atom, while the other terminal sulfur atom is coordinated only to one of these two metal copper atoms, so that five membered CuSSCS chelate rings are formed. The spectral characteristics (electronic, infrared, ^1H and ^{13}C NMR spectra) of the title compound are reported and discussed in comparison with those of the dimeric $[CuS_3C–o\text{-tolyl}]_2\cdot py_2$ and of the polymeric $[CuS_2C–o\text{-tolyl}]_n$ complexes.

Introduction

Recently, dealing with the reactivity of copper *o*-tolyldithiocarboxylato complexes of bipyridine and 1,10-phenanthroline [1], we have isolated a product of formula $[CuS_3C–o\text{-T}]_4$ (*o*-T = *o*-tolyl) (I). The CS_3 groups were at first supposed to be of the trithiocarbonate type, as in the $[Cu_2(dppm)_2(CS_3)]_2$ complex [2], formed by similar parent compounds in the presence of 1,2-bis(diphenylphosphino)methane (dppm), but their spectral properties were unequivocally different. At least the X-ray structure determination has revealed that the new compound is a tetranuclear perthiocarboxylate.

Not many perthiocarboxylates with ascertained structure are known in the literature [3]. In particular for copper(I) only three of such compounds have been recently reported: two perthionaphthoate [4, 5] and a mixed dithioperthiobenzoate [6], all prepared by reaction between $CuCl_2$ and the corresponding dithioacid, followed by recrystallization from carbon disulfide or pyridine and alcohol.

Our product was at first obtained by hydrolysis with HCl of copper(I)–*o*-tolyldithiocarboxylato complexes of bipy and phen, but, once we discovered its nature, other more convenient preparative methods were found. We report here the crystal structure of I and some of its spectral characteristics.

Experimental

Materials

When not otherwise specified the reagents employed were commercial products.

Preparation of the $[CuS_3C–o\text{-T}]_4$ *Compound*

Method A. 0.03 g of sulfur (0.94 mml) were added to a suspension of 0.22 g of $[CuS_2C–o\text{-T}]_n$ [7] (0.95 matom of copper) in 20 ml of toluene and the mixture was refluxed. In some minutes the polymer dissolved to an orange solution. Concentration to about a quarter of the original volume, followed by addition of ether, gave orange microcrystals, in practically quantitative yield. Melting point (m.p.) 233–234 °C after recrystallization from CS_2–ether. *Anal.* Found: C, 36.8; H, 2.71; Cu, 23.99; S, 36.45. Calc. for $C_8H_7CuS_3$: C, 36.55; H, 2.69; Cu, 24.17; S, 36.59%. The solubility of the compound is high in carbon disulfide, fair in hot toluene, moderate in methylene chloride, chloroform, dichloroethane, DMF, low in ether and acetonitrile and very low in pentane, acetone, methanol and carbon tetrachloride.

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In pyridine black needles with a low melting point (<125 °C) precipitated in a few minutes from the solution initially formed. The analysis of this new product corresponds to a rough formula CuS_3C–*o*-T·py. *Anal.* Found: C, 46.5; H, 3.59; Cu, 18.20; N, 3.75; S, 28.4. Calc. for $C_{13}H_{12}CuNS_3$: C, 45.66; H, 3.54; Cu, 18.58; N, 4.10; S, 28.13%.

Method B. A mixture of 16 ml of $(NH_4)_2S$ (C. Erba, 20%), 3 g S and 100 ml THF was refluxed for 15 min. 6 g of *o*-tolualdehyde were then added to the orange–red solution, which was further refluxed for 15 min. The cooled red–brown solution was diluted with 100 ml of water and extracted with 200 ml of diethylether to eliminate the excess of aldehyde and other organic byproducts. 3.0 g of $CuCl_2·2H_2O$ in 30 ml of water were added to the filtered aqueous solution under stirring. The orange–red powder of **I** formed was filtered and washed thoroughly with a mixture of water and methanol and then with diethylether. Yield 3.2 g (69%) of crude product.

