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N-Thiophosphorylthiourea containing an aza-18-crown-6 fragment. The crystal structure of bis[*N*-(*N'*-diisopropoxythiophosphorylamidothiocarbonyl)-aza-18-crown-6]nickel(II)

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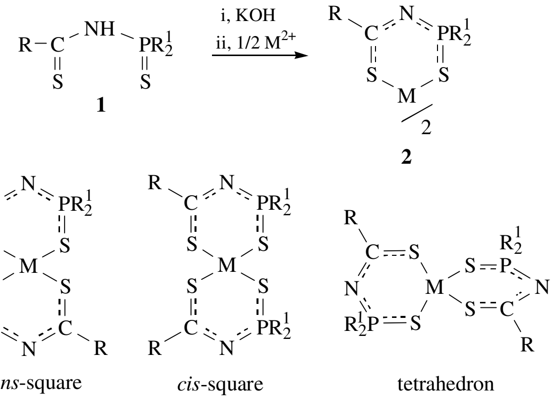
N-(N'-Diisopropoxythiophosphorylamidothiocarbonyl)aza-18-crown-6 (HL) was obtained by the reaction of aza-18-crown-6 with diisopropoxythiophosphorylisothiocyanate, and its chelate with Ni$^{\mathrm{II}}$ was characterised using IR, ^{1}H and ^{31}P NMR spectroscopy and single-crystal X-ray diffraction.

N-Thiophosphorylthioureas (**1**, R = NR^{2}R^3) and thioamides (**1**, R = Alk, Ar) form stable *S,S'*-chelates **2** with divalent metal cations. Previously, we described complexes **2** with M = Co$^{\mathrm{II}}$,[1] Ni$^{\mathrm{II}}$,[2] Pd$^{\mathrm{II}}$,[1,3,4] Pt$^{\mathrm{II}}$,[4] Pb$^{\mathrm{II}}$,[1,5] Cu$^{\mathrm{II}}$,[6,7] Zn$^{\mathrm{II}}$,[1] Cd$^{\mathrm{II}}$,[1] and Hg$^{\mathrm{II}}$.[1,8] The following three forms of chelates **2** are prevailing: *trans*- or *cis*-square-planar (M = Ni$^{\mathrm{II}}$, Pd$^{\mathrm{II}}$, Pt$^{\mathrm{II}}$, Cu$^{\mathrm{II}}$) and tetrahedral (M = Co$^{\mathrm{II}}$, Zn$^{\mathrm{II}}$, Cd$^{\mathrm{II}}$, Hg$^{\mathrm{II}}$) (Scheme 1).



Scheme 1

We synthesised crown-containing *N*-thiophosphorylthioureas[7,9] and thioamides,[10] which comprise two fundamentally different complexing groups in their structures: a chelating fragment and a macrocyclic ring. The structures of these compounds allow them to form complexes with two different metals simultaneously. While crown ethers can form complexes with the ions of alkali and alkaline earth metals, the *N*-(thio)phosphorylurea (or thioamide) fragment forms chelates with divalent transitional metal cations.

Here, we present ligand **1a**[†] (R = *N*-aza-18-crown-6, R^1 = = OPr^i) and the complex of thiourea **1a** with the Ni$^{\mathrm{II}}$ cation (**2a**).[‡] Complex **2a** was obtained by the reaction of an aqueous Ni(NO$_3$)$_2$·6H$_2$O solution with the potassium salt of **1a** in 96% aqueous ethanol.

The structures of **1a** and **2a** were proved by IR, ^{1}H and ^{31}P NMR spectroscopy. The crystal and molecular structure of complex **2a** was determined by single-crystal X-ray diffraction (Figure 1).[§] Complex **2a** is centrosymmetric with the square-planar configuration of the NiS$_4$ core (the sum of bond angles around the nickel atom is 360°). Only a slight distortion of the NiS$_4$ square is observed: the endocyclic S–Ni–S angle [97.79(4)°] is greater than the exocyclic S–Ni–S angle [82.19(4)°]. The ligand molecules in **2a** have planar S(2)–C(1){N(2)}–N(1)–P(1) fragments. Maximum deviations for the P(1) and N(1) atoms are 0.022(1) and –0.035(3) Å, respectively. The NiCNPS$_2$ chelate ring folded about the P(1)···Ni axis. The dihedral angle between S(2)–C(1){N(2)}–N(1)–P(1) and Ni–S(1)–P(1) planes is 55.58(8)°. The structure of chelate **2a** is similar to that of the

