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Insertion reaction of carbon disulfide into copper–carbon bonds of aromatic organocopper(I) compounds, in the presence of 2,2′-bipyridine and 1,10-phenanthroline. X-ray diffraction structures of the [(CuS$_3$C-*o*-tolyl)phen], [(CuS$_3$C-*o*-tolyl)$_2$phen] and [Cu$_2$(S$_3$C-*o*-tolyl)(S$_2$C-*o*-tolyl)bipy] complexes

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Abstract

In the presence of nitrogen chelating ligands (LL = 2,2′-bipyridine, 1,10-phenanthroline) the insertion reaction of CS$_2$ into the copper–carbon bond of arylcopper(I) compounds (Ar = Ph, *o*- and *p*-tolyl) gave adducts of Cu(I) dithiocarboxylates with LL, whose stoicheiometry depended upon the ligand and the aryl moiety. Co-formation of perthio and perthiodithio derivatives was suggested by hydrolysis of the rough products. The adducts were identified by comparison with authentic samples, prepared by other routes and characterized by IR spectra. Crystal structures were established by X-ray diffraction analyses for the [(CuS$_3$C-*o*-T)phen] (I), [(CuS$_3$C-*o*-T)$_2$phen] (II) and [Cu$_2$(S$_3$C-*o*-T)(S$_2$C-*o*-T)bipy] (III) complexes. Crystal data: C$_{20}$H$_{15}$CuN$_2$S$_3$ (I), space group $P\bar{1}$, with a = 14.135(3), b = 7.659(3), c = 9.115(3) Å, α = 73.33(2), β = 96.89(3), γ = 96.73(3)° and Z = 2; C$_{28}$H$_{22}$Cu$_2$N$_2$S$_6$ (II), space group $P\bar{1}$, with a = 12.385(2), b = 11.865(3), c = 11.331(2) Å, α = 114.35(3), β = 89.48(2), γ = 105.75(2)° and Z = 2; C$_{26}$H$_{22}$Cu$_2$N$_2$S$_5$ (III), space group $P2_1/n$, a = 25.057(4), b = 10.188(3), c = 10.960(3) Å, β = 100.58(3)° and Z = 4. In **I** and **II** the original tetrameric structure of the copper perthiocarboxylate, under the action of the new LL ligand, turns to mononuclear and binuclear, respectively, according to the Cu:LL ratios. In **I** the metal atom is pseudo-tetrahedrally coordinated by two N atoms from phen and two S atoms from the bidentate chelating *o*-tolyldithiocarboxylate ligand; complex **II** can be considered arising from **I** by electrophilic attack of the trigonally arranged metal atom of an 'additional' CuS$_3$C-*o*-T chelate unit on the terminal perthio S atom of the tetrahedral moiety. In the structure of **III**, which is the first example of a perthiodithiocarboxylate with an *ortho* substituent in the aryl group, tetrahedral and trigonal arranged copper(I) atoms, doubly bridged by perthio- and dithioarylate groups, are present.

Introduction

In recent years we have been studying the insertion of CS$_2$ in copper–carbon bonds of arylcopper(I) compounds and the complexes formed in the presence of tertiary mono- and bidentate phosphines [1–4]. This paper deals with analogous reactions in the presence of bidentate nitrogen containing ligands, such as 2,2′-bipyridine and 1,10-phenanthroline. These reactions were in effect the first investigated, but owing to the difficulty in recrystallizing the compounds and obtaining reproducible analyses, we were at the time incapable of identifying the products formed. Now our extended knowledge and experience in this field have allowed us to interpret the previous results, often unexpected on the basis of complexation of the organocopper compounds with these nitrogen ligands alone [5]. The structures of the [(CuS$_3$C-*o*-T)phen] (I), [(CuS$_3$C-*o*-T)$_2$phen] (II) and [Cu$_2$(S$_3$C-*o*-T)(S$_2$C-*o*-T)bipy] (III) adducts (*o*-T = *o*-tolyl) were established by X-ray diffraction analysis.

Experimental

The organocopper compounds were prepared by published methods [6]. The copper(I) perthio- and dithiocarboxylates, used for the synthesis of the

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comparison compounds, were also prepared as previously reported [7]. In the reactions with copper(I) aryls dry solvents and anhydrous phenanthroline were employed and the reactions were carried out under nitrogen. An inert atmosphere is also advisable for the other syntheses. Prolonged treatments of the products with chlorinated solvents must be avoided.

Reactions of the arylcopper compounds with CS_2 and LL (bipy or phen)

ArCu (1 g) was suspended in toluene at -40 °C and 5 ml of CS_2 (excess) were slowly added. The temperature was then allowed to rise to 0 °C and the solution filtered clear. The addition of the ligand, in the chosen ratio with the arylcopper (Cu:LL from 0.5 to 3), caused an immediate darkening, followed after some minutes by formation of voluminous red–brown precipitates. After 6 h the products were filtered and washed with toluene and ether. Alternatively the complexes of ArCu with bipyridine or phenanthroline [5] were prepared *in situ* and then CS_2 was added. The products were apparently the same.

Hydrolysis of the above products

We report here, for example, the procedure followed for the hydrolysis of the product obtained from *o*-tolylcopper, CS_2 and bipyridine.

Acid hydrolysis

0.5 g of the powder of approximate composition $(CuS_2C\text{-}o\text{-}T)_3$bipy was hydrolyzed in 25 ml of benzene with 10 ml of aqueous HCl (1:1), under nitrogen, giving rapidly a gelatinous compound, which occluded the aqueous phase. After 24 h it was in part flocculated and could be filtered and washed with acetone, always under nitrogen, leaving a violet product (A), identified later on as $[CuS_2C\text{-}o\text{-}T]_n$ and corresponding to 52% of the initial copper content. The two phases of the filtrate were separated: the aqueous layer, light pink, but which became rapidly green in air, contained 23.5% of the copper initially present; the organic layer, washed with water till neutral reaction and then dried over Na_2SO_4, left, after evaporation of the solvent, a crystalline orange product (B), ($[CuS_3C\text{-}o\text{-}T]_4$, 25% of the total copper) practically pure after having washed away the small amount of a soluble red impurity with pentane.