Method C. A solution of 0.4 g of [*o*-TC(=S)S]$_2$ [8] in 5 ml benzene was added under nitrogen to an equal volume of acetonitrile solution of $[Cu(CH_3CN)_4]ClO_4$ prepared *in situ* from copper powder and 0.45 g of $CuClO_4·6H_2O$. Addition of few drops of a methanolic solution of NaOH 0.2 N caused precipitation of copper oxide, which immediately dissolved, while the colour of the mixture changed from the original red to orange. After half an hour the reaction mixture was filtered and the clear filtrate reduced to about a third of its volume by gentle heating. Orange needles of **I** precipitated by cooling. Yield 0.11 g (35%).

Reaction with Triphenylphosphine (Cu:P = 1)

0.2 g of PPh_3 were added to a suspension of 0.2 g of **I** in toluene (10 ml) under stirring. From the dark red–brown solution, immediately formed, a violet–brown gelatinous product precipitated within some minutes. After half an hour it was filtered and washed thoroughly with toluene. Drying under vacuum dramatically decreased its volume, leaving a film of the same colour, with the characteristics of $[CuS_2C$–*o*-T$]_n$ (**II**) [7]. Yield practically quantitative.

PPh_3S was recovered in consistent amounts from the mother liquor.

Apparatus

IR spectra were run on a P.E. 983 G spectrophotometer as nujol mulls supported on CsI plates or as KBr pellets. ^1H NMR spectra were recorded on a Jeol JNM-C60HL spectrometer in the field sweep-external lock mode; ^{13}C NMR spectra at 80 MHz with a Bruker WP80 equipped with a BNC 28 computer with 8 K data points. Electronic spectra were recorded on a P.E. 550 spectrophotometer.

X-ray Data Collection and Refinement

An irregularly shaped crystal of approximate dimensions 0.20 × 0.32 × 0.35 mm was used for the X-ray analysis. Unit cell parameters were obtained by least-squares refinement of the θ values of 29 carefully centred reflections (with θ in the range 25–35°), chosen from diverse regions of the reciprocal space.

Crystal data. $C_{32}H_{28}Cu_4S_{12}$, M_r = 1051.48, triclinic, a = 12.810(5), b = 13.051(6), c = 12.789(5) Å, α = 94.88(2), β = 98.61(2), γ = 104.11(3)°, V = 2033(1) Å^3, space group $P\bar{1}$, Z = 2, D_c = 1.717 g cm^{-3}, $F(000)$ = 1056, μ(Cu Kα) = 82.20 cm^{-1}. Data were collected at room temperature on a Siemens AED diffractometer using the Ni-filtered Cu Kα radiation (λ = 1.54178 Å) and the θ–2θ scan technique, the individual profiles having been analysed according to Lehmann and Larsen [9]. All the reflections in the range $3 \leqslant \theta \leqslant 70°$ were measured. Of 7684 independent reflections, 4674, having $I \geqslant 2\sigma(I)$, were considered observed and used in the analysis. A correction for the absorption effects was applied [10] using the program ABSORB [11] (maximum and minimum values for the absorption corrections in the polar angles ψ and μ are 1.197 and 0.775 respectively).

The structure was solved by direct and Fourier methods and refined by full-matrix least-squares using the SHELX system of computer programs [12] first with isotropic and then with anisotropic thermal parameters for all non-hydrogen atoms; all the hydrogen atoms were localized from a ΔF map and refined isotropically.

The weighting scheme used in the last cycles of refinement was $w = K[\sigma^2(F_o) + gF_o{}^2]^{-1}$ with K = 0.6313 and g = 0.0059. Final R and R_w values were 0.058 and 0.077 respectively. Atomic scattering factors, corrected for the anomalous dispersion of Cu and S, were taken from ref. 13. Final atomic coordinates for the non-hydrogen atoms are given in Table I.

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) and on the GOULD-SEL 32/77 computer of the 'Centro di Studio per la Strutturistica Diffrattometrica del CNR', Parma.

Results and Discussion

The $[CuS_3C$–*o*-T$]_4$ complex has been prepared easily and in high yield by treatment of the dithiotoluato copper derivative with sulfur (method A).

