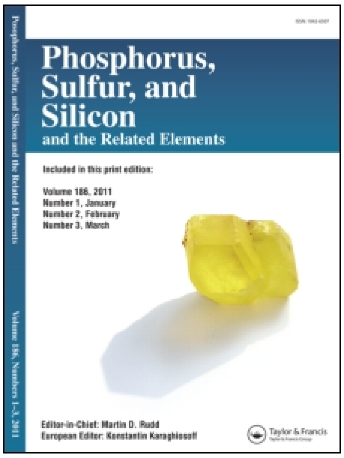

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Safin, Damir A. , Babashkina, Maria G. , Bolte, Michael , Szyrwiel, Łukasz , Klein, Axel and Kozlowski, Henryk(2010) 'Complexes of Co(II) and Zn(II) with *N*-(Thio)phosphorylthioureas AdNHC(S)NHP(O)(O*i*Pr)$_2$ and MeNHC(S)NHP(S)(O*i*Pr)$_2$', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 8, 1739 — 1745

To link to this Article: DOI: 10.1080/10426500903251365

URL: http://dx.doi.org/10.1080/10426500903251365

Phosphorus, Sulfur, and Silicon, 185:1739–1745, 2010
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500903251365

COMPLEXES OF Co(II) AND Zn(II) WITH *N*-(THIO)PHOSPHORYLTHIOUREAS AdNHC(S)NHP(O)(O*i*Pr)$_2$ AND MeNHC(S)NHP(S)(O*i*Pr)$_2$

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The reaction of the potassium salt of the N-(thio)phosphorylated thioureas AdNHC(S)NHP(O)(OiPr)$_2$ (HL^I, Ad = Adamantyl) and MeNHC(S)NHP(S)(OiPr)$_2$ (HL^{II}) with Co(II) and Zn(II) in aqueous EtOH leads to [ML$_2^{I,II}$] chelate complexes. They were investigated by UV-vis, ^{1}H and ^{31}P NMR spectroscopy, and microanalysis. The molecular structures of [ML$_2^I$] were elucidated by single crystal X-ray diffraction analysis. The metal centers in both complexes are found to be in a distorted-tetrahedral O$_2$S$_2$ environment formed by the C=S sulfur atoms and the P=O oxygen atoms of two deprotonated L^I ligands. The photoluminescence properties of [ZnL$_2^{II}$] are also reported.

Keywords Cobalt(II); crystal structure; *N*-phosphorylthiourea; luminescence; zinc(II)

INTRODUCTION

In our prior articles, we have reported complexes of *N*-(thio)phosphorylated thioureas and thioamides RC(S)NHP(X)(O*i*Pr)$_2$ (X = O, S) with Co(II) and Zn(II).[1–13] These complexes showed interesting magnetic[6,7,12] and luminescent properties.[8,11,12] Also, in our previous work we have published data illustrating the complexation properties of two *N*-(thio)phosphorylated thioureas AdNHC(S)NHP(X)(O*i*Pr)$_2$ [X = O (**HL^I**), S], containing the adamantyl substituent at the thiocarbonyl group.[12,14] We have also described the synthesis, magnetic, and luminescent properties of the cobalt(II) and zinc(II) complexes of the common formula [M{AdNHC(S)NP(O)(O*i*Pr)$_2$}]$_2$ **[ML$_2^I$]** (M = Co(II), Zn(II)).[12] Unfortunately, recently we were not successful in our X-ray single crystal investigations of **[ML$_2^I$]**.

The data presented are a continuation of the investigation of the structure of Co(II) and Zn(II) complexes with the *N*-(thio)phosphorylthioureas started in our previous work.[1–13]

Received 16 March 2009; accepted 11 August 2009.

This work was supported by the Russian Science Support Foundation. D.A.S. and M.G.B. thank DAAD for the scholarships (Forschungsstipendien 2008/2009).

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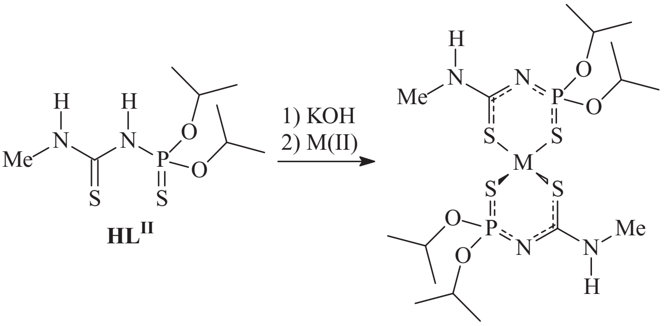
In this article, we report the crystal structures of **[ML$_2^{\mathrm{I}}$]** and new complexes of Co(II) and Zn(II) with *N*-thiophosphorylated thiourea **HL$^{\mathrm{II}}$**.

