Polyhedron 28 (2009) 1504-1510

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Versatile coordination of *N*-(diisopropoxyphosphoryl)-*p*-bromothiobenzamide towards Zn(II) and Cd(II)

Damir A. Safin^{a,*}, Axel Klein^a, Maria G. Babashkina^a, Heinrich Nöth^b, Dmitriy B. Krivolapov^c, Igor A. Litvinov^c, Henryk Kozlowski^d

^a Institut für Anorganische Chemie, Universität zu Köln, Greinstrasse 6, D-50939 Köln, Germany

^b A.E. Arbuzov Institute of Organic and Physical Chemistry, Arbuzov Street 8, 420088, Kazan, Russian Federation

^c Department Chemie und Biochemie der Universität München, Butenandtstrasse 5-13 (Haus D), D-81377 München, Germany

^d Faculty of Chemistry, University of Wroclaw, F. Joliot-Curie Street 14, 50383, Wroclaw, Poland

ARTICLE INFO

Article history: Received 19 January 2009 Accepted 2 March 2009 Available online 18 March 2009

Keywords: Cadmium Zinc Crystal structure Luminescence Thiobenzamide ligands

ABSTRACT

Reaction of the potassium salt of *N*-(diisopropoxyphosphoryl)-*p*-bromothiobenzamide *p*-BrC₆H₄C(S)NHP(O)(OiPr)₂ (**HL**) with Zn(II) and Cd(II) cations in aqueous EtOH leads to the three different complexes: $[Zn(L-O,S)_2]$ (**1**), $[Cd(p-BrC_6H_4C(S)NH_2-S)(L-O,S)_2]$ (**2**) and $[Cd(HL-O)_2(L-O,S)_2]$ (**3**). The structures of these compounds were investigated by single crystal X-ray diffraction analysis, IR, ¹H and ³¹P NMR spectroscopy, MALDI TOF spectrometry, and microanalysis. The Zn(II) atom in complex **1** is in a distorted tetrahedral O₂S₂ environment formed by the C=S sulfur atoms and the P=O oxygen atoms of two deprotonated ligands. Complex **2** has a trigonal-bipyramidal coordination core, Cd(O^{ax})₂(S^{eq})₃, and two deprotonated ligand molecules **L** are coordinated in the axial positions through the oxygen atoms of the P=O groups. The trigonal plane is formed by the sulfur atoms of two anionic ligands and one *p*-bromothiobenzamide. The Cd(II) cation in complex **3** has an octahedral environment, $(O^{ax})_2(O^{eq})_2(S^{eq})_2$, with two neutral ligand molecules coordinated in the axial positions through the oxygen atoms of the P=O groups. The equatorial plane is formed by two anionic ligands in a typical 1,5-O,S-coordination mode. The corresponding neutral and deprotonated ligands are in a *trans* disposition.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Complexes of late transition metal cations are of great interest as precursors for novel materials with nanosized structures [1– 22]. During the last years symmetric or asymmetric organic and organoelement compounds with the **A** and **B** fragments (acetates, carbamates, imides, phosphites, phosphinates, phosphonates, phosphates, imidodiphosphites, imidodiphosphinates, imidodiphosphonates, and imidodiphosphates) (Chart 1) have found application as single-source precursors (SSPs) for the synthesis of thin films, nanocrystals, and semiconductors [13–18]. In this connection the syntheses of new potential SSPs remains actual to this day.

In the literature there are many examples of SSPs, representing Group 12 metal complexes with ligands of common formulas R'R''P(X)-N(H)-P(Y)R'R'' and RC(X)-N(H)-C(Y)R' [16–18]. Compounds with X, Y = S and/or Se have been extensively studied, whereas the corresponding oxygen derivatives are still poorly investigated. Recently, utilization of Cd(II) complexes with *N*,*N*-

* Corresponding author. E-mail address: damir.safin@ksu.ru (D.A. Safin). diethyl-*N*'-benzoylthio(seleno)urea as SSPs was published by Koch et al. [18].

Our scientific groups have been investigating complexes of *N*-(thio)phosphorylated (thio)amides and (thio)ureas RC(X)NHP(Y)R₂ (**HZ**), containing various functional substituents [23–45]. **HZ** contain X, Y donor atoms and an amido nitrogen atom which can be involved in complexation. In terms of reactivity **HZ** compounds are quite different from each other depending on the nature and combination of atoms X and Y in the molecule, as well as the nature of substituents of (thio)carbonyl and (thio)phosphoryl moieties. We possess ample knowledge on the complexation properties of dithioderivatives **HZ** (X = Y = S). These compounds usually form stable chelate complexes with *d*-metal cations, containing a tetrahedral [M(II) = Co(II), Zn(II), Cd(II)] [24–34] or planar [M(II) = Ni(II), Pd(II), Pt(II)] [34–38] MS₄ core. The anionic form **Z** behaves as a bidentate ligand.

Substitution of one sulfur atom in the central coordination sphere by an oxygen atom lowers the degree of stabilization of π -interactions. As a result, the MO₂S₂ core is less stable than the MS₄ fragment. Because of this, **HZ** with X = S and Y = O can show significant changes in complexation properties as compared with dithiophosphoryl analogs.





^{0277-5387/\$ -} see front matter \odot 2009 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2009.03.007

$$\begin{array}{ccc} & & & & & & \\ -C-R & & -P-R' & & & \\ & & & & & \\ & X & & Y & \\ \mathbf{A} & & \mathbf{B} & \end{array}$$

Chart 1.

In this contribution we report the synthesis, structures, and chemical properties of complexes of *N*-(diisopropoxyphosphoryl)*p*-bromothiobenzamide *p*-BrC₆H₄C(S)NHP(O)(OiPr)₂ (**HL**) [45] with Zn(II) ([Zn(L-O,S)₂], **1**) and Cd(II) ([Cd(*p*-BrC₆H₄C(S)NH₂-S)(L-O,S)₂], **2**; [Cd(HL-O)₂(L-O,S)₂], **3**) cations. In the ligand **HL** both -C(X)R and -P(Y)R'R'' functional groups are combined (X = S, Y = O, R = *p*-C₆H₄, R' = R'' = OiPr), and bonded by the NH fragment. The phosphorylated thiobenzamide **HL** is easily deprotonated in alkaline medium, leading to a thioamide with the negative charge delocalized in the O-P-*N*-C-S backbone [23].

The luminescence properties of the novel compounds and previously described [24] complexes of thiobenzamide $C_6H_5C(S)$ -NHP(O)(OiPr)₂ (**HQ**) with Zn(II) and Cd(II) cations: [Zn(Q-O,S)₂] (**4**), [Cd₂(Q-O,S)₄] (**5**), [Cd(HQ-O)₂(Q-O,S)₂] (**6**), were also measured.

2. Results and discussion

The ligand **HL** was prepared by the reaction of *p*-bromothiobenzamide p-BrC₆H₄C(S)NH₂ with diisopropyl chlorophosphate (*i*PrO)₂P(O)Cl [45]. The product was carefully purified by extraction and recrystallization, and it definitely contains no traces of starting thioamide according to the spectral and microanalysis data.

