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Reaction of *N*-diisopropoxyphosphorylthiobenzamide (HL) with the Co$^{\text{II}}$ cation: the crystal structure of CoL$_2$ and CoL$_2$·2HL complexes

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The title complexes CoL$_2$ and CoL$_2$·2HL were synthesised and characterised using IR spectroscopy, mass spectrometry and single-crystal X-ray diffraction analysis.

It is well known,[1–4] that the complexes of deprotonated *N*-thioacylamidothiophosphates RC(S)NHP(S)R$'_2$ contain a tetrahedral CoS$_4$ core, which is highly stable due to π-dative interactions between the central ion and the chelator sulfur atoms. In contrast to dithio derivatives, the Co$^{\text{II}}$ complexes with the anions of *N*-thioacylamidophosphates RC(S)NHP(O)R$'_2$ containing a phosphoryl fragment were not studied earlier. Substitution of two sulfur atoms in the central ion coordination sphere for oxygen atoms lowers the degree of stabilization of π-interactions. It makes the Co$^{\text{II}}$ cation coordinatively unsaturated, and the CoO$_2$S$_2$ core is less stable than the CoS$_4$ fragment. Because of this, *N*-thioacylamidophosphates RC(S)NHP(O)R$'_2$ containing various donor atoms can show significant changes in coordination properties as compared with thiophosphoryl analogues.

This work is devoted to the complexing properties of *N*-diisopropoxyphosphorylthiobenzamide HL[5,6] with the Co$^{\text{II}}$ cation. The reaction of an aqueous Co(NO$_3$)$_2$·6H$_2$O solution with the potassium salt of HL in 96% aqueous ethanol was studied. Two types of complexes were isolated from the reaction mixture: blue crystals of CoL$_2$ **1** and yellow crystals of CoL$_2$·2HL **2**.[†] The structures of complexes **1** and **2** were determined by single-crystal X-ray diffraction.[‡] The Co$^{\text{III}}$L$_3$ complex was precipitated with an insignificant yield (less than 5%).[§]

Complex **1** in a crystal located in a special position at the axis 2 (C_2 symmetry). It is a spirocyclic chelate with a distorted tetrahedral CoO$_2$S$_2$ core (Figure 1). The endocyclic angles S–Co–O are reduced, and the exocyclic angles are increased in comparison with an ideal tetrahedral angle of 109.5° (Table 1). Six-membered chelate rings are practically flat in the molecule of **1**. The maximum deviation from the mean-square plane Co–O–P–N–C–S is observed for P(1) phosphorus [–0.107(1) Å] and O(1) oxygen [0.110(2) Å] atoms. The dihedral angle between chelate planes is 79.97(6)°.

Complex **2** was formed by the hydrolysis of chelate **1** under reaction conditions. *N*-Phosphorylthiobenzamide HL, which is formed at the first stage of a process, serves as a neutral ligand in the coordination sphere of complex **1**. According to the Cambridge Crystallographic Database (November 2002), complex **2** has no structural analogues among *N*-acylamidophosphates and related chelators such as imidodi(thio)phosphinates R$_2$P(X)NHP(Y)R$'_2$ and β-di(thio)carbonyl compounds.

$$\text{CoL}_2 + 2\text{H}_2\text{O} \rightarrow \text{Co(OH)}_2 + 2\text{HL}$$
$$\text{CoL}_2 + 2\text{HL} \rightarrow \text{CoL}_2\cdot 2\text{HL}$$

The mass spectrum of **1** contains the molecular ion peak with *m/z* 659.3 (100.0%). The molecular ion of **2** (*m/z* 1262.28) is

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[†] IR spectra (Nujol) were recorded on a Specord M-80 spectrometer in the range 400–3600 cm^{-1}. Mass spectra were measured on TRACE MS Finnigan MAT instrument. Electron ionization energy was 70 eV. The substance was injected directly into the ion source at 150 °C. Heating was carried out in a programmed mode from 35 to 200 °C at a rate of 35 K/min.

