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Solvent-dependent formation of two different Cd(II) complexes with p-BrC₆H₄C(S)NHP(O)(OiPr)₂ (HL). Crystallographic modification of Cd(HL)₂L₂

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1. Introduction

In the course of our research on transition metal complexes of N-(thio)phosphorylated (thio)amides and (thio)ureas RC(X)NHP- $(Y)(OiPr)_2$ (X, Y = O, S) [1–23] we recently reported on the coordination of *N*-(diisopropoxyphosphoryl)-*p*-bromothiobenzamide p-BrC₆H₄C(S)NHP(O)(OiPr)₂ (HL) towards Zn(II) and Cd(II) [23]. Reaction of the potassium salt of the benzamide with Zn(II) and Cd(II) cations in aqueous EtOH leads to the three different complexes: [Zn(L-O,S)₂] ([**ZnL**₂]), [Cd(HL-O)₂(L-O,S)₂] ([**Cd**(**HL**)₂**L**₂]) and $[Cd(p-BrC_6H_4C(S)NH_2-S)(L-O,S)_2]$ ($[Cd(L^1)L_2]$). The structures of these three compounds were investigated by single crystal X-ray diffraction analysis, IR, ¹H and ³¹P{¹H} NMR spectroscopy, MALDI TOF spectrometry, and microanalysis. Concerning the formation of the *p*-bromothiobenzamine ligand L^{I} we assumed the a priori formation of a binuclear complex (Eq. (1)) and the subsequent hydrolysis of the bridging ligand L (Eq. (2)).

$$2 \ Cd(CH_3COO)_2 + 4 \ KL \rightarrow [Cd_2L_4] + 4 \ CH_3COOK \tag{1a} \label{eq:cd}$$

$$[Cd_2L_4] \leftrightarrow 2[CdL_2] \tag{1b}$$

ABSTRACT

Reaction of the potassium salt of N-(diisopropoxyphosphoryl)-p-bromothiobenzamide p-BrC₆H₄C(S)NHP (O)(OiPr)₂ (HL) with Cd(II) cations in freshly dried and distilled EtOH leads exclusively to the complex $[Cd(p-BrC_6H_4C(S)NH_2-S)(L-O,S)_2]$ ($[Cd(L^I)L_2]$), while the same reaction in H₂O leads to the complex $[Cd(HL-O)_2(L-O,S)_2]$ ($[Cd(HL)_2L_2]$). The corresponding reactions with Zn(II) always lead to the complex [Zn(L-O,S)₂] ([ZnL₂]) regardless of the solvent. The crystal structure of [Cd(HL)₂L₂]²/3H₂O reveals to be a polymorph to the previously reported anhydrous $[Cd(HL)_2L_2]$.

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

Both the structure of a similar binuclear complex $[Cd_2Z_4]$ $(HZ = PhC(S)NHP(O)(OiPr)_2)$ (Chart 1) and its tendency to form monomers in solution was reported earlier [10].

Since usually ligands of this type are rather stable towards hydrolysis we got interested under which conditions this reaction can be observed or inhibited. To this end we carried out the reaction of deprotonated HL towards Zn(II) and Cd(II) in dried and distilled EtOH and alternatively in H₂O, on which we want to report in this contribution.

2. Experimental

2.1. Physical measurements

NMR spectra in CDCl₃ were obtained on a Bruker Avance 300 MHz spectrometer at 25 °C. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to SiMe₄ (¹H) and 85% H₃PO₄ (³¹P{¹H}). Elemental analyses were performed on a CHNS HEKAtech EuroEA 3000 analyzer.

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2.2. Crystal structure determination and refinement

X-ray diffraction data were collected on a Enraf Nonius Kappa CCD diffractometer equipped with a rotating anode generator and with Cu Kα radiation. The structures were solved by direct methods using the SHELXS [24] program and refined first isotropically and then anisotropically using SHELXL97 [24]. Hydrogen atoms were added to the structure model on calculated positions and were refined as rigid atoms. H atoms bonded to N were freely refined. The figure was generated using the program MERCURY [25].