Complexes **1–3** were prepared by the following procedure: the ligand was deprotonated *in situ* using KOH, followed by reaction with salts of the corresponding metals. The compounds obtained are crystalline solids, which are soluble in most polar solvents. The corresponding reaction using ZnCl_2 in aqueous EtOH leads exclusively to the formation of the complex [ZnL_2] (**1**), while the same reaction with Cd(CH₃COO)₂ leads to the formation of two complexes: [Cd(*p*-BrC₆H₄C(S)NH₂)L₂] (**2**) and [Cd(HL)₂L₂] (**3**) (Scheme 1). Complex **3** was separated from the mixture by extraction with *n*-hexane.

The properties of complexes of the "soft", easily polarizable Cd(II) cation differ considerably from those of Zn(II) derivatives with the same ligands. The coordination environment of CdO_2S_2



Scheme 1. Preparation of complexes 1-3 (R = p-BrC₆H₄).

turns out to be considerably less stable than that of CdS_4 or ZnO_2S_2 . As a result, the complexes are hydrolytically unstable and tend to increase the coordination number of the central atom even in dry solvents [24,25].

We assume that the reason for the propensity of Cd(II) complexes to hydrolysis is the formation of dimeric molecules $[Cd_2L_4]$ in the aqueous ethanol medium:

$$2Cd(CH_3COO)_2 + 4KL \rightarrow [Cd_2L_4] + 4CH_3COOK$$

$$[Cd_2L_4] \leftrightarrows 2CdL_2$$
(1)

The structure of a similar dimeric complex **5** was reported earlier [24]. In the dimeric molecule of composition $[Cd_2Q_4]$ the complex units $[CdQ_2]$ are connected by bridging Cd–S–Cd bonds (Scheme 2).

X-ray data have shown that the cyclic bonds in the bridging tridentate ligands \mathbf{Q} are significantly elongated in comparison with terminal bidentate ones. Decrease of the electron density, introduced by the electron-withdrawing effect of the two Cd(II) cations might result in the facilitation of the nucleophilic attack of H₂O molecules and, thus, promote hydrolysis. An assumed reaction of that type is shown in the following equation:

$$\begin{split} [Cd_2L_4] + 3H_2O &\rightarrow [CdL_2] + p\text{-}BrC_6H_4C(S)NH_2 \\ &+ (iPrO)_2P(O)OH + Cd(OH)_2 + HL \end{split} \tag{2}$$

Recently, we have established [24] that the complex **5** is unstable in solution and dissociates to the mononuclear complexes. However, even if the equilibrium is almost quantitatively shifted to the right (Eq. (1)), the small amount of easily hydrolyzing dimer molecules could provide the accumulation of the hydrolysis product in the reaction mixture. Interestingly, Zn(II) complexes exhibit no dimer formation under the same reaction conditions.

N-Phosphoryl-*p*-bromothiobenzamide **HL** and *p*-BrC₆H₄C(S)NH₂, which are formed as a result of hydrolysis (Eq. (2)), can serve as neutral ligands in the coordination sphere of [CdL₂] as in complexes **2** and **3**. In the ³¹P{¹H} spectrum of the reaction mixture there is also a signal at -1.7 ppm, which might correspond to (*i*PrO)₂P(O)OH (δ_P 2.98 ppm in THF-*d*₈ [46]).

The molecular structures of these compounds were investigated by MALDI, IR, ¹H, ³¹P{¹H} NMR spectroscopy and by microanalysis.

In the IR spectrum of **HL** there are bands of all characteristic groups. The P=O group is observed as an intense band at 1256 cm^{-1} . The band at 1504 cm^{-1} corresponds to the S=C-N fragment. The NH group shows a band at 3080 cm^{-1} .

The IR spectrum of **1** in Nujol is similar to the spectrum of **2**. The resonances of the P=O group of the anionic forms of **L** in complexes **1** and **2** are shifted by approximately 100 cm⁻¹ to low frequencies relative to the band of the parent ligand **HL**. This confirms their participation in chelate formation. The spectra contain very intense bands corresponding to the conjugated SCN group at 1512–1544 cm⁻¹. This fact also confirms the formation of the anionic forms of **L** [23–25].

The main difference between the two complexes 1 and 2 involves the absorption bands of the NH₂ group in the IR spectrum of complex 2 while for complex 1 no signals are observed in the



Scheme 2. Structure of 5 [24].

characteristic area of the NH group. There is an intense band at 1664 cm⁻¹ and two bands of low intensity at 3104 and 3280 cm⁻¹.

The IR spectrum of **3** shows two bands for different phosphorus groups. Along with the above band corresponding to the **L** form at 1156 cm⁻¹, a strong P=O band is observed at 1248 cm⁻¹ due to the bound neutral molecules of **HL**. Its frequency also decreases relative to that of the band of the free ligand; however, the shift is only 8 cm⁻¹. The band for the NH group at 3160 cm⁻¹ also indicates the presence of **HL** molecules in complex **3**. The SCN group shows an intense band at 1528 cm⁻¹ and indicates the presence of the anionic form of **L**.

The IR spectra of **HL** and complexes 1-3 exhibit a very intense band at 1000–1008 cm⁻¹ corresponding to the POC group.

The ³¹P{¹H} NMR signals of complexes **1** and **2** appear at δ = 6.9 and 4.3 ppm, respectively, and a down-field shift, relative to that of the free ligand **HL** (δ = -5.9 ppm), is observed.

The ¹H NMR spectra of complexes **1** and **2** contain a single set of signals for the (*i*PrO)₂P(O) and C₆H₄ protons of the anionic form **L**. The *o*-phenylene proton signals in **1** and **2** are shifted down-field relative to that of the free ligand ($\Delta \delta = 0.36$ ppm), while the *m*-C₆H₄ proton signals are practically not shifted ($\Delta \delta = 0.01$ – 0.04 ppm). The signal for the NHP(O) group proton is absent in the ¹H NMR spectra. This confirms the presence of the **HL** anionic form in the structures of complexes **1** and **2**.

The main difference involves the proton signals of the *p*-BrC₆H₄C(S)NH₂ group in the ¹H NMR spectrum of complex **2**. The signals for the C₆H₄ protons of the *p*-bromothiobenzamide are observed at δ = 7.55 and 7.68 ppm. There are two singlets at δ = 7.35 and 9.61 ppm corresponding to the NH₂ group protons due to the constrained rotation around the CN bond, typical for the thioamide group.

There are two singlets at $\delta = -5.3$ and 4.4 ppm, which have identical integrated intensities, in the ³¹P{¹H} NMR spectrum of complex **3**. The signal at $\delta = -5.3$ ppm is in the region characteristic for neutral *N*-phosphorylated thioamides and thioureas, whereas the second signal corresponds to the amidophosphate environment in complexes of *N*-acylamidophosphate anions.