If the hydrolysis was carried out in air A disappeared rapidly, while green crystals (C) were formed at the interphase and the organic layer turned to orange–red. C, separated by filtration and washed repeatedly with CS_2 to eliminate some orange–red precipitate included, was identified as the $[(CubipyCl)_2Cl_2]$ complex. The organic phase, evaporated to dryness and extracted with n-pentane left B (21%), while at least three different red products, of exclusive organic nature, were present in the pentane extract. The most important of these, identified by comparison with an authentic sample, was *o*-TC(S)SSC(S)-*o*-T disulfide; the other two, rather unstable, were not further investigated.

Basic hydrolysis

0.5 g of '$(CuS_2C\text{-}o\text{-}T)_3$bipy' was suspended in toluene and 5 ml of NH_3 20% was added under stirring. Addition of a little acetone favoured the contact between the two phases. The complex went into solution, while the organic layer turned brown–black and the aqueous phase blue. After 15 min a red–violet solid, the complex $[Cu_2(S_3C\text{-}o\text{-}T)(CS_2\text{-}o\text{-}T)bipy]$, began to precipitate. The yield of this product accounted for two thirds of the initial copper, the rest was quantitatively found in the aqueous phase.

Synthesis of comparison compounds, starting from Cu(I) perthio- and dithiocarboxylates

Complexes of Cu(I) perthioarylcarboxylates with phen, [(CuS₃CAr)phen] (Ar=Ph, o-T, p-T)

A suspension of $[CuS_3CAr]_4$ (1.5 mmol Cu) and 1.6 mmol of anhydrous phen in 40 ml of toluene was refluxed under stirring. The reagents went into solution and a microcrystalline dark brown solid precipitated in a short time. After 1 h the heating was interrupted and the product filtered and washed many times, at first with small amounts of toluene and finally with ethyl ether. The products were recrystallized from hot toluene or from CS_2 with addition of ethyl ether and dried *in vacuo*.

$[(CuS_3C\text{-o-}T)_2phen]$ was prepared as above, with a double amount of perthiocarboxylate and recrystallized from hot toluene diluted with n-hexane.

Complexes of Cu(I) perthioarylcarboxylates with bipy

When equivalent amounts of CuS_3CAr and bipy were refluxed in toluene perthiocarboxylates reprecipitated in almost quantitative yield from the solutions at first formed. Even at room temperature the phenyl and *p*-tolyl perthiocarboxylates were the main products recovered. Minor variations in their IR spectra indicated the presence of some bipy, but analyses revealed less than one LL molecule for six copper atoms. The $[(CuS_3C\text{-}o\text{-}T)bipy]$ adduct was formed instead in high yield, together with some $[Cu_2(S_3C\text{-}o\text{-}T)(S_2C\text{-}o\text{-}T)bipy]$ complex, from which the latter could be separated due to its higher solubility.

Complexes of Cu(I) perthiodithioarylcarboxylate with phen, [$Cu_2(S_3CAr)(S_2CAr)$phen] (Ar=Ph, o-T, p-T)

A suspension of $[Cu_2(S_3CAr)(S_2CAr)]_n$ (0.6 meq. Cu) and 0.119 g of phen·H_2O (0.6 mmol) in 20 ml of toluene was heated at reflux for 1 h. The shining crystals formed by cooling of the filtered solution were washed repeatedly with little toluene.

Complexes of Cu(I) perthiodithioarylcarboxylates with bipy

Equivalent amounts of CuS_3CAr, CuS_2CAr and bipy were heated at reflux in toluene (about 0.6 meq. in 25 ml of solvent) for half an hour and, if necessary, the solution was filtered clear. The crystals, which precipitated by standing at room temperature, were collected and washed throughly with Et_2O. Recrystallization was by extraction with CS_2 and concentration of the extract.

Complexes of Cu(I) dithioarylcarboxylates with phen

(CuS_2CAr)phen (Ar=Ph, o-T, p-T). A suspension of $[CuS_2CAr]_4$ (0.8 mmol Cu) and 0.85 mmol phen in 30 ml of toluene was refluxed for 1 h. The brown powders formed were filtered and washed repeatedly with toluene and then with CS_2. Recrystallization was possible only from hot pyridine, and caused isomerization of the product in the case of the *o*-tolyl derivative.

$(CuS_2CAr)_2$phen. The formation of these complexes is questionable, owing to the low solubility in toluene of both copper reagents and products. Recrystallization of the *p*-tolyl derivative from hot toluene gave, however, analyses indicative of the above stoichiometry.

Complexes of Cu(I) dithioarylcarboxylates with bipy

Prolonged stirring of mixtures of the Cu(I) dithioarylates with bipy in toluene, in Cu:L ratios varying from 1 to 3, and repeated washing of the filtered solids with toluene, gave products of approximate stoicheiometry $(CuS_2CAr)_3$bipy. Recrystallization of these products from pyridine caused dissociation of the adducts. Refluxing in toluene increased the Cu:LL ratio to about 4 for the phenyl and *p*-tolyl derivatives.

X-ray data collection and refinement

The X-ray measurements of **I**, **II** and **III** were performed at room temperature on Siemens AED diffractometers using Ni-filtered Cu Kα radiation ($\bar{\lambda}=1.54178$ Å).

The crystal data of the three compounds and some of the most relevant parameters used in the data collections are reported in Table 1.