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) for the Non-hydrogen Atoms[a]

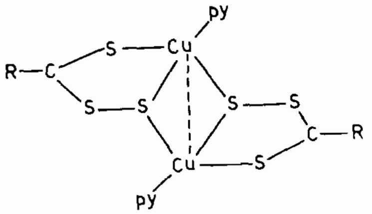
Atom	*x/a*	*y/b*	*z/c*
Cu1	4414(1)	4517(1)	1506(1)
Cu2	3599(1)	2282(1)	1027(1)
Cu3	4041(1)	3442(1)	3235(1)
Cu4	2153(1)	3330(1)	1768(1)
S1	4370(2)	3484(2)	19(2)
S2	5954(2)	3362(2)	295(2)
S3	5052(2)	1726(2)	1677(2)
S4	1810(2)	1650(2)	935(2)
S5	1165(2)	1849(2)	−578(2)
S6	1502(2)	4105(2)	408(2)
S7	5607(1)	4587(1)	3041(2)
S8	5449(1)	5918(1)	3912(2)
S9	3709(2)	5837(1)	2022(1)
S10	2503(2)	3964(1)	3499(2)
S11	1739(2)	2725(2)	4217(2)
S12	3631(2)	1850(1)	3814(2)
C1	6043(6)	2428(6)	1132(6)
C2	7197(6)	2355(7)	1376(6)
C3	7994(8)	3232(9)	1963(9)
C4	9068(9)	3189(11)	2208(11)
C5	9355(8)	2296(10)	1848(10)
C6	8579(8)	1419(11)	1280(9)
C7	7481(7)	1434(7)	1023(7)
C8	6677(10)	517(10)	356(13)
C9	1098(6)	3141(7)	−587(7)
C10	639(8)	3343(7)	−1675(7)
C11	1352(13)	3682(10)	−2351(10)
C12	935(17)	3907(10)	−3345(12)
C13	−141(19)	3847(11)	−3639(13)
C14	−839(15)	3517(11)	−2947(13)
C15	−467(9)	3276(8)	−1947(8)
C16	−1256(10)	2919(13)	−1224(12)
C17	4417(6)	6344(5)	3222(6)
C18	4151(6)	7224(6)	3843(6)
C19	3706(7)	7002(8)	4748(7)
C20	3410(9)	7808(11)	5333(10)
C21	3583(10)	8816(11)	5016(13)
C22	4019(11)	9023(8)	4157(11)
C23	4312(7)	8260(6)	3516(8)
C24	4825(13)	8534(9)	2572(12)
C25	2486(6)	1797(6)	4267(6)
C26	1980(6)	897(6)	4816(7)
C27	2152(9)	1065(10)	5918(8)
C28	1723(10)	246(11)	6489(10)
C29	1107(9)	−718(10)	5925(12)
C30	913(8)	−862(8)	4840(11)
C31	1368(7)	−73(7)	4256(8)
C32	1181(12)	−280(10)	3085(10)

[a] e.s.d.s given in parentheses.

No more than one sulfur atom was added for each copper atom. Alternatively **I** has been obtained from a modification [14] of Bruni and Levi's method for the synthesis of dithiocarboxylates from *o*-tolualdehyde and ammonium polysulfide, employing excess polysulfide and basic medium (method B). Tang Kaluo *et al.* [4] consider $[RC(=S)S]_2$ as intermediate for the formation of copper(I) perthionaphthoate. Although the preparative method B recommends the elimination of disulfides before the metal salt addition, we could obtain **I** also by starting from the corresponding bis(thioaroyl)disulfide and $[Cu(CH_3CN)_4]ClO_4$ (method C).

$[CuS_3C{-}o\text{-}T]_4$ is an orange–red compound, stable in air, which, in agreement with its structure (see below), does not show electrolyte properties. From carbon disulfide, benzene and methylene chloride it recrystallizes as needles with a molecule of solvent, while, from mixtures of these solvents and ether, no solvated red compact microcrystals are formed. The solvates, when heated rapidly, show a double melting point, the first of which is at about 155–160 °C with change of colour to dark red.

The black solvate isolated from pyridine is probably the dimeric $[CuS_3C{-}o\text{-}T]_2py_2$ derivative (**III**), in agreement with the behaviour of the corresponding perthionaphthoate [5].



III

The transition between the dimeric and tetrameric forms is reversible.