The ¹H NMR spectrum contains a double set of equal intensity signals for the $(iPrO)_2P(O)$ and C_6H_4 protons. The assignment of the ¹H NMR spectrum of compound **3** is executed by comparing the spectrum of **3** with those of **HL** and complex **2**. For more exact reference of OCH and C_6H_4 proton signals of complex **3**, the spectrum of **a** mixture of **3** and **HL** was recorded at a molar ratio of 2:1. The increase in intensities of the low-field OCH group signal and the signals for the *m*- and *o*-C₆H₄ protons at δ = 7.47 and 7.81 ppm, respectively, concerning the neutral **HL** form, confirms the reference made by comparison of the spectra. The ¹H NMR spectrum of complex **3** shows a signal for the NH group of the phosphorylamide fragment as a doublet (²*J*_{P,H} = 10.1 Hz).

MALDI experiments on complexes **1** and **2** show peaks for the molecular ions $[M+H]^+$, $[M+Na]^+$ and $[M+K]^+$. These peaks are very intense in the mass spectrum of **1** but have low intensities (less than 8%) in the spectrum of complex **2**. In the MALDI mass spectrum of **2** there are molecular ion peaks corresponding to the additional *p*-bromothiobenzamide ligand.

The molecular ion peak of **3** is not observed under the same measurement conditions, only ions characteristic for the $[CdL_2]$ complex core, $[CdL_2 + H]^+$, $[CdL_2 + Na]^+$ and $[CdL_2 + K]^+$, are found in the MALDI spectrum.

The MALDI data of **1–3** show propensity to dimer formation. The intensity of the $[M_2L_3]^+$ peak in the spectra of complexes **1–3** is in the range of 12–19%. The peaks corresponding to the dimer formation were also observed in the ES (electrospray) mass spectra of complexes **4–6** [24].

The data of the emission spectra for complexes **1–6** in the solid state at room temperature are listed in Table 1 (note that neither

Table 1

Photophysical data for complexes **1–6**^a.

Complex	Emission max, nm	Complex	Emission max, nm
1	395	4	392
2	331, 397	5	322, 394
3	394	6	397

^a Excitation at 249 nm.



Fig. 1. Emission spectra of complexes 1-6 (the excitation wavelength was 249 nm).

parent ligands **HL** and **HQ** nor p-BrC₆H₄C(S)NH₂ show any emission under the same conditions). On first view, all compounds **1–6** exhibit practically the same fluorescence properties, respectively.

Complexes **1**, **3**, **4** and **6** show a blue emission band with the maximum intensity at 392–397 nm upon excitation at 249 nm (Table 1, Fig. 1). Complexes **2** and **5** give a blue emission band at 394–397 nm and additionally exhibit bands of low intensity at 322–331 nm (Table 1, Fig. 1). The emissions of **1–6** are proposed to be the result of the coordination of **L**, **Q** and *p*-BrC₆H₄C(S)NH₂ to Zn(II) or Cd(II), and according to previous data [32,33], these emission bands can be assigned to the emission from a an excited ligand-to-metal charge transfer (LMCT) state.

In the solid state, the emission bands of complexes **1** and **6** have equal intensities. Replacing the *p*-bromosubstituted ligand to the nonsubstituted analog in the complexes with the same environment of the metal cation (compare complexes **1** to **4** and, **3** to **6** respectively), leads to an increase in intensity, which may be due to stronger σ -donation from **Q** and **HQ** than **L** and **HL**.

Emission spectra of **2** and **5** are practically isomorphic and the intensities of both bands in **2** are smaller than in **5**. The Cd(II) cation in complexes **2** and **5** is pentacoordinated with trigonal-bipyramidal O_2S_3 environment, which may lead to the appearance of the low-intensive band at 322–331 nm. There are two metal atoms in a molecule of **5** and only one central cation in **2**. Thus, this fact together with more electron donation from **Q** leads to an increase in intensity of both emission bands in complex **5** compared with **2**.

Crystals of **1–3** were obtained by slow evaporation of the solvent from dichloromethane/*n*-hexane solutions of the complexes. The crystals were measured and the structures were solved under the conditions and with the results outlined in Table 2.

According to the X-ray data, complex **1** in a crystal is a spirocyclic chelate with a distorted tetrahedral ZnO_2S_2 core (Fig. 2). S(1)–Zn-O(1) and O(1)-Zn-O(1)a (1 - x, 1 - y, -z) angles are reduced whereas S(1)-Zn-O(1)a (1 - x, 1 - y, -z) and S(1)-Zn-S(1)a (1 - x, +1, -y, -z) are increased in comparison with an ideal tetrahedral

Table 1	2
---------	---

Crystal data, data collection and refinement details for 1-3.

	1	2	3
Empirical formula	$C_{26}H_{36}Br_2N_2O_6P_2S_2Zn$	C ₃₃ H ₄₂ Br ₃ CdN ₃ O ₆ P ₂ S ₃	C ₅₂ H ₇₄ Br ₄ Cd ₁ N ₄ O ₁₂ P ₄ S ₄
Formula weight	823.82	1086.97	1634.32
Crystal system	monoclinic	monoclinic	triclinic
Space group	C2/c	P2(1)	P-1
a (Å)	13.184(1)	15.144(3)	12.352(14)
b (Å)	21.878(2)	11.918(2)	12.763(15)
<i>c</i> (Å)	13.648(2)	23.868(5)	12.89(3)
α (°)	90	90	101.36(2)
β (°)	117.356(1)	96.41(3)	95.89(2)
γ (°)	90	90	114.90(1)
V (Å ³)	3496.2(7)	4281(2)	1767(5)
Ζ	4	4	1
D_{calc} (Mg m ⁻³)	1.565	1.686	1.533
Absorption coefficient, μ (mm ⁻¹)	3.238	3.574	2.833
F(000)	1664	2160	822
Recording range, θ (°)	2.0-28.0	3.2-25.0	2.8-22.2
Number of recorded reflections	9753	14922	8306
Number of recorded independent reflections (<i>R</i> _{int})	4014 (0.028)	14922 (0.0000)	4006 (0.151)
R indices (all data)	$R_1 = 0.0337$, $wR_2 = 0.0809$	$R_1 = 0.0579, wR_2 = 0.1521$	$R_1 = 0.0711, wR_2 = 0.1381$
S	1.03	1.01	0.90



Fig. 2. Thermal ellipsoid representation of complex **1** (hydrogen atoms are omitted for clarity). Ellipsoids are drawn at the 30% probability level.

angle of 109.5° (Table 3). Similarly to those of the $[Co(II)Q_2]$ [28,29] and complex **4** [24], investigated by us earlier, the six-membered chelate rings are practically planar in the molecule of **1**. The maximum deviation from the best plane Zn–O–P–*N*–C–S is observed for P(1) phosphorus and O(1) oxygen atoms. The phenylene ring is rotated relative to the plane of the conjugated SCN moiety [torsion angles are N(2)–C(1)–C(2)–C(3) 16.1(3)° and S(1)–C(1)–C(2)–C(7) 17.8(3)°].

Complex **2** (Fig. 3) crystallizes in the chiral space group P2(1). The asymmetric unit contains two independent molecules.

