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Studies on zinc(II) complexes with *N*-thioacylamidophosphates: X-ray crystal structure of the $[Zn(RC(S)NP(O)(OiPr)_2)_2]$ (R = NH₂, *t*BuNH, *c*-C₆H₁₁NH)

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ABSTRACT

The photoluminescent properties of 17 zinc(II) chelates $[Zn(RC(S)NP(O)(OiPr)_2-O,S)_2]$ (R = Ph (1a), PhNH (1b), *p*-BrPh (1c), *p*-MeOC₆H₄NH (1d), *p*-BrC₆H₄NH (1e), NH₂ (1f), *i*PrNH (1g), *t*BuNH (1h), Et₂N (1i), *c*-C₅H₁₀N (1j), *c*-OC₄H₈N (1k), *c*-C₆H₁₁NH (1l), aminobenzo-15-crown-5 (1m)) and $[Zn(B) (RC(S)NP(O)(OiPr)_2-O,S)_2]$ (R = Ph, B = 2,2'-bipyridine (2a); R = Ph, B = 1,10-phenanthroline (2b); R = PhNH, B = 2,2'-bipyridine (2c); R = PhNH, B = 1,10-phenanthroline (2b); R = PhNH, B = 2,2'-bipyridine (2c); R = PhNH, B = 1,10-phenanthroline (2d)), are reported. Colorless and air/moisture stable chelate complexes of divalent zinc show blue emission in the solid state when excited with UV light. Complexes 1f, 1h, 1l were investigated by single crystal X-ray diffraction. The zinc(II) atom in complexes 1f, 1h, 1l is in a distorted tetrahedral O₂S₂ environment formed by the C=S sulphur atoms and the P=O oxygen atoms of two deprotonated ligands.

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1. Introduction

Up to now, large numbers of coordination complexes of the Zn(II) cation have been prepared by taking certain factors into account, such as the functionality, flexibility, symmetry and nature of donor centers of organic ligands and the coordination ability of the metal ion [1]. Among these, the construction of complexes with changeable geometry and structure, to the best of our knowledge, has become a widely propagated and popular subject. Such complexes are important in advanced materials such as optical devices, especially with luminescence properties [2]. One of the effective strategies to vary luminescent activity is to change the geometry and structure. This requires the synthesis of complexes by addition of a heteroligand to homoligand luminescence active complexes. These compounds might find applications as receptors with optical detecting properties.

The late transition metal ion complexes of *N*-acylthioureas $R_2NC(S)NHC(O)R'$ [3] and their phosphoryl analogues based on thioureas $R_2NC(S)NHP(O)(OR')_2$ and thioamides RC(S)NHP(O) ($OR')_2$ [4,5, and references therein] are of interest due to their mag-

netic and photophysical properties. The 1,5-X,S-coordination of these ligand anions is typical for chelate complexes (e.g. [4–6]).

However, recent investigations have shown that the coordination mode of these ligands containing the RNH group towards Ni(II), Pd(II), Pt(II) [7,8], Cu(II) [9] and Cd(II) [10] cations depends on the presence of strong intramolecular NH···O=P or NH···O=C bonds. The thiourea ligands of common formula RNHC(S)NHP(O) (OR')₂ (NPTU) [8,9] are able to bind Ni(II), Pd(II) and Cu(II) cations through the C=S sulfur and P–N nitrogen atoms. The thiourea *n*PrNHC(S)NHC(O)*n*Pr [7] forms similar 1,3-*N*,S-chelate with the Pt(II) cation through the C=S sulfur and NC(O) nitrogen atoms.

Interestingly, the *N*-(*o*-nitrophenyl)-*N*'-(methoxycarbonyl)thiourea (HQ) in complex of formula $[Cd(2,2'-bpy)Q_2]$ is also bound in the 1,3-*N*,*S*-fashion via the C=S sulfur and NC(O) nitrogen atoms [10]. However, the sulfur atom of the thiourea HQ does not coordinate to the Zn(II) ion. A monodentate coordination through the deprotonated nitrogen atom of the C(S)NC(O) moiety occurs in the chelate $[Zn(2,2'-bpy)Q_2]$.

In the literature there is no information on crystal structure of NPTU complexes with the Zn(II) cation. In this connection it was interesting to investigate the structure and properties of some complexes of phosphorylated thioureas and thioamides and compares these with heteroligand analogues with participation of 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) as additional donor ligands.



