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Complexes of N-thiophosphorylated thioureas and triphenylphosphine with Cu^{I}

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The complexes $(Pr^{i}O)_2P(S)NHC(S)R$ (R = NEt_2, NHPh), $[(Pr^{i}O)_2P(S)NHC(S)]_2$-1,10-diaza-18-crown-6 have been obtained by the metathesis reaction of potassium salts of corresponding thiophosphorylated thioureas with $(PPh_3)_2CuNO_3$; the crystal structure of $(Ph_3P)_2Cu[Et_2NC(S)NP(S)(OPr^{i})_2]$ has been confirmed by X-ray crystallography.

Complexes of copper(I) have useful luminescent properties, and they can be used in microelectronics and in radiation sensors. Copper(I) complexes catalyse homolytic C–Hal (Hal = Cl, Br) bond cleavage in polyhaloalkanes.[1]

The examination of Cu^{I} phosphine complexes of poly(pyrazolyl)borates has shown[2] that the coordination environment is strictly dependent on both steric and electronic properties of poly(pyrazolyl)borate and phosphine ligands. The synthesis of Cu^{I} complexes containing imidodiphosphinate $Ph_2P(X)NHP(X)Ph_2$ (X = O, S, Se) and triphenylphosphine was reported previously.[3–5] In these complexes, the copper atom is coordinated to two chalcogen atoms of a chelating ligand and one (when X = S, Se) or two (X = O) triphenylphosphine molecules. The complex $\{Cu(PPh_3)[PhC(O)NP(S)Ph_2]\}$ contains a three-coordinated copper atom.[6] The corresponding Cu^{I} complex with a β-diketone (2-thienyltrifluoroacetone) displays the coordination of the copper atom to two triphenylphosphine molecules,[7] while the Cu^{I} trimethylphosphine complex of acetylacetone has the ratio chelating ligand : phosphine = 1:1 or 1:2, depending on reaction conditions.[8] Hence, there is a diverse coordination environment about Cu^{I} in its complexes with chelating and pendant phosphine ligands. That is why we interested in the preparation and investigation of the complexes of thiophosphorylated thioureas and triphenylphosphine with Cu^{I}.

The parent ligands $Et_2NC(S)NHP(S)(OPr^{i})_2$, PhNHC(S)–$NHP(S)(OPr^{i})_2$ and $[(Pr^{i}O)_2P(S)NHC(S)]_2$(1,10-diaza-18-crown-6) were prepared by the addition of a corresponding amine to diisopropylthiophosphoryl isothiocyanate.[9] Complexes **1**–**3** were obtained[3–6] by the metathesis reactions of the potassium salts of corresponding thiophosphorylated thioureas with bis(triphenylphosphine)copper(I) nitrate in an ethanol–methylene chloride solution (Scheme 1).†

Compounds **1**–**3** are colourless crystalline solids, soluble in CH_2Cl_2, $CHCl_3$, acetone and benzene and insoluble in hexane. The complexes were characterised by ^{31}P, ^{1}H NMR and IR spectroscopy and microanalysis.‡ The crystal structure of **1** was confirmed by X-ray crystallography.§ Figure 1 shows its molecular structure.

The IR spectra of **1**–**3** exhibit absorption bands at 1490–1580, 970–1030 and 690–696 cm^{-1}, which were assigned to the group and stretching vibrations of SCN, POC and P–C (P–Ph) groups, respectively. The P=S absorption band shifts to lower frequency from 620–648 cm^{-1} in parent ligands to 560–575 cm^{-1} in complexes. The absorption band of the phosphorylamide NH group disappears upon complexation.

The ^{1}H NMR spectra of **1**–**3** contain the only set of signals, which correspond to the proposed structure. Methyl and ethyl resonance doubling for $P(S)(OPr^{i})_2$ and Et_2N groups is a consequence of hindered rotation that is characteristic of the test derivatives. Such a type of doubling was also observed in the spectra of parent thiourea ligands.[9] The resonance at 51.4–55 ppm in ^{31}P NMR spectra corresponds to the phosphorus of thiophosphoryl groups. The signals of triphenylphosphine were observed at –0.7 to –0.6 ppm and occurred downfield of free PPh_3 (–6.0 ppm).[10] They have the same chemical shift as in the trigonal complex $(Ph_3P)Cu(SPPh_2)_2N$ (–0.7 ppm).[3]

Broad phosphine resonances are a common phenomenon for Cu^{I} phosphine complexes (see ref. 11 and references therein as an example). It can be due to a non-ionic dissociation equilibrium such as that proposed by Pellei *et al.*[2] Fast exchange between free and bound triphenylphosphine in solutions of **1**–**3** results in phosphine signal broadening in ^{31}P NMR spectra.

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† *General procedure for* **1** *and* **2**. To a suspension of $RC(S)NHP(S)(OPr^{i})_2$ (0.5 mmol) in 96% ethanol (25 ml) a KOH (0.5 mmol) in the same solvent (15 ml) was added, and the mixture was stirred until the ligand dissolved completely. To the resulting potassium salt a solution of $(PPh_3)_2CuNO_3$ (0.5 mmol) in CH_2Cl_2 (25 ml) was added dropwise. The mixture was stirred for 1 h, and the precipitate was filtered off. The filtrate was concentrated until crystallization. The isolated crystals were precipitated from a methylene chloride–hexane mixture (1:5, v/v).