RESULTS AND DISCUSSION

The complexes **[ML$_2^{\mathrm{I}}$]** were prepared as described previously.[12] The derivatives **[ML$_2^{\mathrm{II}}$]** were synthesized similarly: the ligand **HL$^{\mathrm{II}}$** was converted into the potassium salt **KL$^{\mathrm{II}}$** and followed by reaction with $CoCl_2$ or $ZnCl_2$ in aqueous EtOH (Scheme 1). The compounds obtained are crystalline solids that are soluble in most polar solvents.



M = Co(II), **[CoL$^{\mathrm{II}}_2$]**; Zn(II), **[ZnL$^{\mathrm{II}}_2$]**

Scheme 1

Investigation of the new cobalt(II) complex **[CoL$_2^{\mathrm{II}}$]** by NMR spectroscopy was not successful because of the presence of the paramagnetic Co(II) cation. The $^{31}P\{^1H\}$ NMR spectrum of **[ZnL$_2^{\mathrm{II}}$]** contains a singlet at 55.6 ppm, which is in the typical range for deprotonated *N*-thiophosphorylated thioureas and thioamides.[15] The ^1H NMR spectrum of **[ZnL$_2^{\mathrm{II}}$]** contains a single set of signals for the *i*Pr and MeNH protons. The isopropyl group is shown as two multiplets for the CH_3 protons at 1.25–1.43 ppm, and for the CH protons at 4.59–4.93 ppm. The doublet for the Me protons was observed at 2.83 ppm, and the NH protons were shown as a broad singlet at 6.05 ppm. The signal for the NHP(S) group proton is absent in the ^1H NMR spectrum of **[ZnL$_2^{\mathrm{II}}$]**. This confirms the presence of **L$^{\mathrm{II}}$** anionic forms in the structure of **[ZnL$_2^{\mathrm{II}}$]**.

Crystals of **[ML$_2^{\mathrm{I}}$]** were obtained by slow evaporation of a saturated solution in CH_2Cl_2/*n*-hexane (v/v 1:3), and the results of the structure solution and refinements are collected in Table I. Representative structures are shown in Figures 1 and 2, and bonding parameters are collected in Table II. Both complexes in the crystal are spirocyclic chelates with a distorted tetrahedral MO_2S_2 core. The six-membered chelate rings are flattened. The *W*-criterion in the structure of complexes is realized with an *anti*-orientation of the N—C—N—H moiety, because of the sterically demanding adamantyl substituents. The crystal structure of **[ZnL$_2^{\mathrm{I}}$]** is stabilized by intermolecular hydrogen bonds in the crystal. As a result of the intermolecular interactions, polymeric chains are formed. The hydrogen bond parameters in **[ZnL$_2^{\mathrm{I}}$]** are as follows: N2—H2A···S2#1 (*x*, 3/2–*y*, 1/2+*z*), *d*(N—H) 0.86 Å, *d*(H···S) 2.81 Å, *d*(N···S) 3.664(3) Å, ∠(N—H···S) 170°; N4—H4A···S1#2 (*x*, 3/2–*y*, −1/2+*z*), *d*(N—H) 0.86 Å, *d*(H···S) 2.87 Å, *d*(N···S) 3.455(4) Å, ∠(N—H···S) 127°.

Table I Crystal structure and data refinement parameters

	[CoL$^{I}_{2}$]	**[ZnL$^{I}_{2}$]**
Empirical formula	$C_{34}H_{60}CoN_4O_6P_2S_2$	$C_{34}H_{60}N_4O_6P_2S_2Zn$
Formula weight	805.87	812.29
Crystal system/space group	Monoclinic/$P2_1$/c	Monoclinic/$P2_1$/c
a/Å	13.1682(8)	12.2550(4)
b/Å	25.5677(14)	25.5295(9)
c/Å	12.3653(7)	13.1492(4)
β/°	106.483(5)	106.609(3)
V/Å^3	3992.1(4)	3939.6(2)
Z	4	4
D$_{calc}$ (g/cm^3)	1.341	1.370
μ (mm^{-1})	0.661	0.858
Crystal size (mm)	0.10 × 0.20 × 0.30	0.20 × 0.23 × 0.25
Temp (K)	293(2)	293(2)
Theta range for collection	3.1–25.1	2.9–39.3
F(000)	1716	1728
Reflections collected	28455	62982
Unique reflections	7084	16673
Observed reflections	5141 ($R_{int} = 0.121$)	9717 ($R_{int} = 0.084$)
R indices, (all data)	$R_1 = 0.1423$, $wR_2 = 0.1912$	$R_1 = 0.0998$, $wR_2 = 0.1811$