Unit cell parameters were obtained by least-squares analysis of the setting angles of 30 carefully centred reflections. The systematic data collections were performed in the range $3 \leqslant \theta \leqslant 70$, operating in θ–2θ step scanning mode, with scan speed 3–12 $\min^{-1}$ and scan width from $(\theta-0.60)°$ to $(\theta+0.60+\Delta\lambda/\lambda\ \mathrm{tg}\theta)°$, were $\Delta\lambda/\lambda=0.142$. The intensities I_{hkl} were determined by the analysis of the reflection profiles [8] and corrected for Lorentz and polarization effects.

Absorption effects were corrected using ABSORB [9]; maximum and minimum values of the absorption coefficients were: 1.18–0.84, 1.11–0.86 and 1.46–0.82 for compounds **I**, **II** and **III**, respectively.

Instrumental linearities and crystals decay were monitored by checking standard reflections every 100 measurements. No significant decreases were detected.

The three structures were solved by automatic Patterson methods using SHELX86 [10] and refined by several cycles of full-matrix least-squares methods. For each of the three compounds the parameters refined were: the overall scale factor, the positional parameters and the anisotropic thermal parameters of all non-hydrogen atoms.

In compound **I** all the hydrogen coordinates were calculated, whereas in compound **II** all the hydrogens were found in the ΔF map and refined with isotropic temperature factors. In compound **III** 14 hydrogens were found in the ΔF map; the others were calculated at their geometrical positions with C–H = 1.08 Å.

Geometrical calculations were obtained by PARST [11] and drawings were made by PLUTO [12].

The weighting scheme used in the last cycles of refinement was $w=K[\sigma^2(F_o)+gF_o^2]^{-1}$ with $K=1.000$ (I) or 0.2917 (III) and $g=0.004744$ (I) or 0.013887 (III). Unit weight was chosen for **II**. The scattering factors were taken from the literature [13]. Final atomic coordinates for the non-hydrogen atoms are given in Tables 2–4.

All the calculations were performed on the Gould 6040 Powernode of the Centro di Studio per la Strutturistica diffrattometrica del C.N.R. Parma.

Results and discussion

The starting organometallic compounds were phenyl and *o*- and *p*-tolyl copper (denoted henceforth by PhCu and *o*- or *p*-TCu, respectively). By reacting them in toluene with carbon disulfide and a nitrogen bidentate ligand LL (bipy or phen), we obtained powders intensely coloured from brown to black, which had low or partial solubilities in common

TABLE 1. Experimental data for the X-ray diffraction studies on **I**, **II** and **III**

	I	**II**	**III**
Crystal habit and colour	brown prisms	brown prisms	brown prisms
Formula	$C_{20}H_{15}CuN_2S_3$	$C_{28}H_{22}Cu_2N_2S_6$	$C_{26}H_{22}Cu_2N_2S_5$
Molecular weight	443.078	705.947	649.865
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	14.135(3)	12.385(2)	25.057(4)
b (Å)	7.659(3)	11.865(3)	10.188(3)
c (Å)	9.115(3)	11.331(2)	10.960(3)
α (°)	73.33(2)	114.35(3)	90
β (°)	96.89(3)	89.48(2)	100.58(3)
γ (°)	96.73(3)	105.75(2)	90
V (Å^3)	934.9(5)	1449.9(7)	2750(1)
Z	2	2	4
D_{calc} (g cm^{-3})	1.574	1.617	1.570
$F(000)$	452	716	1320
Crystal dimensions (mm)	0.5×0.3×0.2	0.4×0.6×0.3	0.4×0.4×0.2
Linear absorption coefficient (cm^{-1})	47.58	59.50	55.33
Reflections measured	$\pm h, \pm k, l$	$\pm h, \pm k, l$	$\pm h, k, l$
Unique total data	3510	5232	5450
Criterion for observations	$I \geqslant 3\sigma(I)$	$I \geqslant 3\sigma(I)$	$I \geqslant 2\sigma(I)$
Unique observed data	2641	3789	3403
Max Δ/σ on last cycle	0.3	0.4	0.4
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.051	0.041	0.047
$R_w = \Sigma w\lvert\Delta F\rvert/\Sigma w\lvert F_o\rvert$	0.065	0.041	0.064

solvents, except in pyridine. The two ligands gave complexes of different stoicheiometries: in a range of Cu:LL ratios from 0.5 to 3 we obtained products with one or two metal atoms for each phenanthroline and at least three copper(I) atoms for each bipyridine. The results were apparently the same by treating the organocopper compounds with carbon disulfide before or after addition of LL. The products could not be recrystallized unchanged and no satisfactory analyses were obtained, but information about their nature could be gained from acid (HCl 1:1) or basic (NH_3 20%) hydrolysis of suspensions of these products in benzene. The reactions followed different routes if carried out under nitrogen or in air, and, in both cases, notwithstanding the different original stoicheiometries, the base products were the same starting from bipy or phen complexes. Copper(I) perthio- and dithiocarboxylates were isolated among the hydrolytic products in acid medium, under nitrogen; in air the latter disappeared rapidly giving $[(CuLLCl)_2Cl_2)]$ complexes and organic sulfurated by-products, the most important of which was the bis(thioaroyl)disulfide, $(ArCS_2)_2$. In basic medium, in air, complexes of perthio- and dithiocarboxylates with LL could be isolated, together with perthiodithio species. The detection of perthio and dithio derivatives among the hydrolysis products, suggests their presence in the original powders, but does not prove it, given that they could originate from by-products of the reactions [14]. Some perthio derivatives were also isolated from the most soluble fractions of original samples.

The new products were identified by analytical data and by comparison with authentic samples prepared by other routes, as specified in 'Experimental'. Table 5 shows the analytical data of the compounds prepared for comparison sake.