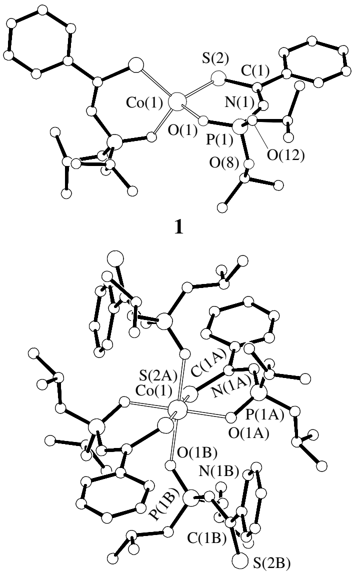
*Bis[*N*-diisopropoxyphosphorylthiobenzamido-*S,O*]cobalt(II)* **1** and *bis[*N*-diisopropoxyphosphorylthiobenzamido-*S,O*]bis[diisopropoxyphosphorylthiobenzamid-O]cobalt(II)* **2**. To a solution of 8.5 mmol HL in 30 ml of 96% EtOH, a solution of 9.0 mmol potassium hydroxide (6% surplus) in 30 ml of EtOH was added. The mixture was stirred for 15 min. An aqueous solution of 4.5 mmol (6% surplus) of Co(NO$_3$)$_2$·6H$_2$O was added to the resulting solution. The complexes formed were extracted with methylene chloride (10×5 ml); the extract was washed with distilled water (15×5 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 **1** was obtained as dark blue crystals: 0.67 g (24%), mp 95 °C (repeated recrystallization from CH$_2$Cl$_2$ + C$_6$H$_{14}$). IR (ν/cm^{-1}): 1528 (SCN), 990–1000 (POC), 1140 (P=O). MS (EI), *m/z*: 659.3 (M$^+$, 100.0%); calc. for Co[PhC(S)NP(O)(OPr^i)$_2$]$_2$, *m/z*: 659.6. Found (%): C, 47.23; H, 5.68; P, 9.45. Calc. for C$_{26}$H$_{38}$CoN$_2$O$_6$P$_2$S$_2$ (%): C, 47.34; H, 5.81; P, 9.39.

After the precipitation of complex **1**, the solution was decanted. Complex **2** was obtained as yellow crystals: 1.1 g (41%), mp 143 °C (repeated recrystallization from CH$_2$Cl$_2$ + C$_6$H$_{14}$). IR (ν/cm^{-1}): 1490 (SCN) for L, 1510 (SCN) for HL, 1000–1010 (POC), 1145 (P=O) for L, 1235 (P=O) for HL. MS (EI), *m/z*: 1262.28 (M$^+$, not observed), 659.3 (M$^+$ of CoL$_2$ complex core, 62.5%); calc. for Co[PhC(S)NP(O)(OPr^i)$_2$]$_2$, *m/z*: 659.6. Found (%): C, 49.70; H, 6.18; P, 10.02. Calc. for C$_{52}$H$_{78}$CoN$_4$O$_{12}$P$_4$S$_4$ (%): C, 49.48; H, 6.23; P, 9.82.

[‡] *X-ray study of complexes* **1** and **2** was carried out on an automatic Enraf-Nonius CAD4 diffractometer at 20 °C. Crystals of compound **1** C$_{26}$H$_{38}$CoN$_2$O$_6$P$_2$S$_2$, monoclinic, a = 18.249(6), b = 9.769(2), c = = 18.220(7) Å, β = 93.23(2)°, V = 3243(1) Å^3, Z = 4, d_{calc} = 1.35 g cm^{-3}, space group $C2/c$. Crystals of compound **2** C$_{52}$H$_{78}$CoN$_4$O$_{12}$P$_4$S$_4$, monoclinic, a = 12.546(3), b = 12.931(2), c = 19.698(7) Å, β = 95.45(4)°, V = 3180(4) Å^3, Z = 2, d_{calc} = 1.32 g cm^{-3}, space group $P2_1/n$. Molecules of **1** and **2** in crystals located in a special position: the molecule of **1** at the axis 2; the molecule of **2** at the symmetry centre. Cell parameters and intensities of 2537 (for **1**) and 8299 (for **2**) independent reflections, from which 1629 (for **1**) and 1776 (for **2**) with $I \geq 3\sigma$, were measured on an Enraf-Nonius CAD-4 diffractometer in the $\omega/2\theta$ scan mode, $\theta \leq 24.62°$ for **1** and ω-scan, $\theta \leq 22.76°$ for **2** (MoKα radiation, graphite monochromator). The intensity falling was not observed at three control measurements, the absorption was not taken into account because it was small [μ(Mo) = 7.9 cm^{-1} for **1**; μ(Mo) = 5.6 cm^{-1} for **2**]. The structure was solved by a direct method using the SIR program.[7] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were solved from difference Fourier maps, and their contribution to structural factors was refined isotropically (**1**) or included with fixed positional and isotropic thermal parameters (**2**) in the last cycles. The final residuals were R = 0.030, R_{w} = 0.036 (**1**) and R = 0.052 and R_{w} = 0.050 (**2**) on 1629 (**1**) and 1776 (**2**) independent reflections $F^2 \geq 3\sigma^2$. All calculations were performed on an Alpha Station 200 computer using the MolEN program package.[8] Intermolecular contact analysis and the figures of molecules were performed with the PLATON program.[9]

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 225507 for **1** and 225508 for **2**. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2004.