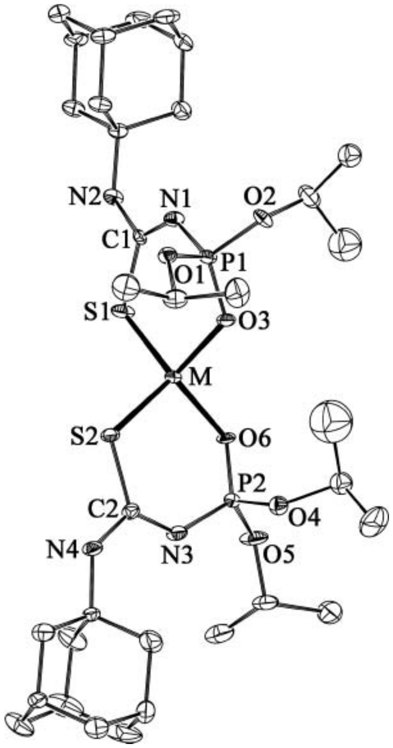


Figure 1 Molecular structure of **[ML$^{I}_{2}$]**. Thermal ellipsoids are drawn at 30% probability. The hydrogen atoms were omitted for clarity.

Table II Selected bond lengths (Å) and bond angles (°) for [$\mathbf{ML^{I}_{2}}$]

	M−O	M−S	C=S	P=O	P−N	C−N(P)	C−N	O−M−S_{endo}	O−M−S_{exo}	O−M−O	S−M−S
[CoL^{I}_{2}]	1.957(5)	2.287(2)	1.766(7)	1.500(6)	1.589(6)	1.316(9)	1.335(9)	99.00(16)	120.54(16)	106.0(2)	113.29(8)
	1.957(5)	2.306(2)	1.770(8)	1.493(6)	1.578(7)	1.313(10)	1.338(10)	100.84(16)	118.03(16)		
[ZnL^{I}_{2}]	1.843(2)	2.3688(9)	1.697(3)	1.426(2)	1.658(3)	1.298(4)	1.380(4)	100.67(7)	115.57(8)	100.76(10)	119.78(3)
	1.930(2)	2.4751(10)	1.693(3)	1.538(2)	1.678(3)	1.272(4)	1.428(5)	103.17(7)	115.73(8)		

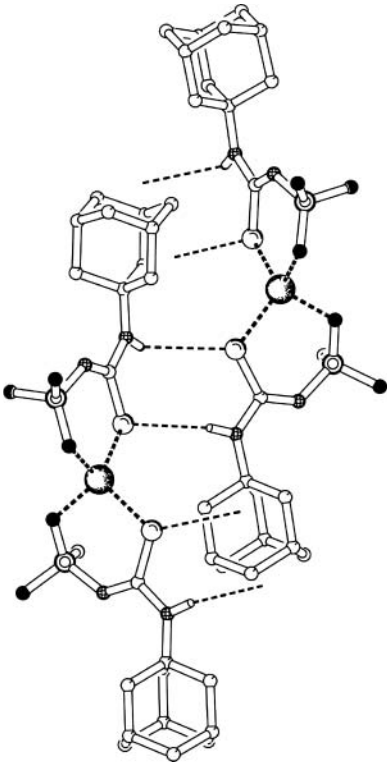


Figure 2 Hydrogen bonded chain in the molecular structure of **[ZnL$^{I}_{2}$]**. The isopropyl and H atoms not involved in hydrogen bonds are omitted for clarity.

In the UV-vis spectrum of **[CoL$^{II}_{2}$]** in CH_2Cl_2 solution, there is a structured absorption with maxima at 563 (ε_{max} 329 mol^{-1} dm^{3} cm^{-1}), 602 (ε_{max} 346 mol^{-1} dm^{3} cm^{-1}), and 664 (ε_{max} 179 mol^{-1} dm^{3} cm^{-1}) nm. The band corresponds to a transition from the basic state $^4A_2$ to a $^4T_1$(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 $^4T_1$(P) and, second, there are resolved transitions in the next doublet states with the same intensity. Other possible transitions, namely $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4T_1$(F), are outside the visible area. The UV-data unequivocally confirm the tetrahedral environment of the Co(II) cation in **[CoL$^{II}_{2}$]**.

The photoluminescence properties of **[ZnL$^{II}_{2}$]** were also investigated in the solid state at room temperature. The complex **[ZnL$^{II}_{2}$]** shows an emission band with maximum intensity at 383 nm upon excitation at 249 nm. The parent ligand **HL^{II}** displays no emission under the same experimental conditions (excitation wavelengths between 300 and 500 nm). The emission of **[ZnL$^{II}_{2}$]** is thus proposed to result from the coordination of two **HL^{II}** ligands to the zinc(II) ion and according to the literature,[8,11,12,16,17] this emission can be assigned to originate from an excited ligand-to-metal charge transfer (LMCT) state.

