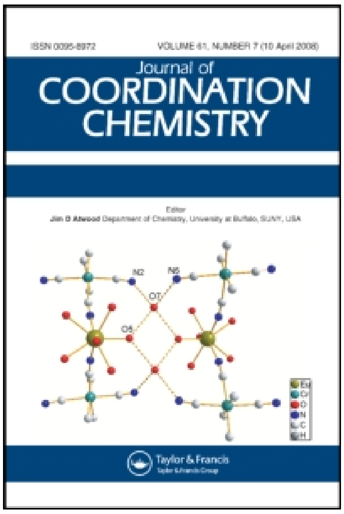

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

MIXED LIGAND COORDINATION COMPOUNDS OF COPPER(I) WITH HETEROCYCLIC THIONES AND TERTIARY PHOSPHINES. THE CRYSTAL STRUCTURE OF BIS (QUINOLINE-2-THIONE) BISTRIPHENYLPHOSPHINO COPPER(I) ETHYLSULFATE HEMIHYDRATE

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To cite this Article Akrivos, Pericles D. , Hadjikakou, Sotiris K. , Karagiannidis, Petros , Luic, Marija and Kojic-prodic, Biserka(1994) 'MIXED LIGAND COORDINATION COMPOUNDS OF COPPER(I) WITH HETEROCYCLIC THIONES AND TERTIARY PHOSPHINES. THE CRYSTAL STRUCTURE OF BIS (QUINOLINE-2-THIONE) BISTRIPHENYLPHOSPHINO COPPER(I) ETHYLSULFATE HEMIHYDRATE', Journal of Coordination Chemistry, 31: 4, 273 — 282

To link to this Article: DOI: 10.1080/00958979408024221

URL: http://dx.doi.org/10.1080/00958979408024221

J. Coord. Chem., 1994, Vol 31, pp. 273–282
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MIXED LIGAND COORDINATION COMPOUNDS OF COPPER(I) WITH HETEROCYCLIC THIONES AND TERTIARY PHOSPHINES. THE CRYSTAL STRUCTURE OF BIS (QUINOLINE-2-THIONE) BISTRIPHENYLPHOSPHINO COPPER(I) ETHYLSULFATE HEMIHYDRATE

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(Received July 14, 1993)

Copper(II) sulfate is reduced in alcoholic media in the presence of heterocyclic thiones (*i.e.* pyridine-2-thione or quinoline-2-thione) and triphenylphosphine. The resulting coordination compounds consist of $Cu(thione)_2(PPh_3)_2$ cationic units; the counteranions are alkyl sulfate monoanions. The crystal structure of the compound prepared using quinoline-2-thione in ethanol reveals that the tetrahedal cationic units and the counteranions are arranged in rows cross-linked through hydrogen bonds formed between the oxygen atoms of the anion and water molecules. The compound crystallizes in the triclinic space group $P\bar{1}$, a = 10.69 (1), b = 13.47 (2), c = 18.75 (2) Å, α = 75.9 (1), β = 85.6 (1), γ = 74.7 (1)°, V = 2525.5 Å^3, Z = 2. The local copper environment is distorted tetrahedal with unequal Cu-S (2.380(2), and 2.341(2) Å) and Cu-P (2.301(2) and 2.316(2) Å) bonds; angles around copper range from 96.37(7) to 121.16(0)°.

INTRODUCTION

Investigation of the structural preferences of copper(I) compounds is an ever growing field of research since understanding of the factors influencing both the local and the overall structure adds to the understanding of the way in which the metal participates as a constituent of the Cu^I/Cu^{II} redox couple in a variety of *in vivo* processes. These factors are mainly the steric demands of the ligated molecules and to a lesser degree the ability of these ligands to form bridges between neighbouring copper atoms. Our interest in the structural conformations of

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monovalent copper has led to the study of a series of copper halide complexes with tertiary phosphines,[1] and heterocyclic thiones[2] as well as mixed ligand complexes possessing ligands of both these classes of compounds,[3] the preparations being almost always carried out in acetonitrile solutions. Within this field of research we have also investigated several copper(I) oxoanion compounds[4] since they are readily prepared in solvents other than acetonitrile from the corresponding copper(II) salts by *in situ* reduction. In this respect and in view of the rather limited data on copper(I) sulfate compounds[5] we launched a more detailed study on the behaviour of copper sulfates. The main feature of the prepared compounds is the presence of alkyl sulfate counteranions instead of the expected sulfate bisanions. Furthermore, the rows formed by the tetrahedal cations and the corresponding counteranions are cross-linked by hydrogen bonds through water molecules, thus giving rise to an interesting, extended three-dimensional structure.