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In this paper, we report on the photoluminescence properties at room temperature of thirteen solid zinc-containing chelating complexes with HL of composition $Zn[RC(S)NP(O)(OiPr)_2-O,S]_2$ (R = Ph **1a**, PhNH **1b**, *p*-BrPh **1c**, *p*-MeOC₆H₄NH **1d**, *p*-BrC₆H₄NH **1e**, NH₂ **1f**, *i*PrNH **1g**, *t*BuNH **1h**, Et₂N **1i**, *c*-C₅H₁₀N **1j**, *c*-OC₄H₈N **1k**, *c*-C₆H₁₁NH **1l**, aminobenzo-15-crown-5 **1m**) and four novel heteroligand complexes of composition $Zn(B)[RC(S)NP(O)(OiPr)_2-O,S]_2$ (R = Ph, B = 2,2'-bipyridine **2a**; R = Ph, B = 1,10-phenanthroline **2b**; R = PhNH, B = 2,2'-bipyridine **2c**; R = PhNH, B = 1,10-phenanthroline **2d**).

2. Experimental

2.1. Physical measurements

Infrared spectra (Nujol) were recorded on 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} spectra were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to SiMe₄ (¹H) and H_3PO_4 (³¹P{¹H}). Electron ionization mass spectra were measured on the TRACE MS Finnigan MAT instrument. Ionization energy was 70 eV. The substance was injected directly into the ion source at 150 °C. Heating was carried out in a programmed mode from 35 to 200 °C at a rate of 35 °C/min. Electrospray ionization mass spectra were measured with a Finnigan-Mat TCQ 700 mass spectrometer on a 10^{-6} M solution in CH₃OH. The speed of a sample submission was 2 $\mu L/min.$ The ionization energy was 4.5 kV. The capillary temperature was 200 °C. Fluorescence measurements were made on a SLM Aminco 500 spectrofluorometer at room temperature. Elemental analyses were performed on a Perkin-Elmer 2400 CHN microanalyser. An ENRAF NONIUS four circle diffractometer, operating with Mo Ka radiation and a graphite monochromator was used for determining the crystallographic parameters and collecting the data sets.

2.2. Synthesis of $[ZnL_2]$ (1a–1m)

Complexes **1a**, **1b**, **1d**, **1e**, **1g**–**1l** were prepared according to the previously described techniques [4,5,11].

Complexes **1c** and **1f** were synthesized for the first time by the method used in [4,5]. A suspension of HL, $R = p-BrC_6H_4$ (1.900 g, 5 mmol) or $R = NH_2$ (1.200 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 $ZnCl_2$ (0.381 g, 2.8 mmol) was added dropwise under vigorous stirring 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 MgSO₄. The solvent was then removed in vacuo. A colourless precipitate was isolated from dichloromethane by *n*-hexane.

2.2.1. $[Zn(p-BrC_6H_4C(S)NP(O)(OiPr)_2)_2]$ (1c)

Yield: 1.73 g (84%), m.p. 143 °C. ¹H NMR (CDCl₃): δ (ppm) = 1.35 (d, ³J_{H,H} = 5.6 Hz, 12 H, CH₃), 1.36 (d, ³J_{H,H} = 5.6 Hz, 12 H, CH₃), 4.71 (d. sept, ³J_{POCH} \approx ³J_{H,H} \approx 6.2 Hz, 4H, OCH), 7.50 (m, 4H, *o*-H, C₆H₄), 8.14 (m, 4H, *m*-H, C₆H₄). ³¹P{¹H} NMR (CDCl₃): 6.9 ppm. IR (cm⁻¹): 1000 (b, vs) (POC); 1152 (vb, s) (P=O); 1544 (s) (SCN). *Anal.* Calc. for C₂₆H₃₆Br₂N₂O₆P₂S₂Zn (823.85): C, 37.90; H, 4.40; N, 3.40. Found: C, 37.86; H, 4.45; N, 3.38%.

