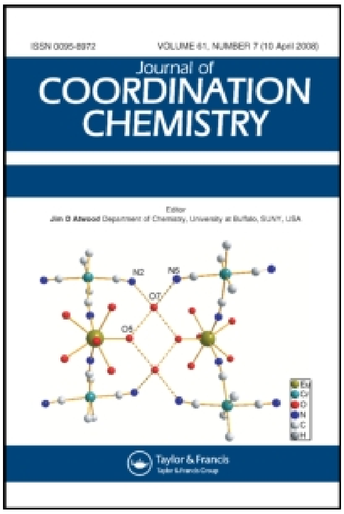

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Transition Metal Complexes with Thiosemicarbazide-Based Ligands. Part 37.* Synthesis and Study of the first Thiosemi-Carbazide-Derived Copper(I) Complexes: Crystal Structure of [2-(Diphenylphosphino)Benzaldehyde Thiosemicarbazonato(-1)] Copper(I)-Nitrate-Methanol Solvate

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TRANSITION METAL COMPLEXES WITH THIOSEMICARBAZIDE-BASED LIGANDS. PART 37.* SYNTHESIS AND STUDY OF THE FIRST THIOSEMI-CARBAZIDE-DERIVED COPPER(I) COMPLEXES: CRYSTAL STRUCTURE OF [2-(DIPHENYLPHOSPHINO)BENZALDEHYDE THIOSEMICARBAZONATO(-1)] COPPER(I)-NITRATE–METHANOL SOLVATE

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The preparation and physical characterization of two copper(I) complexes Cu(HL)NO_3 and $[Cu(HL)_2]NO_3 \cdot MeOH$ formed with a newly synthesized tridentate [S,N,P] HL = 2-(diphenylphosphino)benzaldehyde thiosemicarbazone ligand and the crystal structure analysis of the latter have been carried out. An X-ray study of $[Cu(HL)_2]NO_3 \cdot MeOH$ revealed a copper(I) ion coordinated tetrahedrally to S,N,P,P atoms donated by two HL ligands. One is tridentate [S,N,P], whereas the second HL ligand is monodentate, ligating only its phosphorus atom to the copper. The geometry around the four-coordinate Cu(I) is comparable with Cu{N,S,P,X} tetrahedra (X = N, P, or S) retrieved from the Cambridge Structural Database. In addition, with a restriction to Cu{N,P,X,X} (X = C, N, P) tetrahedra – S is excluded – *ca.* 60 structures against

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three or four cases were found to be maintained by Cu(I) ions substantiating the principal role of the phosphorus ligands in the reduction of Cu(II) to Cu(I).

Keywords: Copper(I) complexes; mono-[P] and tridentate [N,P,S] ligands; X-ray structure

INTRODUCTION

A considerable number of copper complexes with thiosemicarbazide-based ligands of different denticity have been reported.[2–4] A common characteristic of these ligands is that they stabilize copper in its usual (+2) oxidation state. The exceptions include some bidentate SN thiosemicarbazones which can also stabilize copper(I)[5] and the tetradentate N_4 2,4-pentadione bis(S-methylisothiosemicarbazone), which stabilizes copper(III).[6] We recently described[7] the structure of a square-planar nickel(II) complex $[Ni(L)Py]NO_3$, where L is a monoanion of the newly-synthesized tridentate [S,N,P] 2-(diphenylphosphino) benzaldehyde thiosemicarbazone

$$(C_6H_5)_2P{-}C_6H_4{-}CH{=}N{-}NH{-}C({=}S){-}NH_2$$

We present here the syntheses of mono- and bis(ligand) copper(I) complexes of the respective formulae $Cu(HL)NO_3$ and $[Cu(HL)_2]NO_3 \cdot MeOH$, together with the crystal and molecular structure of the latter complex. The copper(I) nuclei have been surveyed by use of the Cambridge Structural Database.[8]

EXPERIMENTAL

Preparation of $[Cu(HL)]NO_3$ and $[Cu(HL)_2]NO_3 \cdot MeOH$

$[Cu(HL)]NO_3$ A mixture of 90 mg (0.6 mmol) of $Cu(NO_3)_2 \cdot 3H_2O$ and 100 mg (~0.3 mmol) of the ligand, obtained by the previously described procedure,[7] was dissolved by heating in 5 mL of MeOH. The readily formed yellow microcrystals were filtered off and washed with MeOH. Yield: 70 mg. m.p. 210–211°C. *Anal.* Found: C, 49.71; H, 4.12; N, 11.39. *Calcd.* for $[Cu(HL)]NO_3$: C, 49.12; H, 3.71; N, 11.12%.

