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X-RAY CRYSTAL STRUCTURE OF (TETRAPHENYLDITHIOIMIDODIPHOSPHINATO) (TRIPHENYLPHOSPHINE)COPPER(I), $(Ph_3P)Cu(SPPh_2)_2N$, A MONOCYCLIC INORGANIC (CARBON-FREE) CHELATE RING COMPOUND

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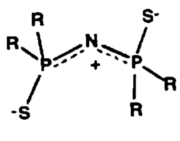
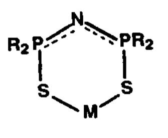
Abstract—The mononuclear $(Ph_3P)Cu(SPPh_2)_2N$ compound was prepared by reacting $(Ph_3P)_2CuNO_3$ with $K[(SPPh_2)_2N]$ in $MeOH/CHCl_3$ solvent mixture. The ^{31}P NMR spectrum has confirmed the loss of a triphenylphosphine molecule and the formation of the title compound. The crystal and molecular structure was determined by X-ray diffractometry. The compound is monoclinic, space group $P2_1/c$, $a = 18.826(2)$, $b = 10.619(2)$, $c = 20.587(2)$ Å, $\beta = 112.46(2)°$, $V = 3803.6(8)$ Å^3, $Z = 4$. The lattice contains monomeric $(Ph_3P)Cu(SPPh_2)_2N$ units, with three-coordinated copper(I) atoms in a distorted trigonal geometry [S(1)—Cu—S(2) 121.5(1), S(1)—Cu—P(3) 126.1(1) and S(2)—Cu—P(3) 112.2(1)°]. The dithioligand is monometallic biconnective and within the resulted CuS_2P_2N inorganic ring the Cu—S [2.215(2), 2.258(2) Å], S—P [2.017(2), 2.012(3) Å] and P—N [1.582(5), 1.592(5) Å] bond lengths suggest a π-electron delocalization over the P—N—P fragment. The conformation of the six-membered ring is non-planar.

Among the ligands able to form inorganic (carbon-free) chelate rings,[1] tetra-alkyl(aryl) dithioimidodiphosphinates, $[(SPR_2)_2N]^-$, are some of the most versatile. Although the non-coordinated anion, e.g. in the potassium(18-crown-6) salt,[2] displays an *anti* conformation (**1**), the molecular skeleton is flexible enough to rotate into a *syn* conformation and to form six-membered chelate rings (**2**). Several transition metal and main group metal chelates have been described,[1] and a renewed interest towards these systems is manifest in a series of recent publications.[3]



1



2

Although copper(II) complexes $Cu[(SPR_2)_2N]_2$ ($R = Me, Ph$) have been isolated (and investigated as potential models for copper enzymes),[4] dithioimidodiphosphinates (like other thio ligands) tend to reduce this metal to the copper(I) oxidation state. Thus, the reaction of copper(II) chloride with $Na[(SPR_2)_2N]$ produces several cluster complexes, including tetranuclear $[Cu^I_4\{(SPPh_2)_2N\}_3][Cu^ICl_2]\cdot CCl_4$, and trinuclear $[Cu_3^{I,II}\{(SPPh_2)_2N\}_4]$ and $[Cu^I_3\{(SPPh_2)_2N\}_3]$[5]. The structure of $[\{Cu_4(SPPh_2)_2N\}][CuCl_2]\cdot CCl_4$ has been investigated by X-ray diffraction.[5a,b] Obviously, in the monocyclic system **2**, with $M = Cu^I$, coordinative saturation of the metal would not be achieved. The formation of the tetranuclear complex, which contains an adamantane type Cu_4S_6 core, allows each copper atom to be connected to three sulphur

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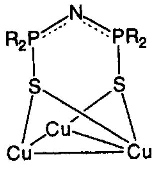
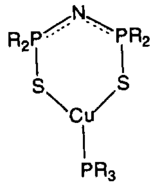
atoms, in addition to the (weak) metal–metal bonds. The resulting structure is rather complex, with the ligand coordinated in a trimetallic tetraconnective fashion on each triangular Cu_3 face of the tetrahedron,[5a,b] as shown in **3**.



3

We were interested in preparing a monocyclic CuS_2P_2N ring system, and to prevent cluster formation, by blocking the unfilled coordination sites in **2** with the aid of additional triphenylphosphine, coordinated to the metal. Thus, the compound **4** (R = Ph) has been obtained, and we now report its molecular structure.



