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(RECOMMENDED CITATION)

Dedicated to Professor Liviu Literat
On the occasion of his 85th birthday

NEW COPPER(I) COMPLEXES WITH ORGANOPHOSPHORUS LIGANDS WITH XPNSO SKELETON

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ABSTRACT. Salt metathesis reactions between $K[\{SP(OEt)_2\}(O_2SC_6H_4Cl\text{-}4)N]$ and the copper(I) species CuCl and $(Ph_3P)_2CuNO_3$, respectively, resulted in the new complexes $[Cu(\{SP(OEt)_2\}(O_2SC_6H_4Cl\text{-}4)N)]$ (**1**) and $[Cu(PPh_3)_2(\{SP(OEt)_2\}(O_2SC_6H_4Cl\text{-}4)N)]$ (**2**). The two compounds were characterized by multinuclear NMR (^1H, ^{13}C, ^{31}P). Single-crystal X-ray diffraction studies revealed a monomeric structure with a bidentate, monometallic biconnective behavior of the organophosphorus(V) ligand in case of compound **2**. For compound **1** the NMR spectra suggest intermolecular associations in solution.

Keywords: *Organophosphorus ligands, copper(I) complexes, structure elucidation*

INTRODUCTION

The tetraorganodichalcogenoimidodiphosphinato ligands of type $[(XPR_2)(YPR'_2)N]^-$ (X, Y = chalcogen, R, R' = alkyl, aryl, OR) were intensively studied in last decades in relation with their versatility towards main group and transition metals, as well as due to the different applications of their metal complexes in catalysis, materials science and biology [1-9]. Copper complexes with such ligands were described as structural models for the active sites in copper containing enzymes [10-12] and found applications as precursors for nanomaterials for opto-electronic devices [13,14].

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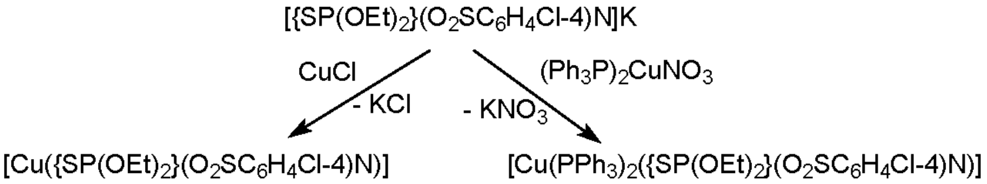
Bis(organosulfonyl)imides of type $(O_2SR)_2NH$ (R = alkyl, aryl) were also studied as ligands towards different metals, including also copper [15-17]. During last years we introduced a new type of organophosphorus ligands, respectively $[(XPR_2)(O_2SR')NH$ (X = S,O; R, R'= alkyl, aryl, OR) and we obtained several complexes with late transition metals (Cu, Au, Ag, Pd) [15,18-20]. It was observed that such ligands behave as bidentate, monometallic biconnective, *O,S*- or *N,S*- chelating units.

In order to extend our studies upon ligands containing alkoxi groups attached to phosphorus, we investigated two Cu(I) complexes with the anionic ligand $[\{SP(OEt)_2\}(O_2SC_6H_4Cl\text{-}4)N]^-$, one of them bearing two additional bulky triphenylphosphane ligands. We report here the synthesis of the complexes $[Cu(\{SP(OEt)_2\}(O_2SC_6H_4Cl\text{-}4)N)]$ (**1**) and $[Cu(PPh_3)_2(\{SP(OEt)_2\}(O_2SC_6H_4Cl\text{-}4)N)]$ (**2**), as well as their solution behavior and the single-crystal X-ray structure of compound **2**.

RESULTS AND DISCUSSION

Synthesis and spectroscopy

The new copper(I) complexes $[Cu(\{SP(OEt)_2\}(O_2SC_6H_4Cl\text{-}4)N)]$ (**1**) and $[Cu(PPh_3)_2(\{SP(OEt)_2\}(O_2SC_6H_4Cl\text{-}4)N)]$ (**2**) were prepared by salt metathesis reactions between CuCl and $(Ph_3P)_2CuNO_3$, respectively, and the potassium salt $[\{SP(OEt)_2\}(O_2SC_6H_4Cl\text{-}4)N]K$, as depicted in Scheme 1.