$[Cu(HL)_2]NO_3 \cdot MeOH$ To a warm solution of $[Cu(o\text{-phen})_3](NO_3)_2$ (215 mg; 0.27 mmol) in 5 mL of MeOH was added 100 mg (0.27 mmol) of the ligand and mildly heated for 5 min. The solution changed color from blue to green. Keeping at room temperature, to partly evaporate the solvent,

the orange single crystals of the title complex (~50 mg) then separated from the mixture of a green microcrystalline product of undefined composition by decanting with acetone. m.p. 227–228°C. *Anal.* Found: C, 55.02; H, 4.23; N, 11.46. *Calcd.* for $[Cu(HL)_2]NO_3 \cdot MeOH$: C, 55.68; H, 4.56; N, 11.09%.

Physical Methods

Magnetic susceptibilities were observed by a magnetic susceptibility balance MSB-MKI (Scherwood Scientific Ltd. Cambridge, UK), while infrared spectra (KBr disc) were recorded on a Perkin-Elmer FT-IR 1726X spectrophotometer. Melting points were determined on a Boetius HPMK 05 apparatus with correction. Molar conductivities of freshly prepared 10^{-3} M EtOH solutions were measured at room temperature using a digital conductivity meter (Jenway 4010).

X-Ray Structure Determination

$[Cu(HL)_2]NO_3 \cdot MeOH$ Formula $C_{41}H_{40}CuN_7O_4P_2S_2$, $M_r = 884.40$, crystal dimensions 0.40 × 0.20 × 0.15 mm, crystal system triclinic; space group P-1 (No. 2), Z = 2; cell dimensions: $a = 10.746(1)$ Å, $b = 12.723(2)$ Å, $c = 16.315(2)$ Å, $\alpha = 77.55(1)°$, $\beta = 85.87(1)°$, $\gamma = 72.29(1)°$, $V = 2074.9(5)$ Å^3, $\rho_{calc} = 1.416\ \mathrm{g\,cm^{-3}}$, $F(000) = 916$, graphite monochromated Mo-Kα radiation ($\lambda = 0.71070$ Å), $\mu = 0.755\ \mathrm{mm^{-1}}$ $T = 293$ K. Enraf-Nonius CAD-4 diffractometer, ω–2θ scan in the range $2.21° < \theta < 30.86°$, total 13 796 observations. Lattice parameters were refined by least-squares fit for 25 reflections ($11.46° < \theta < 12.41°$). After standard Lp correction $T_{max}/T_{min} = 1.000/0.972$ was determined by a semi-empirical psi scan.[9] Crystal decay was not indicated by standard reflections. The crystallographic phase problem was solved by direct methods using SHELXS-86.[10] The atomic positions were refined with anisotropic displacement parameters (515 variables) in F^2 mode for 13 080 unique reflections ($R_{int} = 0.0126$) using SHELXL-93.[11] Hydrogen positions were generated from idealized geometries and refined using a riding model with associated isotropic displacement parameters. The final R factors $R_1 = 0.0439$ for 6868 reflections with $I > 2\sigma(I)$, w$R^2 = 0.1038$, R_1(all data) = 0.1373 wR^2(all data) = 0.1314, $S = 1.005$, largest peak (hole) 0.371 (−0.380) e Å^{-3}. Scattering factors, including anomalous dispersions, were taken from Ref. [12]. Fractional coordinates of the non-hydrogen atoms are listed in Table I. Selected bond distances and angles are given in Table II.

