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# Synthesis, Crystal Structure and Magnetic Properties of the Complex $Co[Me_2NC(S)NP(S)(OPr\text{-}i)_2]_2$[1]

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**Abstract**—The reaction of *N*-(diisopropoxyphosphorothioyl)-*N*',*N*'-dimethylthiourea [$Me_2NC(S)NHP(S)(OPr\text{-}i)_2$, HL) potassium salt with Co(II) cation in aqueous ethanol gave the chelate complex $Co(L\text{-}S,S')_2(CoL_2)$. The structure of the resulting compound was studied by means of IR spectroscopy, microanalysis, and X-ray analysis. The metal center was found to occur in a tetrahedral $S_4$ environment formed by the C=S and P=S sulfur atoms of two deprotonated ligands L. Magnetic properties of the complex $CoL_2$ were also studied.

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Acylamidophosphates and their thio analogs of the general formula $RC(X)NHP(Y)R'_2$ (X, Y = O, S) form fairly stable chelates with a series of double-charged metal ions, in particular, with Co(II) ions [1]. The presence of coordination-active (thio)carbonyl and (thio)phosphoryl groups and of a relatively acidic proton in molecules of *N*-(thio)phosphorylated (thio) ureas and (thio)amides predetermines the possibility of chelation through the sulfur and oxygen donor centers with formation of a stable six-membered chelate ring [2, 3].

Recent progress in the synthesis and characterization of metal phosphonate compounds has been driven by the need to understand their novel physical properties and their potential interesting magnetic, sensing, catalytic, and ion-exchange properties [6–10]. Amidophosphates $RC(S)NHP(S)R'_2$ have long attracted attention of researchers due to their ability to form stable chelates with Group IB, IIB, and VIIIB transition metal cations. These compounds and their complexes exhibit antiviral activity [11].

The present work continues our previous studies on the structure and magnetic properties of Co(II) complexes with *N*-(thio)phosphorylthioureas [12–18]. As ligand we used *N*-(diisopropoxyphosphorothioyl)-*N*',*N*'-dimethylthiourea (HL). It was converted into potassium salt KL which was brought into reaction with cobalt(II) nitrate in aqueous ethanol. The resulting coordination compound ($CoL_2$) was isolated as a crystalline solid that is soluble in most polar solvents.

The IR spectrum of $CoL_2$ contains an absorption band of the P=S group in anionic form L, which is displaced by 45 $cm^{-1}$ toward low frequencies relative to the corresponding band of parent ligand HL. A strong absorption band was also observed at 1540 $cm^{-1}$ due to the conjugated SCN fragment, while no band assignable to NH group was present. These findings indicated complex formation through the P=S groups in the deprotonated ligand. The presence of a strong broadened band in the region 993–1019 $cm^{-1}$ (POC) confirmed conservation of the thiophosphate fragment.

The variable-temperature magnetic susceptibility data for a crystalline sample of complex $CoL_2$ was measured in the temperature range from 1.9 to 300 K with an applied field of 5 T. The temperature dependences of the magnetic susceptibility $\chi_M$, the reciprocal magnetic susceptibility $\chi_M^{-1}$, and the product $\chi_M T$ are shown in Fig. 1. Complex $CoL_2$ revealed complicated magnetic behavior. Variable-temperature magnetic susceptibility of a powdered sample of $CoL_2$ showed a clear discontinuity near 50 K. In this case, $\chi_M T$ steadily increases upon cooling until $T_c$ = 50 K. At lower temperatures, $\chi_M T$ sharply increases, reaching a maximum at about 45 K (Fig. 1). The high-temperature behavior of the magnetic susceptibility is consistent

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[1] The text was submitted by the authors in English.

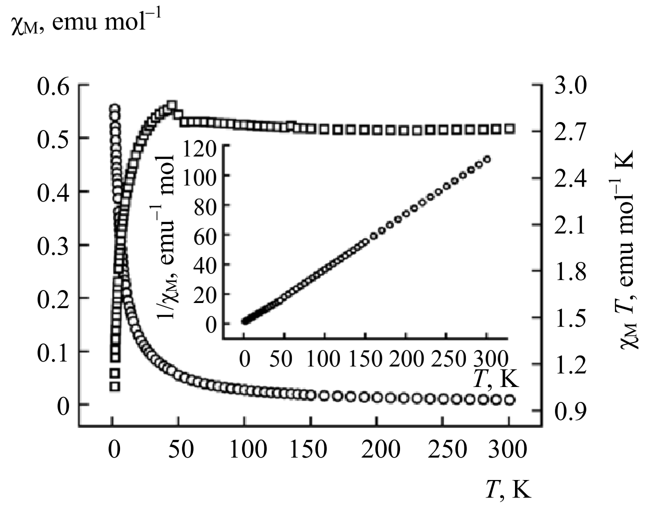

**Fig. 1.** Magnetic susceptibility $\chi_M$ (open circles) and the product $\chi_M T$ (open squares) plotted as a function of temperature for powder samples $CoL_2$. The insets show the inverse magnetic susceptibility $\chi_M^{-1}$.