Like the mononuclear perthiocarboxylates of other metals [15a] **I** is easily partially desulfurated in solution by triphenylphosphine, with formation of PPh_3S. In the presence of a Cu:ligand ratio = 1 the other product was the $[CuS_2C{-}o\text{-}T]_n$ complex, following eqn. (1)

$$1/4[CuS_3C{-}o\text{-}T]_4 + PPh_3 \longrightarrow m[CuS_2C{-}o\text{-}T]_n + PPh_3S \qquad (1)$$

$(m = 1/n)$

The products were identified by comparison with authentical samples.

Although the existence of a copper(I) dithioperthiobenzoate is proved [6], we tried unsuccessfully to obtain the corresponding *o*-tolyl derivative by this method. The reaction of **I** with triphenylphosphine in a Cu:P ratio = 2 in various solvents always gave the $[CuS_2C{-}o\text{-}T]_n$ complex and unreacted starting reagent. Work is in progress on some new complexes obtained with tertiary phosphines from different Cu:ligand ratios.

Crystal Structure of the $[CuS_3C{-}o\text{-}T]_4$ *Complex*

Discrete $[CuS_3C{-}o\text{-}T]_4$ tetramers, whose perspective view is shown in Fig. 1, are present in the

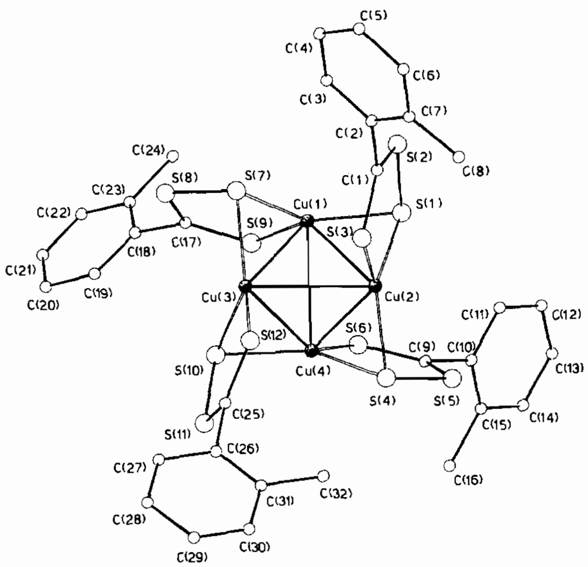


Fig. 1. View of the tetrameric $[CuS_3C\text{–}o\text{-tolyl}]_4$ complex with the atomic numbering scheme.

crystal structure. Relevant bond distances and angles are given in Table II. The four copper atoms are in a tetrahedral arrangement with the four shortest edges [Cu(1)–Cu(3) = 2.757(2), Cu(2)–Cu(4) = 2.782(2), Cu(3)–Cu(4) = 2.795(2) and Cu(1)–Cu(2) = 2.872(2) Å *versus* Cu(2)–Cu(3) = 2.994(2) and Cu(1)–Cu(4) = 3.015(2) Å] bridged by the terminal perthio atom from four *o*-tolylperthiocarboxylato ligands. The other terminal sulfur atom of each ligand coordinates to only one copper atom, so that five membered CuSSCS chelate rings are formed. The symmetry of the tetranuclear complex is only approximately S_4, the methyl groups playing, as shown in the Figure, a fundamental role in the deviation from this symmetry. For all four metals the Cu–S bond involving the perthio atom from the associated chelate ring (average 2.271(1) Å) is longer than the one involving the other perthio atom. Each copper atom interacts with six atoms, three copper and three sulfur atoms. The three sulfur atoms bonded to each copper atom are roughly coplanar with the metal, the displacements of the metal atoms from the plane through the sulfur atoms being −0.060(2), −0.095(2), 0.130(2), and 0.128(2) Å for Cu(1), Cu(2), Cu(3) and Cu(4) atoms respectively. Furthermore in each five-membered CuSSCS chelate ring, in which the S–S distance is normal (average S–S = 2.050(1) Å), the Cu–S bond adjacent to the C–S bond is shorter than the Cu–S bond involving the perthio atom and the C–S bond to the uncoordinated S atom is longer than the other C–S bond, suggesting that the double bond is strongly localized in the latter. In the few structures of perthiocarbonato complexes of metal ions with partially filled shells [16–18] MSSCS chelating rings are present with the M–S bond adjacent to the C–S group longer than the M–S bond involving the perthio atom and with C–S distances almost equal. The presence in our compound of homonuclear metal ions with completely filled d shells and of bent *o*-tolyl groups replacing, by comparison with the MCS_4 complexes, the extra-annular sulfur atoms, seems to justify the non-ability of the S–S group to enhance S–M, p_π–d_π bonding and the localization of the double bond in the ring.