There are intra- and intermolecular hydrogen bonds of the type N–H···O in the crystal of complex **2**. The intramolecular H-bond is formed between the oxygen atom of the P=O group of the anionic ligand **L** and one of the hydrogen atom of the NH₂ fragment of *p*-bromothiobenzamide. The intramolecular hydrogen bond parameters in Molecule 1 are as follows: N(3)–H(3 M)···O(4), *d*(H···O) 2.2(1) Å, *d*(N···O) 2.93(1) Å, \leq (N–H···O) 158(1)°. The hydrogen bond parameters in Molecule 2 are as follows: N(6)–H(6 M)···O(10), *d*(H···O) 2.1(1) Å, *d*(N···O) 2.86(1) Å, \leq (N–H···O) 157(1)°.

As a result of the intermolecular H-bonds chains along the *b* axis are formed. The intermolecular H-bonds are as follows: $N(3)-H(3 N)\cdots O(1) (-1-x, 1/2+y, 2-z), d(H\cdots O) 1.91(9) Å, d(N\cdots O) 2.93(1) Å, <(N-H\cdots O) 172.1(8)^{\circ} N(6)-H(6 N)\cdots O(7) (-1-x, 1/2-y, 3-z), d(H\cdots O) 2.3(1) Å, d(N\cdots O) 3.0(1) Å, <(N-H\cdots O) 169(1)^{\circ}.$

Table 3

Selected bond lengths (Å), and bond angles (°) for complex 1.

Bond lengths			
Zn(1)-O(1)	1.960(2)	Zn(1)-S(1)	2.2980(7)
P(3)-O(1)	1.490(2)	N(2)-C(1)	1.286(3)
P(3)-O(2)	1.568(2)	O(2)-C(8)	1.466(3)
P(3)-O(3)	1.551(2)	O(3)-C(11)	1.481(3)
P(3)-N(2)	1.607(2)	S(1)-C(1)	1.734(2)
Bond angles			
O(1) - Zn(1) - O(1)a	107.6(1)	O(3) - P(3) - N(2)	101.8(1)
O(1) - Zn(1) - S(1)	103.31(5)	O(2)-P(3)-N(2)	107.1(2)
O(1) - Zn(1) - S(1)a	111.70(6)	N(2)-C(1)-C(2)	115.7(2)
S(1) - Zn(1) - S(1)a	118.98(4)	N(2)-C(1)-S(1)	129.0(2)
C(1)-S(1)-Zn(1)	107.45(9)	C(2)-C(1)-S(1)	115.3(2)
P(3) - O(1) - Zn(1)	124.8(1)	C(1)-N(2)-P(3)	133.6(2)
O(1)-P(3)-O(3)	113.2(1)	C(8)-O(2)-P(3)	122.8(2)
O(1) - P(3) - O(2)	104.7(1)	C(11)-O(3)-P(3)	121.9(2)
O(3)-P(3)-O(2)	108.8(1)	O(3)-C(11)-C(12)	106.7(3)
O(1) - P(3) - N(2)	120.9(1)	O(3)-C(11)-C(13)	106.7(3)
Torsion angles			
O(1)-Zn(1)-S(1)-C(1)	110.0(1)	O(2)-P(3)-O(1)-Zn(1)	129.5(1)
S(1)a-Zn(1)-S(1)-C(1)	-129.75(9)	O(3)-P(3)-O(1)-Zn(1)	-112.2(1)
O(1)a-Zn(1)-S(1)-C(1)	-5.3(1)	N(2)a-P(3)-O(1)-Zn(1)	8.8(2)
S(1)-Zn(1)-O(1)-P(3)	127.6(1)	O(2)-P(3)-N(2)a-C(1)a	-130.2(3)
S(1)a-Zn(1)-O(1)-P(3)	-1.4(1)	O(3)-P(3)-N(2)a-C(1)a	115.8(3)
O(1)a-Zn(1)-O(1)-P(3)	-119.7(1)	S(1)-C(1)-N(2)-P(3)a	1.5(4)
Zn(1)-S(1)-C(1)-N(2)	6.2(3)	C(1)-C(1)-N(2)-P(3)a	-177.9(2)
Zn(1)-S(1)-C(1)-C(2)	-174.4(2)		
(1 - x, 1 - y, -z)			

The Cd(II) cations are present in a distorted trigonal-bipyramidal environment (O_2S_3) . The axial positions are occupied by the oxygen atoms of the phosphoryl groups. Three sulfur atoms, corresponding to the two anionic forms L and one p-bromothiobenzamide, lie in its base. The six-membered Cd-O-P-N-C-S cycles have a distorted boat conformation with the C=S sulfur atom and the P=O oxygen atom in apical positions (Table 4). The lengths of the Cd-S bonds in the chelate rings of the Molecule 1 are practically equivalent, but in the Molecule 2 the difference is about 0.014(1) Å. The third Cd-S bonds in both molecules are almost equal to each other ($\Delta \approx 0.003$ Å). The bonds with the oxygen atoms in the chelate rings of the Molecule 1 differ on 0.08 Å, but the Cd-O bonds difference in the Molecule 2 is only 0.03 Å. The Cd(1)-O(1) and Cd(2)-O(7) bonds in the Molecules 1 and 2, respectively, deviate from the normal to the CdS_3 plane [O(1)-Cd(1)-O(4)] $169.3(2)^{\circ}$ and O(7)-Cd(2)-O(10) $171.1(2)^{\circ}$, while the Cd(1)-O(4)



Fig. 3. Thermal ellipsoid representation of one of the two independent molecules of complex **2** (hydrogen atoms are omitted for clarity). Ellipsoids are drawn at the 30% probability level.

Sciected bond icitetiis (11), and bond angles (7101 complex a	Selected bond le	engths (Å),	and bond	angles (°) for complex 2
--	------------------	-------------	----------	-----------	-----------------