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[†] The IR spectra were recorded in Nujol in the range 400–3600 cm^{-1} on a Specord M80 spectrometer. The ^{1}H (300 MHz) and ^{31}P (122.4 MHz, 85% phosphoric acid) NMR spectra were obtained using a Varian Unity-300 NMR in [^{2}H]benzene.

N-(N'-diisopropoxythiophosphorylamidothiocarbonyl)aza-18-crown-6 **1a**. A solution of 7.0 mmol (Pr^{i}O)$_2$P(S)NCS in 20 ml of benzene was added dropwise to a solution of 7.0 mmol of aza-18-crown-6 in 30 ml of benzene. The mixture was stirred for 1 h, and the solvent was removed in a vacuum. The residue was crystallised from a methylene chloride–hexane mixture (1:5, by volume). Tiourea **1a** is a colourless oil: n_{D}^{20} 1.5261. ^{1}H NMR, δ: 1.49, 1.50 (2d, 12H, CH*Me*$_2$, $^3J_{\mathrm{HH}}$ 6.3 Hz), 3.66 (s), 3.64-4.20 (m) (24H, CH$_2$ crown), 5.06 (d sept, 2H, C*H*Me$_2$, $^3J_{\mathrm{HH}}$ 6.3 Hz, $^3J_{\mathrm{PH}}$ 10.6 Hz), 9.08 (NH). ^{31}P{^{1}H} NMR, δ: 59.1. IR (ν/cm^{-1}): 3180 (NH), 1512 (SCN), 1320 (C=S), 1000 (POC), 1110 (COC), 650 (P=S). Found (%): C, 45.30; H, 7.80; P, 6.13. Calc. for $C_{19}H_{39}N_2O_7PS_2$ (%): C, 45.36; H, 7.76; P, 6.17.

[‡] *Bis[N-(N'-diisopropoxythiophosphorylamidothiocarbonyl)aza-18-crown-6]nickel(II)* **2a**. To a solution of 6.0 mmol of **1a** in 30 ml of 96% EtOH, a solution of 6.0 mmol of potassium hydroxide in 30 ml of EtOH was added, and the mixture was stirred for 15 min. An aqueous solutoin of 15.0 mmol of Ni(NO$_3$)$_2$·6H$_2$O was added to the resulting solution. The product was extracted with methylene chloride; the extract was washed with distilled water (10×5 ml) and dried over magnesium sulfate; the solvent was removed in a vacuum. The residue was recrystallised from a methylene chloride–hexane mixture (1:5, by volume). Complex **2a** was obtained as dark violet crystals, mp 125 °C. ^{1}H NMR, δ: 1.43, 1.52 (2d, 12H, CH*Me*$_2$, $^3J_{\mathrm{HH}}$ 6.1 Hz), 3.59–3.71 (m, 18H, NCH$_2$ + OCH$_2$ crown), 3.84–3.87 (m, 4H, OCH$_2$ crown), 4.22–4.30 (m, 2H, OCH$_2$ crown), 4.98 (d sept, 2H, C*H*Me$_2$, $^3J_{\mathrm{HH}}$ 6.1 Hz, $^3J_{\mathrm{PH}}$ 9.9 Hz). ^{31}P{^{1}H} NMR, δ: 50.0. IR (ν/cm^{-1}): 1504 (SCN), 1100–1150 (COC), 980–1010 (POC), 568 (P=S). Found (%): C, 43.01; H, 7.27; Ni, 5.55; P, 5.79. Calc. for $C_{38}H_{76}N_4NiO_{14}P_2S_4$ (%): C, 42.98; H, 7.21; Ni, 5.53; P, 5.83.