EXPERIMENTAL

Materials and measurements

Copper(II) sulfate (Merck), triphenylphosphine (BDH) and the thiones used, *i.e.*, pyridine-2-thione (pytH) and quinoline-2-thione (quintH) (Aldrich) were used as obtained. Reagent grade alcohols (95% ethanol, propanol, butanol) and chloroform were used as solvents. Reactions were carried out in air without any precausions to exclude moisture from the reaction medium. Infrared spectra were recorded in KBr pellets on a Perkin Elmer 1430 spectrometer; electronic spectra were recorded on a Shimadzu 160A spectrophotometer and ^1H NMR spectra were obtained in deuterated chloroform, relative to internal TMS standard, on a Bruker AW 80 spectrometer.

Preparative

Syntheses were carried out in alcoholic media and follow the presently described route which refers to the reaction which led to the preparation of the compound structurally characterized.

Copper(II) sulfate (1 mmol) was initially suspended in 20 cm^3 of 95% ethanol and subsequently 2 mmol triphenylphosphine was added with stirring at ambient temperature. A pale green suspension was immediately formed and which was dissolved by the subsequent addition of 2 mmol of quinoline-2-thione. The colour of the solution turned orange and after 10 min of gentle heating a transparent solution resulted, and which was further refluxed for about 2 h. The viscous solution obtained was allowed to evaporate slowly at room temperature, thus depositing a microcystalline solid. Dissolving the solid product from the reaction with quinoline-2-thione in hot chloroform: ethanol (1:1) mixture and allowing it to evaporate slowly at room temperature led to the formation of light, red coloured crystals, which were subjected to X-ray structural determination.

Crystal data collection

Intensities were collected on a Enraf-Nonius CAD4F diffractometer (graphite monochromatized Mo Kα radiation) using the ω-2θ scan mode. Reference reflections showed a loss of intensity of about 7.9% during data collection; correction to the intensities was applied. Data reduction performed by the SDP VAX package.[6] Lorenz and polarization effects were corrected. Absorption correction of the $\bar{1}05$, $\bar{1}07$, $\bar{1}08$, $\bar{1}09$, $\bar{1}010$ and $\bar{1}011$ reflections was performed by a Ψ-scan; minimum transmission was 0.94.

The copper coordinates were derived from a Patterson map (SHELX86 program);[7] the other non-hydrogen atoms were located by a subsequent difference Fourier synthesis (SHELX-77).[8] NH hydrogen atoms were located by difference Fourier maps and adjusted to theoretical positions; all other hydrogen atoms were located on stereochemical grounds on the pivot atoms. All phenyl rings were treated as regular hexagons with bond lengths equal to 1.395 Å. Copper scattering factors and anomalous dispersion values were taken from *International Tables for X-ray Crystallography*,[9] while for the rest of the atoms, the values included in SHELX-77 were adopted. The oxygen atom of the water molecule is located at an inversion centre and since the symmetry of the water molecule is incompatible with it, a disorder of H_2O is observed. Collection data are given in Table 1.