Phenanthroline is the best of the two LL ligands for the formation of 1:1 complexes with Cu(I) perthioarylates. While the starting $[CuS_3CAr]_4$ species are tetranuclear, molecular weights measurements in toluene had suggested a mononuclear structure for their complexes with phenanthroline. This was then confirmed by X-ray diffraction analysis of single crystals (Fig. 1). The *o*-tolyl derivative also gave an adduct with two Cu(I) perthiocarboxylato groups for each phenanthroline and the structure of the latter compound, the determined by X-ray diffraction methods, is shown in Fig. 2. Species with a Cu:L ratio >1 seem to form also for the phenyl and *p*-tolyl derivatives, but were not definitely characterized. The perthioarylate adducts with bipyridine are rather unstable and decompose by heating in solution or even only by washing with solvents. The most stable

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

Atom	*x/a*	*y/b*	*z/c*
Cu1	1883(1)	2509(1)	1774(1)
S1	2509(1)	3579(1)	−485(1)
S2	3470(1)	5569(1)	−58(1)
S3	2658(1)	4518(1)	2985(1)
N1	1751(2)	−61(4)	3479(3)
N2	423(2)	1707(4)	1398(4)
C1	3403(2)	5771(4)	1718(4)
C2	4117(2)	7244(4)	2073(4)
C3	3857(3)	9025(5)	1638(5)
C4	4501(3)	10434(6)	1921(6)
C5	5393(3)	10043(6)	2650(6)
C6	5655(3)	8269(6)	3061(5)
C7	5025(2)	6831(5)	2794(4)
C8	5331(3)	4913(5)	3242(5)
C9	2407(3)	−884(5)	4526(5)
C10	2177(3)	−2393(5)	5772(4)
C11	1251(3)	−3053(5)	5925(4)
C12	531(3)	−2215(5)	4822(4)
C13	815(2)	−717(4)	3617(4)
C14	112(2)	193(4)	2474(4)
C15	−856(2)	−499(5)	2515(4)
C16	−1507(3)	419(6)	1336(5)
C17	−1190(3)	1901(6)	215(5)
C18	−215(3)	2507(5)	286(5)
C19	−1122(3)	−2041(5)	3756(5)
C20	−467(3)	−2860(5)	4870(5)

is the 1:1 complex of the *o*-tolylperthiocarboxylate, but even this loses part of its bipyridine by recrystallization.

Perthiodithiocarboxylato adducts with one LL moiety each two copper atoms were formed both by phenanthroline and bipyridine. X-ray diffraction analysis showed a dinuclear structure for the latter complexes, $[Cu_2(S_3CAr)(S_2CAr)bipy]$ (Fig. 3)*. The phenyl and *p*-tolyl derivatives lose bipyridine by recrystallization from CH_2Cl_2, while upon recrystallization from pyridine the LL is substituted by two molecules of this solvent [15].

The dithioarylates gave preferentially complexes with a Cu:LL ratio of 1:1 with phenanthroline, but usually there was a higher copper content in the adducts with bipyridine. The Cu:LL ratio of about 3:1 moved towards 4:1 for the phenyl and *p*-tolyl derivatives by refluxing in toluene.

Perthio and dithio adducts are slowly autoxidized also in the solid state and, after some months of storage in air, sulfates could be detected in the filtrates of their aqueous suspensions. Dramatic alterations were noted in some samples of phenyl derivatives.

TABLE 3. Fractional atomic coordinates ($\times 10^4$) for the non-hydrogen atoms with e.s.d.s in parentheses for **II**

Atom	*x/a*	*y/b*	*z/c*
Cu1	1549(1)	1234(1)	2492(1)
Cu2	3900(1)	3142(1)	4396(1)
S1	2246(1)	3329(1)	3971(1)
S2	2639(1)	4231(1)	2752(1)
S3	1708(1)	1521(1)	666(1)
S4	5334(1)	3477(2)	3241(2)
S5	4582(1)	2285(2)	5493(2)
S6	6007(1)	2102(2)	4663(2)
N1	129(3)	152(4)	2966(4)
N2	2185(4)	−174(4)	2585(4)
C1	2261(4)	3095(4)	1177(4)
C2	2449(4)	3733(5)	266(5)
C3	1726(6)	4453(6)	246(6)
C4	1870(7)	5097(7)	−557(8)
C5	2729(7)	5007(7)	−1319(7)
C6	3433(7)	4303(7)	−1329(7)
C7	3310(5)	3639(5)	−514(6)
C8	4091(7)	2878(10)	−534(10)
C9	−868(5)	352(6)	3220(5)
C10	−1715(5)	−446(7)	3597(6)
C11	−1530(5)	−1476(6)	3707(6)
C12	−496(5)	−1735(5)	3433(5)
C13	317(4)	−878(5)	3080(4)
C14	1404(4)	−1070(5)	2841(4)
C15	1647(5)	−2134(5)	2916(5)
C16	2728(6)	−2271(6)	2661(6)
C17	3507(6)	−1362(7)	2421(6)
C18	3212(5)	−318(6)	2410(6)
C19	778(7)	−2993(6)	3257(6)
C20	−218(7)	−2798(6)	3525(6)
C21	6192(4)	2789(5)	3612(5)
C22	7275(4)	2757(4)	3023(5)
C23	8275(4)	3594(5)	3768(6)
C24	9290(5)	3643(6)	3243(7)
C25	9301(5)	2839(6)	1969(7)
C26	8318(5)	1978(6)	1230(6)
C27	7290(4)	1911(5)	1735(5)
C28	6215(7)	926(11)	911(8)

Crystal structures of the $[(CuS_3C\text{-}o\text{-}T)phen]$ *(I),* $[(CuS_3C\text{-}o\text{-}T)_2phen]$ *(II) and* $[Cu_2(S_3C\text{-}o\text{-}T)(S_2C\text{-}o\text{-}T)(bipy)]$ *(III) complexes*

Views of the $[(CuS_3C\text{-}o\text{-}T)phen]$ (**I**), $[(CuS_3C\text{-}o\text{-}T)_2phen]$ (**II**) and $[Cu_2(S_3C\text{-}o\text{-}T)(S_2C\text{-}o\text{-}T)bipy]$ (**III**) complexes are shown in Figs. 1, 2 and 3, respectively, together with the atomic numbering schemes. Selected bond distances and angles for **I**, **II** and **III** are given in Table 6.