[§] *X-ray crystallography of NiL$_2$* **2a**: $C_{38}H_{76}N_4NiO_{14}P_2S_4$, *M* 1061.94, triclinic, space group $P\bar{1}$, a = 9.015(3), b = 9.670(3), c = 16.116(4) Å, α = 75.11(3), β = 79.46(3), γ = 88.31(3)°, V = 1335.7(7) Å^3, Z = 1, d_{calc} = = 1.32 g cm^{-3}. Cell parameters and intensities of 5757 independent reflections (2666 with $I \geq 3\sigma$) were measured on an Enraf-Nonius CAD-4 diffractometer in the $\omega/2\theta$-scan mode, $\theta \leq 26.6°$, using MoKα radiation with a graphite monochromator. Data were corrected for the absorption effect [μ(MoKα) = 5.1 cm^{-1}]. The structure was solved by a direct method using the SIR program[11] and refined by the full matrix least-squares using the MolEN program package.[12] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were solved from difference Fourier maps, and its contribution on structural factors was included with fixed positional and thermal parameters in the last cycles. The final residuals were R_1 = 0.040 and wR_2 = 0.042. All calculations were performed on an Alpha Station 200 computer. The figures of molecules were drawn with the PLATON program.[13]

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 199832. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2003.

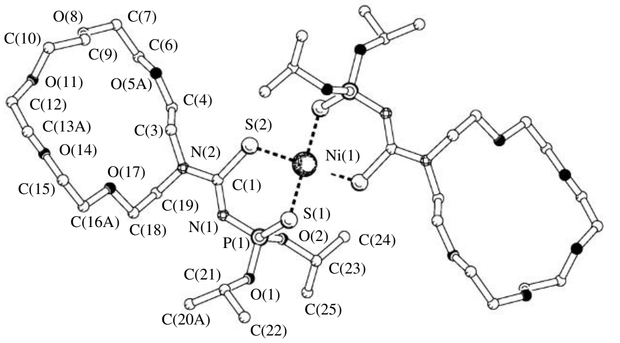

Figure 1 Crystal structure of complex **2a** (hydrogen atoms are not shown). Selected bond lengths (Å) and angles (°): Ni(1)–S(1) 2.2110(8), Ni(1)–S(2) 2.219(1); S(1)–P(1) 2.000(1), P(1)–N(1) 1.583(3), N(1)–C(1) 1.303(5), S(2)–C(1) 1.754(4), N(2)–C(1) 1.349(4), S(2)–Ni(1)–S(1) 97.79(4), S(1)–Ni(1)–S(1a) 82.19(4).

complex $\mathrm{Pd[PhC(S)NP(S)(OPr^{i})_2}$-*S*,*S*′$]_2$.[3]

The crown ether rings in **2a** are significantly flattened. A maximum deviation from a least-square plane of the crown ring is 0.823(4) Å for the C(3) atom. A minimum deviation is 0.010(5) Å for the C(4) atom. The crown ether rings of neighbouring molecules are close in a crystal. The distances between opposite donor atoms are in the range 4.11–4.91 Å.

The low-spin ($S = 0$) *trans*-square-planar form of complex **2a** does not change in solution. The ^{31}P NMR spectrum exhibits a singlet at 50.00 ppm with a line-width of 22 Hz at half height. There are not considerable changes in the ^{1}H NMR spectrum of the crown ether part of molecule **2a** in comparison to that in free ligand **1a**.

The *N*-thiophosphorylthiourea fragment in **2a** and related (similar) compounds plays the role of an orienting group. Mutual orientation of crown ether rings in such compounds depends on the geometry of a chelate core and the nature of the metal cation. A *cis*-square or tetrahedron chelate core makes crown-ether rings closeness. It can promote the formation of sandwich host–guest complexes. *trans*-Square complexes can form supramolecular chain structures under simulated conditions.

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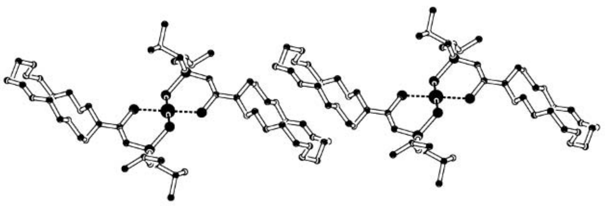

Figure 2 Mutual orientation of crown ether rings in crystals of the complex **2a**.

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