with the presence of a ferromagnetic exchange between cobalt(II) atoms in two neighboring molecules. We suppose that this result agrees with a spin-canted ferromagnetic behavior [19, 20] and antiferromagnetic ordering below 45 K. The plot of $\chi_M^{-1}$ versus $T$ for $CoL_2$ revealed two linear regions on account of the presence of two structural phases. Fitting the data to the Curie–Weiss equation yields $C$ = 2.70 emu mol$^{-1}$ and $\theta$ = 1.45 K ($\chi_M^{-1} = 0.371T - 0.5387$; $r = 1$) for the temperature range 300–50 K and $C$ = 3.07 emu mol$^{-1}$ and $\theta$ = –3.54 K ($\chi_M^{-1} = 0.3254T + 1.1518$; $r = 0.9999$) for the temperature range 40–2 K.

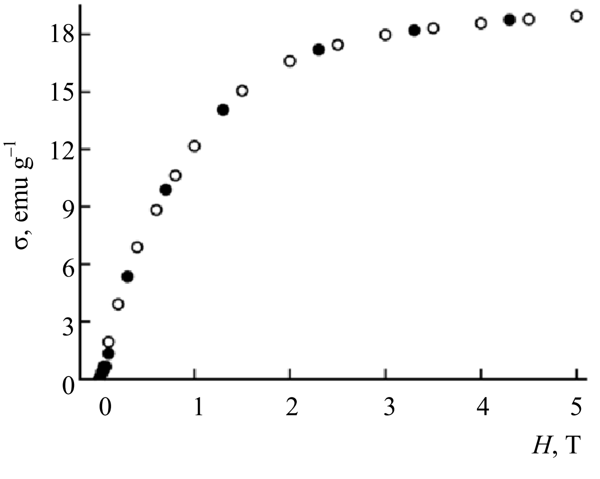

**Fig. 2.** $\sigma$ vs. $H$ plot with the magnetic field increased (open circles) and decreased (full circles) at $T$ = 2 K for complex $CoL_2$.

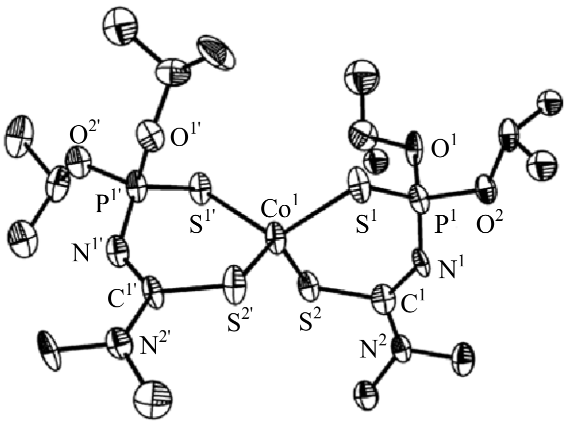

**Fig. 3.** Molecular structure of complex $CoL_2$ according to the X-ray diffraction data. Hydrogen atoms are not shown for clarity. Selected bond distances (Å) and angles (deg): $Co^1–S^1$ 2.337(6), $Co^1–S^{1'}$ 2.330(5), $Co^1–S^2$ 2.289(6), $Co^1–S^{2'}$ 2.295(5), $P^1–O^1$ 1.594(13), $P^1–O^2$ 1.573(13), $P^1–N^1$ 1.558(19), $P^1–S^1$ 2.012(6), $S^1–C^1$ 1.78(2), $N^1–C^1$ 1.33(3), $N^2–C^1$ 1.31(3); $S^{1'}Co^1S^1$ 121.6(2), $S^2Co^1S^1$ 108.02(19), $S^2Co^1S^{1'}$ 96.98(19), $S^2Co^1S^{2'}$ 125.3(3), $S^{2'}Co^1–S^1$ 99.0(2), $S^{2'}Co^1S^{1'}$ 108.03(19), $O^2P^1O^1$ 101.4(7), $O^2P^1S^1$ 108.6(5), $O^1P^1S^1$ 110.7(6), $N^1P^1O^2$ 102.7(8), $N^1P^1O^1$ 115.9(8), $N^1P^1S^1$ 115.9(6), $P^1S^1Co^1$ 101.4(2), $C^1S^2Co^1$ 108.4(6), $C^1N^1P^1$ 136.6(16), $N^2C^1N^1$ 119.6(18), $N^2C^1S^2$ 116.9(15), $N^1C^1S^2$ 123.4(17).