Molecule 1		Molecule 2	
Bond lengths			
Cd(1) - O(1)	2.418(6)	Cd(2)-O(7)	2.355(6)
Cd(1)-O(4)	2.339(6)	Cd(2)-O(10)	2.323(6)
Cd(1)-S(1)	2.514(3)	Cd(2)-S(4)	2.516(3)
Cd(1)-S(2)	2.519(2)	Cd(2)-S(5)	2.530(2)
Cd(1)-S(3)	2.570(3)	Cd(2)-S(6)	2.567(2)
P(1)-O(1)	1.493(6)	P(3)-O(7)	1.467(6)
P(1)-O(2)	1.565(7)	P(3)-O(8)	1.587(9)
P(1)-O(3)	1.556(7)	P(3)-O(9)	1.524(8)
P(1)-N(1)	1.637(8)	P(3)-N(4)	1.620(8)
P(2)-O(4)	1.491(6)	P(4)-O(10)	1.494(6)
P(2)-O(5)	1.567(7)	P(4)-O(11)	1.579(7)
P(2)-O(6)	1.563(7)	P(4)-O(12)	1.558(7)
P(2)-N(2)	1.613(8)	P(4)-N(5)	1.623(8)
Bond angles			
O(4) - Cd(1) - O(1)	169.3(2)	O(4)-Cd(1)-S(1)	88.9(2)
O(1)-Cd(1)-S(1)	91.1(2)	O(4) - Cd(1) - S(2)	94.5(2)
O(1)-Cd(1)-S(2)	94.2(2)	S(1)-Cd(1)-S(2)	126.4(1)
O(4)-Cd(1)-S(3)	93.9(2)	O(1)-Cd(1)-S(3)	76.7(2)
S(1)-Cd(1)-S(3)	118.2(1)	S(2)-Cd(1)-S(3)	114.86(9)
O(10)-Cd(2)-O(7)	171.1(2)	O(10)-Cd(2)-S(4)	96.5(2)
O(7)-Cd(2)-S(4)	91.6(2)	O(10)-Cd(2)-S(5)	92.3(2)
O(7)-Cd(2)-S(5)	86.8(2)	S(4)-Cd(2)-S(5)	120.70(9)
O(10)-Cd(2)-S(6)	93.8(2)	O(7)-Cd(2)-S(6)	78.8(2)
S(4)-Cd(2)-S(6)	120.27(9)	S(5)-Cd(2)-S(6)	117.42(9)
C(1)-S(1)-Cd(1)	111.6(3)	C(51)-S(4)-Cd(2)	108.9(3)
C(8)-S(2)-Cd(1)	107.5(3)	C(58)-S(5)-Cd(2)	110.0(3)
C(15)-S(3)-Cd(1)	114.6(3)	C(65)-S(6)-Cd(2)	112.8(3)
P(1) - O(1) - Cd(1)	110.6(3)	P(3) - O(7) - Cd(2)	119.2(4)
P(2)-O(4)-Cd(1)	113.3(3)	P(4)-O(10)-Cd(2)	114.7(3)
Torsion angles			
S(2)-Cd(1)-S(1)-C(1)	105.6(4)	O(2)-P(1)-O(1)-Cd(1)	171.6(3)
S(3)-Cd(1)-S(1)-C(1)	-65.8(4)	O(3)-P(1)-O(1)-Cd(1)	58.5(4)
O(1)-Cd(1)-S(1)-C(1)	9.7(4)	N(1)-P(1)-O(1)-Cd(1)	-68.5(5)
O(4)-Cd(1)-S(1)-C(1)	-159.6(4)	O(1)-P(1)-N(1)-C(1)	61.3(9)
S(1)-Cd(1)-O(1)-P(1)	31.6(4)	O(2)-P(1)-N(1)-C(1)	-174.7(8)
S(2)-Cd(1)-O(1)-P(1)	-95.0(4)	O(3)-P(1)-N(1)-C(1)	-64.4(9)
S(3)-Cd(1)-O(1)-P(1)	150.4(4)	O(5)-P(2)-O(4)-Cd(1)	68.4(4)
S(1)-Cd(1)-O(4)-P(2)	-108.7(3)	O(6)-P(2)-O(4)-Cd(1)	-173.3(3)
S(2)-Cd(1)-O(4)-P(2)	17.7(3)	N(2)-P(2)-O(4)-Cd(1)	-56.6(5)
S(3)-Cd(1)-O(4)-P(2)	133.1(3)	P(1)-N(1)-C(1)-S(1)	-1.6(1)
Cd(1)-S(1)-C(1)-N(1)	-27.0(1)		



Fig. 4. Thermal ellipsoid representation of complex **3** (hydrogen atoms are omitted for clarity). Ellipsoids are drawn at the 30% probability level.

and Cd(2)–O(10) bonds stay practically perpendicular to the \mbox{CdS}_3 plane.

The molecule of complex **3** in the crystal is located in a special position at the symmetry centre. The coordination geometry of the Cd(II) atom is tetragonal bipyramidal ($D_{2 h}$) (Fig. 4). Isostructural complexes of Co(II) [28,29], Ni(II) [35] with **HQ** and Cd(II), Ni(II) with **HL** [24,45] have been synthesized and structurally characterized by us previously.

The equatorial positions of the bipyramid are occupied by two *N*-phosphoryl-*p*-bromothiobenzamide anions **L**, bonded through sulfur atoms and oxygen atoms of thiocarbonyl and phosphoryl groups, respectively. The six-membered Cd–O–P–*N*–C–S cycle lies between a boat and a chair conformations since the O–P–*N*–C–S backbone is flat (Table 5). The ligands show *trans* configuration. Neutral ligand molecules are coordinated in the axial positions through the oxygen atoms of the phosphoryl groups. The lengths of the Cd–O bonds in the chelate rings are 2.300(9) Å while the bonds with the axial oxygen atoms are 2.419(9) Å.

There are two intramolecular NH···O bonds between the oxygen atom of the P=O group of the anionic ligand **L** and the hydrogen atom of the NH fragment of the neutral ligand **HL** in the crystal of complex **3**. The hydrogen bond parameters are as follows: N(1B)–H(1B)···O(1A) (1 - x, -y, -z), d(H···O) 2.11 Å, d(N···O) 2.92(1) Å, \leq (N–H···O) 157°.

3. Experimental

Infrared spectra (Nujol) were recorded with a Specord M-80 spectrometer in the range 400–3600 cm⁻¹. NMR spectra were obtained on a Varian Unity-300 NMR spectrometer at 25 °C. ¹H and ³¹P{¹H} NMR spectra (CDCl₃) were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to SiMe₄ (¹H) and H₃PO₄ (³¹P{¹H}). MALDI mass spectra of **1–3** were obtained using a Bruker Reflex IV spectrometer. Fluorescence measurements were made on a SLM Aminco 500 spectrofluorometer at room temperature. Elemental analyses were performed on a Perkin–Elmer 2400 CHN microanalyser.

3.1. Syntheses

p- $BrC_6H_4C(S)NHP(O)(OiPr)_2$ (**HL**). N-(diisopropoxyphosphoryl)p-bromothiobenzamide was prepared according to previously described methods [45].

Table

Selected bond lengths (Å), and bond angles (°) for complex 3.