Both tetrahedral arrangement of Cu atoms, with comparable Cu–Cu distances (four in the range 2.701–2.901 Å and two in the range 2.991–3.064 Å) and similar ligand behaviour of perthiocarboxylato –C(S)SS groups have been reported, to the best of our knowledge, only in the structure of the CS_2 solvate of the tetra-α-perthionaphthoato tetracopper(I) complex [4]: in this compound naphthalene rings replace the *o*-tolyl groups of the present compound.

The CuSSCS chelating rings, which are roughly planar (the maximum deviation from the mean plane passing through the five-membered ring being 0.011(8), −0.022(3), 0.048(3) and −0.057(2) Å for the C(1), S(4), S(10) and S(7) atoms respectively) are tilted to each other consecutively by angles ranging from 84.0(1) to 88.8(2)°. The dihedral angles these rings form with the associated *o*-tolyl moieties are 65.3(2), 68.2(2), 80.2(2) and 89.3(3)° for the chelating rings individuated by Cu(1), Cu(2), Cu(3) and Cu(4) metal atoms respectively. The largest dihedral angle, involving *o*-tolyl moieties with facing methyl groups on the C(16) and C(32) atoms, could be due to the greater steric demand of these groups. In the related tetra-α-perthionaphthoatotetracopper(I) complex, of approximate C_2 symmetry, the naphthoato groups are rotated with respect to the associated five-membered chelate ring by angles (ranging from 59° to 80°) narrower than those found for the *o*-tolyl groups, probably as a consequence of the different steric request of the naphthalene ring.

Dihedral angles of nearly 90° between *o*-tolyl groups and CS_2 moieties have been found in already studied (diphenylphosphino)methane dithio–*o*-toluato copper(I) complexes, where four-membered CuSCS chelating rings are present [19].

Normal van der Waals contacts join the tetranuclear complexes in the present structure.

Electronic Spectra

Electronic spectra of **I** have been recorded in solution of various solvents. The spectra are similar in methylene chloride, benzene and carbon disulfide, characterized by a maximum in the 420 nm region (λ_{max} = 415 nm, ϵ = 2900; λ_{max} = 418 nm, ϵ = 2800; λ_{max} = 428 nm, ϵ = 3550) and a shoulder at about 520 nm. In pyridine the pattern is different, with two absorption maxima at 430 (ϵ = 3220) and 512 nm (ϵ = 1950).

TABLE II. Relevant Bond Distances (Å) and Angles (°)

