

Short communication

Synthesis and Characterization of Co(II) Complexes of *N*-Thiophosphorylated Thioureas $\text{RC}(\text{S})\text{NHP}(\text{S})(\text{O}i\text{Pr})_2$ ($\text{R} = \text{Me}_2\text{N}$, $2\text{-MeC}_6\text{H}_4\text{NH}$, $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NH}$, $2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{NH}$)

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Abstract

Reaction of the potassium salts of *N*-thiophosphorylthioureas $\text{RC}(\text{S})\text{NHP}(\text{S})(\text{O}i\text{Pr})_2$ ($\text{R} = \text{Me}_2\text{N}$, HL^{I} ; $2\text{-MeC}_6\text{H}_4\text{NH}$, HL^{II} ; $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NH}$, HL^{III} ; $2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{NH}$, HL^{IV}) with Co(II) cations in aqueous EtOH leads to the complexes $[\text{Co}(\text{L}^{\text{I-IV}}\text{-S,S}')_2]$ ($[\text{CoL}^{\text{I-IV}}]_2$). The structures of the complexes were studied by IR, UV-Vis spectroscopy and microanalysis. The crystal and molecular structure of $[\text{CoL}^{\text{I}}]_2$ was elucidated by single crystal X-ray diffraction. The metal center is found in a tetrahedral S_4 environment formed by the C=S and P=S sulfur atoms of two deprotonated ligands L^{I} . Magnetic properties of $[\text{CoL}^{\text{I}}]_2$ were also investigated.

Keywords: Cobalt(II), crystal structure, *N*-thiophosphorylthiourea, magnetic properties

1. Introduction

Phosphorylated amides and ureas, and their thioanalogues of the general formula $\text{RC}(\text{X})\text{NHP}(\text{Y})\text{R}'_2$ ($\text{X}, \text{Y} = \text{O}, \text{S}$) form fairly stable complexes with a series of double-charged metal ions, in particular, with Co(II).¹ The presence of (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 chelating coordination of these ligands through the sulfur and oxygen donor centers with the formation of a stable six-membered chelate ring.^{2,3}

Recent progress in the synthesis and characterization of metal phosph(on)ate compounds has been driven by the need to understand the novel physical properties and their interesting magnetic, catalytic and ionexchange properties.⁴⁻⁸

Thiophosphorylated thioamides $\text{RC}(\text{S})\text{NHP}(\text{S})\text{R}'_2$ and thioureas $\text{R}^1\text{R}^2\text{NC}(\text{S})\text{NHP}(\text{S})\text{R}'_2$ have long attracted attention of researchers due to their ability to form stable complexes with IB, IIB, and VIIIIB group transition metal

cations. These compounds and their complexes exhibit antiviral activity.⁹

Herein we describe Co(II) complexes of *N*-thiophosphorylated thioureas $\text{RC}(\text{S})\text{NHP}(\text{S})(\text{O}i\text{Pr})_2$ ($\text{R} = \text{Me}_2\text{N}$, $2\text{-MeC}_6\text{H}_4\text{NH}$, $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NH}$, $2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{NH}$). The data presented is a continuation of investigations devoted to the structures and magnetic properties of Co(II) complexes with *N*-(thio)phosphorylthioamides and thioureas.¹⁰⁻²¹

2. Experimental

N-Thiophosphorylated thioureas $\text{HL}^{\text{I-IV}}$ were prepared according to previously described techniques.²¹⁻²³ The complex $[\text{CoL}^{\text{I}}]_2$ was prepared according to the previously described method.²¹

2. 1. Synthesis of $[\text{CoL}^{\text{II-IV}}]_2$

A suspension of $\text{HL}^{\text{II-IV}}$ (0.768, 1.038, 1.080 or 1.122 g, respectively; 3 mmol) in 96% aqueous EtOH

(20 mL) was mixed with an 96% aqueous EtOH solution of KOH (0.185 g, 3.3 mmol). An aqueous (20 mL) solution of $\text{Co}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ (0.582 g, 2 mmol) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for a further 3 h and left overnight. The resulting complex was extracted with CH_2Cl_2 , washed with water and dried with anhydrous MgSO_4 . The solvent was then removed in vacuo. A precipitate was isolated from a CH_2Cl_2 solution by slowly adding *n*-hexane.