TABLE I Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for non-hydrogen atoms

	x	*y*	*z*	*U*(eq)
Cu(1)	1594(1)	7794(1)	7062(1)	38(1)
P(1)	2659(1)	6883(1)	6004(1)	35(1)
P(2)	2027(1)	9319(1)	7344(1)	35(1)
S(1)	−431(1)	7608(1)	7510(1)	54(1)
N(2)	−724(3)	5806(3)	8570(2)	81(1)
C(3)	101(3)	6300(3)	8125(2)	53(1)
N(4)	1356(2)	5681(2)	8200(1)	51(1)
N(5)	2311(2)	6081(2)	7751(1)	42(1)
C(6)	3473(3)	5411(2)	7808(2)	48(1)
S(1A)	3025(1)	4978(1)	10217(1)	65(1)
N(2A)	3880(2)	6636(2)	9352(2)	62(1)
C(3A)	2881(3)	6294(2)	9671(2)	47(1)
N(4A)	1687(2)	7033(2)	9538(1)	48(1)
N(5A)	1535(2)	8105(2)	9074(1)	43(1)
C(6A)	377(3)	8769(2)	9044(2)	49(1)
C(11)	2209(2)	5606(2)	6007(2)	39(1)
C(12)	902(3)	5683(2)	5992(2)	56(1)
C(13)	521(3)	4732(3)	5994(2)	68(1)
C(14)	1438(4)	3712(3)	6014(2)	65(1)
C(15)	2731(4)	3620(2)	6047(2)	66(1)
C(16)	3130(3)	4559(2)	6036(2)	54(1)
C(21)	2923(2)	7418(2)	4896(2)	41(1)
C(22)	2970(3)	8519(2)	4654(2)	60(1)
C(23)	3175(4)	8972(3)	3826(2)	77(1)
C(24)	3313(4)	8350(3)	3224(2)	79(1)
C(25)	3258(4)	7265(3)	3449(2)	85(1)
C(26)	3068(4)	6794(3)	4281(2)	64(1)
C(31)	4321(2)	6301(2)	6439(2)	39(1)
C(32)	4529(3)	5693(2)	7274(2)	43(1)
C(33)	5789(3)	5280(2)	7590(2)	56(1)
C(34)	6839(3)	5493(3)	7115(2)	63(1)
C(35)	6633(3)	6081(3)	6306(2)	60(1)
C(36)	5403(3)	6471(2)	5968(2)	49(1)
C(41)	2073(2)	10232(2)	6310(2)	38(1)
C(42)	3170(3)	10528(2)	5974(2)	45(1)
C(43)	3155(3)	11129(2)	5152(2)	55(1)
C(44)	2066(3)	11460(2)	4674(2)	58(1)
C(45)	955(3)	11189(2)	5009(2)	58(1)
C(46)	963(3)	10571(2)	5816(2)	49(1)
C(51)	3592(2)	9150(2)	7799(2)	41(1)
C(52)	4702(3)	8412(2)	7531(2)	52(1)
C(53)	5919(3)	8265(3)	7842(2)	68(1)
C(54)	6053(4)	8827(4)	8433(3)	85(1)
C(55)	4961(4)	9546(4)	8721(3)	94(1)
C(56)	3722(3)	9732(3)	8404(2)	68(1)
C(61)	828(3)	10298(2)	7905(2)	45(1)
C(62)	99(3)	9935(2)	8594(2)	48(1)
C(63)	−912(3)	10743(3)	8914(2)	67(1)
C(64)	−1127(4)	11872(3)	8608(2)	79(1)
C(65)	−357(4)	12234(3)	7970(2)	77(1)
C(66)	592(3)	11459(2)	7613(2)	63(1)
N(10)	1541(3)	2917(3)	9331(2)	74(1)

TABLE I (*Continued*)

	x	*y*	*z*	*U*(eq)
O(11)	2089(3)	3323(2)	8697(2)	89(1)
O(12)	505(3)	3547(2)	9577(2)	87(1)
O(13)	1986(3)	1937(3)	9680(2)	112(1)
O(80)	4753(5)	2491(4)	8342(4)	173(2)
C(81)	5235(7)	2337(7)	9138(5)	177(3)

TABLE II Selected bond lengths [Å] and angles [°]