Cu(1)–Cu(2)	2.827(2)	Cu(2)–S(1)	2.251(3)
Cu(1)–Cu(3)	2.757(2)	Cu(2)–S(3)	2.232(3)
Cu(1)–Cu(4)	3.015(2)	Cu(2)–S(4)	2.220(3)
Cu(2)–Cu(3)	2.994(2)	Cu(3)–S(7)	2.251(2)
Cu(2)–Cu(4)	2.782(2)	Cu(3)–S(10)	2.297(3)
Cu(3)–Cu(4)	2.795(2)	Cu(3)–S(12)	2.233(2)
Cu(1)–S(1)	2.221(3)	Cu(4)–S(4)	2.264(3)
Cu(1)–S(7)	2.280(2)	Cu(4)–S(6)	2.240(3)
Cu(1)–S(9)	2.228(3)	Cu(4)–S(10)	2.235(3)
S(1)–S(2)	2.054(4)	S(7)–S(8)	2.052(2)
S(2)–C(1)	1.702(9)	S(8)–C(17)	1.711(8)
S(3)–C(1)	1.656(8)	S(9)–C(17)	1.653(7)
S(4)–S(5)	2.051(4)	S(10)–S(11)	2.041(3)
S(5)–C(9)	1.710(9)	S(11)–C(25)	1.716(9)
S(6)–C(9)	1.638(9)	S(12)–C(25)	1.644(9)
Cu(3)–Cu(1)–Cu(4)	57.7(1)	Cu(2)–S(1)–S(2)	100.4(2)
Cu(2)–Cu(1)–Cu(4)	56.8(1)	S(1)–S(2)–C(1)	108.9(3)
Cu(2)–Cu(1)–Cu(3)	64.8(1)	Cu(2)–S(3)–C(1)	103.4(3)
Cu(1)–Cu(2)–Cu(4)	65.0(1)	S(2)–C(1)–S(3)	127.4(5)
Cu(1)–Cu(2)–Cu(3)	56.5(1)	S(3)–C(1)–C(2)	122.7(6)
Cu(3)–Cu(2)–Cu(4)	57.7(1)	S(2)–C(1)–C(2)	109.8(6)
Cu(1)–Cu(3)–Cu(2)	58.7(1)	Cu(2)–S(4)–S(5)	103.6(2)
Cu(2)–Cu(3)–Cu(4)	57.3(1)	S(4)–S(5)–C(9)	108.8(3)
Cu(1)–Cu(3)–Cu(4)	65.8(1)	Cu(4)–S(6)–C(9)	103.8(3)
Cu(2)–Cu(4)–Cu(3)	64.9(1)	S(5)–C(9)–S(6)	127.7(6)
Cu(1)–Cu(4)–Cu(3)	56.5(1)	S(6)–C(9)–C(10)	120.8(7)
Cu(1)–Cu(4)–Cu(2)	58.2(1)	S(5)–C(9)–C(10)	111.5(6)
S(7)–Cu(1)–S(9)	98.2(1)	Cu(1)–S(7)–S(8)	101.1(1)
S(1)–Cu(1)–S(9)	138.3(1)	S(7)–S(8)–C(17)	108.4(3)
S(1)–Cu(1)–S(7)	122.8(1)	Cu(1)–S(9)–C(17)	105.0(3)
S(3)–Cu(2)–S(4)	133.8(1)	S(8)–C(17)–S(9)	126.8(5)
S(1)–Cu(2)–S(4)	124.5(1)	S(9)–C(17)–C(18)	120.7(6)
S(1)–Cu(2)–S(3)	99.9(1)	S(8)–C(17)–C(18)	112.4(6)
S(10)–Cu(3)–S(12)	98.7(1)	Cu(3)–S(10)–S(11)	100.3(2)
S(7)–Cu(3)–S(12)	134.3(1)	S(10)–S(11)–C(25)	109.2(3)
S(7)–Cu(3)–S(10)	123.3(1)	Cu(3)–S(12)–C(25)	104.3(3)
S(6)–Cu(4)–S(10)	126.9(1)	S(11)–C(25)–S(12)	127.2(5)
S(4)–Cu(4)–S(10)	131.2(1)	S(12)–C(25)–C(26)	121.7(6)
S(4)–Cu(4)–S(6)	99.2(1)	S(11)–C(25)–C(26)	111.0(6)

Infrared Spectra

The infrared spectrum of **I** shows three main peaks at 1020s,br (with shoulders at 1053, 1035, 1010 cm^{-1}), 896m and 752s cm^{-1} respectively. Its pattern is very similar to that of $[CuS_2C\text{–}o\text{-}T]_n$, with the maximum of the first band slightly shifted to higher energies with respect to that of this compound (1005 cm^{-1}), as repeatedly found for perthiocarboxylates in comparison with the corresponding dithioderivatives [15]. The second peak is sharper than in **II** and at a frequency of some cm^{-1} lower; the third peak, due to the benzene ring, occurs at the same frequency as in the dithiocarboxylato derivative, but it is markedly higher than the corresponding band in $[CuS_2C\text{–}o\text{-}T]_n$. In general the spectrum of **I** is richer in peaks than that of **II**: in particular a new band of weak intensity appears at 486 cm^{-1}, which could be reasonably assigned to the sulfur–sulfur stretching vibration in agreement with attributions for similar complexes [15b]. It seems difficult to accept the assignation of Maltese and Zennaro [15c], who, in the bis-perthiobenzoates of Zn(II) and Ni(II), associate this vibration to an absorption at 655 or 659 cm^{-1} respectively. In effect the spectrum of **I** shows a weak peak in this region (647 cm^{-1}), but in the other complex – which on the basis of its formula does not contain S–S stretchings – an absorption of corresponding intensity is also present at the same frequency.