Compound **3** was prepared similarly to compounds **1** and **2** using a double amount of KOH and $(PPh_3)_2CuNO_3$.

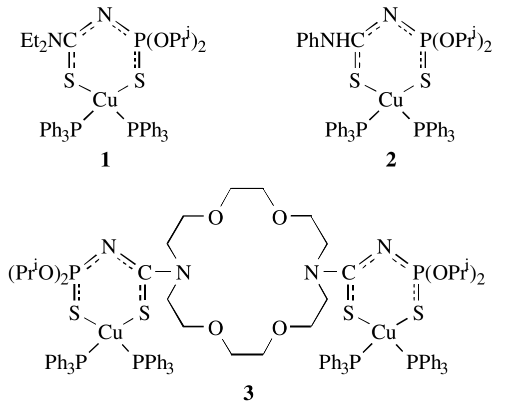
‡ Infrared spectra (Nujol) were recorded on a Specord M-80 spectrometer in the range 400–3600 cm^{-1}. ^{1}H NMR (299.942 MHz) and ^{31}P (120.420 MHz) spectra in $CDCl_3$ and C_6D_6 solutions were obtained on a Varian Unity-300 NMR spectrometer at 25 °C. Mass spectra were measured on an TRACE MS Finnigan MAT instrument. Electron ionization energy was 70 eV. The substance was injected directly into the ion source at 150 °C.

*[*N,N*-Diethyl-*N'*-(diisopropoxythiophosphoryl)thiocarbamido]-bis(triphenylphosphine)copper(I)* **1**: yield 60%, mp 104 °C (CH_2Cl_2 + C_6H_{14}, 1:5). ^{1}H NMR (C_6D_6) δ: 1.26 (t, 3H, CH_2Me, $^{3}J_{HH}$ 7.2 Hz), 1.37 (t, 3H, CH_2Me, $^{3}J_{HH}$ 7.2 Hz), 1.53 (d, 6H, CH*Me*, $^{3}J_{HH}$ 6.3 Hz), 1.55 (d, 6H, CH*Me*, $^{3}J_{HH}$ 6.9 Hz), 3.67 (q, 2H, CH_2Me, $^{3}J_{HH}$ 7.0 Hz), 4.04 (q, 2H, CH_2Me, $^{3}J_{HH}$ 7.1 Hz), 5.19 [d sept, 2H, CH (Pr^{i}), $^{3}J_{HH}$ + $^{3}J_{PH}$ 10.3 Hz], 7.2–7.3 (m, 12H, P–Ph), 7.7–7.8 (m, 18H, P–Ph). ^{31}P NMR (C_6D_6) δ: –0.70 (PPh_3), 54.96 (thiourea ligand). IR (Nujol, ν/cm^{-1}): 564 (P=S), 690 (P–C), 970–1030 (POC), 1580 (SCN). Found (%): C, 60.25; H, 6.12; N, 3.45; P, 10.39; S, 6.45. Calc. for $C_{47}H_{54}CuN_2O_2P_3S_2$ (%): C, 62.76; H, 6.05; N, 3.11; P, 10.33; S, 7.13.

*[*N*-Phenyl-*N'*-(diisopropoxythiophosphoryl)thiocarbamido]-bis(triphenylphosphine)-copper(I)* **2**: yield 42%, mp 146 °C (CH_2Cl_2 + C_6H_{14}, 1:3). ^{1}H NMR ($CDCl_3$) δ: 1.33 (d, 6H, Me, $^{3}J_{HH}$ 6.3 Hz), 1.36 (d, 6H, Me, $^{3}J_{HH}$ 6.2 Hz), 4.79 [d sept, 2H, CH (Pr^{i}), $^{3}J_{HH}$ 6.2 Hz, $^{3}J_{PH}$ 10.6 Hz], 7.08 (t, 1H, *p*-Ph, $^{3}J_{HH}$ 7.1 Hz), 7.24–7.5 (m, 32H, P–Ph and *o*-Ph), 7.57 (d, 1H, NH, $^{4}J_{PNCNH}$ 7.9 Hz), 7.73 (t, 2H, *m*-Ph, $^{3}J_{HH}$ 8.4 Hz). ^{31}P NMR ($CDCl_3$) δ: –0.70 (PPh_3), 54.96 (dt, thiourea ligand A_2MX, $^{3}J_{POCH}$ + $^{4}J_{PNCNH}$ 9.3 Hz). IR (Nujol, ν/cm^{-1}): 560 (P=S), 696 (P–C), 984 (br., POC), 1538 (SCN), 3260 (N–H). Found (%): C, 63.15; H, 6.02; N, 3.14; P, 10.77; S, 6.16. Calc. for $C_{49}H_{50}CuN_2O_2P_3S_2$ (%): C, 64.00; H, 5.48; N, 3.05; P, 10.11; S, 6.97.

