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1,2-Benzo-15-crown-5 containing an *N*-thiophosphorylthiobenzamide fragment

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A crown-containing *N*-thiophosphorylthioamide has been synthesised by a reaction between diisopropyl thiophosphate chloride and (4-amidothiocarbonyl-1,2-benzo)-15-crown-5, and its chelate complex with nickel(II) has been obtained.

Earlier, we have reported on the synthesis of crown-containing *N*-thiophosphorylthioureas, which comprise two fundamentally different complexing groups: a chelating fragment and a crown ether (or its open-chained analogue, *i.e.*, a podand).[1–3] The structure of these compounds allows them to form complexes with two different metals simultaneously. Podands (or crown ethers) form complexes with alkali and alkaline earth metal ions, whereas *N*-(thio)phosphorylthiourea forms stable chelates with divalent transition metals. Such complexes are interesting as potential binuclear complex catalysts, models for studying redox processes within complexes, and reagents for supramolecular synthesis.[4]

There is no published data on compounds combining crown and chelating *N*-(thio)phosphorylthioamide groups in their structures. However, the above chelating fragment is more stable in a coordination sphere and less exposed to oxidation as compared to the *N*-(thio)phosphorylthiourea group. This is important, for example, for the synthesis of Hg^{II} complexes.[5,6]

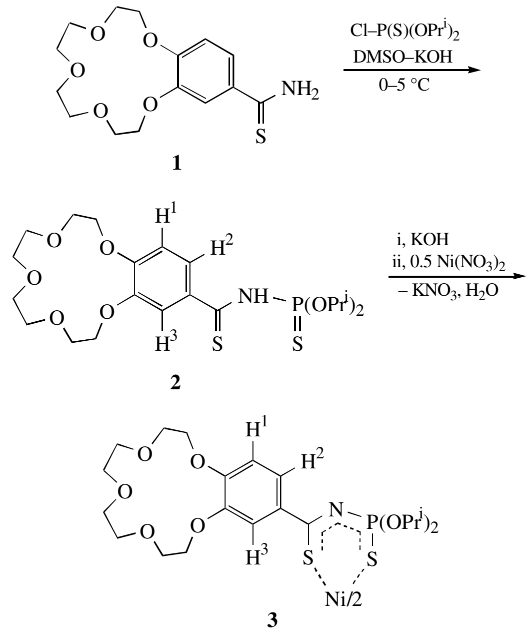
The crown-containing *N*-thiophosphorylthioamide has been obtained by a reaction between diisopropyl thiophosphate chloride and (4-amidothiocarbonyl-1,2-benzo)-15-crown-5 **1** under superbase conditions (DMSO–KOH). Thioamide **2**[†] forms orange crystals.

Data obtained by IR, ^{1}H and ^{31}P NMR spectroscopy and microanalysis confirm the proposed structure completely.

The ^{31}P-{^{1}H} NMR spectrum exhibits a singlet signal at $\delta^{31}P$ 58.74 ppm, which is similar to the chemical shift of its acyclic analogue [PhC(S)NHP(S)(OPr^{i})$_2$] $\delta^{31}P$ 58.72 ppm.[7] The IR spectrum contains intense absorption bands at 1100, 1120 and 980, 1000 cm^{-1}, which correspond to the vibrations of COC and POC groups. This fact confirms the presence of macrocyclic and thiophosphoryl fragments.

The crown-ether fragment manifests itself in the ^{1}H NMR spectrum as a multiplet at 3.62–3.90 ppm. The NH proton appears as a doublet signal at 8.37 ppm with a characteristic $^{2}J_{PNH}$ constant of 14.1 Hz.[3,8] The H(1) (6.45 ppm) and H(3) (7.77 ppm) protons appear in the ^{1}H NMR spectrum as doublets with $^{3}J_{H(1)H(2)}$ and $^{4}J_{H(2)H(3)}$ constants of 8.5 Hz and 2.3 Hz, respectively. The signal of the H(2) proton appears as a doublet of doublets with identical constants. The structure of thioamide **2** has been confirmed using single crystal X-ray diffraction analysis.

Thioamide **2** reacts with nickel(II) in aqueous ethanol to form chelate complex NiL_2 **3**. The phosphorus nucleus produces a narrow singlet signal with a chemical shift of 54.7 ppm, which is typical of nickel(II) complexes with a square-planar coordination.[3,9] Without decoupling, the spectrum looks like a triplet with a $^{3}J_{PH}$ constant of 9.2 Hz, which is typical of isopropoxythiophosphoryl derivatives. In the ^{1}H NMR spectrum, the H(2)-proton (δ_H 8.49 ppm, dd) of complex **3**[‡] is downfield shifted by 1.2 ppm relative to the signal of initial thioamide **2**.



The band due to the P=S group in complex **3** is shifted by 45 cm^{-1} to a lower frequency, indicating the participation in coordination with a nickel(II) cation. This behaviour is typical of chelate complexes.[3,6,8,9]

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References

1 N. G. Zabirov, N. I. Galyautdinov, V. A. Shcherbakova and R. A. Cherkasov, *Zh. Obshch. Khim*, 1990, **60**, 1247 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1990, **60**, 1112].