1 **2**

Scheme 1

Both copper(I) complexes are colorless solid species, soluble in common organic solvents. They were characterized by solution multinuclear NMR (^1H, ^{13}C, ^{31}P). The proton NMR spectra have the expected pattern for the organic groups attached either to phosphorus or to sulfur: multiplet resonances for the *ortho*, *meta* and *para* C_6H_5 protons in PPh_3, doublet resonances for the *ortho* and *meta*, respectively, protons in the C_6H_4Cl-4 group attached to sulfur. The ethoxy protons give two resonances in a 2:3 ratio, with aspect of a doublet of quartets (CH_2) and a triplet (CH_3), as result of the proton-proton and phosphorus-proton couplings. In case of the copper complex **1** the ^1H NMR spectrum contains two sets of resonances both for the CH_2 and the

C*H*$_3$ protons, suggesting the non-equivalence of the ethyl groups in solution. Moreover, in both compounds the C*H*$_2$ protons in the ethyl groups appear as AB spin systems, due to diastereotopicity. In compound **1** two AB spin systems are present, one of them centered at δ 3.92 ppm and the other at δ 4.40 ppm, in accordance with the non-equivalent O*Et* groups, while in compound 2 one AB spin system centered at δ 3.73 ppm was observed. The aspect of the resonances corresponding to the C*H*$_2$ protons is complex, due to the proton-proton and phosphorus-proton couplings in combination with the AB spin systems.

For both species, the ^{13}C NMR resonances appear as singlets for the organic groups attached to sulfur and as doublets in case of the organic groups attached to phosphorus, due to the phosphorus-carbon couplings. The ^{13}C NMR spectrum of compound **1** contains in the aliphatic region a doublet resonance for the *C*H$_3$ carbons and two doublet resonances for the *C*H$_2$ carbons. This is in accordance with the nonequivalence of the O*Et* groups attached to the same phosphorus atom, assuming that the two *C*H$_3$ groups have, by coincidence, the same chemical shift.

Only one ^{31}P resonance was observed for complex **1** (δ 45.08 ppm), while for compound **2** two broad resonances were observed, one of them at δ 48.06 ppm, corresponding to the P(V) atom, and the other at δ -4.52 ppm, corresponding to the PPh$_3$ ligands, in a 1:2 ratio. The δ(^{31}P) values are shifted in comparison with the starting materials.

Copper(I) is expected to be either di-coordinated in a linear environment, trigonal-planar, or tetra-coordinated with a tetrahedral environment, depending on the ligands in a molecular unit. Such a coordination geometry can not be realized only by a bidentate chelating ligand. Taking into account the NMR observations for compound **1**, we assume that the non-equivalence of the O*Et* groups in the molecular unit might be the result of an intermolecular interaction of one *O*Et oxygen atom with a neighboring molecule, as was also previously observed in K[(SPPh$_2$){OP(OEt)$_2$}N]·H$_2$O [21]. The [{SP(OEt)$_2$}(O$_2$SC$_6$H$_4$Cl-4)N]$^-$ units can behave as a bimetallic triconnective ligand (Figure 1) resulting in an oligomeric (dimeric, trimeric, etc.) or a polymeric structure, the latter being less probable taking into account the good solubility of compound **1** in common organic solvents.

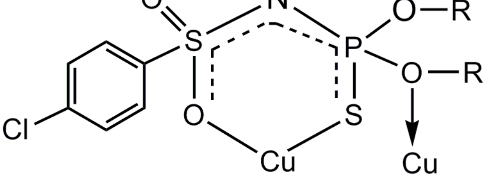


Figure 1. Proposed coordination pattern of the ligand in compound **1**

Single-crystal X-ray diffraction studies

For compound **2** the molecular structure was determined by single-crystal X-ray diffraction. The Ortep-like diagram with the atom numbering Scheme is given in Figure 2, while important interatomic distances and angles are given in Table 1.

Table 1. Important interatomic distances (Å) and angles (deg.) in **2**.