2.3. Synthesis

2.3.1. [ZnL₂]

A suspension of **HL** (0.38 g, 1 mmol) in distilled EtOH or H_2O (10 mL) was admixed to a solution of potassium hydroxide (0.056 g, 1 mmol) in distilled EtOH or H_2O . To this mixture a solution of ZnCl₂ (0.068 g, 0.5 mmol) in distilled EtOH or H_2O (10 mL) was added dropwise under vigorous stirring. The mixture was stirred at room temperature for further 5 h and left overnight. The complex was obtained by extraction of the reaction mixture using several portions of dichloromethane and drying of the combined extracts using anhydrous MgSO₄. After filtration the solvent was removed in vacuo. The colorless precipitate was recrystallized from a dichloromethane/*n*-hexane mixture. Yield: 0.395 g (96%) for the

synthesis in distilled EtOH; 0.292 g (71%) for the synthesis in H₂O. M.p. 142–143 °C. (*Anal.* Calc. for $C_{26}H_{36}Br_2N_2O_6P_2S_2Zn$: C, 37.90; H, 4.40; N, 3.40. Found: C, 37.84; H, 4.42; N, 3.34%). ν_{max}/cm^{-1} 1546 (SCN), 1150 (P=O), 1001 (POC). δ_H 8.16 (4H, m, ³J 8.3, o-H, C_6H_4), 7.51 (4H, m, ³J 8.3, m-H, C_6H_4), 4.73 (4H, d sept, ³J 6.1, OCH), 1.36 (12H, d, ³J 5.7, CH₃), 1.34 (12H, d, ³J 5.8, CH₃). δ_P 6.8.

2.3.2. $[Cd(L^{I})L_{2}]$ and $[Cd(HL)_{2}L_{2}]$

A suspension of **HL** (0.38 g, 1 mmol) in distilled EtOH or H_2O (10 mL) was admixed to a solution of potassium hydroxide (0.056 g, 1 mmol) in distilled EtOH or H_2O . To this mixture a solution of Cd(CH₃COO)₂ (0.115 g, 0.5 mmol) in distilled EtOH or H_2O (10 mL) was added dropwise under vigorous stirring. The mixture was stirred at room temperature for further 5 h and left overnight. The complex was obtained by extraction of the reaction mixture using several portions of dichloromethane and drying the collected extracts using anhydrous MgSO₄. After filtration the solvent was removed in vacuo. The colorless precipitate was recrystallized from a dichloromethane/*n*-hexane mixture.

2.3.3. $[Cd(L^{I})L_{2}]$

Yield 0.315 g (87%). M.p. 129–130 °C. (*Anal.* Calc. for $C_{33}H_{42}Br_3CdN_3O_6P_2S_3$: C, 36.46; H, 3.89; N, 3.87. Found: C, 36.38; H, 3.95; N, 3.82%). v_{max}/cm^{-1} 3283, 3108, 1666 (NH₂), 1515 (SCN), 1154 (P=O), 1003 (POC). δ_H 9.63 (1H, br. s, NH₂), 8.15 (4H, m, ³J 8.4, o-H, C₆H₄, L), 7.69 (2H, m, ³J 8.3, o-H, C₆H₄), 7.57 (2H, m, ³J 8.5, *m*-H, C₆H₄), 7.49 (4H, m, ³J 8.4, *m*-H, C₆H₄, L), 7.36 (1H, s, NH₂), 4.74 (4H, d sept, ³J 6.1 Hz, OCH), 1.33 (24H, d, ³J 6.2, CH₃). δ_P 4.4.

2.3.4. [Cd(HL)₂L₂]

Yield 0.334 g (82%). M.p. 114 °C. (*Anal.* Calc. for $C_{52}H_{74}Br_4CdN_4O_{12}P_4S_4$: C, 38.28; H, 4.57; N, 3.43. Found: C, 38.39; H, 4.50; N, 3.48%). v_{max}/cm^{-1} 3164 (NH), 1531 (SCN), 1249 (P=O, HL), 1158 (P=O, L), 1006 (POC). δ_H 9.03 (2H, d, ³*J* 10.0, NH), 8.15 (4H, m, ³*J* 7.7, o-H, C_6H_4 , L), 7.79 (4H, m, ³*J* 8.2, o-H, C_6H_4 , HL), 7.50 (4H, m, ³*J* 7.9, *m*-H, C_6H_4 , L), 7.49 (4H, m, ³*J* 8.0, *m*-H, C_6H_4 , HL), 4.79 (4H, d sept, ³*J* 6.2, OCH, HL), 4.63 (4H, d sept, *m*-H, C_6H_4 , HL), 4.63 (4H, d sept, *m*-H, C





Fig. 1. Thermal ellipsoid representation of the two independent molecules found in the crystal structure of [Cd(HL)₂L₂]·2/3H₂O. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms except of NH and H₂O were omitted for clarity.