[CoL^{II}₂]. Yield 0.889 g (79%), green viscous oil. IR: ν 602 (P=S), 1002 (POC), 1569 (SCN), 3283 (NH) cm^{-1} . UV-Vis λ_{max} (ϵ , $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$): 559 (302), 608 (327), 670 (163) nm. Anal. Calcd for $\text{C}_{28}\text{H}_{44}\text{CoN}_4\text{O}_4\text{P}_2\text{S}_4$: C 44.76, H 5.96, N 7.39. Found: C 44.85, H 5.91, N 7.47.

[CoL^{III}₂]. Yield 1.072 g (92%), green viscous oil. IR: ν 599 (P=S); 1011 (POC); 1558 (SCN); 3299 (NH) cm^{-1} . UV-Vis λ_{max} (ϵ , $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$): 567 (294), 602 (339), 661 (157) nm. Anal. Calcd for $\text{C}_{30}\text{H}_{48}\text{CoN}_4\text{O}_4\text{P}_2\text{S}_4$: C 46.32, H 6.22, N 7.20. Found: C 46.40, H 6.17, N 7.14.

[CoL^{IV}₂]. Yield 1.051 g (87%), green viscous oil. IR: ν 606 (P=S); 998 (POC); 1549 (SCN); 3270 (NH) cm^{-1} . UV-Vis λ_{max} (ϵ , $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$): 562 (292), 611 (337), 672 (165) nm. Anal. Calcd for $\text{C}_{32}\text{H}_{52}\text{CoN}_4\text{O}_4\text{P}_2\text{S}_4$: C 47.69, H 6.50, N 6.95. Found: C 47.78, H 6.61, N 7.02.

2. 2. Physical Measurements

Infrared spectra (Nujol) were recorded with a Specord M-80 spectrometer in the range 400–3600 cm^{-1} . Electronic absorption spectra of CH_2Cl_2 solutions were recorded in the range 200–900 nm on a Perkin-Elmer Lambda 35 spectrophotometer. Magnetic susceptibility measurements were performed on MPMS-5 Quantum Design instrument in the temperature range 1.9–300 K and field range 0–5 T using polycrystalline samples of **[CoL^I₂]**. Elemental analyses were performed on a Perkin-Elmer 2400 CHN microanalyzer.

2. 3. Crystal Structure Determination and Refinement

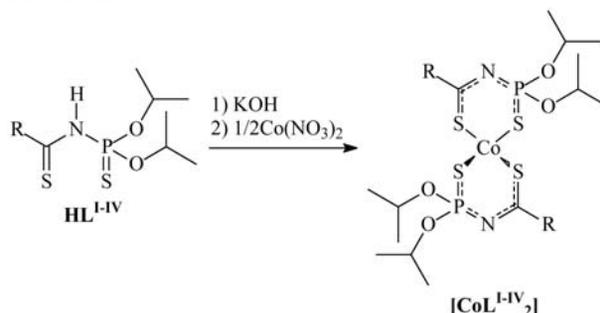
The X-ray data were collected on STOE IPDS-II diffractometer with graphite-monochromatized Mo-K α radiation generated by fine-focus X-ray tube operated at 50 kV and 40 mA. The images were indexed, integrated and scaled using the X-Area data reduction package.²⁴ Data were corrected for absorption using the PLATON program.²⁵ The structure was solved by direct method using the SHELXS-97 program²⁶ and refined on F^2 with full-matrix least-squares using SHELXL-97.²⁷

CCDC 692850 contains the supplementary crystallographic data for **[CoL^I₂]**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ,

UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

3. Results and Discussion

Complexes **[CoL^{II-IV}₂]** were prepared by the following procedure: the corresponding ligand was converted into the potassium salt and followed by reaction with $\text{Co}(\text{NO}_3)_2$ in aqueous EtOH (Scheme 1). The compounds **[CoL^{II-IV}₂]** are viscous oils, which are soluble in most polar solvents.