Bond lengths			
Cd(1)-O(1A)	2.300(9)	P(1B)-O(1B)	1.475(8)
Cd(1)-O(1B)	2.419(9)	P(1B)-O(2B)	1.557(9)
Cd(1)-S(1A)	2.570(7)	P(1B)-O(3B)	1.57(1)
N(1A)-C(1A)	1.28(2)	P(1A)-N(1A)	1.61(1)
N(1B)-C(1B)	1.42(2)	P(1B)-N(1B)	1.66(1)
P(1A)–O(1A)	1.509(9)	S(1A)-C(1A)	1.74(1)
P(1A)–O(2A)	1.54(1)	S(2B)-C(1B)	1.61(1)
P(1A)–O(3A)	1.59(2)		
Bond angles			
O(1A)-Cd(1)-O(1B)	89.7(2)	O(1A)-P(1A)-O(3A)	103.8(6)
$O(1A)-Cd(1)-O(1A_a)$	180.00	O(1A)-P(1A)-N(1A)	122.2(5)
$O(1A)-Cd(1)-O(1B_a)$	90.3(2)	O(1B)-P(1B)-O(2B)	114.9(5)
$S(1)-Cd(1)-O(1^{a})$	89.6(2)	O(1B)-P(1B)-O(3B)	116.0(5)
S(1)-Cd(1)-O(1a)	90.4(2)	O(1B)-P(1B)-N(1B)	108.0(4)
S(1A)-Cd(1)-O(1B)	90.2(2)	O(2A)-P(1A)-O(3A)	110.2(7)
$S(1A)-Cd(1)-O(1B_a)$	89.8(2)	O(2A)-P(1A)-N(1A)	101.8(5)
$S(1A)-Cd(1)-S(1a_a)$	180.00	O(3A)-P(1A)-N(1A)	104.7(6)
$Cd(1)-S(1A)-C(1^{a})$	108.5(4)	O(2B)-P(1B)-O(3B)	101.2(5)
$Cd(1)-O(1A)-P(1^{a})$	124.6(4)	O(2B)-P(1B)-N(1B)	108.7(4)
Cd(1)-O(1B)-P(1B)	136.1(4)	O(3B)-P(1B)-N(1B)	107.6(5)
O(1A)-P(1A)-O(2A)	113.7(5)		
Torsion angles			
$O(1A)-Cd(1)-S(1^{a})-C(1A)$	-30.8(5)	Cd(1)-O(1A)-P(1A)-O(3A)	-126.2(6)
$O(1B)-Cd(1)-S(1^{a})-C(1A)$	58.9(5)	Cd(1)-O(1A)-P(1A)-N(1A)	-8.7(8)
$O(1A_a)-Cd(1)-S(1A)-C(1A)$	149.2(5)	Cd(1)-O(1B)-P(1B)-O(2B)	-136.2(6)
$O(1B_a)-Cd(1)-S(1A)-C(1A)$	-121.1(5)	Cd(1)-O(1B)-P(1B)-O(3B)	106.2(6)
S(1A)-Cd(1)-O(1A)-P(1A)	27.7(5)	Cd(1)-O(1B)-P(1B)-N(1B)	-14.7(8)
O(1B)-Cd(1)-O(1A)-P(1A)	-62.5(5)	C(1A)-N(1A)-P(1A)-O(1A)	-19.9(2)
$S(1a_a)-Cd(1)-O(1A)-P(1A)$	-152.3(5)	C(1A)-N(1A)-P(1A)-O(2A)	-148.0(1)
$O(1B_a)-Cd(1)-O(1A)-P(1A)$	117.5(5)	C(1A)-N(1A)-P(1A)-O(3A)	97.3(2)
S(1A)-Cd(1)-O(1B)-P(1B)	80.3(6)	C(1B)-N(1B)-P(1B)-O(1B)	-168.6(1)
O(1A)-Cd(1)-O(1B)-P(1B)	169.9(7)	C(1B)-N(1B)-P(1B)-O(2B)	-43.4(1)
$S(1A_a)-Cd(1)-O(1B)-P(1B)$	-99.7(6)	C(1B)–N(1B)–P(1B)–O(3B)	65.5(1)
$O(1A_a)-Cd(1)-O(1B)-P(1B)$	-10.1(7)	N(1A)-C(1A)-S(1A)-Cd(1)	21.6(1)
Cd(1)-O(1A)-P(1A)-O(2A)	114.1(5)	S(2B)-C(1B)-N(1B)-P(1B)	-11.9(2)

 $[ZnL_2]$ (1). A suspension of HL (1.9 g, 5 mmol) in aqueous ethanol (20 mL) was mixed with an ethanol solution of potassium hydroxide (0.28 g, 5 mmol). An aqueous (20 mL) solution of ZnCl₂ (0.82 g, 2.8 mmol) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for further 3 h and left overnight. The complex was obtained by extraction of the reaction mixture by dichloromethane, washed with water and dried using anhydrous MgSO₄. The solvent was then removed in vacuo. A colorless precipitate was recrystalized from a dichloromethane/n-hexane mixture. Yield 1.73 g (84%), m.p. 143 °C. (Found: C, 37.82; H, 4.47; N, 3.31%. C₂₆H₃₆Br₂N₂O₆P₂S₂Zn requires C, 37.90; H, 4.40; N, 3.40%.). v_{max}/ cm⁻¹ 1544 (SCN), 1152 (P=O), 1000 (POC). $\delta_{\rm H}$ 8.14 (4H, m, ³J 8.4, o-H, C₆H₄), 7.50 (4H, m, ³J 8.4, m-H, C₆H₄), 4.71 (4H, d sept, ³J 6.2, OCH), 1.36 (12H, d, ${}^{3}J$ 5.6, CH₃), 1.35 (12H, d, ${}^{3}J$ 5.6, CH₃). δ_{P} 6.9. m/z (MALDI) 826 (81) [M+H]⁺, 849 (100) [M+Na]⁺, 864 (52) $[M+K]^+$, 1271 (12) $[Zn_2L_3]^+$.

[$Cd(p-BrC_6H_4C(S)NH_2)L_2$] (**2**) and [$Cd(HL)_2L_2$] (**3**). A suspension of **HL** (1.91 g, 5 mmol) in aqueous ethanol (20 mL) was mixed with an ethanol solution of potassium hydroxide (0.28 g, 5 mmol). An aqueous (20 mL) solution of $Cd(CH_3COO)_2 \cdot 2H_2O$ (0.82 g, 2.8 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 complex was obtained by extraction of the reaction mixture by dichloromethane, washed with water and dried with anhydrous MgSO₄. The solvent was then removed in vacuo. The residue was extracted using *n*-hexane. The hexane insoluble residue was recrystallized from a dichloromethane/*n*-hexane mixture, and complex **2** was isolated. Complex **2** was obtained as colorless crystals. Yield 0.44 g, mp 129 °C. (Found: C, 36.35; H, 3.96; N, 3.81%. C₃₃H₄₂Br₃CdN₃O₆P₂S₃