2.2.2. $[Zn(NH_2C(S)NP(O)(OiPr)_2)_2]$ (1f)

Yield: 1.24 g (91%), m.p. 182 °C. ¹H NMR (CDCl₃): δ (ppm) = 1.29 (d, ³*J*_{H,H} = 6.2 Hz, 12H, CH₃), 1.30 (d, ³*J*_{H,H} = 6.2 Hz, 12H, CH₃), 4.58 (d. sept, ³*J*_{POCH} = 7.6 Hz, ³*J*_{H,H} = 6.2 Hz, 4H, OCH), 5.81 (br. s, 1H,

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NH₂), 5.97 (br. s, 1H, NH₂). ${}^{31}P{}^{1}H$ NMR (CDCl₃): 6.2 ppm. IR (cm⁻¹): 992 (b, vs) (POC); 1132 (vb, s) (P=O); 1512 (s) (SCN); 1620 (s), 3136 (b, s), 3272 (s); 3496 (s) (NH₂). *Anal.* Calc. for C₁₄H₃₂N₄O₆P₂S₂Zn (542.05): C, 30.92; H, 5.93; N, 10.30. Found: C, 30.90; H, 5.91; N, 10.33%.

2.3. Synthesis of $[Zn(B)L_2]$ (**2a–2d**)

A solution of complexes **1a** (0.30 g, 0.45 mmol) or **1b** (0.31 g, 0.45 mmol) in benzene (10 mL) was added dropwise whilst stirring to a solution of 2,2'-bipyridine (0.07 g, 0.45 mmol) or 1,10-phenanthroline (0.08 g, 0.45 mmol) in benzene (10 mL). After complete addition, the solution was stirred for an hour. The solvent was then removed in vacuo. The residue was recrystallized from a methylene chloride/*n*-hexane mixture. The complexes **2a-2d** were isolated as colorless powders.

2.3.1. [Zn(2,2'-bpy)(PhC(S)NP(O)(OiPr)₂)₂] (**2a**)

Yield: 0.28 g (75%), m.p. 102 °C. ¹H NMR (CDCl₃): δ (ppm) = 1.36 (d, ³*J*_{H,H} = 6.1 Hz, 24H, CH₃), 4.74 (d. sept, ³*J*_{POCH} ≈ ³*J*_{H,H} ≈ 6.5 Hz, 4H, OCH), 7.21–8.76 (m, 18H, C₆H₅ + bpy). ³¹P{¹H} NMR (CDCl₃): 5.9 ppm. IR (cm⁻¹): 996 (b, vs) (POC); 1168 (b, s) (P=O); 1464 (s) (SCN). EI-MS: *m*/*z* (%) = 665 (73) [ZnL₂]⁺, 301 (61) [HL]⁺, 156 (13) [bpy]⁺. ES (positive ion): *m*/*z* (%) = 522.2 (100) [M−PhC(S)NP(O) (OiPr)₂]⁺. Anal. Calc. for C₃₆H₄₆N₄O₆P₂S₂Zn (820.16): C, 52.59; H, 5.64; N, 6.81. Found: C, 52.62; H, 5.60; N, 6.78%.

2.3.2. [*Zn*(1,10-*phen*)(*PhC*(*S*)*NP*(*O*)(*OiPr*)₂)₂] (**2b**)

Yield: 0.31 g (82%), m.p. 154 °C. ¹H NMR (CDCl₃): δ (ppm) = 1.32 (d, ³*J*_{H,H} = 6.0 Hz, 24H, CH₃), 4.72 (d. sept, ³*J*_{POCH} ≈ ³*J*_{H,H} ≈ 6.5 Hz, 4H, OCH), 7.28–8.42 (m, 18H, C₆H₅ + phen). ³¹P{¹H} NMR (CDCl₃): 6.1 ppm. IR (cm⁻¹): 996 (b, vs) (POC); 1172 (b, s) (P=O); 1492 (s) (SCN). EI-MS: *m/z* (%) = 665 (100) [ZnL₂]⁺, 301 (29) [HL]⁺, 180 (54) [phen]⁺. ES (positive ion): *m/z* (%) = 546.3 (100) [M–PhC(S)NP(O)(OiPr)₂]⁺. Anal. Calc. for C₃₈H₄₆N₄O₆P₂S₂Zn (844.16): C, 53.93; H, 5.48; N, 6.62. Found: C, 53.96; H, 5.51; N, 6.59%.