The other two peaks at low frequencies, *i.e.* 525 and 443 cm^{-1}, are probably due to benzene ring and to metal–sulfur stretching absorptions, the latter hence at values higher than usual.

The similarity of the infrared patterns of **I** and **II** suggests that the two compounds have an analogous crystal structure. **II**, however, must have a higher degree of polymerization, given that its solubility is very low in all kinds of solvents, except pyridine.

The initial presence in **II** of tetrameric groupings of copper atoms is also supported by the rapid and complete transformation of $[CuS_2C\text{–}o\text{-}T]_n$ in **I** by treatment with sulfur. This implies that in **II** the dithiocarboxylic groups are in such a position to be easily approached by the sulfur atoms, which cause the chelate ring expansion. This reaction does not require basic solvents or photochemical excitation, as found for dithiocarboxylates of other metals [20]. The spectrum of the $[CuS_3C\text{–}o\text{-}T]_2py_2$ compound is practically an overposition of those of **I** and of pyridine, with a slight shift (5–15 cm^{-1}) of the main absorption peaks of the first compound towards higher frequencies. Furthermore the broad peak of **I** in the 1050–1000 cm^{-1} region is splitted (1038 and 1027 cm^{-1}). The absorption of the pyridine at 1030 (mw) cm^{-1} should not be responsible for the new peak observed, because an identical pattern is shown in this region by the product recrystallized from deuteropyridine, where, as expected, all the other absorption bands of the solvent are shifted to lower frequencies.

NMR Spectra

In agreement with its formula the ^1H NMR spectrum of the $[CuS_3C\text{–}o\text{-}T]_4$ compound in CS_2 shows only two peaks: a singlet for the aliphatic hydrogens of the methyl group at 2.35 ppm and a multiplet, due to the benzene ring hydrogens, at 7.25 ppm. The ratio of aliphatic:aromatic hydrogens is correct at 3:4. The methyl signal, as already observed for some copper(I) derivatives of a similar type [21], is broader than usual: this can be ascribed to interconversion of the methyl groups, sterically differentiated among themselves in the structure. Furthermore no specially deshielded aromatic proton is present and in effect the aromatic ring is rotated out of the plane of the five-membered chelate ring, so that the effect of the ring current is ruled out.

It has been suggested that the position of the aromatic ring is caused by S–H contacts that arise when the S–C–S angle opens under the insertion of another sulfur atom in the four-membered ring [20], but we observed this effect also in some copper(I) *ortho* substituted derivatives with CS_2 groups as ligands [19].

The ^{13}C NMR spectrum (in deuteroacetone:CS_2 = 1:2) shows the methyl signal at 20.2 ppm, a multiplet due to the aromatic carbons in the 127–141 ppm region and, downfield, at 231.2 ppm, a peak of low intensity, which we attribute to C(S)SS.

The spectra of the other two compounds could be run only in pyridine and are scarcely significant, because of the background of this solvent in the aromatic region. In the ^1H NMR spectra the methyl signal of **II** is found at 2.5 ppm and that of the dimer (2.4 ppm) is particularly broad. In the ^{13}C NMR spectra the low solubility did not allow us to assign the peaks of CS_2 and CS_3 in the above compounds even after 100.000 scans, as the pyridine again affects the region of the aromatic carbons. The methyl group resonates at 20.19 ppm in **II** and at 19.83 ppm in $[CuS_3C\text{–}o\text{-}T]_2\cdot(py\text{-}d_5)_2$.

Supplementary Material

Atomic coordinates of the hydrogen atoms, atomic thermal parameters and a list of calculated and observed structure factors are available from the authors on request.

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