R = Me₂N (**HL^I**, **[CoL^I₂]**); 2-MeC₆H₄NH (**HL^{II}**, **[CoL^{II}₂]**);

2,6-Me₂C₆H₃NH (**HL^{III}**, **[CoL^{III}₂]**); 2,4,6-Me₃C₆H₂NH (**HL^{IV}**, **[CoL^{IV}₂]**)

Scheme 1

The IR spectra of **[CoL^{II-IV}₂]** exhibit bands for the P=S group of the anionic forms **L^{II-IV}** at 599–606 cm^{-1} . There is also an intense band at 1549–1569 cm^{-1} corresponding to the conjugated SCN fragment. This fact confirms unequivocally the complex formation. Furthermore broad intense bands were observed for the POC group at 998–1011 cm^{-1} . This confirms the conservation of the structure of the ligands in the obtained complexes. There is no band for the PNH group, which testifies the deprotonated form of the ligands. The band for the arylNH group was found at 3270–3299 cm^{-1} .

In the UV-Vis spectra of **[CoL^{II-IV}₂]** in CH_2Cl_2 solution there is a structured absorption with maxima at 559–567 (ϵ_{max} 292–302 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$), 602–611 (ϵ_{max} 327–339 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$), and 661–672 (ϵ_{max} 157–165 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$) nm. The band corresponds to a transition from the ground state $^4\text{A}_2$ to the $^4\text{T}_1(\text{P})$ state. The fine structure is caused by the spin-orbital interaction as a result of which, first, there is a splitting of the state $^4\text{T}_1(\text{P})$ and, second, there are resolved transitions in the next doublet states with the same intensity. Other possible transitions, namely $^4\text{A}_2 \rightarrow ^4\text{T}_2$ and $^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{F})$ are outside the visible area. The UV-data confirm the tetrahedral environment of the Co(II) cation in **[CoL^{II-IV}₂]**.^{13–15}

The variable temperature magnetic susceptibility data for the crystalline sample of **[CoL^I₂]** were measured

in the temperature range 1.9–300 K with an applied field of 0.1 T. The temperature dependence of the magnetic susceptibility (χ_M), the reciprocal magnetic susceptibility (χ_M^{-1}), and the product $\chi_M T$ are shown in Figure 1.

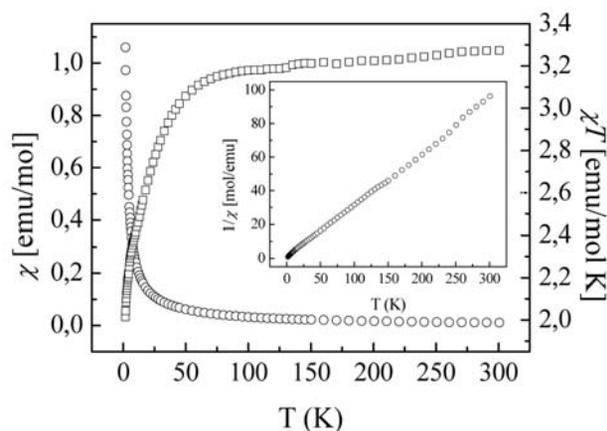


Figure 1. Magnetic susceptibility χ_M (open circles) and the product $\chi_M T$ (open squares) plotted as a function of temperature for powder samples $[\text{CoL}_2]$. The insets show the inverse magnetic susceptibility χ_M^{-1} .

The magnetic susceptibility for $[\text{CoL}_2]$ follows the Curie-Weiss law: $[\chi_M^{-1} = 0.2104 T + 0.8871]$ ($r = 0.9998$), with $C = 4.75$ emu K/mol and $\theta = -4.22$ K. From the equation, $\mu_{\text{eff}} = (8\chi_M T)^{1/2}$, one obtains the effective magnetic moment per metal atom, $\mu_{\text{eff}} = 4.89$ μB , which is considerably higher than the reported spin-only value of 3.87 μB for non interaction of one $S = 3/2$ spin of Co(II). The effective magnetic moments for Co(II) compounds around room temperature are between 4.4 and 5.0, which is characteristic for mononuclear, high-spin, tetrahedral Co(II) complexes.^{28–31} This is consistent with experimental values observed for other systems at room temperature and is attributed to the orbital contribution of the Co(II) ion.