requires C, 36.46; H, 3.89; N, 3.87%.). v_{max}/cm⁻¹ 3280, 3104, 1664 (NH₂), 1512 (SCN), 1157 (P=O), 1000 (POC). $\delta_{\rm H}$ 9.61 (1H, br. s, NH₂), 8.14 (4H, m, ³/ 8.5, o-H, C₆H₄, L), 7.68 (2H, m, ³/ 8.4, o-H, C_6H_4), 7.55 (2H, m, ³J 8.4, m-H, C_6H_4), 7.47 (4H, m, ³J 8.5, m-H, C₆H₄, L), 7.35 (1H, s, NH₂), 4.72 (4H, d sept, ³J 6.3 Hz, OCH), 1.34 (24H, d, ${}^{3}J$ 6.1, CH₃). δ_{P} 4.3. m/z (MALDI) 217 (100) [p- $BrC_6H_4C(S)NH_2 + H]^+$, 240 (13) $[p-BrC_6H_4C(S)NH_2 + Na]^+$, 217 (5) $[p-BrC_6H_4C(S)NH_2 + K]^+$, 873 (34) $[CdL_2 + H]^+$, 896 (48) $[CdL_2 + Na]^+$, 1089 (6) $[M + H]^+$, 1112 (3) $[M + Na]^+$, 1128 (7) $[M + K]^+$, 1364 (19) $[Cd_2L_3]^+$. At the solvent-removal stage (hexane soluble), product 3 was isolated. Complex 3 was obtained as orange crystals. Yield 0.21 g, m.p. 114 °C. (Found: C, 38.37; H, 4.46; N, 3.50%. $C_{52}H_{74}Br_4CdN_4O_{12}P_4S_4$ requires C, 38.28; H, 4.57; N, 3.43%.). v_{max}/cm⁻¹ 3160 (NH), 1528 (SCN), 1248 (P=O, HL), 1156 (P=O, L), 1004 (POC). $\delta_{\rm H}$ 9.00 (2H, d, ³J 10.1, NH), 8.13 (4H, m, ³J 7.9, o-H, C₆H₄, L), 7.81 (4H, m, ³J 8.3, o-H, C₆H₄, HL), 7.53 (4H, m, ³J 7.9, *m*-H, C₆H₄, L), 7.47 (4H, m, ³J 7.9, *m*-H, C₆H₄, HL), 4.83 (4H, d sept, ³J 6.3, OCH, HL), 4.65 (4H, d sept, ³J 6.2, OCH, L), 1.36 (12H, d, ${}^{3}J$ 6.3, CH₃, L), 1.30 (36H, br s, CH₃, L + HL). δ_{P} 4.4 (2P, L), -5.3 (2P, HL). m/z (MALDI) 873 (67) $[CdL_2 + H]^+$, 896 (100) $[CdL_2 + Na]^+$, 912 (17) $[CdL_2 + K]^+$, 1364 (15) $[Cd_2L_3]^+$.

3.2. Structure determination

The data for **1** and **3** were collected at 20 °C using a Bruker Smart Apex2 diffractometer and graphite-monochromated Mo K α radiation generated from Diffraction X-ray tube operated at 50 kV and 30 mA. The images were indexed, integrated and scaled using the APEX2 data reduction package [47]. All raw data were corrected for absorption using sADABS [48] The structure was solved by heavy atom and direct method using SIR [49] program and the refinement was carried out with SHELXL [50] using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure model on calculated positions and were refined as rigid atoms. All calculations were performed on PC computer using WINGX [51] program.

X-ray diffraction data for **2** were collected on a Enraf Nonius Kappa CCD diffractometer equipped with a rotating anode generator and with Mo $K\alpha$ radiation. The structure solutions were found with SHELXS [52], and the refinement was carried out with SHELXL [50] using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure model on calculated positions and were refined as rigid atoms.

All figures were made using the program PLATON [53].

4. Conclusions

The data obtained testify that the structure of the chelate complexes of 12 Group metal cations with *N*-phosphorylated thioamides of general formula RC(S)NHP(O)R'R'' depends on the nature of the central ion, and unlike dithioanaloges RC(S)NHP(S)R'R'' which form only complexes with a MS₄ core. For the ligands containing different donor atoms, sulfur and oxygen simultaneously, the increase in the coordination number of the central atom by dimerization or interaction with nucleophilic species is observed for complexes of Cd(II), while only tetracoordinated [M{RC(S)NP(O)R'R''}-O,S)₂] complexes of Zn(II) have been obtained [24,25].

We assume, that dimerization of the Cd(II) compounds in aqueous ethanol media can promote their hydrolysis, while the mononuclear Zn(II) compounds are obtained in good yield and show no tendency to hydrolytic destruction.

The luminescent properties of the new complexes has shown that the observed emission bands can be assigned ligand-to-metal charge transfer (LMCT).

Acknowledgments

This work was supported by the Russian Science Support Foundation and partly by University of Wroclaw. M.G.B. and D.A.S. thank DAAD for the scholarships (Forschungsstipendien 2008/ 2009). We also thank Dr. P. Mayer for collecting the data sets for the crystal structure determination.

Appendix A. Supplementary data

CCDC 664765, 682366 and 664766 contain the supplementary crystallographic data for (1), (2) and (3). 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.

References

- S. Blaurock, F.T. Edelman, I. Haiduc, P. Poremba, Inorg. Chim. Acta 361 (2008) 407.
- [2] F.T. Edelman, A. Fischer, I. Haiduc, Inorg. Chem. Commun. 656 (2003) 225.
- [3] I. Haiduc, J. Organomet. Chem. 623 (2001) 29.
- [4] A. Silvestru, D. Bilc, R. Roesler, J.E. Drake, I. Haiduc, Inorg. Chim. Acta 305 (2000) 106.
- [5] I. Szekely, C. Silvestru, J.E. Drake, G. Balazs, S.I. Farcas, I. Haiduc, Inorg. Chim. Acta 299 (2000) 247.
- [6] J. Novosad, M. Necas, J. Marek, P. Veltsistas, C. Papadimitriou, I. Haiduc, M. Watanabe, J.D. Woollins, Inorg. Chim. Acta 290 (1999) 56.
- [7] (a) J.E. Drake, A. Silvestru, J. Yang, I. Haiduc, Inorg. Chim. Acta 271 (1998) 75;
 (b) I. Haiduc, Coord. Chem. Rev. 158 (1997) 325.
- [8] C. Silvestru, I. Haiduc, Coord. Chem. Rev. 147 (1996) 117.
- [9] C. Silvestru, J.E. Drake, Coord. Chem. Rev. 223 (2001) 117.
- [10] C.W. Liu, T.S. Lobana, B.K. Santra, C.-M. Hung, H.-Y. Liu, B.-J. Liaw, J.-C. Wang, Dalton Trans. (2006) 560.