4

RESULTS AND DISCUSSION

The reaction between bis(triphenylphosphine) copper(I) nitrate and potassium tetraphenyldithioimidodiphosphinate in methanol–chloroform, produced the ring compound **4**, via loss of one molecule of triphenylphosphine:

$$\mathrm{(PPh_3)_2CuNO_3 + K(SPPh_2)_2N \rightarrow \underset{\mathbf{4}}{Ph_3PCu(SPPh_2)_2N} + PPh_3 + KNO_3.} \tag{1}$$

The compound is a colourless, crystalline solid (m.p. 234.6–235.3°C), moderately soluble in several common organic solvents, e.g. chloroform. The ^{31}P NMR spectrum gave the first indication that only one molecule of triphenylphosphine remained coordinated to the metal, since the integrated intensity ratio of the $P_{\mathrm{ligand}} : P_{\mathrm{phosphine}}$ signals was 2 : 1.

A single crystal X-ray diffraction study of **4** revealed that the compound is monocyclic and contains three-coordinate copper(I). The molecular structure is shown in Fig. 1 and important interatomic distances and bond angles are listed in Table 1.

The six-membered ring is somewhat unsymmetric. The P—S bonds are equal, with interatomic distances in the range characteristic for single P—S bonds.[6] The P—N bonds are also equal within the e.s.d. measured [1.582(5) and 1.592(5) Å], but the slight difference in the Cu—S bond lengths [2.215(2) and 2.258(2) Å] seems to be significant. The P—N bond lengths are comparable with values normally observed in cyclophosphazenes, i.e. 1.58–1.60 Å,[7] and suggest a partial double bond character, i.e. a π-electron delocalization over the P—N—P fragment. With these molecular dimensions, the structural diagram **4** seems to best reflect the bonding situation in the ring.

Table 1. Important interatomic distances (Å) and bond angles (°)

Cu—S(1)	2.215(2)	P(1)—C(1)	1.817(6)
Cu—S(2)	2.258(2)	P(1)—C(7)	1.819(6)
Cu—P(3)	2.216(2)	P(2)—C(13)	1.809(6)
P(1)—S(1)	2.017(2)	P(2)—C(19)	1.806(6)
P(2)—S(2)	2.012(3)	P(3)—C(25)	1.822(6)
P(1)—N(1)	1.582(5)	P(3)—C(31)	1.821(5)
P(2)—N(1)	1.592(5)	P(3)—C(37)	1.825(6)
S(1)—Cu—S(2)	121.5(1)	S(1)—P(1)—C(1)	108.9(2)
Cu—S(1)—P(1)	100.1(1)	S(1)—P(1)—C(7)	107.0(2)
Cu—S(2)—P(2)	100.7(1)	S(2)—P(2)—C(13)	108.8(2)
P(1)—N(1)—P(2)	134.6(3)	S(2)—P(2)—C(19)	108.6(2)
S(1)—P(1)—N(1)	118.9(2)	N(1)—P(1)—C(1)	110.2(2)
S(2)—P(2)—N(1)	119.4(2)	N(1)—P(1)—C(7)	104.5(3)
S(1)—Cu—P(3)	126.1(1)	N(1)—P(2)—C(13)	108.1(3)
S(2)—Cu—P(3)	112.2(1)	N(1)—P(2)—C(19)	105.5(2)
		C(1)—P(1)—C(7)	106.5(3)
		C(13)—P(2)—C(19)	105.5(3)