2.3.3. [Zn(2,2'-bpy)(PhNHC(S)NP(O)(OiPr)₂)₂] (2c)

Yield: 0.25 g (65%), m.p. 101 °C. ¹H NMR (CDCl₃): δ (ppm) = 1.15–1.33 (m, 24H, CH₃), 4.48–4.65 (m, 4H, OCH), 6.89–8.46 (m, 18H, C₆H₅ + bpy), 8.58–8.63 (m, 2H, PhNH). ³¹P{¹H} NMR (CDCl₃): 6.5 ppm. IR (cm⁻¹): 1008 (b, vs) (POC); 1140 (b, s) (P=O); 1560 (s) (SCN); 3312 (NH). EI-MS: m/z (%) = 695 (22) [ZnL₂]⁺, 316 (100) [HL]⁺, 56 (74) [bpy]⁺. ES (positive ion): m/z (%) = 537.3 (100) [M–PhNHC(S)NP(O)(OiPr)₂]⁺. Anal. Calc. for C₃₆H₄₈N₆O₆P₂S₂Zn (850.18): C, 50.73; H, 5.68; N, 9.86. Found: C, 50.70; H, 5.72; N, 9.84%.

2.3.4. [*Zn*(1,10-*phen*)(*PhNHC*(*S*)*NP*(O)(OiPr)₂)₂] (**2d**)

Yield: 0.31 g (82%), m.p. 104 °C. ¹H NMR (CDCl₃): δ (ppm) = 0.96–1.32 (m, 24H, CH₃), 4.39–4.66 (m, 4H, OCH), 6.85– 8.45 (m, 18H, C₆H₅ + phen), 9.18–9.40 (m, 2H, PhNH). ³¹P{¹H} NMR (CDCl₃): 6.6 ppm. IR (cm⁻¹): 1020 (b, vs) (POC); 1144 (b, s) (P=O); 1504 (s) (SCN); 3288 (NH). EI-MS: m/z (%) = 695 (34) [ZnL₂]⁺, 316 (57) [HL]⁺, 180 (91) [phen]⁺. ES (positive ion): m/z(%) = 561.2 (100) [M–PhNHC(S)NP(O)(OiPr)₂]⁺. Anal. Calc. for C₃₈H₄₈N₆O₆P₂S₂Zn (874.18): C, 52.08; H, 5.52; N, 9.59. Found: C, 52.04; H, 5.47; N, 9.64%.

2.4. Crystal structure determination and refinement

The selected crystal was coerced with lithelene and mounted on a glass fibre. It was then cooled to -60 °C on the goniometer head of a Kappa Nonius diffractometer operated with a rotating anode. After alignment the unit cell parameters were calculated from a se-

lected data set, and data collection was performed by using an area detector. For data reduction the program SMART was used, and for structure solution and refinement the program package SHELXTL PLUS. All plots of the molecules are shown with a 50% probability for the thermal ellipsoids. The numbering of the atoms is shown in Figs. 1–3 (ORTEP) [12] (see Table 1).



Fig. 1. An ORTEP view of $[Zn(H_2NC(S)NP(O)(OiPr)_2)_2]$ (1f). Displacement ellipsoids are drawn at the 50% probability level.



Fig. 2. An ORTEP view of $[Zn(tBuNHC(S)NP(O)(OiPr)_2)_2]$ (**1h**). Displacement ellipsoids are drawn at the 50% probability level.



Fig. 3. An ORTEP view of $[Zn(c-C_6H_{11}NHC(S)NP(O)(OiPr)_2)_2]$ (11). Displacement ellipsoids are drawn at the 50% probability level.

3. Results and discussion

3.1. Synthesis

Complexes **1a–1m** were prepared by the following procedure: the ligand was converted to the potassium salt, followed by reaction with ZnCl₂ (Scheme 1). The compounds obtained are crystal-line solids soluble in most polar solvents.

Unsaturation of the ZnO₂S₂ coordination environment opens up possibilities for the synthesis of a large number of heteroligand complexes. They are obtained by the interaction of these complexes with various donor agents.