The structure was refined with a full-matrix least-squares procedure, hydrogen; oxygen and the ethylsulfate carbon atoms were refined isotropically. Final atomic coordinates and equivalent thermal parameters for the non-hydrogen atoms are listed in Table 2, selected bond lengths and angles in Table 3. Molecular geometry drawings were carried out using the EUCLID package of programs.[10]

Table 1 Summary of crystal and intensity collection data

Formula	$C_{56}H_{51}CuN_2O_{4.5}P_2S_3$
fw	1045.72
a(Å)	10.69 (1)
b(Å)	13.47 (2)
c(Å)	18.75 (2)
α(deg)	75.9 (1)
β(deg)	85.6 (1)
γ(deg)	74.7 (1)
V(Å^3)	1666.5 (3)
Z	2525.5
D_{calcd} (Mg m^{-3})	1.37
Space group	$P\bar{1}$,
Crystal dimensions (mm)	0.3 x 0.24 x 0.21
Linear absorption coefficient (cm^{-1})	6.18
F(000)	1088
Radiation	Cu Kα (graphite monochromator)
Temperature (K)	297 ± 1
θ range (deg) for cell detn.	7, 12
No of reflections for cell detn.	25
θmin, θmax	2, 25
$\omega/2\theta$ scan (A)	$\Delta\omega = 0.80 + 0.35\tan\theta$
$h\ k\ l$ limits	$0 \rightarrow 10$, $0 \rightarrow 18$, $-14 \rightarrow 14$
Reflections collected	17776
Reflections with $I > 4\sigma(I)$	5114
No. of refined parameters	310
Weighting scheme $\Sigma w\|\|F_o\| - \|F_c\|\|^2$	$1/w = \sigma^2(F_o) + 0.007F_o^2$
R, R_w	0.069, 0.078
$(\Delta/\sigma)_{max}$	0.114 (N1, x)

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters for the complex

Atom	*x/a*	y/b	z/c	U(eq), Å^2
Cu	0.09855 (8)	0.13643 (6)	0.23882 (4)	0.0387 (3)
S (1)	0.32177 (17)	0.13281 (15)	0.24279 (10)	0.0493 (6)
S (2)	-0.02322 (17)	0.17815 (13)	0.34156 (9)	0.0437 (5)
P (1)	0.06893 (16)	-0.02329 (13)	0.23017 (9)	0.0388 (5)
P (2)	0.04476 (17)	0.28493 (13)	0.14296 (9)	0.0413 (5)
N (1)	0.5068 (5)	0.0869 (4)	0.3387 (3)	0.0376 (17)
N (2)	-0.1109 (6)	0.3635 (5)	0.3741 (3)	0.0418 (19)
C (1)	0.4084 (6)	0.0558 (5)	0.3171 (3)	0.041 (2)
C (2)	0.3879 (7)	-0.0416 (6)	0.3577 (4)	0.052 (3)
C (3)	0.4674 (7)	-0.1026 (6)	0.4144 (4)	0.051 (2)
C (4)	0.5739 (6)	-0.0693 (5)	0.4335 (4)	0.042 (2)
C (5)	0.6597 (7)	-0.1284 (5)	0.4906 (4)	0.050 (3)
C (6)	0.7605 (7)	-0.0912 (6)	0.5047 (4)	0.056 (3)
C (7)	0.7780 (7)	0.0038 (6)	0.4635 (4)	0.053 (3)
C (8)	0.6949 (6)	0.0649 (6)	0.4091 (4)	0.046 (2)
C (9)	0.5928 (6)	0.0284 (5)	0.3937 (3)	0.0366 (17)
C (10)	-0.0066 (6)	0.2947 (5)	0.3549 (3)	0.0348 (19)
C (11)	0.1123 (7)	0.3224 (6)	0.3521 (4)	0.045 (2)
C (12)	0.1196 (7)	0.4136 (6)	0.3677 (4)	0.054 (3)
C (13)	0.0064 (7)	0.4833 (6)	0.3874 (4)	0.049 (3)
C (14)	0.0076 (10)	0.5801 (7)	0.4056 (5)	0.069 (3)
C (15)	-0.1052 (11)	0.6436 (7)	0.4262 (6)	0.082 (4)
C (16)	-0.2200 (11)	0.6140 (7)	0.4302 (6)	0.085 (4)
C (17)	-0.2238 (9)	0.5198 (7)	0.4141 (6)	0.074 (3)
C (18)	-0.1100 (7)	0.4570 (5)	0.3904 (4)	0.046 (2)
C (19)	0.13141	-0.12993	0.30959	0.0400
C (20)	0.23156	-0.21895	0.30537	0.0546
C (21)	0.28178	-0.29186	0.36956	0.0654
C (22)	0.23186	-0.27574	0.43795	0.0654
C (23)	0.13172	-0.18672	0.44216	0.0617
C (24)	0.08149	-0.11381	0.37798	0.0507
C (25)	0.15647	-0.07179	0.15307	0.0473
C (26)	0.10457	-0.12075	0.10922	0.0736
C (27)	0.17885	-0.15809	0.05223	0.1034
C (28)	0.30502	-0.14648	0.03910	0.1029
C (29)	0.35692	-0.09752	0.08295	0.0806
C (30)	0.28265	-0.06017	0.13994	0.0641
C (31)	-0.09387	-0.03824	0.22278	0.0473
C (32)	-0.18633	0.04649	0.18265	0.0640
C (33)	-0.31157	0.03694	0.17630	0.0745
C (34)	-0.34436	-0.05735	0.21009	0.0777
C (35)	-0.25190	-0.14209	0.25022	0.0753
C (36)	-0.12666	-0.13253	0.25657	0.0692
C (37)	0.13778	0.26863	0.05860	0.0491
C (38)	0.13388	0.18064	0.03289	0.0703
C (39)	0.20580	0.15979	-0.02949	0.0798
C (40)	0.28163	0.22693	-0.06616	0.0930
C (41)	0.28553	0.31491	-0.04046	0.1116
C (42)	0.21361	0.33576	0.02192	0.0758
C (43)	-0.12402	0.32601	0.11289	0.0476
C (44)	-0.22202	0.30982	0.16458	0.0629
C (45)	-0.35055	0.33669	0.14226	0.0796
C (46)	-0.38108	0.37975	0.06825	0.0755
C (47)	-0.28308	0.39594	0.01656	0.0720
C (48)	-0.15455	0.36907	0.03888	0.0554
C (49)	0.07359	0.40532	0.15965	0.0507