Cu(1)–N(5)	2.158(2)	P(2)–C(61)	1.842(3)	C(3A)–N(4A)	1.340(3)
Cu(1)–P(2)	2.2705(7)	S(1)–C(3)	1.699(3)	N(4A)–N(5A)	1.378(3)
Cu(1)–S(1)	2.3102(8)	N(2)–C(3)	1.325(3)	N(5A)–C(6A)	1.271(3)
Cu(1)–P(1)	2.3239(7)	C(3)–N(4)	1.338(4)	C(6A)–C(62)	1.457(4)
P(1)–C(21)	1.824(2)	N(4)–N(5)	1.377(3)	N(10)–O(13)	1.216(4)
P(1)–C(11)	1.830(2)	N(5)–C(6)	1.277(3)	N(10)–O(11)	1.246(3)
P(1)–C(31)	1.842(3)	C(6)–C(32)	1.465(4)	N(10)–O(12)	1.255(4)
P(2)–C(51)	1.821(3)	S(1A)–C(3A)	1.686(3)	O(80)–C(81)	1.386(7)
P(2)–C(41)	1.837(2)	N(2A)–C(3A)	1.311(3)		
N(5)–Cu(1)–P(2)	126.1(1)	C(41)–P(2)–Cu(1)	104.6(1)	N(5A)–C(6A)–C(62)	120.5(2)
N(5)–Cu(1)–S(1)	84.1(1)	C(61)–P(2)–Cu(1)	120.9(1)	C(12)–C(11)–P(1)	118.6(2)
P(2)–Cu(1)–S(1)	115.0(1)	C(3)–S(1)–Cu(1)	97.4(1)	C(16)–C(11)–P(1)	122.7(2)
N(5)–Cu(1)–P(1)	78.9(1)	N(2)–C(3)–N(4)	114.5(3)	C(26)–C(21)–P(1)	123.8(2)
P(2)–Cu(1)–P(1)	122.8(1)	N(2)–C(3)–S(1)	121.5(3)	C(22)–C(21)–P(1)	118.2(2)
S(1)–Cu(1)–P(1)	118.4(1)	N(4)–C(3)–S(1)	124.1(2)	C(36)–C(31)–P(1)	121.6(2)
C(21)–P(1)–C(11)	103.8(1)	C(3)–N(4)–N(5)	120.4(2)	C(32)–C(31)–P(1)	120.5(2)
C(21)–P(1)–C(31)	103.8(1)	C(6)–N(5)–N(4)	116.8(2)	C(42)–C(41)–P(2)	124.0(2)
C(11)–P(1)–C(31)	102.0(1)	C(6)–N(5)–Cu(1)	129.5(2)	C(46)–C(41)–P(2)	117.3(2)
C(21)–P(1)–Cu(1)	131.4(1)	N(4)–N(5)–Cu(1)	113.7(2)	C(52)–C(51)–P(2)	118.6(2)
C(11)–P(1)–Cu(1)	112.0(1)	N(5)–C(6)–C(32)	121.2(2)	C(56)–C(51)–P(2)	122.9(2)
C(31)–P(1)–Cu(1)	99.8(1)	N(2A)–C(3A)–N(4A)	117.6(2)	C(66)–C(61)–P(2)	118.9(2)
C(51)–P(2)–C(41)	103.2(1)	N(2A)–C(3A)–S(1A)	123.4(2)	C(62)–C(61)–P(2)	122.9(2)
C(51)–P(2)–C(61)	104.4(1)	N(4A)–C(3A)–S(1A)	118.9(2)	O(13)–N(10)–O(11)	120.5(3)
C(41)–P(2)–C(61)	101.3(1)	C(3A)–N(4A)–N(5A)	120.3(2)	O(13)–N(10)–O(12)	121.9(3)
C(51)–P(2)–Cu(1)	119.5(1)	C(6A)–N(5A)–N(4A)	115.4(2)	O(11)–N(10)–O(12)	117.5(3)

RESULTS AND DISCUSSION

Both elemental analysis and diamagnetism of a novel product (yellow microcrystals) described by stoichiometry of Cu(HL)NO_3 revealed reduction of the Cu(II) cation to Cu(I) in a reaction of warm MeOH solutions of $Cu(NO_3)_2 \cdot 3H_2O$ with the ligand 2-(diphenylphosphino)benzaldehyde thiosemicarbazone (HL). Similarly, another Cu(I) complex {[Cu(HL)$_2$]$NO_3 \cdot$MeOH} was obtained in the form of orange single crystals when warm MeOH solutions of [Cu(*o*-phen)$_3$]$(NO_3)_2$ were reacted with HL. However, in this reaction, irrespective of the 1 : 1 stoichiometric ratio of the reactants, *o*-phen was completely replaced and a bis(ligand) complex was