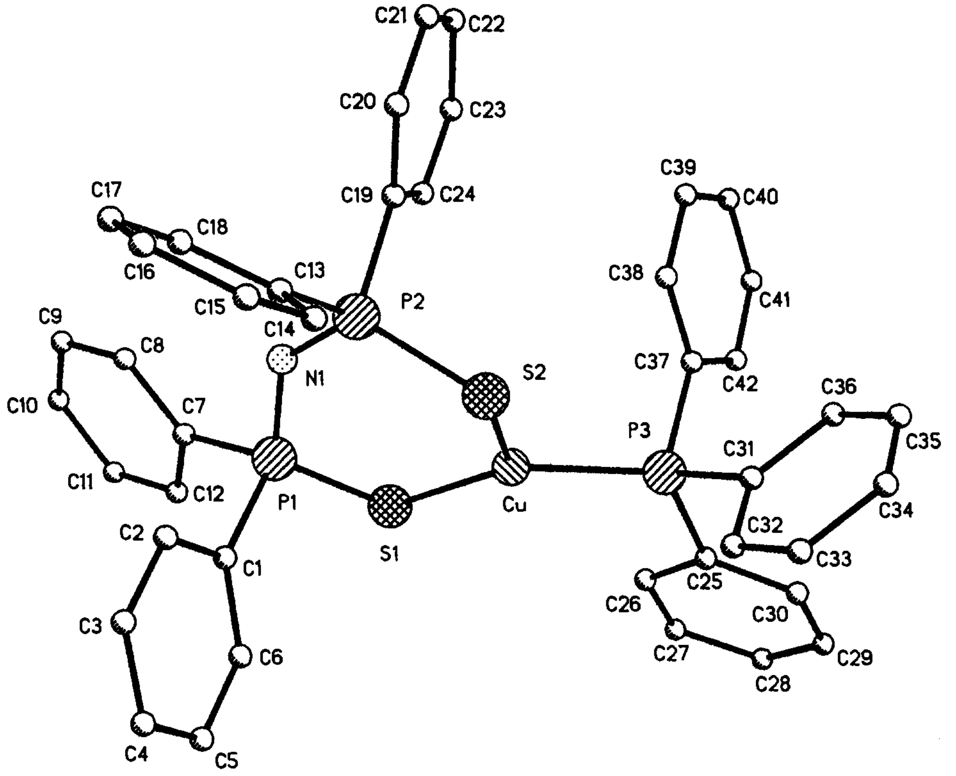


Fig. 1. ORTEP-like view of the $(Ph_3P)Cu(SPPh_2)_2N$ molecule.

The most notable difference is observed between the external bond angles S(1)—Cu—P(3) [126.1(1)°] and S(2)—Cu—P(3) [112.2(1)°], which distort the trigonal coordination geometry around the copper atom. The molecular dimensions in **4** do not differ much from those observed in the tetranuclear cluster $[Cu^I_4\{(SPPh_2)_2N\}_3]^+$. In the latter the bond lengths are: Cu—S, 2.257–2.278 Å; P—S, 2.044–2.063 Å; P—N, 1.58–1.59 Å. The bond angles are: S—Cu—S, 123.6° (average); P—N—P, 138° (average).[5b]

The six-membered CuS_2P_2N ring is non-planar and its conformation can be described as distorted boat. The distortions seem to be imposed by the bond angles observed in the ring, i.e. P—S—Cu 100.4(1)° and P—N—P 134.6°. Figure 2 clearly shows that the two sulphur atoms are on opposite sides of an imaginary P_2Cu plane, the nitrogen atom also being out-of-plane. The deviations of the sulphur and nitrogen atoms from the plane determined by two phosphorus and one copper atom are given in Table 2. The crystal packing is shown in Fig. 3.

Most dithioimidodiphosphinato complexes contain a "naked" metal atom as coordination centre and thus are bi- or tricyclic chelate complexes $[M\{(SPR_2)_2N\}_n]$, with $n = 2$ (divalent M) or 3 (trivalent M).[1] Few monocyclic compounds are known, either with organometallic coordination centres, $R_mM(SPR_2)_2N$ ($R_mM = TlPh_2$,[8] $AuMe_2$[9]) or with halogen substituents, like $X_mM(SPR_2)_2N$ ($MX_2 = AuCl_2$),[10] or mixed ligand complexes, e.g. the rhenium compounds $[ReNCl\{(SPPh_2)_2N\}(PPh_3)]$[3b] and $[ReOCl_2\{(SPPh_2)_2N\}(PPh_3)]$.[3a]

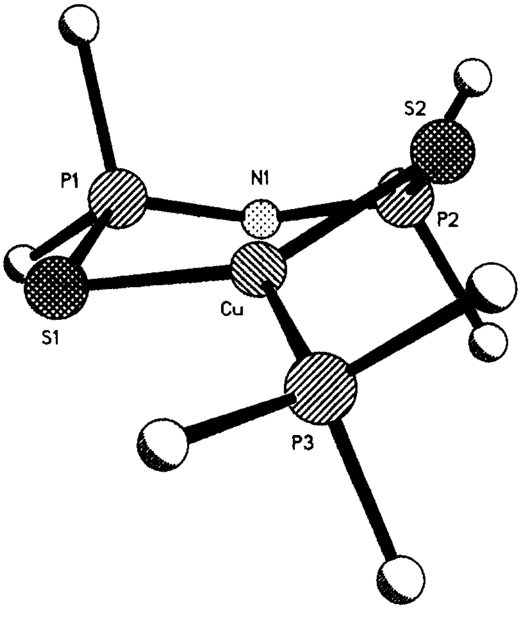


Fig. 2. Conformation of the six-membered CuS_2P_2N ring in the title compound (for clarity only *ipso* carbons of phenyl groups are shown).