Figure 2 shows the field strength dependence of $\sigma$ for complex $CoL_2$ at $T$ = 2 K. In these measurements, the field was initially increased (light circles) and then decreased (dark circles). No differences were observed between the $\sigma$ plots measured with increase or decrease of the magnetic field strength.

The molecular structure of complex $CoL_2$ in crystal is shown in Fig. 3; selected bond lengths and bond angles are also given. Complex $CoL_2$ is a spirocyclic chelate with a distorted tetrahedral $CoS_4$ coordination entity. The endocyclic angle SMS is reduced, while the exocyclic one is increased in comparison with an ideal tetrahedral angle of 109.5°. The six-membered CoSPNCS rings have a distorted *boat* conformation with planar PNCS fragment. The phosphorus atoms are in a distorted tetrahedral $NO_2S$ environment.

In summary, a novel Co(II) complex with *N*-thiophosphorylated thiourea $Me_2NC(S)NHP(S)(OPr\text{-}i)_2$ has been successfully synthesized. IR spectroscopy has shown that the thiourea in this complex acts as a 1,5-*S,S'*-ligand. The central cobalt(II) ion has a tetrahedral configuration. Interesting spin-canted magnetic behavior of $CoL_2$ should also be noted; it is related to the presence of methyl substituents and ligands coordinated to tetrahedral metal center, obviously without intermolecular hydrogen bonds.

## EXPERIMENTAL

The IR spectra (Nujol) were recorded in the range 400–3600 cm$^{-1}$ using a Specord M-80 spectrometer. Magnetic susceptibility measurements for a polycrystalline sample of $CoL_2$ were performed on MPMS-5 Quantum Design instrument in the temperature range 1.9–300 K at a magnetic field strength of 0 to 5 T. Elemental analyses were performed on a Perkin–Elmer 2400 CHN microanalyzer.

**Bis[*N*-(diisopropoxyphosphorothioyl)-*N'*,*N'*-dimethylthiocarbamido-*S*,*S'*]cobalt(II) ($CoL_2$).** A suspension of 0.852 g (3 mmol) of *N*-(diisopropoxyphosphorothioyl)-*N'*,*N'*-dimethylthiourea (HL) in 20 ml of aqueous ethanol was mixed with a solution of 0.185 g (3.3 mmol) of potassium hydroxide in ethanol. An aqueous solution of 0.582 g (2 mmol) of $Co(NO_3)_2 \cdot 6H_2O$ was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred for 3 h at room temperature and left overnight. The resulting complex was extracted with methylene chloride, the extract was washed with water and dried over anhydrous $MgSO_4$, the solvent was removed under reduced pressure, and the residue was recrystallized from methylene chloride–*n*-hexane. Complex $CoL_2$ was isolated as green crystals, yield 0.685 g (73%), mp 84°C. IR spectrum, ν, cm$^{-1}$: 596 (P=S); 993, 1019 (POC); 1540 (SCN). Found, %: C 34.43; H 6.51; N 8.87. $C_{18}H_{40}CoN_4O_4P_2S_4$. Calculated, %: C 34.55; H 6.44; N 8.95.

The X-ray diffraction data were collected on a STOE IPDS-II diffractometer with graphite-monochromatized Mo$K_\alpha$ radiation generated by fine-focus X-ray tube operating at 50 kV and 40 mA. The images were indexed, integrated and scaled using the X-Area data reduction package [21]. Data were corrected for absorption using PLATON program [22]. The structure was solved by the direct method using SHELXS-97 program [23] and refined on $F^2$ with full-matrix least-squares approximation using SHELXL-97 [24]. $C_{18}H_{40}CoN_4O_4P_2S_4$, *M* 625.65; triclinic crystals, space group *P*-1; unit cell parameters: $a = 9.672(2)$, $b = 10.289(2)$, $c = 16.678(5)$ Å; $\alpha = 72.18(2)$, $\beta = 77.14(2)$, $\gamma = 78.02(2)°$; $V = 1523.0(6)$ Å$^3$; $Z = 2$; $\rho = 1.364$ g cm$^{-3}$; $\mu(MoK_\alpha) = 0.972$ mm$^{-1}$. Total of 13288 reflections were collected, 5346 of which were unique with $R_{int} = 0.3151$. Final divergence factors (all reflections): $R_1 = 0.2792$, $wR_2 = 0.5375$. The complete set of crystallographic data was deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 692850) and are available free of charge via *http://www.ccdc.cam.ac.uk/conts/retrieving.html* or upon request by e-mail: *deposit@ccdc.cam.ac.uk* (12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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