In the monomeric complex **I** the copper atom is pseudotetrahedrally coordinated by two sulfur atoms from the chelating *o*-tolylperthiocarboxylate anion and by the two nitrogen atoms of the phen ligand, so that two roughly planar pentaatomic chelate rings are formed around the metal atom.

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*A corresponding structure was observed also for the *p*-tolyl derivative, but, not furnishing substantially new information, it was not refined.

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

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu1	60(1)	1968(1)	3223(1)
Cu2	−20(1)	1190(1)	890(1)
S1	406(1)	65(1)	2555(1)
S2	1202(1)	476(1)	2563(1)
S3	−846(1)	2136(1)	3022(1)
S4	−889(1)	1626(1)	290(1)
S5	717(1)	2054(1)	327(1)
N1	320(2)	3895(4)	3067(4)
N2	486(2)	2294(4)	5001(3)
C1	1233(2)	1497(5)	1359(4)
C2	1808(2)	1868(5)	1287(5)
C3	2035(3)	1301(7)	346(7)
C4	2574(3)	1608(8)	257(10)
C5	2864(3)	2469(10)	1114(12)
C6	2636(3)	3017(10)	1996(11)
C7	2096(3)	2769(7)	2125(7)
C8	1843(4)	3484(9)	3084(8)
C9	207(3)	4673(5)	2052(6)
C10	353(3)	5990(6)	2100(7)
C11	597(3)	6527(6)	3195(7)
C12	714(2)	5760(5)	4257(6)
C13	566(2)	4426(4)	4162(4)
C14	666(2)	3535(4)	5235(4)
C15	927(2)	3902(6)	6418(5)
C16	1000(3)	2979(7)	7358(5)
C17	828(2)	1718(6)	7113(5)
C18	578(2)	1409(5)	5919(5)
C19	−1152(2)	2096(4)	1524(4)
C20	−1730(2)	2509(7)	1299(5)
C21	−2099(3)	1740(10)	1883(7)
C22	−2632(3)	2083(14)	1733(10)
C23	−2809(4)	3173(15)	1067(11)
C24	−2480(4)	3936(15)	518(11)
C25	−1912(3)	3591(9)	617(7)
C26	−1563(4)	4422(9)	58(12)

In the dimeric complex **II** (distance between the Cu(1) and Cu(2) copper atoms 3.281(2) Å) the Cu(1) atom shows a coordination arrangement very similar to that found for the metal in **I**, while the Cu(2) copper atom is trigonally coordinated by two sulfur atoms from the second chelating anion and by a bridging perthio sulfur atom from the perthioarylato group chelating the Cu(1) atom. So complex **II** can be considered arising by electrophilic attack of the metal atom of an 'additional' CuS_3C-*o*-T chelate unit on the terminal perthio sulfur atom of the tetrahedral moiety.

In both complexes **I** and **II** the values of the N(1)–Cu(1)–N(2) (78.8(1) and 80.4(2)°), S(1)–Cu(1)–S(3) (99.2(1) and 99.0(1)°) and some N–Cu(1)–S bond angles (ranging from 131.9(1) to 136.2(1)° in **I** and from 115.1(1) to 127.0(1)° in **II**) differ significantly from the values expected for a regular tetrahedron. The values of the bite angles are in agreement with those generally found in this class of chelate rings; the other are probably due to the steric hindrance inside the Cu(1) coordination sphere of the two pentaatomic rings. The Cu–N (2.099(3)–2.134(3) and 2.070(4)–2.087(4) Å) and the Cu–S (2.235(2)–2.253(2) and 2.230(2)–2.271(2) Å) bond lengths in the tetrahedral moieties support asymmetrical bonding of the nitrogen and sulfur atoms in both compounds. The introduction of the CuS_3C-*o*-T chelate unit, which accommodates nearly orthogonal to the perthiocarboxylato ring of the tetrahedral portion of **II** (the dihedral angle between the involved chelate rings is 96.8(1)°) seems to cause significant differences only in the values of the dihedral angles between the pentaatomic chelate rings (113.7(1)° in **I** and 97.0(1)° in **II**). The nearly theoretical value of 90° found in **II**, could be attributable to the increase of the distance of the Cu(1) metal atom from the associated terminal perthio sulfur atom (2.271(2) in **II** versus 2.235(2) Å in **I**), leading to narrower ring–ring repulsion.

In the dimeric complex **III** the two metal atoms (Cu(1)–Cu(2) distance 2.649(4) Å) are bridged by the sulfur atoms of a bidentate dithio-*o*-toluate and by the terminal sulfur atom of a perthioarylate, which also acts as a chelating ligand for the Cu(2) atom. The latter is therefore trigonally coordinated by three sulfur atoms, while the environment of the Cu(1) atom is completed to tetrahedral by the two nitrogen atoms of the bipy molecule, acting as a bidentate planar system, like phen in **I** and **II**. So the dimeric **II** and **III** complexes, stoicheiometrically differing for a perthio- replacing a dithio-*o*-toluate anion, show tetrahedrally and trigonally arranged copper(I) atoms bridged by one sulfur atom; in complex **III** the bidentate bridging dithio-*o*-toluate gives rise to an hexaatomic $\overline{\text{CuSCuSCS}}$ bimetallic ring of half-chair conformation, the two planar CuSCu and CuSCSCu moieties forming a dihedral angle of 51.1(1)°.