Table 2 Continued

Atom	x/a	y/b	z/c	U(eq), Å^2
C (50)	0.19842	0.40594	0.17608	0.0627
C (51)	0.22064	0.49571	0.19201	0.0775
C (52)	0.11803	0.58485	0.19150	0.0927
C (53)	-0.0068	0.58422	0.17508	0.1101
C (54)	-0.02902	0.49446	0.15915	0.0811
S (3)	0.51718 (17)	0.36736 (16)	0.35771 (12)	0.0540 (7)
				U, Å^2
O (1)	0.6423 (8)	0.3319 (6)	0.3846 (5)	0.113 (2)
O (2)	0.4782 (8)	0.3100 (6)	0.3147 (4)	0.112 (2)
O (3)	0.4862 (9)	0.4823 (7)	0.3186 (5)	0.127 (3)
O (4)	0.4294 (13)	0.3739 (10)	0.4217 (8)	0.198 (5)
O (5)	1/2	1/2	1/2	0.285 (12)
C (55)	0.5780 (18)	0.5090 (15)	0.2595 (10)	0.168 (6)
C (56)	0.557 (2)	0.6325 (17)	0.2282 (12)	0.192 (8)

U(eq) = 1/3 of the trace of the orthogonalized U. The atoms from O1 to C56 were refined isotropically. Carbons in the phenyl rings were converted into regular hexagonal arrays with C– equal to 1.395 Å, and treated as rigid groups.

RESULTS AND DISCUSSION

Spectroscopic characterization

The compounds are either yellow (pyridine-2-thione complexes) or red (quinoline-2-thione) microcrystalline substances behaving as 1:1 electrolytes in 10^{-3} M methanol and ethanol solutions. Even in these media the compounds tend to precipitate. Lower solubilities are observed in chloroform and related solvents.

The IR spectra of the compounds show broad medium intensity bands in the region 3300–3200 cm^{-1} attributed to ν(NH), indicative therefore of S-coordinated thiones; furthermore split medium-to-strong intensity bands in the region 1110 and 980 cm^{-1} attributed to the ν_3 and ν_1 vibrations of SO_4 are indicative of an asymmetric SO_4 unit. The coordination of triphenylphosphine is verified by the presence of characteristic bands in the region 740–680 cm^{-1} which are slightly shifted relative to those observed for the free ligand.