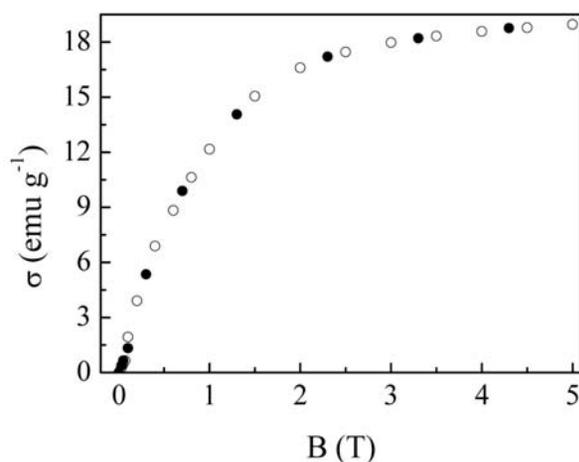


Figure 2. σ vs. $B(T)$ plot with the magnetic field increased (open circles) and decreased (full circles) at $T = 2$ K for $[\text{CoL}_2]$.

The μ_{eff} values slowly decrease until approximately 90 K, below which they drop gradually, reaching 3.92 μB at 1.9 K; this drop is likely due the prevalence of zero-field splitting effects of the Co(II) centers.^{32,33} On cooling down from room temperature, the $\chi_M T$ value decreases continuously indicating weak antiferromagnetic interactions between the Co(II) centers. This is confirmed by the negative Weiss constant, determined by the magnetic susceptibility data.

Figure 2 shows the field dependence of σ for the complex $[\text{CoL}_2]$ at $T = 2$ K. In these measurements, the field has been increased (open circles) and then decreased (full circles). No differences were observed between σ curves measured with increase or decrease of the magnetic field strength for the complex.

Table 1. Crystal Structure and Data Refinement Parameters for $[\text{CoL}_2]$

Empirical Formula	$\text{C}_{18}\text{H}_{40}\text{CoN}_4\text{O}_4\text{P}_2\text{S}_4$
Formula Weight	625.65
Crystal System / Space Group	triclinic / $P-1$
$a / \text{\AA}$	9.672(2)
$b / \text{\AA}$	10.289(2)
$c / \text{\AA}$	16.678(5)
$\alpha / ^\circ$	72.18(2)
$\beta / ^\circ$	77.14(2)
$\gamma / ^\circ$	78.02(2)
$V / \text{\AA}^3$	1523.0(6)
Z	2
$D_{\text{calc}} (\text{g/cm}^3)$	1.364
$\mu (\text{mm}^{-1})$	0.972
Crystal size (mm)	$0.19 \times 0.16 \times 0.03$
Temp (K)	173(2)
Theta range for collection	3.58–25.02
$F(000)$	658
Reflections Collected	13288
Observed Reflections	5346 ($R_{\text{int}} = 0.0581$)
R indices, (all data)	$R_1 = 0.0792$, $wR_2 = 0.1375$

Crystals of $[\text{CoL}_2]$ were obtained by slow evaporation of a saturated solution in CH_2Cl_2 – n -hexane (v/v 1:3). Results of the structure solution and refinements are collected in Table 1, the molecular structure is shown in Figure 3, bonding parameters are collected in Table 2.

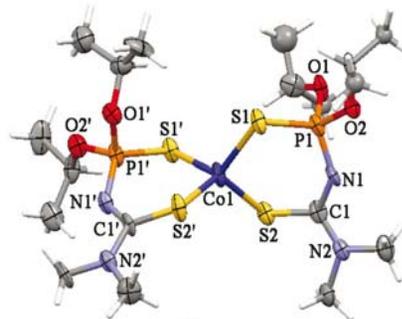


Figure 3. Thermal ellipsoid representation of $[\text{CoL}_2]$. Ellipsoids are drawn at the 30% probability level.

Table 2. Selected Bond Lengths (Å), and Bond Angles (°) for [CoL₂]

<i>Bond lengths</i>			
Co1–S1	2.337(6)	P1–N1	1.558(19)
Co1–S1'	2.330(5)	P1–S1	2.012(6)
Co1–S2	2.289(6)	S1–C1	1.78(2)
Co1–S2'	2.295(5)	N1–C1	1.33(3)
P1–O1	1.594(13)	N2–C1	1.31(3)
P1–O2	1.573(13)		
<i>Bond angles</i>			
S1'–Co1–S1	121.6(2)	N1–P1–O2	102.7(8)
S2–Co1–S1	108.02(19)	N1–P1–O1	115.9(8)
S2–Co1–S1'	96.98(19)	N1–P1–S1	115.9(6)
S2–Co1–S2'	125.3(3)	P1–S1–Co1	101.4(2)
S2'–Co1–S1	99.0(2)	C1–S2–Co1	108.4(6)
S2'–Co1–S1'	108.03(19)	C1–N1–P1	136.6(16)
O2–P1–O1	101.4(7)	N2–C1–N1	119.6(18)
O2–P1–S1	108.6(5)	N2–C1–S2	116.9(15)
O1–P1–S1	110.7(6)	N1–C1–S2	123.4(17)