Cu(1)–O(1)	2.231(3)	O(1)–Cu(1)–P(1)	96.96(10)
Cu(1)–P(1)	2.2638(11)	O(1)–Cu(1)–P(2)	112.54(10)
Cu(1)–P(2)	2.2751(12)	P(1)–Cu(1)–P(2)	126.67(4)
Cu(1)–S(2)	2.3611(14)	O(1)–Cu(1)–S(2)	102.30(9)
N(1)–P(3)	1.527(5)	P(1)–Cu(1)–S(2)	115.04(5)
N(1)–S(1)	1.584(5)	P(2)–Cu(1)–S(2)	101.22(5)
O(1)–S(1)	1.437(4)	P(3)–N(1)–S(1)	136.3(3)
O(2)–S(1)	1.435(4)	P(3)–S(2)–Cu(1)	105.83(7)
O(3)–P(3)	1.612(4)	S(1)–O(1)–Cu(1)	127.3(2)
O(4)–P(3)	1.570(4)		
P(3)–S(2)	1.9364(18)		

The compound has a monomeric structure, with a distorted tetrahedral coordination geometry around copper. The anionic ligand acts as a *S,O* bidentate monometallic biconnective moiety.

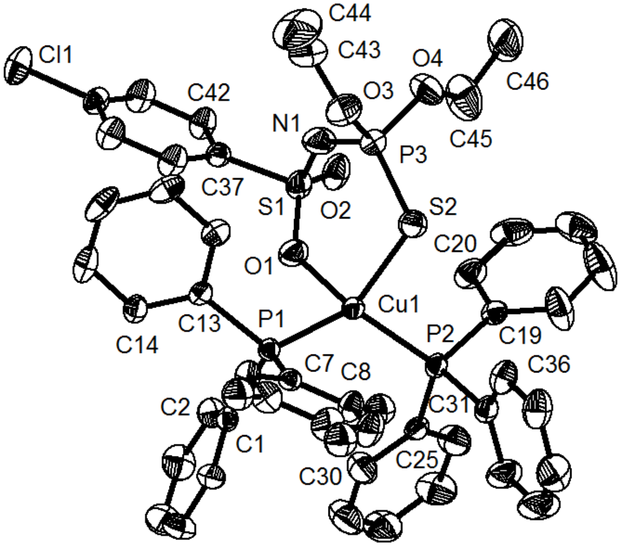


Figure 2. Ortep-like diagram with 30% probability elipsoids of compound **2**. Hydrogen atoms are omitted for clarity.

The Cu–S and Cu–O interatomic distances [Cu(1)–S(2) 2.3611(14) Å and Cu(1)–O(1) 2.231(3) Å] are of similar magnitude with those found in the related complexes [$(Ph_3P)_2Cu\{(SPPh_2)(O_2SMe)N\}$] (Cu–S 2.3912(11) and Cu–O 2.188(2) Å) and [$(Ph_3P)_2Cu\{(SPPh_2)(O_2STol\text{-}p)N\}$] $0.5C_6H_5CH_3$ (Cu–S 2.3761(18) and Cu–O 2.160(4) Å] [19]. The phosphorus–sulfur bond length [P(3)–S(2) 1.9364(18) Å] and the phosphorus–nitrogen interatomic distance [P(3)–N(1) 1.527(5) Å] are shorter than those observed in the related compounds [$(Ph_3P)_2Cu\{(SPPh_2)(O_2SMe)N\}$] [1.9886(14) and 1.602(3) Å] and [$(Ph_3P)_2Cu\{(SPPh_2)(O_2STol\text{-}p)N\}$]$\cdot 0.5C_6H_5CH_3$ [1.995(2) and 1.605(6) Å]. They are also different than those found in the free acid $\{SP(OEt)_2\}(O_2SC_6H_4Cl\text{-}4)NH$ [P–N 1.683(3) and P=S 1.9138(11) Å] [18].

The sulfur–nitrogen interatomic distance [S(1)–N(1) 1.584(5) Å] is longer than in the above mentioned complexes [1.552(3) and 1.558(6) Å]. The sulfur–oxygen bond lengths [S(1)–O(1) 1.437(4) and S(1)–O(2) 1.435(4) Å] are almost equal and in the range found for the other two copper complexes mentioned above [1.427(1) – 1.446(1) Å] [19]. The bond lengths suggest the delocalization of the π electrons on the SPNSO skeleton. The six-membered $CuOS_2PN$ ring exhibits a twisted boat conformation with S(1) and S(2) in apices.

CONCLUSIONS

Our studies revealed a bidentate monometallic biconnective behavior of the anionic organophosphorus ligand [$\{SP(OEt)_2\}(O_2SC_6H_4Cl\text{-}4)N]^-$ in compound **2**. The NMR spectra suggest that in the absence of the bulky PPh_3 groups the copper(I) atom in compound **1** tends to increase its coordination number by intermolecular interactions in which one *O*Et group is involved.