^{1}H NMR spectra serve as a further verification of the sulfur coordination of the thione ligands. The imino proton resonance signal is not observed, probably due to participation in hydrogen bond formation. It should be noted that during multiple scanning measurements for its location, the compounds precipitated in the nmr tube. The aromatic protons of both ligands give rise to a complicated pattern in the region 6.62–8.04 ppm within which it is practically impossible to carry out a assignment. The compounds prepared in ethanol present a quartet at 4.12 ppm and a triplet at 1.32 ppm, in close analogy with the characteristic pattern of ethyl protons in diethyl sulfate (4.3 and 1.4 ppm, respectively). Analogous studies of the spectra of compounds prepared in isopropanol and butanol reveal that in these cases the corresponding alkyl sulfates play the role of the counteranion. The peaks observed are 4.04 ppm (1H,s), 1.28 (6H,d) and 3.78 (2H,m), 1.53 (4H,m), 1.04 (3H,m), respectively.

The electronic spectra of the pyridine-2-thione complexes present three distinct bands in the regions 356–360 (ε ranging between 9000 and 11000 M^{-1} cm^{-1}),

Table 3 Selected bond distances (angstroms) and angles (degrees)

Coordination sphere			
Cu-S(1)	2.380(2)	S(1)-Cu-S(2)	114.24(7)
Cu-S(2)	2.3405(19)	S(1)-Cu-P(1)	112.34(7)
Cu-P(1)	2.3006(19)	S(1)-Cu-P(2)	96.37(7)
Cu-P(2)	2.3156(18)	S(2)-Cu-P(1)	105.95(7)
		S(2)-Cu-P(2)	106.89(7)
Quinoline-2-thione		P(1)-Cu-P(2)	121.16(7)
S(1)-C(1)	1.692(6)		
C(1)-C(2)	1.410(10)		
C(2)-C(3)	1.368(11)		
C(3)-C(4)	1.427(10)		
C(4)-C(5)	1.404(10)		
C(4)-C(9)	1.403(9)		
C(5)-C(6)	1.369(11)		
C(6)-C(7)	1.375(11)		
C(7)-C(8)	1.361(10)		
C(8)-C(9)	1.385(10)		
C(9)-N(1)	1.377(8)		
N(1)-C(1)	1.352(9)		
		Cu-S(1)-C(1)	118.5(2)
S(2)-C(10)	1.704(7)	Cu-S(2)-C(10)	110.4(2)
C(10)-C(11)	1.410(10)		
C(11)-C(12)	1.353(11)		
C(12)-C(13)	1.408(11)		
C(13)-C(14)	1.429(12)		
C(13)-C(18)	1.374(11)		
C(14)-C(15)	1.371(15)		
C(15)-C(16)	1.378(17)		
C(16)-C(17)	1.385(14)		
C(17)-C(18)	1.396(12)		
C(18)-N(2)	1.369(9)	Cu-P(1)-C(19)	112.55(8)
N(2)-C(10)	1.337(9)	Cu-P(1)-C(25)	113.53(8)
		Cu-P(1)-C(31)	120.32(9)
		C(19)-P(1)-C(25)	103.16(9)
Triphenylphosphine		C(19)-P(1)-C(31)	101.89(8)
		C(25)-P(1)-C(31)	103.40(8)
P(1)-C(19)	1.8251(17)	Cu-P(2)-C(37)	112.88(9)
P(1)-C(25)	1.8227(17)	Cu-P(2)-C(43)	116.27(9)
P(1)-C(31)	1.8232(18)	Cu-P(2)-C(49)	115.24(8)
P(2)-C(37)	1.8307(17)	C(37)-P(2)-C(43)	103.47(8)
P(2)-C(43)	1.8321(19)	C(37)-P(2)-C(49)	103.68(9)
P(2)-C(49)	1.8299(18)	C(43)-P(2)-C(49)	103.80(9)

280–284 (ε between 22000 and 35000) and 215–221 nm (ε from 43000 to 52000) respectively. The second band is generally asymmetric with a shoulder appearing clearly in the ethylsulfate compound at 262 nm. Investigation of the spectra derivatives verifies the presence of an absorbtion in the region 260–265 nm. The great similarity of the spectra apparently originates from the common tetrahedral copper(I) environment. The complexes of quinoline-2-thione possess an analogous chromophore and the general pattern of the spectra is similar. The bands observed are in the regions 382–387 (ε ranging between 10000 and 13000), 272–278 (ε between 19000 and 27000) and 224–228 nm (ε from 41000 to 49000), respectively.