2 A. L. Konkin, V. G. Shtyrlin, N. G. Zabirov, A. V. Aganov, L. E. Zapechelnyuk, S. V. Kashevarov and A. V. Zakharov, *Zh. Neorg. Khim.*, 1996, **41**, 1156 (*Russ. J. Inorg. Chem.*, 1996, **41**, 1107).

[†] *[4-(*N*-Diisopropoxythiophosphoryl)amidothiocarbonyl-1,2-benzo]-15-crown-5* **2**: yield 53%, mp 89–91 °C ($CH_2Cl_2 + C_6H_{14}$, 1:5). ^{1}H NMR (300 MHz, C_6D_6) δ: 1.49 (d, 6H, Me, J_{HH} 6.2 Hz), 1.50 (d, 6H, Me, J_{HH} 6.2 Hz), 3.62–3.90 (m, 16H, OCH_2 crown), 5.30 [d sept, 2H, CH (Pr^{i}), J_{HH} 6.2 Hz, J_{PH} 10.7 Hz], 6.45 [d, 1H, H(1) (Ph), $J_{H(1)H(2)}$ 8.45 Hz], 7.33 [dd, 1H, H(2) (Ph), $J_{H(1)H(2)}$ 8.5 Hz, $J_{H(2)H(3)}$ 2.3 Hz], 7.77 [d, 1H, H(3) (Ph), $J_{H(2)H(3)}$ 2.3 Hz], 8.37 (br. d, 2H, NH, J_{PH} 14.1 Hz). ^{31}P-{^{1}H} NMR (121.4 MHz, C_6D_6) δ: 58.74. IR (Nujol, ν/cm^{-1}): 625 (P=S), 980, 1000 (POC), 1100, 1120 (COC), 1600 (weak, Ph), 3200 (br., NH). Found (%): C, 49.77; H, 6.87; P, 6.45. Calc. for $C_{21}H_{34}NO_7PS_2$ (%): C, 49.69; H, 6.75; P, 6.10.

[‡] *Bis{[4-(*N*-diisopropoxythiophosphoryl)amidothiocarbonyl-1,2-benzo]-15-crown-5-S,S'}nickel(II)* **3**: yield 47%, mp 163 °C ($C_6H_6 + C_6H_{14}$, 1:3). ^{1}H NMR (300 MHz, C_6D_6) δ: 1.54 (d, 6H, Me, J_{HH} 6.2 Hz), 1.67 (d, 6H, Me, J_{HH} 6.2 Hz), 3.66–3.70, 3.80–3.94 (2m, 16H, OCH_2 crown), 5.55 [d sept, 2H, CH (Pr^{i}), J_{HH} 6.2 Hz, J_{PH} 10.3 Hz], 6.67 [d, 1H, H(1) (Ph), $J_{H(1)H(2)}$ 8.4 Hz], 8.31 [d, 1H, H(3) (Ph), $J_{H(2)H(3)}$ 2.2 Hz] 8.49 [dd, 1H, H(2) (Ph), $J_{H(1)H(2)}$ 8.4 Hz, $J_{H(2)H(3)}$ 2.2 Hz]. ^{31}P-{^{1}H} NMR (121.4 MHz, C_6D_6) δ: 54.7. IR (Nujol, ν/cm^{-1}): 580 (P=S), 980, 1000 (POC), 1100, 1120 (COC), 1600 (weak, Ph). Found (%): C, 47.06; H, 6.18; Ni, 5.45; P, 5.67. Calc. for $C_{42}H_{66}N_2NiO_{14}P_2S_4$ (%): C, 47.06; H, 6.21; Ni, 5.48; P, 5.78.

3 N. G. Zabirov, V. V. Brusko, S. V. Kashevarov, F. D. Sokolov, V. A. Shcherbakova, A. Yu. Verat and R. A. Cherkasov, *Zh. Obshch. Khim.*, 2000, **70**, 1294 (*Russ. J. Gen. Chem.*, 2000, **70**, 1214).

4 F. C. J. M. van Vegel, W. Verboom and D. N. Reinhoudt, *Chem. Rev.*, 1994, **94**, 279.

5 A. F. Grapov, V. N. Zontova and N. N. Melnikov, *Dokl. Akad. Nauk SSSR*, 1980, **251**, 882 [*Dokl. Chem.* (*Engl. Transl.*) 1980, **251**, 158].

6 N. G. Zabirov, V. N. Solov'ev, F. M. Shamsevaleev, R. A. Cherkasov and I. V. Martynov, *Zh. Obshch. Khim.*, 1991, **61**, 1748 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1991, **61**, 1608].

7 F. Kh. Karataeva, N. G. Zabirov and V. V. Klochkov, *Zh. Obshch. Khim.*, 1997, **67**, 1080 (*Russ. J. Gen. Chem.*, 1997, **67**, 1017).

8 V. V. Brusko, A. I. Rakhmatullin and N. G. Zabirov, *Zh. Obshch. Khim.*, 2000, **70**, 1705 (*Russ. J. Gen. Chem.*, 2000, **70**, 1603).

9 V. V. Brusko, A. I. Rakhmatullin, V. G. Shtyrlin and N. G. Zabirov, *Zh. Obshch. Khim.*, 2000, **70**, 1618 (*Russ. J. Gen. Chem.*, 2000, **70**, 1521).

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