 3J 6.1, OCH, L), 1.33 (12H, d, 3J 6.1, CH₃, L), 1.29 (36H, br s, CH₃, L + HL). δ_P 4.5 (2P, L), –5.5 (2P, HL).

3. Results and discussion

The ligand **HL** was prepared as described previously [22,23]. The syntheses of the complexes were carried out as follows: the ligand was deprotonated in situ using KOH, followed by reaction with salts of the corresponding metals in freshly dried and distilled EtOH or alternatively in H₂O. The compounds obtained are crystal-line solids, which are soluble in most polar solvents. The structures of these compounds were investigated by single crystal X-ray diffraction analysis, IR, ¹H and ³¹P{¹H} NMR spectroscopy and micro-analysis. It was established that all three complexes are identical to those described by us earlier [23]: [**ZnL**₂], [**Cd**(**L**¹)**L**₂], and [**Cd**(**HL**)₂**L**₂].

The corresponding reaction using ZnCl_2 both in distilled EtOH or H_2O leads exclusively to the complex $[\text{ZnL}_2]$, in both cases. The same reaction using anhydrous $\text{Cd}(\text{CH}_3\text{COO})_2$ leads to the exclusive formation of either $[\text{Cd}(\text{L}^1)\text{L}_2]$ (in freshly dried and distilled EtOH) or $[\text{Cd}(\text{HL})_2\text{L}_2]$ (in H_2O) (Scheme 1). The corresponding synthesis in aqueous EtOH leads to a mixture of the complexes $[\text{Cd}(\text{L}^1)\text{L}_2]$ and $[\text{Cd}(\text{HL})_2\text{L}_2]$ [23]. Interestingly, the formation of the similar Cd(II) complex $[\text{Cd}(\text{HZ})_2\text{Z}_2]$, described by us earlier [10], does not depend on the solvent. Reaction of the potassium salt KZ with Cd(CH₃COO)₂ both in freshly dried and distilled EtOH or H₂O leads to the exclusive formation of $[\text{Cd}(\text{HZ})_2\text{Z}_2]$. Thus, both the nature of the solvent (EtOH or H₂O) and the influence of the *p*-Br substituent affect considerably the complex formation.

In addition to the selectivity of the reaction we were interested to find evidence for the formation of the binuclear complex following Eq. (1b). However, neither in the isolated products nor in the reaction mixture we found evidence for such species (NMR). At the moment we have no explanation for this failure, since from the related ligand **HZ** such a binuclear complex was isolated and characterized (Chart 1). The *p*-Br (electron-demanding) substituent seems thus to be responsible for this very different behavior. Thus, in further experiments we will investigate this phenomenon by further variation of this substituent. Furthermore, we will explore the reaction under strict anhydrous conditions, since it is clear, that the water necessary for the hydrolysis of the ligand (in dried EtOH) was formed in the deprotonation reaction HL + KOH \rightarrow H₂O + KL. In

any case, the high selectivity and yield is remarkable and deserves further investigation.

In addition to the recently reported crystal structure of the complex [**Cd**(**HL**)₂**L**₂] [23] we can report here on a second crystallographic modification of this complex. Crystals of [**Cd**(**HL**)₂**L**₂]·**2**/**3H**₂**O** were obtained by slow evaporation of the solvent from dichloromethane/*n*-hexane solution. The structure of [**Cd**(**HL**)₂**L**₂]·**2**/**3H**₂**O** is shown in Fig. 1, while the crystal and structure refinement data are given in Table 1. Isostructural complexes of Co(II) [8,17], Ni(II) [21] with **HZ**, and Cd(II), Ni(II) with **HL** [9,10] have been synthesized and structurally characterized previously.