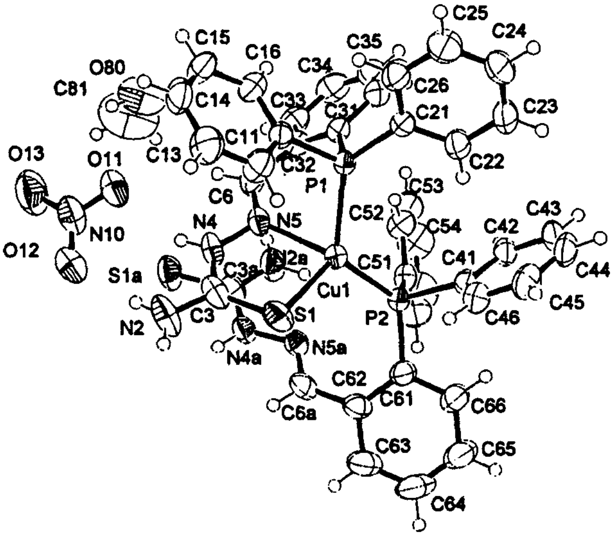

FIGURE 1 Perspective view of the structure of $[Cu(HL)_2]NO_3 \cdot MeOH$ showing thermal ellipsoids at 50% probability level and atomic numbering scheme.

formed. X-ray diffraction revealed (Figure 1) one HL molecule coordinated *via* the P,N,S set of donors, whereas the other HL acts as a monodentate ligand donating only the phosphorus atom. The measured molar conductivities of DMF solutions ($C = 10^{-3}$ M) of both complexes of about 65 S cm^2 mol^{-1} correspond to 1 : 1 electrolyte in the given solvent[13] and suggest that the NO_3 group is non-coordinated consistent with the crystal packing revealed by X-ray diffraction in the bis(ligand) complex. Non-coordination gives rise to a very strong $\nu(NO_3)$ band at 1385 cm^{-1} in the IR spectra (KBr) of both complexes. For the monoligand complex, this would mean that Cu(I) has a less common trigonal planar configuration[14] formed by the tridentate PNS-ligand. The mere fact that the synthesis is accompanied by the reduction of Cu(II) to Cu(I) suggests that the phosphorus atom is coordinated. Coordination of the S atom was concluded from the shift of the moderately strong ν(CS) band in the ligand spectrum, observed at 811 cm^{-1}, to lower energies (below 750 cm^{-1}). In contrast, the ν(CS) band in the spectrum of $\{[Cu(HL)_2]NO_3 \cdot MeOH\}$ generated by HL with a non-coordinated CS group is shifted to higher energies (825 cm^{-1}). This can be attributed to the absence of hydrogen bonds (Table III) around the free CS group in the crystal structure of $\{[Cu(HL)_2]NO_3 \cdot MeOH\}$. In the crystals of the free ligand, similar to other thiosemicarbazones[15,16] intermolecular hydrogen bonds involving CS groups can be expected.

TABLE III Hydrogen bond contacts D–H···A

	H···A (Å)	D···A (Å)	D–H···A (°)
N2–H2A···O12	2.090(4)	2.945(4)	172.7(1)
N4–H4···O11	2.031(4)	2.807(4)	149.7(1)
N4A–H4A···O12 [$-x, -y+1, -z+2$]	2.029(3)	2.878(3)	169.3(1)
O80–H80···O11	2.216(5)	2.799(5)	117.3(2)

The reduction of Cu(II) to Cu(I) in the above reactions is not surprising if one bears in mind the nature of the donor atoms P and S which, being soft bases, stabilize Cu(I) as a typical soft acid.[14] Taking into account the fact that the tridentate XNS (X = O, N) thiosemicarbazones stabilize Cu(II),[2–4] it can be concluded that the presence of the phosphorus donor atom in our ligand has a *decisive role* in the reduction of Cu(II). This should be emphasized, since it is commonly known that the tetradentate N_2S_2 thiosemicarbazones stabilize Cu(II).[2,17] Our conclusion on the role of the phosphorus ligand(s) in the reduction of Cu(II) to Cu(I) is supported by numerous crystal structures retrieved from the copper complexes archived in CSD[8] with ligands N, P, S, and/or C, respectively. A list of the relevant structures with chemical names and formulae is given in Table IV.