[§] The structure and properties of the latter compound will be published elsewhere.



1

2

Figure 1 Molecular structures of complexes **1** and **2** (hydrogen atoms are not shown).

unstable under measurement conditions, and the heaviest molecular ion observed in the spectra of **2** corresponds to the neutral $\mathrm{CoL_2}$ complex core, *m*/*z* 659.3 (62.5%).

The structures of complexes **1** and **2** are precisely reflected by IR-spectroscopic data. The absorption bands of the P=O group of anionic forms L in complexes **1** and **2** are shifted by approximately 100 $\mathrm{cm^{-1}}$ at low frequencies[†] concerning parent ligand HL band [ν(P=O) 1252 $\mathrm{cm^{-1}}$], this confirms their participation in the chelate formation.

The IR spectrum of **2** contains two bands of different phosphorus groups. Along with the above band corresponding to the L form, a strong P=O band is observed at 1235 $\mathrm{cm^{-1}}$ due to the bounded neutral molecules of HL. Its frequency also decreases in comparison with that of the band of the free ligand; however, the shift is 17 $\mathrm{cm^{-1}}$. The absorption band of the NH group at 3140 $\mathrm{cm^{-1}}$ also proves the presence of HL molecules in complex **2**.

The molecule of **2** in a crystal is located in a special position at the symmetry centre. The coordination polyhedron of the $\mathrm{Co^{II}}$ atom is a distorted tetragonal bipyramid (D_{2h}) (Figure 1, Table 1).

Equatorial positions of the bipyramid are occupied by two *N*-phosphorylthiobenzamide anions bound through sulfur and oxygen atoms of phosphoryl groups. The six-membered Co–O–P–N–C–S ring has a distorted boat conformation: the O–P–N–C–S fragment is flat within the limits of 0.029(7) Å, the deviation of the cobalt atom is 0.979 Å. Ligands are situated in a *trans* configuration. In the chelate rings of complexes **1** and **2**, the bond lengths differ insignificantly. A negative charge delocalization in the S–C–N–P–O pentade takes place in both cases. It leads to the contraction of C–N and P–N bonds and also to the lengthening of C=S and P=O bonds in comparison with the free ligand HL[5] (Table 1).

Neutral ligand molecules are coordinated in axial positions through the oxygen atoms of phosphoryl groups. There are two intramolecular NH···S bonds between the neutral and anionic ligands in a crystal of complex **2**. The hydrogen bond parameters are as follows: N(1B)–H(1B)···S(2A) (–*x*, –*y*, –*z*), *d*(N–H) 1.02 Å, *d*(H···S) 2.46 Å, *d*(N···S) 3.381(7) Å, ∠(NH…S) 150.70°.

Table 1 Selected bond lengths (Å) and valent and torsion angels (°) in complexes **1** and **2** and the free ligand $\mathrm{PhC(S)NHP(O)(OPr^i)_2}$ (HL).

	HL (ref. 5)	$\mathrm{CoL_2}$	$\mathrm{CoL_2{\cdot}2HL}$	
			L	HL
Co–S	—	2.2894(9)	2.452(3)	—
Co–O	—	1.939 (2)	2.052(6)	2.197(6)
C–S	1.646	1.731(3)	1.72(1)	1.62(1)
C–N	1.360	1.296(3)	1.29(1)	1.41(1)
P–N	1.672	1.610(2)	1.612(8)	1.646(8)
P=O/P–O	1.457	1.489(2)	1.486(7)	1.467(7)
S–Co–O (endocyclic)	—	101.25(6)	90.5(2)	—
S–Co–O (exocyclic)	—	116.49(6)	89.5(2)	—
S–C–N–P	7.57	3.1(5)	7(1)	–2(1)
O–P–N–C	177.1	–15.7(3)	–7(1)	177.3(8)

The conformations of neutral molecules and the lengths of P=O and P–N bonds in a crystal are practically identical to the data for free *N*-phosphorylthiobenzamide HL.[5] Only some lengthening of C–S and C–N bonds is observed, which is connected with the displacement of electronic density in the SCNPO pentade on the oxygen atom of the phosphoryl group (Table 1).

The instability of the $\mathrm{CoO_2S_2}$ core coordination environment in the chelates of tetracoordinated $\mathrm{Co^{II}}$ cations with $\mathrm{RC(S)NHP(O)R'_2}$ ligands provides an opportunity to synthesise a wide range of stable mixed complexes similar to compounds **2** by interaction with σ-donor ligands. The $\mathrm{CoO_2S_2}$ core structure can be used in homogeneous catalysis and for the synthesis of new metal-containing macrocyclic and supramolecular compounds.

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