EXPERIMENTAL SECTION

Starting materials, *i.e.* K[$\{SP(OEt)_2\}(O_2SC_6H_4Cl\text{-}4)N$] [18] and $(Ph_3P)_2CuNO_3$ [22], were prepared according to literature procedures. Other reagents including ^nBuLi, Ph_3P, CuCl and $Cu(NO_3)_2$ were purchased from Aldrich and used without further purification. All manipulations involving air sensitive compounds were carried out under vacuum or argon, using Schlenk techniques. Solvents were dried and distilled prior to use. Elemental analyses were performed on a Flash EA 1112 machine. Melting points have been determined with an ELECTROTHERMAL 9200 apparatus and they are not corrected. Multinuclear NMR spectra (^1H, ^{13}C and ^{31}P) were recorded on a BRUKER 300 Avance instrument operating at 300.11, 75.5 and 121.4 MHz, respectively, using $CDCl_3$ solutions. The chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (ref. $CHCl_3$: ^1H 7.26, ^{13}C 77.0 ppm) and H_3PO_4 85%. The ^1H and ^{13}C chemical shifts were assigned based on 2D experiments (COSY, HSQC and HMBC) using standard BRUKER XWIN-NMR pulse sequences. The NMR spectra were processed using the MestReC and MestReNova software [23].

Preparation of [Cu{SP(OEt)$_2$}(O$_2$SC$_6$H$_4$Cl-4)N] (1)

A reaction mixture of CuCl (0.122 g, 1.23 mmol) and K[{SP(OEt)$_2$}(O$_2$SC$_6$H$_4$Cl-4)N] (0.47 g, 1.23 mmol) in 25 mL of anhydrous dichloromethane was stirred at room temperature for 16 hours. The solvent was removed under vacuum and the remained solid product was washed with n-hexane and dried under vacuum. The title compound was obtained as a colorless powder which was recrystallized from a dichloromethane/n-hexane mixture (1:3, v/v). Yield 0.361 g (72%), m.p. 199°C. Anal. Calc. for $C_{10}H_{14}ClCuNO_4PS_2$ (M = 406.32): C 29.56% H 3.47%, N 3.45%. Found: C 29.42%, H 3.32%, N 3.51%. ^{1}H NMR: δ 1.18t (3H, OCH$_2$C*H*$_3$, $^3J_{HH}$ 6.5 Hz), 1.35t (3H, OCH$_2$C*H*$_3$, $^3J_{HH}$ 6.5 Hz), 3.92 AB spin system with δ_A 3.78dq (1H, OC*H*$_2$CH$_3$, $^3J_{HH}$ 7.5 Hz, $^3J_{PH}$ 14.2 Hz) and δ_B 4.06dq (1H, OC*H*$_2$CH$_3$, $^3J_{HH}$ 7.5 Hz, $^3J_{PH}$ 14.7 Hz), 4.40 AB spin system with δ_A 4.39dq (1H, OC*H*$_2$CH$_3$, $^3J_{HH}$ 7.3 Hz, $^3J_{PH}$ 13.4 Hz) and δ_B 4.41dq (1H, OC*H*$_2$CH$_3$, $^3J_{HH}$ 7.3 Hz, $^3J_{PH}$ 13.5 Hz), 7.44d (2H, C$_6$*H*$_4$-*meta*, $^3J_{HH}$ 8.3 Hz), 7.92d (2H, C$_6$*H*$_4$-*ortho*, $^3J_{HH}$ 8.3 Hz). ^{13}C NMR: δ 15.46d (OCH$_2$*C*H$_3$, $^3J_{PC}$ 8.6 Hz), 66.26d (O*C*H$_2$CH$_3$, $^2J_{PC}$ 6.9 Hz), 67.15d (O*C*H$_2$CH$_3$, $^2J_{PC}$ 6.8 Hz), 128.66s (*C*$_6$H$_4$-*meta*), 128.87s (*C*$_6$H$_4$-*ortho*), 138.4s (*C*$_6$H$_4$-*ipso*), 141.9s (*C*$_6$H$_4$-*para*). ^{31}P NMR: δ 45.08s.