N,N'*-Bis[*N''*-(diisopropoxythiophosphoryl)amidothiocarbonilato-bis-(triphenylphosphine)-copper(I)]-1,10-diaza-18-crown-6* **3**: yield 76%, mp 144–145 °C (CH_2Cl_2 + C_6H_{14}, 1:5). ^{1}H NMR ($CDCl_3$) δ: 1.28 (d, 12H, Me, $^{3}J_{HH}$ 6.3 Hz), 1.36 (d, 12H, Me, $^{3}J_{HH}$ 6.0 Hz), 3.59–3.65 (m, 8H, NCH_2), 3.75 (t, 4H, NCH_2CH_2O, $^{3}J_{HH}$ 6.3 Hz), 3.85 (t, 4H, NCH_2CH_2O, $^{3}J_{HH}$ 5.4 Hz), 3.96 (t, 4H, OCH_2CH_2O, $^{3}J_{HH}$ 5.8 Hz), 4.21 (t, 4H, OCH_2CH_2O, $^{3}J_{HH}$ 5.4 Hz), 4.73 [d sept, 4H, CH (Pr^{i}), $^{3}J_{HH}$ + $^{3}J_{PH}$ 8.7 Hz], 7.32–7.76 (m, 60H, P–Ph). ^{31}P {^{1}H} NMR ($CDCl_3$) δ: –0.60 (PPh_3), 51.51 (s, thiourea ligand). IR (Nujol, ν/cm^{-1}): 575 (P=S), 696 (P–C), 1000 (br., POC), 1480 (SCN). Found (%): C, 60.42; H, 5.82; N, 2.77; P, 10.15; S, 6.34. Calc. for $C_{98}H_{112}Cu_2N_4O_8P_6S_4$ (%): C, 61.46; H, 5.89; N, 2.93; P, 9.70; S, 6.70.

$$(PPh_3)_2CuNO_3 + K[RC(S)NP(S)(OPr^i)_2] \longrightarrow (Ph_3P)_2Cu[RC(S)NP(S)(OPr^i)_2] + KNO_3$$



Scheme 1

Full widths at half peak maximum are 40, 47 and 30 Hz for complexes **1**, **2** and **3**, respectively.

The parent ion was not observed in the mass spectra of **1** and **2**. The absence of the parent ion was reported previously for the similar compound $\{Cu(PPh_3)[PhC(O)NP(S)Ph_2]\}$.[6]

Thus, we found that thiophosphorylated thioureas form heteroligand triphenylphosphine Cu^I complexes. The copper atom is bound to two sulfur atoms of phosphorylated urea and two phosphorus of PPh_3. Compound **3** contains a diaza-crown ether ring, which is capable to bind alkali metal cations. Thus, it can be used for the preparation of hard-soft heteronuclear metal complexes. According to our preliminary results, the test compounds have greater reactivity than tris(triphenylphosphine)-copper(I)[1] and phoshphine platinum(II) complexes.

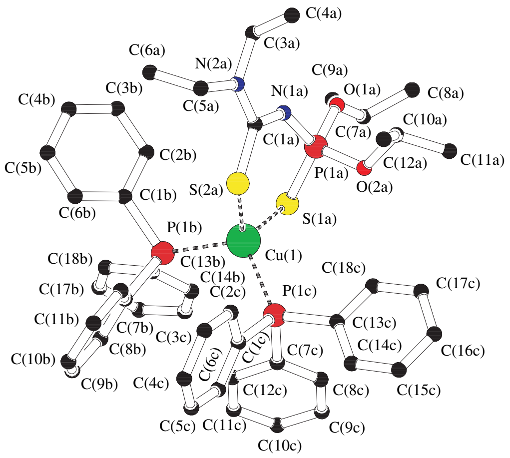


Figure 1 Molecular structure of complex **1** (H atoms omitted for clarity). Selected bond lengths (Å): Cu(1)–S(1a) 2.338(2), Cu(1)–S(2a) 2.307(3), Cu(1)–P(1b) 2.331(3), Cu(1)–P(1c) 2.296(3).

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§ *X-ray crystallography of* **1**: $C_{47}H_{54}CuN_2O_2P_3S_2$, M = 899.52, monoclinic, space group $P2_1/n$, a = 13.058(2), b = 20.931(2), c = 17.560(6) Å, β = 108.62(2)°, V = 1616(1) Å^3, Z = 4, d_{calc} = 1.31 g cm^{-3}. Cell parameters and intensities of 3562 independent reflections were measured on an Enraf-Nonius CAD-4 diffractometer in the $\omega/2\theta$-scan mode, $\theta \le 24.62°$, using MoKα radiation with a graphite monochromator. Data were corrected for the absorption effect. The structure was solved by a direct method using the SIR program[12] and refined by the full matrix least-squares using the MolEN program package.[13] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were solved from difference Fourier maps, and the contribution of structural factors was included with fixed positional and thermal parameters in the last cycles. The final residuals were R_1 = 0.060 and wR_2 = 0.062. All calculations were performed on an Alpha Station 200 computer. The molecular structure of **1** was drawn using the PLATON program.[14]

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 199834. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2003.