A search for complexes built on Cu{N,S,P,X} (X = N, P, or S) tetrahedra was performed revealing 11 structures possessing exclusively Cu(I) nuclei. Among them – similar to the title compound – five structures were found to possess Cu(I) coordinated with two Ph_3P or $MePh_2P$ ligands:

Cu{N,P,P,S}: S1,[18] S2,[19] S3,[20] S4,[21] S5.[22]

In the coordination tetrahedra of four structures, one of the P ligands is replaced either by a second sulfur or nitrogen atom:

Cu{N,P,S,S}: S6,[23] S7,[24] S8;[25]
Cu{N,N,P,S}: S9,[26]

while in two compounds Cu(I) is trigonal-planar coordinated with three different ligands:

Cu{N,P,S}: S10,[19] S11.[27]

In nine structures S1–S9 with tetrahedrally-coordinated copper(I) the Cu–P bond length varies between 2.212(8) and 2.324(2) Å with a mean value of 2.272 Å (r.m.s. is 0.026 Å). In the title compound both Cu–P

TABLE IV A list of the crystal structures (S1–S18) retrieved from CSD.[8] Each structure received a reference number when first mentioned

S1[18]	μ-dithiocyanato-tetrakis(triphenylphosphine)dicopper(I), $C_{74}H_{60}Cu_2N_2P_4S_2$
S2[19]	(N-phenylimino(2,6-dimethylphenoxy)methanethiolato)-bis(triphenylphosphine)-copper(I), $C_{51}H_{44}CuNOP_2S$
S3[20]	hydrogensulfido-pyridine-bis(triphenylphosphine)-copper(I), $C_{41}H_{36}CuNP_2S$
S4[21]	μ-dithiocyanatotetrakis(methyldiphenylphosphine)dicopper(I), $C_{54}H_{52}Cu_2N_2P_4S_2$
S5[22]	bis(triphenylphosphine)-(N-methylimino(2,6-dimethylphenoxy) methanethiolato)-copper(I), $C_{46}H_{42}CuNOP_2S$
S6[23]	tetrakis(μ-2-mercaptothiazolinato-N,S)-bis(triphenylphosphine)-tetra-copper(I), $C_{48}H_{46}Cu_4N_4P_2S_2$
S7[24]	(μ-pyridine-2-thiolato)-tris((μ-sulfido)-triphenylphosphine-copper(I))-oxomolybdenum, $C_{59}H_{49}Cu_3MoNOP_3S_4$
S8[25]	tetrakis((μ-1-3-benzoxazoline-2-thionato)-triphenylphosphine-copper(I)) toluene solvate, $C_{100}H_{76}Cu_4N_4O_4P_4S_4 + 3C_4H_8$
S9[26]	(6,7,15,16-tetrahydrodibenzo(f,m)(1,8,4,11)dithiadiazacyclotetradecine-S,N,N′)-triphenylphosphine-copper(I) perchlorate acetone solvate, $C_{36}H_{33}CuN_2P_2S_2 \cdot ClO_4 + \frac{1}{2}(C_3H_6O)$
S10[19]	bis(μ-(N-phenylimino(2,6-di-*t*-butylphenoxy)methanethiolato)-trimethylphosphito)-copper(I), $C_{50}H_{74}Cu_2N_2O_8P_2S_2$
S11[27]	bis(μ-trithiocyanuric acid)-hexakis((triphenylphosphine)-copper(I)) chloroform solvate, $C_{114}H_{90}Cu_6N_6P_6S_6 + 3CHCl_3$
S12[28]	tetrakis(trimethylphosphine)-copper(I) hexafluorophosphate, $C_{72}H_{60}CnP_4 + F_6P$
S13[29]	(acetonitrile-N)-tris(triphenylphosphine)-copper(I) perchlorate, $C_{56}H_{48}CuNP_3 \cdot ClO_4$
S14[31]	N,N′-bis(*o*-(diphenylphosphino)-benzylidene)-ethylenediamine-N,N′,P,P′-copper(I) perchlorate ethylene chloride solvate, $C_{40}H_{34}CuN_2P_2 \cdot ClO_4 + CH_2Cl_2$
S15[31]	N,N′-bis(*o*-(diphenylphosphino)-benzylidene)-ethylenediamine-N,P,P′-*t*-butylisocyanide-copper(I) perchlorate, $C_{45}H_{43}CuN_3P_2 \cdot ClO_4$
S16[33]	tris(triphenylphosphine)-(tetracyanoethylene-N)-copper(II) acetonitrile solvate, $C_{60}H_{45}CuN_4P_3 \cdot C_2H_3N$
S17[34]	(N,N′bis(2-(diphenylphosphino)phenyl)propane-1,3-diamine)-(perchlorato-O)-copper(II) perchlorate benzene solvate, $C_{39}H_{36}ClCuN_2O_4P_2 \cdot ClO_4 + C_6H_6$
S18[34]	(N,N′-bis(2-(diphenylphosphino)phenyl)propane-1,3-diamine)-(perchlorato-O)-copper(II) perchlorate dichloromethane solvate, $C_{39}H_{36}ClCuN_2O_4P_2 \cdot ClO_4 + \frac{1}{2}CH_2Cl_2$