Crystal structure

The molecular structure of the title compound is presented in Figure 1; the packing within the unit cell is depited in Figure 2. The local metal environment is an irregular tetrahedron with unequally bonded ligands, a feature common to other cationic complexes of the formula $[Cu(tzt)_2(PPh_3)_2]^+$ as well.[4b,11] The close resemblance of the overall geometry as well as the individual bond length and bond angle differences with respect to the closely related compounds $[Cu(pyrimidine\text{-}2\text{-}thione)_2(PPh_3)_2](ClO_4)$ and $[Cu(thiazoline\text{-}2\text{-}thione)_2(PPh_3)_2](NO_3)$, which will be refered to as complexes **I** and **II**, respectively, will be presently discussed. Structures of other mononuclear monovalent copper sulfates are not similar since they correspond to three-coordinate copper ligated to sulfur donating molecules[5] and, furthermore, the packing within the unit cell is rather simple, probably due to the absence of an extensive hydrogen bonding network.

In all three complexes the two phosphine ligands reveal different degrees of

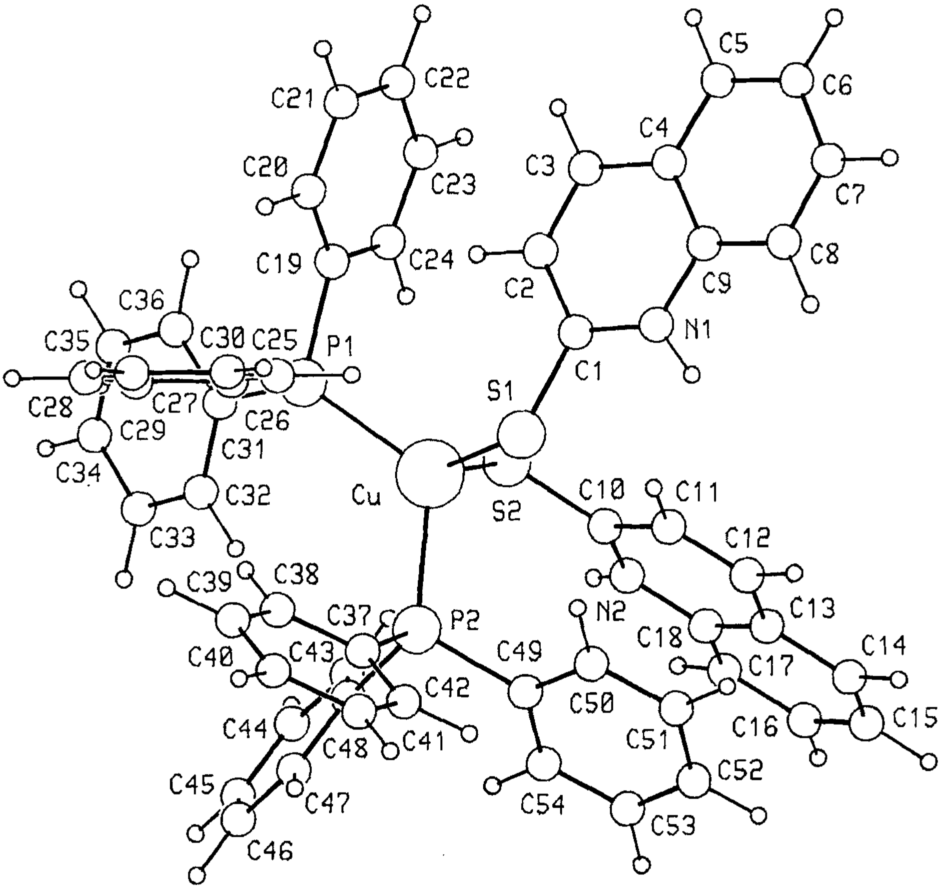


Figure 1 An ORTEP view of the cationic unit $[Cu(quinoline\text{-}2\text{-}thione)_2(PPh_3)_2]^+$ with atom numbering.