The complex [CoL₂] is a spirocyclic chelate with a distorted tetrahedral CoS₄ core. The endocyclic angle S–M–S is reduced and exocyclic one is increased in comparison with an ideal tetrahedral angle of 109.5°. The six-membered CoSPNCS cycles have the conformation of a distorted boat with a planar PNCS fragment. The phosphorus atoms are in a distorted tetrahedral NO₂S environment. The complex structure is typical for Co(II) complexes with *N*-(thio)phosphorylated thioamides RC(S)NHP(X)R'₂ and thioureas R¹R²NC(S)NHP(X)R'₂ (X = O, S).^{10–21}

4. Conclusions

In summary, novel Co(II) complexes with *N*-thiophosphorylated thioureas HL^{I–IV} have been successfully synthesized. IR spectroscopy has shown that the deprotonated thioureas act as 1,5-*S,S'*-ligands forming complexes with tetrahedrally configured Co(II). This is confirmed by UV-Vis spectroscopy and XRD on one of the complexes. Magnetic properties of [CoL₂] were investigated and weak antiferromagnetic interactions between the Co(II) centers were established.

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6. References

- V. P. Botha, A. Ziegler, I. Haiduc, *Inorg. Chim. Acta* **1976**, *17*, 13–16.
- T. Q. Ly, J. D. Woollins, *Coord. Chem. Rev.* **1998**, *176*, 451–481.
- Z. Zak, T. Glowiak, E. Hermann, *Z. Anorg. Allg. Chem.* **1990**, *586*, 136–140.
- J. Zhu, X. Bu, P. Feng, G. D. Stucky, *J. Am. Chem. Soc.* **2000**, *122*, 11563–11564.
- A. Subbiah, D. Pyle, A. Rowland, J. Huang, R. A. Narayanan, P. Thiyagarajan, J. Zon, A. Clearfield, *J. Am. Chem. Soc.* **2005**, *127*, 10826–10827.
- A. K. Cheetham, G. Ferey, T. Loiseau, *Angew. Chem.* **1999**, *111*, 3466–3492.
- C. Maillot, P. Janvier, M. Pipelier, T. Praveen, Y. Andres, B. Bujoli, *Chem. Mater.* **2001**, *13*, 2879–2884.
- K. D. Demadis, S. D. Katarachia, R. G. Raptis, H. Zhao, P. Baran, *Cryst. Growth. Des.* **2006**, *6*, 836–838.
- N. G. Zabiroy, O. K. Pozdeev, F. M. Shamshevaleev, R. A. Cherkasov, G. Kh. Gilmanova, *Pharm. Chem. J. (Engl. Transl.)* **1989**, *23*, 423–425.
- F. D. Sokolov, D. A. Safin, N. G. Zabiroy, L. N. Yamaliev, D. B. Krivolapov, I. A. Litvinov, *Mendeleev Commun.* **2004**, *14*, 51–52.
- M. P. Kutyreva, M. S. Starikova, N. A. Ulakhovich, F. D. Sokolov, D. A. Safin, N. G. Zabiroy, E. E. Gubina, V. M. Amirkhanov, *Russ. J. Gen. Chem.* **2005**, *75*, 480–481.
- D. A. Safin, M. G. Babashkina, F. D. Sokolov, N. G. Zabiroy, *Inorg. Chem. Commun.* **2006**, *9*, 1133–1135.
- D. A. Safin, F. D. Sokolov, N. G. Zabiroy, V. V. Brusko, D. B. Krivolapov, I. A. Litvinov, R. C. Luckay, R. A. Cherkasov, *Polyhedron* **2006**, *25*, 3330–3336.
- D. A. Safin, P. Mlynarz, F. E. Hahn, M. G. Babashkina, F. D. Sokolov, N. G. Zabiroy, J. Galezowska, H. Kozlowski, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1472–1479.
- D. A. Safin, P. Mlynarz, F. D. Sokolov, M. Kubiak, F. E. Hahn, M. G. Babashkina, N. G. Zabiroy, J. Galezowska, H. Kozlowski, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2089–2096.
- D. A. Safin, F. D. Sokolov, V. V. Brusko, M. G. Babashkina, D. R. Chubukaeva, D. B. Krivolapov, I. A. Litvinov, *Z. Anorg. Allg. Chem.* **2008**, *634*, 967–971.
- D. A. Safin, F. D. Sokolov, H. Nöth, M. G. Babashkina, T. R. Gimadiev, J. Galezowska, H. Kozlowski, *Polyhedron* **2008**, *27*, 2022–2028.
- D. A. Safin, M. G. Babashkina, T. R. Gimadiev, M. Bolte, M. V. Pinus, D. B. Krivolapov, I. A. Litvinov, *Polyhedron* **2008**, *27*, 2978–2982.
- D. A. Safin, M. Bolte, M. G. Babashkina, *Transition Met. Chem.* **2009**, *34*, 43–49.
- D. A. Safin, M. G. Babashkina, F. D. Sokolov, S. V. Baranov, F. E. Hahn, T. Pape, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1613–1619.
- D. A. Safin, M. Bolte, M. G. Babashkina, H. Kozlowski, *Polyhedron* **2010**, *29*, 488–492.
- M. G. Babashkina, D. A. Safin, M. Bolte, A. Klein, *Inorg. Chem. Commun.* **2009**, *12*, 678–681.
- D. A. Safin, M. G. Babashkina, M. Bolte, A. Klein, *in preparation*.