CONCLUSIONS

In summary, novel Co(II) and Zn(II) complexes with *N*-thiophosphorylated thiourea **HL^{II}** have been synthesized. NMR and UV-vis experiments in solutions have shown that the thiourea acts as a 1,5-*S*,*S*′-ligand in **[CoL$_2^{II}$]** and **[ZnL$_2^{II}$]**. The crystal structures of previously synthesized Co(II) and Zn(II) complexes with *N*-phosphorylated thiourea **HL^{I}**[12] have been described. X-ray data have shown that the deprotonated thiourea **L^{I}** is a 1,5-*O,S*-ligand in both complexes, and the central cation is in a tetrahedral environment. Moreover, in a crystal, both complexes form polymeric chains due to the intermolecular hydrogen bonds. The data presented show that the central cation is in a tetrahedral environment.

The luminescent complex **[ZnL$_2^{II}$]** may find use as new light-converting molecular devices since it is air/moisture stable, shows luminescent properties in the solid state, and at the same time, the ligand can be easily prepared.[18]

EXPERIMENTAL

N-(Thio)phosphorylated thioureas **HL^{I,II}** and complexes **[ML$_2^{I}$]** were prepared according to the previously described techniques.[12,14,18]

Synthesis of [ML$_2^{II}$]

A suspension of **HL^{II}** (0.135 g, 0.5 mmol) in aqueous EtOH (10 mL) was mixed with an aqueous EtOH solution of potassium hydroxide (0.031 g, 0.55 mmol). An aqueous EtOH (10 mL) solution of $CoCl_2$ or $ZnCl_2$ (0.039 or 0.041 g, 0.3 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 dichloromethane, washed with water, and dried with anhydrous $MgSO_4$. The solvent was then removed in vacuo. A green (**[CoL$_2^{II}$]**) or colorless (**[ZnL$_2^{II}$]**) precipitate was isolated from a CH_2Cl_2 solution by slowly adding *n*-hexane.

[CoL$_2^{II}$]. Yield: 0.138 g (92%). Mp 73°C. UV–vis spectrum, [λ_{max}, nm (ε, mol^{-1} dm^3 cm^{-1})]: 563 (329), 602 (346), 664 (179). Calcd. for $C_{16}H_{36}CoN_4O_4P_2S_4$ (597.61): C, 32.16; H, 6.07; N, 9.38. Found: C, 32.29; N, 6.02; N, 9.43.

[ZnL$_2^{II}$]. Yield: 0.131 g (87%). Mp 84°C. ^{1}H NMR: $\delta = 1.25$–1.43 (m, 24H, CH_3, *i*Pr), 2.83 (d, $^3J_{H,H} = 4.8$ Hz, 6H, CH_3, Me), 4.59–4.93 (m, 4H, OCH), 6.05 (br. s, 2H, NH) ppm. $^{31}P\{^1H\}$ NMR: $\delta = 55.6$ ppm. Calcd. for $C_{16}H_{36}N_4O_4P_2S_4Zn$ (604.05): C, 31.81; H, 6.01; N, 9.28. Found: C, 31.73; N, 6.08; N, 9.15.

Physical Measurements

NMR spectra were obtained on a Bruker Avance 300 MHz spectrometer at 25°C. ^{1}H and $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$) were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to $SiMe_4$ (^{1}H) and H_3PO_4 ($^{31}P\{^1H\}$). Electronic absorption spectra of CH_2Cl_2 solutions were recorded in the range 200–900 nm on a Perkin-Elmer Lambda 35 spectrophotometer. Fluorescence measurements were carried out on a Spex FluoroMax-3 spectrofluorometer at room temperature. Elemental analyses were performed on a CHNS HEKAtech EuroEA 3000 analyzer.

Crystal Structure Determination and Refinement

The X-ray data for complexes **[ML$_2^{I}$]** were collected at −173°C, using a KM4CCD diffractometer and graphite-monochromated Mo-*K*α radiation generated from a diffraction

X-ray tube operated at 50 kV and 35 mA. The images were indexed, integrated, and scaled using the KUMA data reduction package.[19] Data were corrected for absorption using the PLATON program.[20] The structure was solved by direct methods using SHELXS-97 program[21] and refined on F^2 with full-matrix least-squares using SHELXL-97.[22]

CCDC 723954 and 723955 contain the supplementary crystallographic data for **[CoL$^{I}_{2}$]** and **[ZnL$^{I}_{2}$]**, respectively. 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.

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