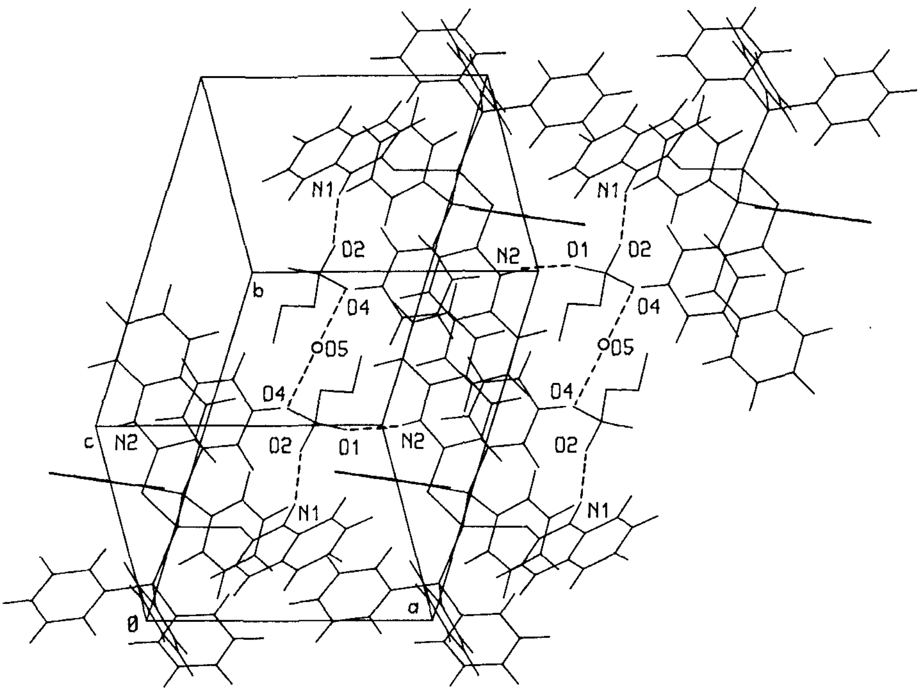


Figure 2 Representation of the packing within the crystal unit.

interaction to the metal reflected in the different Cu-P bond lengths which usually differ by 15–20 pm. The two Cu-P bond lengths are indeed 2.301(1) and 2.316(0) Å, identical to 2.301(1) and 2.315(1) Å in **I** and close to 2.292(1) ans 2.310(1) Å in **II**. In all the compounds the phosphine ligand more strongly bound to the metal is subject to the most pronounced stereoelectronic interactions which are reflected in the wide range of the P—C distances and C—P—C bond angles, relative to the less strongly bound phosphine. An expected difference between the two unequally bonded phosphine ligands is that the more strained one adopts shorter meant P—C bond distances, though individual values vary significantly and smaller mean C—P—C angles (C—P 1.820 to 1.837 in **I**, 1.834–1.844 in **II**, mean C—P—C angle *ca* 103° in both complexes) than those in the less strained one (C—P 1.820–1.824 in **I** and 1.842–1.849 in **II**, mean C—P—C angles *ca* 103.5° in both cases but individual values not so widespread). In the present compound the more weakly metal-bonded phosphine ligand is under the close influence of a quinoline-2-thione molecule, the corresponding S—Cu—P angle (96.37 (7)°) being the smaller within the chromophore; consequently smaller differeces in the mean P—C bond lengths and C—P—C angles are observed and individual values do not varying significantly (see Table 3).