distances of 2.271(1) and 2.234(1) Å fall in this range. However, in accordance with steric hindrance between the bulkier ligands like PPh_3 in tetrakis(triphenylphosphine) copper(I) hexafluorophosphate S12,[28] the mean Cu(I)–P bond length is much longer: 2.542 Å (r.m.s. 0.051 Å), while in S13,[29] where one of the four PPh_3 ligands is replaced by a smaller acetonitrile moiety, the mean Cu(I)–P distance for the remaining three phosphorus ligands drops back to 2.332 Å (r.m.s. is 0.014 Å). In these salts the CuP_4 tetrahedron is almost regular whereas in the title compound (Table II) it is substantially distorted: the r.m.s. of the mean bond angle (107.6°) is 20.6°. This can be attributed to two small "bite" angles, P1–Cu–N5 = 78.9(1)° and N5–Cu–S = 84.1(1)° formed within the tridentate PNS ligand. The first is formed in a constrained six-membered ring, while the second is embedded in a five-membered ring, respectively. A similarly distorted coordination tetrahedron (the mean bond angle is 106.8° with r.m.s. of 20.3°) is formed in S5[22] where, beside two monodentate PPh_3 ligands, there is a bidentate anion with a rather small S–Cu–N bite angle of 68.8(1)°.

The title compound (Figure 1) and the crystal structures with Cu{N,P,P,S} tetrahedra can also be characterized by the P–Cu(I)–P angle varying in a narrow range 122.8(1)°–126.9(6)° with a mean value of 124.7° (r.m.s. is 2.0°). As predicted by the VSEPR rules,[30] the wider P–Cu(I)–P angles in S14[31] are formed by the shorter Cu(I)–P bonds of 2.227(2), 2.219(2), 2.221(2) and 2.222(2) Å; the smaller angle of 123.7(2)° in S15[31] is closed by the longer Cu(I)–P = 2.255(5) and 2.301(5) Å bond lengths, respectively. A similar phenomenon is shown by the title compound, Cu(I)–P bond lengths 2.271(1) and 2.324(1) Å with an angle of 122.8(1)°.

CONCLUSION

The CSD search gave ample evidence of the predominant role of phosphorus ligand(s) in the reduction of Cu(II) to Cu(I) while bidentate thiosemicarbazone ligands prefer Cu(II) nuclei. To substantiate the independent "sulfur free" effect of the phosphorus ligand(s) Cu-complexes possessing CuX_4 tetrahedra with phosphorus ligands accompanied either by N, or C, or both, were also screened. In 60 crystal structures of this type there are exclusively Cu(I) nuclei. This is in agreement with Gringras and Sirianai:[5a] "with thiosemicarbazones $R^1R^2C{=}N{-}NH{-}C(S){-}NH_2$ the reaction proceeds with the reduction of Cu(II) and only Cu(I) chelates of the parent thiosemicarbazone ligand were isolated." Furthermore, the thioamido group, *e.g.* in 2-mercapto thiazoline, ligands may also give rise to a Cu(II) → Cu(I) reduction.[32] Among the complexes with phosphorus ligands, only three structures (S16,[33] S17[34] and S18[34]) were reported with a Cu(II) core. In the latter two complexes there is a common tetradentate (N,P,N,P) ligand.

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Supplementary Material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 104397. Copies of data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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