24. Stoe & Cie. X-Area. Area-Detector Control and Integration Software. Stoe & Cie, Darmstadt, Germany, 2001.
25. A. L. Spek, *J. Appl. Cryst.* **2003**, A36, 7–13.
26. G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, 46, 467–473.
27. G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, 46, 112–122.
28. W. R. Gemmil, M. D. Smith, B. A. Reisner, *J. Solid State Chem.* **2005**, 178, 2658–2662.
29. R. L. Carlin, *Magneto-Chemistry*; Springer-Verlag: New York, 1986.
30. D. Kong, Y. Li, X. Ouyang, A. V. Prosvirin, H. Zhao, J. H. Ross, K. R. Dunbar, A. Clearfield, *Chem. Mater.* **2004**, 16, 3020–3031.
31. A. Cukurovali, I. Yilmaz, *Transition Met. Chem.* **2006**, 31, 207–213.
32. J.-S. Sun, H. Zhao, X. Ouyang, R. Clerac, J. A. Smith, J. M. Clemente-Juan, C. Gomez-Garcia, E. Coronado, K. R. Dunbar, *Inorg. Chem.* **1999**, 38, 5841–5855.
33. H. Sakiyama, R. Ito, H. Kumagai, K. Inoue, M. Sakamoto, Y. Nishida, M. Yamasaki, *Eur. J. Inorg. Chem.* **2001**, 2027–2032.

Povzetek

Reakcije kalijevih soli *N*-tiofosforiltiosečnin RC(S)NHP(S)(O*i*Pr)₂ (R = Me₂N, **HL**^I; 2-MeC₆H₄NH, **HL**^{II}; 2,6-Me₂C₆H₃NH, **HL**^{III}; 2,4,6-Me₃C₆H₂NH, **HL**^{IV}) s Co(II) kationi v etanolnih raztopinah vodijo do nastanka kompleksov strukturnega tipa [Co(L^{I-IV}-S,S')₂] ([CoL^{I-IV}]₂). Kompleksi so bili okarakterizirani z IR in UV-Vis spektroskopijo ter mikroanalizo. Molekulska struktura [CoL^I]₂ je bila določena z rentgensko strukturno analizo na monokristalu. Kovinski center je v tetraedričnem S₄ okolju, ki ga tvorijo C=S in P=S atomi žvepla dveh deprotoniranih ligandov L^I. Predstavljeni so tudi rezultati študija magnetnih lastnosti sintetiziranih kompleksov.