In compounds **II** and **III** the Cu–N bond lengths of the Cu(1) tetrahedral arrangements are very similar (2.079(4)(av.) versus 2.078(4)(av.) Å) and the Cu–S distances slightly different (2.251(3)(av.) versus 2.273(2)(av.) Å), but the structure of **III** shows a significant shortening of the Cu–Cu distance (2.649(2) versus 3.281(2) Å) and a remarkable enlargement of the S(1)–Cu(1)–S(3) bond angle (117.8(1) versus 99.0(1)°) due to the steric demand of the additional –S–C–S– bridge formed by the dithioarylate anion. As a consequence the perthiocarboxylato ring at Cu(2) in **III** forms with the planar bipy molecule a dihedral angle of 54.3(1)°, while the perthioarylate ring at Cu(2) in **II** gives rise to a dihedral angle of 31.0(1)° with the phen system.

TABLE 5. Analytical data of the compounds

Compound	Colour	Decomposition point	Analysis[a] (%)				
			C	H	Cu	N	S
[CuS$_3$CPh·phen]	brown-violet	196–198	52.9 (53.18)	3.1 (3.05)	14.5 (14.81)	6.0 (6.53)	22.5 (22.42)
[Cu$_2$(S$_3$CPh)(S$_2$CPh)phen]	dark brown	187–189	48.2 (48.35)	2.8 (2.81)	19.6 (19.68)	4.2 (4.34)	24.7 (24.83)
[Cu$_2$(S$_3$CPh)(S$_2$CPh)bipy][b]	brown–violet	163–164	45.6 (46.35)	2.9 (2.92)	20.4 (20.44)	4.0 (4.50)	26.0 (25.79)
CuS$_2$CPh·phen[c]	dark brown	175–179	57.0 (57.48)	3.7 (3.30)	15.9 (16.01)	6.9 (7.06)	16.0 (16.16)
[CuS$_3$C-*o*-T·phen]	dark brown	184–186	53.5 (54.21)	3.2 (3.41)	14.1 (14.34)	6.1 (6.32)	21.5 (21.71)
[CuS$_3$C-*o*-T·bipy][c]	red–brown	119–121	50.3 (51.59)	3.8 (3.61)	14.8 (15.16)	6.0 (6.68)	22.9 (22.96)
[(CuS$_3$C-*o*-T)$_2$(phen)]	orange–brown	168–170	47.0 (47.63)	3.7 (3.16)	17.9 (18.00)	3.5 (3.97)	27.3 (27.25)
[Cu$_2$(S$_3$C-*o*-T)(S$_2$C-*o*-T)phen]	orange	216–217	48.6 (49.9)	3.3 (3.29)	18.9 (18.86)	3.8 (4.16)	23.3 (23.79)
[Cu$_2$(S$_3$C-*o*-T)(S$_2$C-*o*-T)bipy]	amaranth	215–216	47.8 (48.05)	3.3 (3.41)	19.5 (19.56)	4.3 (4.31)	24.6 (24.67)
CuS$_2$C-*o*-T·phen[d]	ochre	224–232	58.5 (58.44)	3.5 (3.68)	15.4 (15.46)	6.7 (6.81)	15.2 (15.60)
[CuS$_3$C-*p*-T·phen]	dark brown	215–216	53.4 (54.21)	3.3 (3.41)	14.1 (14.34)	6.0 (6.32)	21.6 (21.71)
[Cu$_2$(S$_3$C-*p*-T)(S$_2$C-*p*-T)phen]	brown–black	205–207	49.5 (49.90)	3.3 (3.29)	18.7 (18.86)	3.9 (4.16)	23.5 (23.79)
[Cu$_2$(S$_3$C-*p*-T)(S$_2$C-*p*-T)bipy][b,e]	dark brown	188–190	47.6 (48.05)	3.5 (3.41)	19.9 (19.56)	4.0 (4.31)	24.35 (24.67)
CuS$_2$C-*p*-T·phen	dark brown	212–214	58.5 (58.44)	4.0 (3.68)	15.4 (15.46)	6.7 (6.81)	15.4 (15.60)
(CuS$_2$C-*p*-T)$_2$phen	orange–brown	≈155 black 185–190	51.0 (52.40)	4.7 (3.46)	19.5 (19.80)	4.1 (4.36)	19.0 (19.98)

[a] Calculated values in parentheses. [b] Recrystallized from pyridine and n-pentane gave [Cu$_2$(S$_3$CAr)(S$_2$CAr)py$_2$]. [c] Reacted with CCl$_4$. [d] Orange–red by recrystallization from py; dec. pt. 235–237. [e] Dissociated in CH$_2$Cl$_2$ with formation of CuS$_3$C-*p*-T and CuS$_2$C-*p*-T compounds.

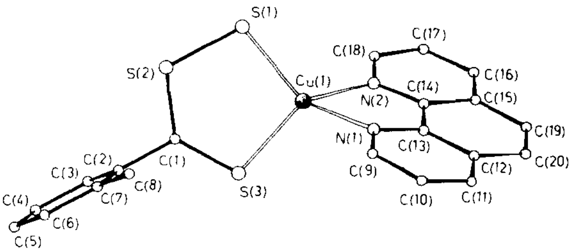

Fig. 1. Perspective view of the [Cu(S$_3$C-*o*-tolyl)phen] complex (I), with the atomic numbering scheme.

The trigonal arrangements around the Cu(2) atom in **II** and **III** show different and justifiable trends of the associated Cu–S and S–Cu–S bond distances and angles. In **II** the two Cu–S distances involving the Cu(2) atom and the perthio sulfur atoms are close to each other (2.196(3) and 2.198(2) Å) and significantly shorter than the other Cu–S bond (2.242(2) Å); of the two very asymmetrical S–Cu–S non-bite angles (136.7(1) and 121.7(1)°) that associated with the shortest Cu–S bonds and adjacent to the bulky phen molecule is the largest, to minimize steric hindrance. In **III** the Cu(2)–S(4) distance, involving a sulfur atom of the bridging dithiocarboxylato group, is significantly shorter (2.201(1) Å) than the other Cu–S bonds involving sulfur atoms of the chelate ring (2.233(2) and 2.251(2) Å); the non-bite S–Cu–S bond angles, in the absence of