In order to obtain the heteroligand complexes, we have combined HL and two aromatic chelate ligands, (2,2'-bipyridine or 1,10-phenanthroline) in experiments based on the following considerations: (i) the steric hindrance at the metal center will be increased when the aromatic 1,4-donor ligand binds to the metal ion; this ensures the formation of the lower dimensional structure and on the other hand (ii) metal complexes of 2,2'-bipyridine or 1,10-phenanthroline and their derivatives exhibit excellent luminescent properties [13], which can be used not only as efficient blue emitters in electroluminescent devices but also as chemical sensors for specific organic molecules [14].

Complexes **2a**–**2d** were prepared by the following procedure: a benzene solution of 2,2′-bipyridine or 1,10-phenanthroline was added dropwise to a benzene solution of **1a** or **1b** (Scheme 1). The compounds obtained **2a**–**2d** are crystalline solids soluble in most polar solvents.

3.2. IR and NMR spectroscopy

It is shown that all listed complexes **1a–1m** have a similar coordination environment at the zinc atom. The IR, ¹H, ³¹P{¹H} NMR [4,11] and X-ray [4] data confirm that in a CDCl₃ solution and in the solid state only [ZnL₂] chelates with a tetrahedral ZnO₂S₂ core exist. The 1,5-0,S-coordination appears to be the most steric favorable in this case because it provides a maximal bite angle for the ligand's anionic form L⁻.

The additional ligands bpy or phen in a molecule of complex could affect on the coordination mode of the anionic thiourea ligands. The bond angles in the cation environment decrease in comparison with the tetrahedral core and requirements to the bite angle are softened, thus the situation becomes ambiguous. The structures of the thiourea HQ chelates with the Zn(II) and Cd(II) cations demonstrate the examples of such changes in the coordination modes [10].

There is a strong (20-25 kJ/mol) hydrogen bond of type PhNH \cdots O=P in the thiourea PhNHC(S)NHP(O)(OiPr)₂ and its complexes [8,9]. It prevents the coordination through the P=O group in square planar complexes of the Ni(II), Pd(II) and Cu(II) cations.

Thus, the presence the bpy or phen in the coordination sphere of Zn(II) makes possible the three coordination modes of PhNHC(S)NHP(O)(OiPr)₂ (HL): (i) preservation of the 1,5-O,S-coordination for L⁻ (Scheme 2A); (ii) 1,3-*N*,S-coordination of L⁻ (Scheme 2B); (iii) monodentate *N*-coordination (Scheme 2C). Neither of them could be discarded *a priori*.

The 1,5-O,S-coordination (Scheme 2A) is a unique variant is for complexes of the thioamide $PhC(S)NHP(O)(OiPr)_2$ due to absence of the intramolecular H-bonds.

Unfortunately, we could not get suitable crystals of complexes **2a–2d**, for X-ray structure analysis. However, according to the IR, ¹H, ³¹P{¹H} NMR and luminescence data, obtained in a CDCl₃ solution and in the solid state, complexes **2a–2d** have a $ZnO_2S_2N_2$ core (Scheme 2A). The comparative analysis of IR spectra of the initial ligands RC(S)NHP(O)(OiPr)₂ (R = Ph and PhNH), their complexes

Table 1
Crystal data and data collection parameters for 1f , 1h and 1l

	Compound			
	1f	1h	11	
Chemical formula	$C_{14}H_{32}N_4O_6P_2S_2Zn$	$C_{22}H_{48}N_4O_6P_2S_2Zn$	C ₂₆ H ₅₂ N ₄ O ₆ P ₂ S ₂ Zn	
Formula weight	543.91	656.11	708.19	
Crystal size (mm)	$0.06 \times 0.14 \times 0.19$	$0.22\times0.30\times0.35$	0.15 imes 0.21 imes 0.25	
Crystal system	monoclinic	monoclinic	monoclinic	
Space group	$P2_1/n$	Сс	$P2_1/c$	
a (Å)	15.9479(4)	24.776(5)	14.912(5)	
b (Å)	9.1698(2)	9.350(2)	17.531(5)	
c (Å)	17.4946(4)	14.476(3)	15.153(5)	
β (°)	104.0098(1)	98.41(3)	115.410(5)	
V (Å ³)	2482.29(10)	3317.3(12)	3578(2)	
Ζ	4	4	4	
ρ (calc.) (Mg/m ³)	1.455	1.314	1.315	
$\mu ({\rm mm^{-1}})$	1.321	1.001	0.933	
F(000)	1136	1392	1504	
Index range	$-18\leqslant h\leqslant 18,-10\leqslant k\leqslant 10,-20\leqslant l\leqslant 20$	$-30 \leqslant h \leqslant 30, -11 \leqslant k \leqslant 11, -17 \leqslant l \leqslant 17$	$-18\leqslant h\leqslant 18,-21\leqslant k\leqslant 20,-18\leqslant l\leqslant 18$	
2θ (°)	50.02	52.22	52.02	
Temperature (K)	200	193	193	
Reflections collected	8389	6192	13268	
Reflections unique	4358	6187	7020	
Reflections observed (4σ)	3598	5724	5853	
R(int.)	0.017	0.005	0.026	
Number of variables	294	337	538	
Weight. scheme ^a , x/y	0.0511/1.1243	0.0495/7.0103	0.0500/0.8394	
Goodness-of-fit	1.05	1.01	1.02	
Final R (4 σ)	0.0337	0.0387	0.0319	
Final wR ₂	0.0927	0.1028	0.0882	
Larg. res. peak (ɛ/ų)	0.29	0.43	0.38	