Preparation of [Cu(PPh$_3$)$_2${SP(OEt)$_2$}(O$_2$SC$_6$H$_4$Cl-4)N] (2)

A reaction mixture of (Ph$_3$P)$_2$CuNO$_3$ (0.289 g, 0.445 mmol) and K[{SP(OEt)$_2$}(O$_2$SC$_6$H$_4$Cl-4)N] (0.17 g, 0.445 mmol) in 25 mL of anhydrous dichloromethane was stirred at room temperature for 24 hours. The solvent was removed under vacuum, when a colorless viscous oil was obtained. After washing with n-hexane, the title compound resulted as a colorless microcrystalline solid. Yield 0.244 g (59%), m.p. 162°C. Anal. Calc. for $C_{46}H_{44}ClCuNO_4P_3S_2$ (M = 930.90): C 59.35%, H 4.76%, N 1.50%. Found: C 59.64%, H 4.92%, N 1.55%. ^{1}H NMR: δ 1.07t (6H, C*H*$_3$, $^3J_{HH}$ 7.02 Hz); 3.73 AB spin system with δ_A 3.72dq (2H, C*H*$_2$, $^3J_{HH}$ 7.5 Hz, $^3J_{PH}$ 14.5 Hz) and δ_B 3.74dq (2H, C*H*$_2$, $^3J_{HH}$ 7.5 Hz, $^3J_{PH}$ 14.6 Hz); 7.04d (2H, C$_6$*H*$_4$, $^3J_{HH}$ 8.3 Hz); 7.25m (12H, C$_6$*H*$_5$-*ortho*) 7.35m (18H, C$_6$*H*$_5$-*meta*+*para*); 7.51d (2H, C$_6$*H*$_4$, $^3J_{HH}$ 8.3 Hz). ^{13}C NMR: δ 15.76d (OCH$_2$*C*H$_3$, $^3J_{PC}$ 8.8 Hz), 62.72d (O*C*H$_2$CH$_3$, $^2J_{PC}$ 6.5 Hz), 127.95s (*C*$_6$H$_4$-*para*), 128.45d (*C*$_6$H$_5$-*ortho*, $^2J_{PC}$ 7.3 Hz), 129.44s (*C*$_6$H$_4$-*ortho* + *C*$_6$H$_4$-*meta*), 133.5d (*C*$_6$H$_5$-*ipso*, $^1J_{PC}$ 106.3 Hz), 133.95d (*C*$_6$H$_5$-*meta*, $^3J_{PC}$ 14.4 Hz), 136.28 (*C*$_6$H$_4$-*ipso*), 143.95 (*C*$_6$H$_4$-*para*). ^{31}P NMR: δ -4.52s, br. (Ph$_3$*P*); 48.06s [(EtO)$_2$*P*(S)].

X-ray Crystallographic Studies

X-ray quality crystals of compound **2** were grown by slow diffusion from a mixture of CH_2Cl_2/n-hexane (1/5, v/v). The crystal was attached with paraton/N oil to a cryoloop. Data collection and processing was carried on a Bruker SMART APEX CCDC system, using graphite-monochromated Mo Kα radiation (k = 0.71073 Å). Details of the crystal structure determination and refinement for compound **2** are given in Table 2.

Table 2. Crystalllographic data for compound **2**.

Empirical formula	$C_{46}H_{44}ClCuNO_4P_3S_2$
Formula weight	930.84
Temperature, K	297(2)
Wavelength, Å	0.71073
Crystal system	Triclinic
Space group	P-1
Crystal size, mm	0.60 x 0.48 x 0.38
Unit cell dimensions	
a, Å	9.7281(9)
b, Å	11.4567(10)
c, Å	21.5866(19)
α, °	103.838(2)
β, °	93.523(2)
γ, °	103.242(2)
V, $Å^3$	2256.7(3)
Z, Calculated density	2, 1.370 Mg/m^3
F(000)	964
Refinement method	Full-matrix least-squares on F^2
Θ Range for data collection	0.98 to 25.00
Reflections collected	21771
Independent reflections [R_{int}]	7940 [R_{int} = 0.0312]
Data/restraints/parameters	7940 / 0 / 525
Goodness-of-fit on F^2	1.114
Final *R* indices [I>2sigma(I)]	R1 = 0.0674, wR2 = 0.1519
R indices (all data)	R1 = 0.0795, wR2 = 0.1585
Largest diff. peak and hole, (e $Å^{-3}$)	1.274 and -0.621

The structure was refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. The software package SHELX-97 was used for structure solving and refinement [24]. The drawings were created with the DIAMOND program [25].

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SUPPLEMENTARY DATA

CCDC 961231 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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