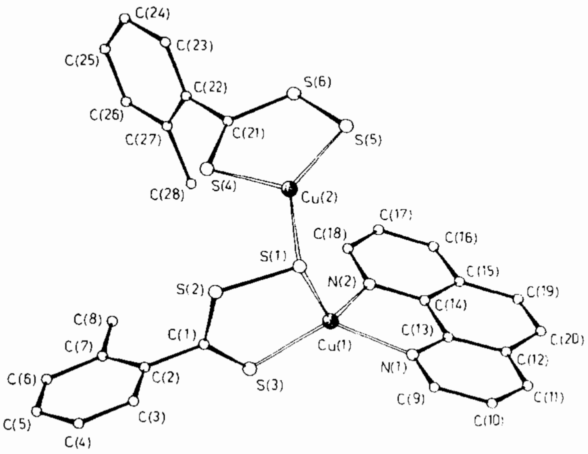

Fig. 2. Perspective view of the [(CuS$_3$C-*o*-tolyl)$_2$phen] complex (II), with the atomic numbering scheme.

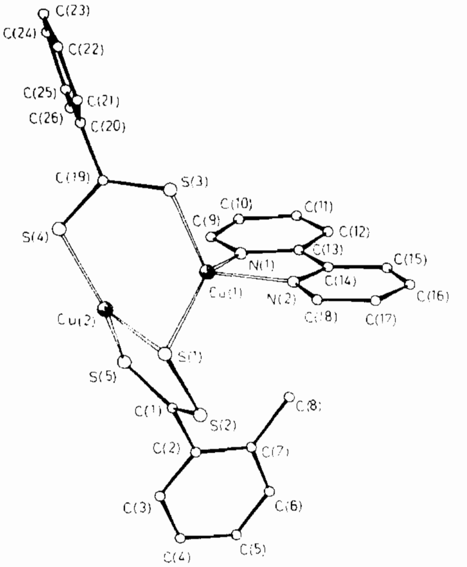

Fig. 3. Perspective view of the [Cu$_2$(S$_3$C-*o*-tolyl)(S$_2$C-*o*-tolyl)bipy] complex (III), with the atomic numbering scheme.

adjacent bulky ligands, are almost symmetrical (129.9(2) and 131.4(1)°).

The C–S bond distances in the perthio- and dithiocarboxylato groups and their dihedral angles with the associated aryl moieties also deserve some comment. Only the C–S bonds values in the perthiocarboxylato group of **I** and in the dithiocarboxylato moiety of **III** agree with delocalization of the double bond in the relative CS$_2$ portion; this last is tilted with respect to the associated aryl group by 93.7(1)° in **I** and 112.5(1)° in **II**. In the perthiocarboxylato groups of **II** and **III** instead, the C–S bonds to the uncoordinated S atom are longer than the other ones, where the double bond should be

TABLE 6. Relevant bond distances (Å) and angles (°) in [(CuS$_3$C-*o*-tolyl)phen] (**I**), [(CuS$_3$C-*o*-tolyl)$_2$phen] (**II**) and [Cu$_2$(S$_3$C-*o*-tolyl)(S$_2$C-*o*-tolyl)bipy] (**III**) complexes

	I	II	III
Cu(1)–S(1)	2.235(2)	2.271(2)	2.298(2)
Cu(1)–S(3)	2.253(2)	2.230(2)	2.247(3)
Cu(1)–N(1)	2.134(3)	2.087(4)	2.085(4)
Cu(1)–N(2)	2.099(3)	2.070(6)	2.070(4)
S(1)–Cu(1)–S(3)	99.2(1)	99.0(1)	117.8(1)
N(1)–Cu(1)–N(2)	78.8(1)	80.4(2)	79.1(2)
S(1)–Cu(1)–N(2)	109.3(1)	120.4(1)	106.0(1)
S(3)–Cu(1)–N(1)	106.3(1)	127.0(1)	104.2(1)
S(3)–Cu(1)–N(2)	131.9(1)	116.7(1)	114.7(1)
S(1)–Cu(1)–N(1)	136.2(1)	115.1(1)	128.8(2)
Cu(2)–S(1)		2.198(2)	2.251(2)
Cu(2)–S(4)		2.242(2)	2.201(2)
Cu(2)–S(5)		2.196(3)	2.233(2)
S(1)–Cu(2)–S(4)		121.7(1)	129.9(1)
S(1)–Cu(2)–S(5)		136.7(1)	97.6(1)
S(4)–Cu(2)–S(5)		100.2(1)	131.4(1)
S(1)–S(2)	2.012(2)	2.053(2)	2.037(4)
S(2)–C(1)	1.685(4)	1.706(4)	1.693(5)
S(3)–C(1)	1.668(3)	1.647(4)	
C(1)–C(2)	1.503(4)	1.496(9)	1.506(7)
N(1)–C(13)	1.366(4)	1.360(9)	1.357(6)
N(2)–C(14)	1.353(4)	1.357(7)	1.351(6)
C(13)–C(14)	1.434(4)	1.431(8)	1.470(6)
S(5)–C(1)			1.654(5)
Cu(1)–S(1)–S(2)	100.9(1)	100.6(1)	104.6(1)
Cu(2)–S(1)–S(2)		100.7(1)	102.5(1)
S(1)–S(2)–C(1)	100.7(2)	108.8(2)	107.9(2)
S(2)–C(1)–S(3)	126.0(2)	127.3(3)	
S(2)–C(1)–S(5)			127.0(3)
S(2)–C(1)–C(2)	111.9(3)	110.1(4)	112.1(4)
S(3)–C(1)–C(2)	122.1(3)	122.6(4)	
S(5)–C(1)–C(2)			120.9(4)
C(1)–S(3)–Cu(1)	103.1(1)	104.3(2)	
C(1)–S(5)–Cu(2)			105.0(2)
Cu(1)–N(1)–C(13)	111.5(2)	112.0(3)	113.6(3)
N(1)–C(13)–C(14)	117.6(3)	117.4(5)	116.4(4)
C(13)–C(14)–N(2)	117.2(3)	117.5(5)	115.1(4)
C(14)–N(2)–Cu(1)	113.6(3)	112.6(4)	115.2(3)
Cu(1)–S(1)–Cu(2)		94.5(1)	71.2(1)
S(5)–S(6)		2.014(2)	
S(6)–C(21)		1.682(7)	
S(4)–C(21)		1.654(7)	
C(21)–C(22)		1.496(7)	
S(3)–C(9)			1.680(4)
S(4)–C(19)			1.679(5)
C(19)–C(20)			1.485(7)
Cu(2)–S(5)–S(6)		100.5(1)	
S(5)–S(6)–C(21)		110.0(2)	
S(6)–C(21)–S(4)		126.6(3)	
S(6)–C(21)–C(22)		112.6(4)	
S(4)–C(21)–C(22)		120.8(4)	
C(21)–S(4)–Cu(2)		102.1(2)	
S(3)–C(19)–S(4)			128.2(3)
S(3)–C(19)–C(20)			114.3(4)
S(4)–C(19)–C(20)			117.5(4)