^a $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP; P = (F_o^2 + 2F_c^2)/3.$







Scheme 2. Proposed modes of the ligand coordination in complexes $[Zn(B)L_2]\ (2).$ R'=OiPr.

with the Zn(II) cation **1a** and **1b**, and adducts **2a–2d** confirms the preservation of the 1,5-*O*,*S*-coordination in the $[ZnL_2]$ core of **2a–2d**.

There is a series of the P=O group absorption bands in the IR spectra of complexes 2a-2d in the area close to the appropriate 1,5-O,S-chelate complexes of type [ML₂] [4–6], and there is also

an intense absorption band of the SCN fragment. This confirms the 1,5-*O*,*S*-coordination of the ligand anions.

It is important to note, that the band of the PhNH group in **2c**, **2d** is in the field of 3288–3312 cm⁻¹, which is characteristic for

1,5-O,S-isomers, showing the weak intermolecular H-bonding in the solid state [5,8]. The isomers B and C must have the NH-group absorption band up to $3100-3160 \text{ cm}^{-1}$ [8] due to formation of the strong intramolecular hydrogen bond (Scheme 2).

The ³¹P{¹H} NMR signals of complexes **2a–2d** appear at δ = 5.9– 6.7 ppm, i. e. there is a down-field shift relative to that of the free ligand RC(S)NP(O)(OiPr)₂ (R = Ph, δ = -5.6 ppm and PhNH, δ = -5.3 ppm). Full width at half peak heights is in the range 3.0– 9.0 Hz. However, the shift of the signals in **2a–2d** is more than 0.2–0.4 ppm, compared to the complexes **1a** and **1b** [11]. The signals are in the region that is characteristic to the amidophosphate environment in complexes of *N*-acylamidophosphate anions.

The ¹H NMR spectra of complexes **2a–2d** contain a set of signals for the $(iPrO)_2P(O)$ and C_6H_5 protons. There are also signals corresponding to the polyaromatic chelate ligand. Analysis of the integral intensities of the proton signal testifies about complexes **2a– 2d** structure of $[Zn(2,2'-bpy)L_2]$ (**2a**, **2c**) or $[Zn(1,10-phen)L_2]$ (**2b**,**2d**).

Thus, IR and NMR spectroscopy data confirm the structure of the adducts **2a–2d** in solution and solid state. The donor polyaromatic ligands, as well as anionic ligands, are coordinated to the Zn(II) cation.

3.3. EI mass spectrometry

Molecular ions of complexes **2a–2d** are unstable under the conditions of measurement, and the heaviest molecular ion, observed in the spectra of **2a–2d**, corresponds to the neutral [ZnL₂] complex core. In the EI mass spectra there are also peaks of the parent amidophosphate ligands, 2,2'-bipyridine and 1,10-phenanthroline, respectively.

3.4. Molecular structure of ZnL₂ complexes 1f, 1h, 1l

According to the X-ray data complexes **1f**, **1h**, **1l** are spirocycling bis-chelates with a distorted-tetrahedral ZnO_2S_2 core. All complexes contain structurally independent ligand moieties. The selected bond lengths and torsion angles are given in Table 2. Intermolecular hydrogen bond parameters are given in Table 3.