As the anhydrous polymorph $[Cd(HL)_2L_2]$ the complex $[Cd(HL)_2L_2] \cdot 2/3H_2O$ crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit of the complex contains one and a half independent complex molecules as one (Cd2, Molecule B) sits on a centre of inversion whilst another (Cd1, Molecule A) is in general space. Additionally one water molecule is found in the unit cell. In the structure of $[Cd(HL)_2L_2]$ [23] one complex molecule is located in a special position at the symmetry centre. The cell of the new polymorph is thus markedly larger. The overall

Table 1					
Crystal data	and data	collection	details for	[Cd(HI) _a]	-1.5/3H-O

Formula	$(C_{52}H_{74}Br_4CdN_4O_{12}P_4S_4)_3 \cdot 2H_2O$
Formula weight	4929.96
Crystal system	triclinic
Space group	ΡĪ
a (Å)	12.7023(4)
b (Å)	12.8401(3)
<i>c</i> (Å)	34.8219(12)
α (°)	98.860(2)
β (°)	95.901(2)
γ (°)	101.500(2)
$V(Å^3)$	5446.5(3)
Ζ	1
D_{calc} (g cm ⁻³)	1.503
T (K)	293(2)
F (0 0 0)	2486
μ (mm ⁻¹)	7.346
Reflections collected	40 301
Unique reflections	13 861
Observed reflections (R_{int})	6234 (0.0124)
R indices (all data)	$R_1 = 0.0736, wR_2 = 0.1671$

Table 2	
Selected bond lengths (Å) and bond angles (°) for $[Cd(HL)_2L_2]$ ·2/3H ₂ O.	

Molecule A		Molecule B	
Bond lengths			
Cd(1)-S(1)	2.555(3)	Cd(2)-S(5)	2.566(2)
Cd(1) - S(2)	2.571(3)	Cd(2) = O(13)	2.291(5)
Cd(1) = O(1)	2332(5)	Cd(2) = O(14)	2 391(5)
Cd(1) = O(2)	2.332(3)	S(5) - C(53)	1.731(10)
Cd(1) = O(2)	2.200(3)	S(5) = C(53)	1.731(10) 1.637(10)
Cu(1) = O(3)	2.591(0)	S(0) - C(34)	1.027(10)
C(1) = O(4)	2.405(6)	P(5) = O(13)	1.461(6)
S(1) - C(1)	1.719(9)	P(5) - N(9)	1.569(8)
S(2) - C(2)	1.736(10)	P(6) = O(14)	1.4/1(6)
S(3) - C(3)	1.611(10)	P(6) - N(10)	1.660(7)
S(4) - C(4)	1.619(11)	N(9)-C(53)	1.301(12)
P(1) - O(1)	1.470(6)	N(10)-C(54)	1.357(12)
P(1) - N(1)	1.595(8)		
P(2) - O(2)	1.475(6)		
P(2) - N(2)	1.569(9)		
P(3)-O(3)	1.462(7)		
P(3)-N(3)	1.660(8)		
P(4) - O(4)	1.470(7)		
P(4) - N(4)	1.660(8)		
N(1)-C(1)	1.314(12)		
N(2) - C(2)	1.326(13)		
N(3)-C(3)	1.355(12)		
N(4) - C(4)	1.372(13)		
Dand analas			
$S(1) \subset I(1) \subseteq S(2)$	179.20(0)	S(5) C4(2) O(12)	00 75(14)
S(1) - Cd(1) - S(2)	178.20(9)	S(5) - Cd(2) - O(13)	88.75(14)
S(1) - Cd(1) - O(1)	87.97(14)	S(5) - Cd(2) - O(14)	90.14(14)
S(1) - Cd(1) - O(2)	92.12(14)	$S(5) - Cd(2) - S(5)^{**}$	180.00
S(1) - Cd(1) - O(3)	90.01(14)	$S(5) - Cd(2) - O(13)^{+1}$	91.25(14)
S(1) - Cd(1) - O(4)	89.99(16)	$S(5)-Cd(2)-O(14)^{m}$	89.87(14)
S(2) - Cd(1) - O(1)	91.19(14)	O(13) - Cd(2) - O(14)	89.38(19)
S(2)-Cd(1)-O(2)	88.79(14)	$O(13)-Cd(2)-S(5)^{+1}$	91.25(14)
S(2)-Cd(1)-O(3)	88.43(14)	$O(13)-Cd(2)-O(13)^{m}$	180.00
S(2)-Cd(1)-O(4)	91.61(16)	$O(13)-Cd(2)-O(14)^{*1}$	90.62(19)
O(1)-Cd(1)-O(2)	177.46(19)	$O(14)-Cd(2)-S(5)^{\#1}$	89.87(14)
O(1)-Cd(1)-O(3)	92.85(19)	$O(14)-Cd(2)-O(13)^{\#1}$	90.62(19)
O(1)-Cd(1)-O(4)	89.7(2)	$O(14)-Cd(2)-O(14)^{\#1}$	180.00
O(2)-Cd(1)-O(3)	89.69(19)	$S(5)^{\#1}-Cd(2)-O(14)^{\#1}$	88.75(14)
O(2)-Cd(1)-O(4)	87.75(19)	$S(5)^{\#1}-Cd(2)-O(14)^{\#1}$	90.14(14)
O(3)-Cd(1)-O(4)	177.4(2)	$O(13)^{\#1}-Cd(2)-O(14)^{\#1}$	89.38(19)
Cd(1)-S(1)-C(1)	107.4(3)	Cd(2)-S(5)-C(53)	109.4(3)
Cd(1)-S(2)-C(2)	110.2(3)	O(13)-P(5)-N(9)	121.9(4)
O(1)-P(1)-N(1)	122.9(4)	O(14)-P(6)-N(10)	107.3(3)
O(2)-P(2)-N(2)	122.1(4)	Cd(2)-O(13)-P(5)	127.0(3)
O(3) - P(3) - N(3)	108.2(4)	Cd(2)-O(14)-P(6)	137.2(3)
O(4) - P(4) - N(4)	107.5(4)	P(5)-N(9)-C(53)	135.3(6)
Cd(1)-O(1)-P(1)	122.5(3)	P(6)-N(10)-C(54)	130.5(6)
Cd(1)-O(2)-P(2)	128.1(3)	S(5)-C(53)-N(9)	127.5(7)
Cd(1)-O(3)-P(3)	136.4(3)	S(6)-C(54)-N(10)	124.4(7)
Cd(1) - O(4) - P(4)	136.2(3)		
P(1)-N(1)-C(1)	132.7(6)		
P(2) - N(2) - C(2)	134.4(6)		
P(3) - N(3) - C(3)	129.9(7)		
P(4) = N(4) = C(4)	130 8(7)		
S(1) = C(1) = N(1)	128 8(7)		
S(1) = C(1) = N(1) S(2) = C(2) = N(2)	120.0(7) 128 $A(7)$		
S(2) - C(2) - IN(2) S(3) - C(3) - IN(2)	120.4(7) 124.7(7)		
S(3) - C(3) - IN(3) S(4) - C(4) - IN(4)	124.7(7)		
S(4) - C(4) - N(4)	125.2(8)		