Table 2. Deviations of the sulphur and nitrogen atoms from the P(1)—P(2)—Cu plane

Equation of plane: $11.169X+5.983Y+6.2732Z = 7.8686$

Deviation (Å)	
Cu	0.0000
S(1)	−0.4449
S(2)	0.8614
P(1)	0.0000
P(2)	0.0000
P(3)	−0.4905
N(1)	−0.3428

EXPERIMENTAL

Preparation of $(R_3P)Cu(SPPh_2)_2N$

A solution of 0.34 g (5 mmol) $(Ph_3P)_2CuNO_3$ dissolved in 25 cm^3 chloroform was mixed with stirring with a solution of 0.27 g (5 mmol) $K[(SPPh_2)_2N]$ dissolved in 50 cm^3 methanol. After stirring under reflux for 1 h, and leaving for 3 h at room temperature, a white solid deposited and was filtered and the filtrate was concentrated, to deposit a colourless crystalline material. Yield 0.35 g. $(PPh_3)Cu(SPPh_2)_2N$, m.p. 234.6–235.4°C. Found: C, 65.1; H, 4.5; N, 1.8. Calc. for $C_{42}H_{35}CuNP_3S_2$: C, 64.4; H, 4.5; N, 1.8%. ^{31}P NMR (δ, in $CDCl_3$, rel. to 85% H_3PO_4): 35.5 (s, SPNPS), −0.7 (s, PPh_3). IR (KBr pellets, cm^{-1}): 1478s, 1435vs (Ph), 1223s ($\nu_{as}P_2N$), 1092s, 1024m, 906m, 790m (Ph), 740s, 695vs (νPC), 565 (νPS), 518vs, 503s, 490s (Ph). Mass spectrum (FAB, high resolution): M, 774.1628; Calc. 774.3. Also observed: m/z 512 ($M-PPh_3$, 48.6%), 480 ($M-Ph_3-S$, 15%), 262 (PPh_3, 100%).

Crystallographic data

$C_{42}H_{35}CuNP_3S_2$, $M = 774.3$, monoclinic, space group $P2_1/c$; $a = 18.826(2)$, $b = 10.619(2)$, $c = 20.587(2)$ Å, $\beta = 112.46(2)°$; $V = 3803.6(8)$ Å^3; $Z = 4$; $D_{calc} = 1.352$ g cm^{-3}, absorption coefficient 0.841 mm^{-1}, $F(000) = 1600$. A colourless crystal of the dimensions 0.68 × 0.36 × 0.22 mm was measured at 293 K on a Siemens P3/PC four-circle diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Within the 2θ range from 3.0 to 60.0° 11,122 reflections were collected, of which 10,817 were independent reflections ($R_{int} = 2.16\%$) and 4289 with $F > 4.0\sigma(F)$ were used in calculations. The structure was solved by direct methods and full-matrix least square refinement of data. The quantity minimized was $\Sigma[w(F_0-F_c)^2]$ with weights $w^{-1} = \sigma^2(F)+0.0008F^2$. The residual electron density was in the range −0.44 to 0.51 e Å^{-3}. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms positioned geometrically but not refined. Further details of the crystal structure investigation are available as supplementary material, which was deposited with the Cambridge Crystallographic Data Centre.

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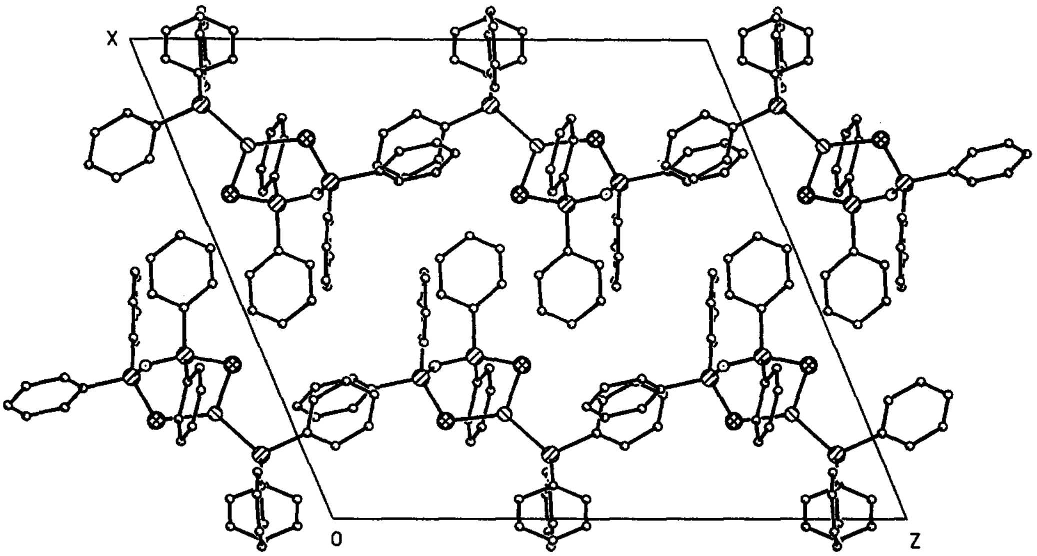

Fig. 3. Crystal packing of $(Ph_3P)Cu(SPPh_2)_2N$.

"Babeş-Bolyai" University of Cluj-Napoca, Romania, for a leave of absence.

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