Bond lengths (S)C–N and P–N in complexes are shortened (Table 2) and the C=S and P=O(Zn) distances are considerably lengthened in comparison with typical interatomic distances reported for *N*-phosphorylated thioureas [6]. The bond lengths distribution in the ligand moieties confirms the superiority of *S*-enolic tautomeric form S–C=N–P=O for all compounds.

Six-membered Zn–O–P–N–C–S cycles have the asymmetrical boat conformation. The maximal deviation of atoms from the least square plane (LSP) of the cycles is observed for the phosphorus, sulphur and zinc atoms. Chelate cycles in **1f** are almost planar; the deviation from LSP is the smallest among the presented structures.

Complexes **1f**, **1l** show a remarkably different H-bonding pattern in the crystal (Scheme 3). Molecules of **1f** are connected to endless chains by H-bonds between the NH_2 group proton and the nitrogen atom of the N–P group. The chelates **1h** and **1l** form hydrogen-bonded chains with the RNH proton and the sulphur atom of neighbor chelate molecule.

3.5. Photoluminescent properties

The data of the emission spectra for complexes **1a–1m** and **2a–2d** in the solid state at room temperature are listed in Table 4 (note that the parent ligands have no emission). Interestingly, they exhibit practically the same fluorescent properties.

Complexes **1a–1m** show a blue emission band with the maximum intensity at 394–399 nm upon excitation at 249 nm (Table

Table 2

Selected bond distances (Å) bond and torsion angles (°) for six-membered cycles Zn-S-C-N-P-O in complexes **1f**, **1h** and **1l**^a

	Complexes of general formula [ZnL ₂]			
	1f	1h	11	
Zn-O	1.957(2)	1.964(3)	1.973(2)	
	1.954(2)	1.948(3)	1.973(2)	
Zn-S	2.2945(9)	2.2894(12)	2.3077(9)	
	2.2890(8)	2.2850(11)	2.2970(9)	
C-S	1.749(2)	1.767(4)	1.770(2)	
	1.751(2)	1.752(4)	1.766(2)	
(S)C–N	1.315(3)	1.314(5)	1.310(3)	
	1.314(3)	1.302(5)	1.303(3)	
(S)C–N (exocyclic)	1.329(4)	1.349(4)	1.331(3)	
	1.334(4)	1.338(4)	1.330(3)	
P-N	1.598(2)	1.603(3)	1.602(2)	
	1.606(2)	1.599(4)	1.593(2)	
Р-О	1.494(2)	1.495(3)	1.4996(14)	
	1.496(2)	1.492(3)	1.4961(14)	
S–Zn–O (endocyclic)	109.53(6)	103.00(9)	101.38(4)	
	102.00(6)	101.89(9)	99.70(4)	
P-N-C-S	3.5(4)	-7.0(6)	7.8(3)	
	4.5(4)	-8.0(7)	3.5(3)	
O-P-N-C	-17.1(3)	32.6(4)	-45.3(2)	
	-25.9(3)	-13.5(5)	-23.8(3)	
Zn-S-C-N	11.7(3)	176.3(2)	29.1(2)	
	11.0(3)	16.1(4)	26.5(2)	
N–P–O–Zn	10.4(2)	21.1(3)	29.50(14)	
	27.0(2)	-42.9(3)	2.20(2)	
S-Zn-O-P	3.20(14)	28.8(2)	6.50(11)	
	-11.19(14)	-10.1(2)	23.41(12)	
0-Zn-S-C	$-12.49(11) \\ -6.77(11)$	-6.1(2) -6.6(2)	-31.18(9) -33.51(9)	

 $^{\rm a}\,$ Presented data relate to the two independent ligand moieties with P(1) and P(2) atoms, respectively.

Table 3

Intermolecular hydrogen bond parameters for 1f, 1h and 1l

D−H···A	D-H	H···A	$D{\cdots}A$	D−H···A
1f				
$N(2)-H(2N)\cdots N(3)\#^{a}$	0.83(3)	2.30(3)	3.131(3)	175(3)
$N(4)-H(4N)\cdots N(1)\#^{b}$	0.83(3)	2.20(3)	3.007(3)	166(3)
1h				
$N(1)-H(1N)\cdots S(2)\#^{c}$	1.02(4)	2.56(4)	3.559(4)	169(3)
$N(3)-H(3N)\cdots S(1)\#^{d}$	0.68(5)	2.87(5)	3.536(4)	167(4)
11				
$N(2)-H(2)\cdots S(2)\#^{e}$	0.80(2)	2.65(2)	3.400(2)	158(2)
$N(4)-H(4)\cdots S(1)\#^{f}$	0.78(3)	2.77(3)	3.531(2)	166(2)

^a [-1/2 + x, 1/2 - y, -1/2 + z].