localized, as found in the tetrameric $[CuS_3C\text{-}o\text{-}T]_4$ complex [7]; the dihedral angles that the perthio SCSS moieties form with the associated aryl group range from 70.9(1) to 73.5(1)°.

Finally, it has to be noted that the introduction of additional LL ligands (LL = bipy, phen) reduces the degree of association of the starting copper(I) perthio- [7, 14, 16] and dithio- [17, 18] carboxylates, usually tetrameric. In these the four copper atoms, roughly tetrahedrally arranged, are each trigonally coordinated to sulfur atoms, one half of which bridges two metal atoms and the other half coordinates to one copper atom. The steric demand of the ligands, whose nitrogen donor atoms also satisfy the well known tendency of copper(I) to be four-coordinated, seems responsible for the low nuclearity of the present compounds. The same effect was previously observed even with the less bulky pyridine moiety in the $[CuS_3C(\alpha\text{-}C_7H_{10})py]_2$ and $[CuS_3C\text{-}o\text{-}Tpy]_2$ complexes [19, 20].

Infrared spectra

In the IR spectra of the adducts, the main absorption bands of the perthio- and dithioarylates are easily assigned occurring at frequencies almost unchanged (± 5–10 cm^{-1}) with respect to those of the parent compounds. In the perthio- and perthiodithiocarboxylates the CS_3 stretches move to lower frequencies and the out-of-plane (oop) bending CH-absorptions of the aryl groups to higher frequencies, while in the dithiocarboxylates the $\nu(CS_2)_{asym}$ are shifted to the opposite direction. In the bipy adduct of the Cu dithio-*o*-tolylcarboxylate this absorption band is extra broad and undergoes splitting by refluxing in toluene. The intensities of the $\nu(CS_2)_{asym}$ are always significantly lower than in the parent Cu(I) compounds.

We did not try to assign the frequencies in the region under 700 cm^{-1}, where several weak bands are present and the original patterns are remarkably altered. A weak-medium band appears at 540 cm^{-1} in the perthio complexes and moves to 520 cm^{-1} in the $[Cu_2(S_3CAr)(S_2CAr)LL]$ compounds.

The good correspondence of the spectra, with regard to the common features, suggests that the bonding mode of LL is the same in all the adducts*, i.e. that bipyridine and phenanthroline act as chelating ligands, as established by the X-ray structures (Figs. 1–3). In agreement with literature data for IR spectra of chelating LL [21], bonded phenanthroline causes a weak band at about 1620 cm^{-1} and two strong absorptions close to 840 and 725 cm^{-1}. Bipyridine introduces (or more often enhances) a band at 1593 cm^{-1}; of its splitted oop bending CH-absorptions one is at about 730 cm^{-1} and the other usually overlaps with those of the aryls, being clearly distinguishable only in the $[Cu_2(S_3C\text{-}o\text{-}T)(S_2C\text{-}o\text{-}T)bipy]$ complex (bipy, 763 cm^{-1}).

Comparison of spectra of adducts with different stoicheiometry evidentiates a variation in the intensity ratios between the oop bending CH-absorptions of LL and Ar, ratios which are in agreement with the proposed formulae.

After months of storage in air new absorption bands were detected in several samples. They are mainly attributable to SO_4^{2-} groups, in agreement with the autoxidative reaction occurring for some Cu(1) dithiocarboxylates derivatives in pyridine [17].

From this systematic investigation it appears that the stoicheiometry of the above complexes is influenced by the geometry of the LL ligand but also by the nature of the aryl bonded to the sulfurated groups, phenyl and *p*-tolyl derivatives showing a rather similar behaviour, different from that of the *o*-tolyl ones. The differences observed reflect the structural position of the benzene ring with respect to the plane of CS_2 or CS_3 groups, roughly coplanar in the phenyl and *p*-tolyl, but approximately orthogonal in the *o*-tolyl complexes. Noteworthy is the stabilizing effect of LL on the perthiodithio-*o*-tolylcarboxylate moiety, mixed complexes with such an aryl group never having been obtained before for copper(I) derivatives, although well known for phenyl and *p*-tolyl derivatives [15, 22].

Supplementary material

Listing of observed and calculated structure factors, thermal anisotropic parameters and fractional coordinates of the hydrogen atoms are available from the authors on request.

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*Refluxing in toluene (under nitrogen) or recrystallization from pyridine of the $[Cu(S_2C\text{-}o\text{-}T)phen]$ complex causes a dramatic change in its spectrum, in which the $\nu(CS_2)_{asym}$ is shifted to 990 cm^{-1} (shoulder 974 cm^{-1}) and the first oop bending band of phenanthroline occurs at 830 cm^{-1}. Similar changes were not observed for the corresponding phenyl and *p*-tolyldithiocarboxylates.

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