quality of both crystal structures makes us confident, that both structure solution and refinement are correct for the new polymorph. The bonding parameters are essentially the same for the two independent molecules in $[Cd(HL)_2L_2] \cdot 2/3H_2O$ (Table 2) and also very similar to the recently reported values in $[Cd(HL)_2L_2]$ [23]. There are two intramolecular N-H···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 $[Cd(HL)_2L_2] \cdot 2/3H_2O$. The hydrogen bond parameters are shown in Table 3. Similar hydrogen bonding was also observed in the crystal of the anhydrous polymorph $[Cd(HL)_2L_2]$ [23].

Table 3

Hydrogen bond lengths (Å) and angles (°) for $[Cd(HL)_2L_2]\cdot 2/3H_2O$.

D−H···A	d(D-H)	d(H···A)	$d(D \cdots A)$	∠(DHA)
$\begin{array}{l} N(3) - H(1) \cdots O(1) \\ N(4) - H(2) \cdots O(2) \\ N(10) - H(75) \cdots O(13)^{\#1} \end{array}$	0.86	2.21	3.022(9)	158
	0.86	2.03	2.841(9)	156
	0.86	2.10	2.923(9)	159

Symmetry transformations used to generate equivalent atoms: #1 - 1 - x, -2 - y, -z.