^b [1/2 + x, 1/2 - y, 1/2 + z].

^c [x, 1 - y, -1/2 + z].

^d [x, 1 - y, 1/2 + z].

e [x, 1/2 - y, -1/2 + z].

^f [x, 1/2 - y, 1/2 + z].

4 and Fig. 4). Complexes **2a–2d** give a strong blue emission band at 413–419 nm when irradiated at wavelength 249 nm (Table 4 and Fig. 4). In order to understand the nature of these emission bands, we analyzed the photoluminescence properties of free HL. For excitation wavelengths between 300 and 500 nm, there is no obvious emission observed for free HL under the same experimental conditions. Therefore, the fluorescent emissions in the compounds **1a–1m** are proposed to originate from the coordination of two L⁻ to the zinc atom and according to the literature [15], these emission bands can be assigned to the emission of ligandto-metal charge transfer (LMCT).



Scheme 3. Intermolecular hydrogen bonds patterns in a crystal of **1f** (A) and **1h** (R = tBu), **1l** $(R = c-C_6H_{11})$ (B). R' = OiPr.

 Table 4

 Photophysical data for complexes 1a-1m and 2a-2d^a

	Emission max (nm)		Emission max (nm)
1a	394	1j	398
1b	397	1k	399
1c	395	11	399
1d	398	1m	398
1e	398	2a	415
1f	397	2b	418
1g	398	2c	413
1h	399	2d	419
1i	398		

^a Excitation at 249 nm.



Fig. 4. Fluorescent emission spectra of complexes 1a (curve 1; spectra of complexes 1b-1m are similar) and 2a (curve 2; spectra of complexes 2b-2d are similar).

In the solid state, the emission bands increase in intensity and with a notable shift in energy. As it has been told above, there are no emission bands of HL found at 300–500 nm and it is known that the free 2,2'-bipyridine molecule displays a very weak luminescence at 530 nm in the solid state at room temperature [15b]. Thus, compared with **1a**, **1b**, the emission peaks of **2a–2d** exhibit a clear bathochromic shift, which may be due to σ -donations from both the L⁻ and 2,2'-bipyridine or 1,10-phenanthroline ligands to the Zn(II) ion.

Easily synthesized *N*-thioacylamidophosphates HL do not have absorption in the visible region and their Zn(II) chelates are colourless. Therefore they could be excited with UV light that has been shown by us during the experiment. The presence of the bpy or phen ligands in the coordination sphere of the Zn(II) cation allows increasing the emission that might be easily used in non-linear optical devices.

4. Conclusion

N-Phosphorylated thioamides and thioureas HL form with the Zn(II) cation only [ZnL₂] chelates with a tetrahedral ZnO₂S₂ core. 1,5-*O*,*S*-Coordination of the deprotonated form of the ligand, generating a maximal bite angle for L⁻, appears as much as possible favorable on the steric reasons.

The ZnO_2S_2 core in these complexes shows a coordination unsaturation. The $[ZnL_2]$ complexes tends to increase the coordination number of the central atom with neutral donor ligands like 2,2'-bipyridine or 1,10-phenanthroline. The adducts of common formula $[Zn(bpy)L_2]$ and $[Zn(phen)L_2]$ have been obtained and characterized. The preservation of the 1,5-0,S-coordination mode of L^- in the adducts have been established on the basis of the IR and NMR data comparison.

Luminescent zinc *N*-thioacylamidophosphates can be used as new light-converting molecular devices since they (i) are air/moisture stable, (ii) show luminescent properties in the solid state, and at the same time (iii) ligands can be easily prepared from widely used amines and isothiocyanates [4,11].

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Appendix A. Supplementary data

CCDC 646784–646786 contain the supplementary crystallographic data for **1f**, **1h** and **1l**, 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.03.005.

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