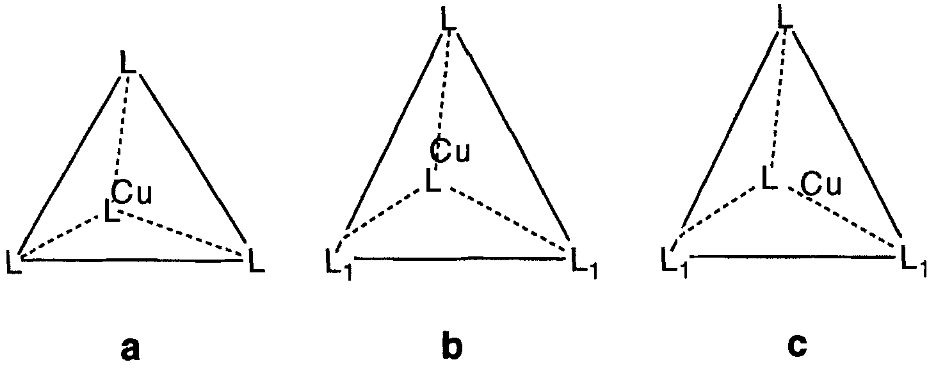
The tetrahedral environment around copper is flattened towards the side of the two phosphine ligands as an effect of their enhanced steric demands; the P—Cu—P angle is 121.16 (7)° and represents the largest deviation of the ideal tetrahedral arrangement around the metal atom. This value is close to analogous values of

121.5(0)° and 123.2(0)° observed in **I** and **II**, respectively. The dihedral angle between the Cu—P(1)—P(2) and Cu—S(1)—S(2) planes is 84.8°. Interactions of the two quinoline-2-thione ligands are comparable to those between the thiazoline-2-thione ligands in **II** and larger than those between pyridine-2-thione molecules in **I**, as envisaged through the corresponding S—Cu—S angle (114.24(0)°) in the present case and 101.3(0)° and 115.4(0)° in **I** and **II**, respectively.

Both ions present in the crystal unit participate in hydrogen bonding, in which crystalline water molecules are involved as well. In this way infinite chains are formed along *a*. The cations are connected along this axis through intermolecular hydrogen bonds with anions: N(2)-H . . . $O(1)^i$, $i = x - 1, y, z$, 2.77 (2) Å. Two parallel chains thus formed are linked through two neighbouring anions, the connections being provided by a water molecule located on an inversion centre (at 1/2, 1/2, 1/2); the oxygen atom O(5) of the water molecule occupies the inversion centre [N(1)-H . . . O(2), 2.86 (2) Å and O(4)-H . . . O(5), 2.79 (2) Å]. Owing to the special position of the water molecule, which is not compatible with an inversion centre, disorder results in its location.

Computational considerations

The salient feature of the title compound structure as well as of complexes **I** and **II** discussed already is the departure of the copper atom from the centre of the tetrahedron defined by the two sulfur and two phosphorus atoms of the chromophore towards one of its edges, *i.e.*, a tendency towards a two-coordination scheme. Such a property of copper(I), especially in "soft" environments provided by neighbouring S atoms, has been observed in several copper-containing solids and has been dealt with by Extended Hückel calculations.[12] In an analogous treatment the construction of a symmetric tetrahedral $Cu(S{=}CH_2)_2(PMe_3)_2$ cation adopting the mean values of the Cu—S and Cu—P bonds observed in the three abovementioned compounds was followed by the displacement of the copper atom along the bisector of one P—Cu—S angle (Scheme 1 (c)). A maximum displacement of 3 pm was investigated in steps of 0.5 pm. The net atomic charges and the Cu—P and



Scheme 1 (a) Regular tetrahedron with four identical ligands L; (b) symmetrically distorted tetrahedron with two sets of ligands, L and L_1; (c) displacement of the central copper atom towards an edge of a asymmetric $CuL_2(L_1)_2$ tetrahedron.

Cu—S overlap populations appeared insensitive to this movement, the latter being uniformly shifted to higher and lower values for the atoms approaching and departing from copper, respectively, not exceeding at the most 0.006 e. An overall orbital stabilization of 11.5 kJ mol^{-1} was calculated but the individual energy levels were only slightly affected both in energy and in constitution during this process. Core-core repulsions, providing a stabilization of 21.5 kJ mol^{-1}, seem to be more important in defining the final position of the metal atom within the chromophore.

Supplementary data

Full lists of H coordinates, thermal parameter, bond lengths, angles and observed and calculated structure factors are available from the authors upon request.

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