4. Conclusions

In summary, the reaction of the in situ deprotonated thiobenzamide ligand p-BrC₆H₄C(S)NHP(O)(OiPr)₂ (**HL**) with ZnCl₂ both in freshly dried and distilled EtOH or H₂O leads exclusively to the formation of the complex [**ZnL**₂], while the same reaction with anhydrous Cd(CH₃COO)₂ leads to the exclusive formation of either $[Cd(L^{I})L_{2}]$ in dried and distilled EtOH, or $[Cd(HL)_{2}L_{2}]$ in H₂O. The corresponding synthesis in aqueous EtOH gave a mixture of the complexes [**Cd**(**L**¹)**L**₂] and [**Cd**(**HL**)₂**L**₂]. The water for the hydrolysis of the ligand, allowing the formation of [Cd(L¹)L₂], comes from the deprotonation reaction. It was assumed that a binuclear complex [Cd₂L₄] is responsible for the activation of the normally hydrolysis-stable ligand, but no evidence could be found for such a complex (which has previously been observed for the phenyl derivative $C_6H_5C(S)NHP(O)(OiPr)_2$). Further investigations will thus be necessary to elucidate this interesting hydrolysis reaction, one approach will be the variation of the para substituent, which might play an important role.

5. Supplementary data

CCDC 766627 (**[Cd(HL)₂L₂]·2/3H₂O**) contains the supplementary crystallographic data. 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 email: deposit@ccdc.cam.ac.uk.

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References

- V.N. Soloviev, A.N. Chechlov, N.G. Zabirov, I.V. Martynov, Dokl. Chem. 341 (1995) 502.
- [2] 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.
- [3] 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.
- [4] V.V. Brusko, A.I. Rakhmatullin, N.G. Zabirov, Russ. J. Gen. Chem. 70 (2000) 1603.
- [5] N.G. Zabirov, V.V. Brusko, A.Yu. Verat, D.B. Krivolapov, I.A. Litvinov, R.A. Cherkasov, Phosphorus, Sulfur Silicon 17 (2002) 1869.
- [6] F.D. Sokolov, N.G. Zabirov, V.V. Brusko, D.B. Krivolapov, I.A. Litvinov, Mendeleev Commun. 13 (2003) 72.
- [7] N.G. Zabirov, A.Yu. Verat, F.D. Sokolov, M.G. Babashkina, D.B. Krivolapov, V.V. Brusko, Mendeleev Commun. 13 (2003) 163.
- [8] F.D. Sokolov, D.A. Safin, N.G. Zabirov, L.N. Yamalieva, D.B. Krivolapov, I.A. Litvinov, Mendeleev Commun. 14 (2004) 51.
- [9] F.D. Sokolov, D.A. Safin, N.G. Zabirov, P.V. Zotov, R.A. Cherkasov, Russ. J. Gen. Chem. 75 (2005) 1919.
- [10] 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.
- [11] D.A. Safin, M.G. Babashkina, F.D. Sokolov, N.G. Zabirov, Inorg. Chem. Commun. 9 (2006) 1133.

- [12] 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.
- [13] 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.
- [14] 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.
- [15] F.D. Sokolov, V.V. Brusko, N.G. Zabirov, R.A. Cherkasov, Curr. Org. Chem. 10 (2006) 27.
- [16] A. Zazybin, O. Osipova, U. Khusnutdinova, I. Aristov, B. Solomonov, F. Sokolov, M. Babashkina, N. Zabirov, J. Mol. Catal. A: Chem. 253 (2006) 234.
- [17] 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.
- [18] D.A. Safin, M.G. Babashkina, F.D. Sokolov, N.G. Zabirov, J. Galezowska, H. Kozlowski, Polyhedron 26 (2007) 1113.

- [19] F.D. Sokolov, M.G. Babashkina, D.A. Safin, A.I. Rakhmatullin, F. Fayon, N.G. Zabirov, M. Bolte, V.V. Brusko, J. Galezowska, H. Kozlowski, Dalton Trans. (2007) 4693.
- [20] D.A. Safin, F.D. Sokolov, H. Nöth, M.G. Babashkina, T.R. Gimadiev, J. Galezowska, H. Kozlowski, Polyhedron 27 (2008) 2022.
- [21] 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.
- [22] 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.
- [23] D.A. Safin, A. Klein, M.G. Babashkina, H. Nöth, D.B. Krivolapov, I.A. Litvinov, H. Kozlowski, Polyhedron 28 (2009) 1504.
- [24] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
- [25] I.J. Bruno, J.C. Cole, P.R. Edgington, M. Kessler, C.F. Macrae, P. McCabe, J. Pearson, R. Taylor, Acta Crystallogr., Sect. B 58 (2002) 389.