- [11] I. Haiduc, in: J. McCleverty, T.J. Mayer (Eds.), Comprehensive Coordination Chemistry II, vol. II, Pergamon, London, 2004, pp. 323–348.
- [12] I.P. Gray, A.M.Z. Slawin, J.D. Woollins, Dalton Trans. (2005) 2188.
- [13] A.A. Memon, M. Afzaal, M.A. Malik, C.Q. Nguyen, P. O'Brien, J. Raftery, Dalton Trans. (2006) 4499.
- [14] M.C. Copsey, A. Panneerselvam, M. Afzaal, T. Chivers, P. O'Brien, Dalton Trans. (2007) 1528.
- [15] M. Afzaal, D.J. Crouch, P. O'Brien, J. Raftery, P.J. Skabara, A.J.P. White, D.J. Williams, J. Mater. Chem. 14 (2004) 233.
- [16] D. Fan, M. Afzaal, M.A. Mallik, C.Q. Nguyen, P. O'Brien, P.J. Thomas, Coord. Chem. Rev. 251 (2007) 1878.
- [17] J.S. Ritch, T. Chivers, M. Afzaal, P. O'Brien, Chem. Soc. Rev. 10 (2007) 1622.
- [18] J.C. Bruce, N. Revaprasadu, K.R. Koch, New J. Chem. 9 (2007) 1647.
- [19] C.C. Landry, J. Lockwood, A.R. Barron, Chem. Mater. 7 (1995) 699.
- [20] A.D. Garnovskii, D.A. Garnovskii, I.S. Vasilchenko, A.S. Burlov, A.P. Sadimenko, I.D. Sadekov, Russ. Chem. Rev. 66 (1997) 389.
- [21] T.Q. Ly, J.D. Woollins, Coord. Chem. Rev. 176 (1998) 451.
- [22] V.V. Skopenko, V.M. Amirkhanov, T.Yu. Sliva, I.S. Vasilchenko, E.L. Anpilova, A.D. Garnovskii, Russ. Chem. Rev. 73 (2004) 737.
- [23] F.D. Sokolov, V.V. Brusko, N.G. Zabirov, R.A. Cherkasov, Curr. Org. Chem. 10 (2006) 27.
- [24] F.D. Sokolov, D.A. Safin, N.G. Zabirov, V.V. Brusko, B.I. Khairutdinov, D.B. Krivolapov, I.A. Litvinov, Eur. J. Inorg. Chem. (2006) 2027.
- [25] F.D. Sokolov, D.A. Safin, N.G. Zabirov, P.V. Zotov, R.A. Cherkasov, Russ. J. Gen. Chem. 75 (2005) 1919.
- [26] N.G. Zabirov, V.V. Brusko, A.Yu. Verat, D.B. Krivolapov, I.A. Litvinov, R.A. Cherkasov, Phosphorus Sulfur Silicon 17 (2002) 1869.
- [27] V.V. Brusko, A.I. Rakhmatullin, N.G. Zabirov, Russ. J. Gen. Chem. 70 (2000) 1603.
- [28] F.D. Sokolov, D.A. Safin, N.G. Zabirov, L.N. Yamalieva, D.B. Krivolapov, I.A. Litvinov, Mendeleev Commun. 14 (2004) 51.
- [29] D.A. Safin, P. Mlynarz, F.E. Hahn, M.G. Babashkina, F.D. Sokolov, N.G. Zabirov, J. Galezowska, H. Kozlowski, Z. Anorg. Allg. Chem. 633 (2007) 1472.
- [30] D.A. Safin, M.G. Babashkina, F.D. Sokolov, N.G. Zabirov, Inorg. Chem. Commun. 9 (2006) 1133.
- [31] D.A. Safin, F.D. Sokolov, N.G. Zabirov, V.V. Brusko, D.B. Krivolapov, I.A. Litvinov, R.A. Cherkasov, Polyhedron 25 (2006) 3330.
- [32] D.A. Safin, F.D. Sokolov, H. Nöth, M.G. Babashkina, T.R. Gimadiev, J. Galezowska, H. Kozlowski, Polyhedron 27 (2008) 2022.
- [33] D.A. Safin, H. Nöth, F.D. Sokolov, M.G. Babashkina, N.G. Zabirov, J. Galezowska, H. Kozlowski, in: Proceedings of the VII Science Conference on "Materials and technologies of XXI centuries", Kazan, Russia, 2007, p. 111.
- [34] F.D. Sokolov, N.G. Zabirov, L.N. Yamalieva, V.G. Shtyrlin, Ruslan R. Garipov, V.V. Brusko, A.Yu. Verat, S.V. Baranov, P. Mlynarz, T. Glowiak, H. Kozlowski, Inorg. Chim. Acta 359 (2006) 2087.
- [35] A.Yu. Verat, B.I. Khairutdinov, V.G. Shtyrlin, F.D. Sokolov, L.N. Yamalieva, D.B. Krivolapov, N.G. Zabirov, I.A. Litvinov, V.V. Klochkov, Mendeleev Commun. 18 (2008) 150.
- [36] F.D. Sokolov, N.G. Zabirov, V.V. Brusko, D.B. Krivolapov, I.A. Litvinov, Mendeleev Commun. 13 (2003) 72.
- [37] V.V. Brus'ko, F.D. Sokolov, N.G. Zabirov, R.A. Cherkasov, A.I. Rakhmatullin, A.Yu. Verat, Russ. J. Gen. Chem. 69 (1999) 664.
- [38] N.G. Zabirov, I.A. Litvinov, O.N. Kataeva, S.V. Kashevarov, F.D. Sokolov, R.A. Cherkasov, Russ. J. Gen. Chem. 68 (1998) 1408.
- [39] F.D. Sokolov, M.G. Babashkina, D.A. Safin, A.I. Rakhmatullin, F. Fayon, N.G. Zabirov, M. Bolte, V.V. Brusko, J. Galezowska, Henryk Kozlowski, Dalton Trans. (2007) 4693.
- [40] D.A. Safin, M.G. Babashkina, F.D. Sokolov, N.G. Zabirov, J. Galezowska, H. Kozlowski, Polyhedron 26 (2007) 1113.
- [41] A. Zazybin, O. Osipova, U. Khusnutdinova, I. Aristov, B. Solomonov, F. Sokolov, M. Babashkina, N. Zabirov, J. Mol. Catal. A: Chem. 253 (2006) 234.
- [42] A.Y. Verat, F.D. Sokolov, N.G. Zabirov, M.G. Babashkina, D.B. Krivolapov, V.V. Brusko, I.A. Litvinov, Inorg. Chim. Acta 359 (2006) 475.
- [43] N.G. Zabirov, A.Yu. Verat, F.D. Sokolov, M.G. Babashkina, D.B. Krivolapov, V.V. Brusko, Mendeleev Commun. 13 (2003) 163.
- [44] V.N. Soloviev, A.N. Chechlov, N.G. Zabirov, I.V. Martynov, Dokl. Chem. 341 (1995) 502.
- [45] D.A. Safin, F.D. Sokolov, S.V. Baranov, Ł. Szyrwiel, M.G. Babashkina, E.R. Shakirova, F.E. Hahn, H. Kozlowski, Z. Anorg. Allg. Chem. 634 (2008) 835.
- [46] R.R. Abdreimova, D.N. Akbayeva, G.S. Polimbetova, A.-M. Caminade, J.-P. Majorals, Phosphorus Sulfur Silicon Relat. Elem. 156 (2000) 239.
- [47] APEX2 (Version 2.1), SAINTPLUS. Data Reduction and Correction Program (Version 7.31A, Bruker Advanced X-ray Solutions, BrukerAXS Inc., Madison, WI, USA, 2006.
- [48] G.M. Sheldrick, sADABS, Program for Empirical X-ray Absorption Correction, Bruker-Nonius, 1990–2004.
- [49] A. Altomare, G. Cascarano, C. Giacovazzo, D. Viterbo, Acta Crystallogr., Sect. A. 47 (1991) 744.
- [50] G.M. Sheldrick, SHELXL-97 2 Program for Crystal Structure Refinement, University of Goettingen, Germany, 1997.
- [51] L.J. Farrugia, WINGX 1.64.05 An Integrated System of Windows Programs for the solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data, J. Appl. Crystal. 32 (1999) 837.
- [52] G.M. Sheldrick, SHELXS-97 Program for Crystal Structure Solution, University of Goettingen, Germany, 1997.
- [53] A.L. Spek, Acta Crystallogr., Sect. A 46 (1990) 34.