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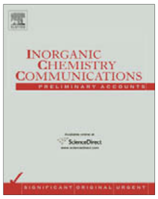

C–Cl bond cleavage of CH_2Cl_2 by the zinc(II) complex **[Zn(phen)L_2]** (L = PhC(S)NP(O)(O*i*Pr)$_2^-$) with the formation of **[Zn(phen)LCl]** and $CH_2[PhC(S)NP(O)(OiPr)_2]_2$

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ABSTRACT

The reaction of **[Zn(phen)L_2]** (L = PhC(S)NP(O)(O*i*Pr)$_2^-$) with CH_2Cl_2 leads to the formation of complex **[Zn(phen)LCl]** and *S,S*′-bis(benzimidothio-*N*-diisopropoxyphosphoryl)methane **L–CH_2–L** in high yields. Using $CHCl_3$ or CCl_4 instead of CH_2Cl_2 does not lead to the formation of chlorine substituted products even under reflux conditions. Compounds obtained were investigated by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, and microanalysis. The crystal structure of **[Zn(phen)LCl]** was elucidated by X-ray diffraction. The Zn(II) atom in the complex is in a distorted tetragonal-pyramidal ClN_2OS environment. The structure is stabilized by the intermolecular hydrogen bonds of the type C–H···Cl–Zn and π···π stacking interactions between the phenanthroline rings.

Coordination compounds of Zn(II) with amidothiophosphate ligands RC(X)NHP(Y)R'_2, which simultaneously contain donor atoms of sulfur and oxygen (X ≠ Y), remain poorly explored in comparison with dithioanalogues. Recently, we have reported on complexes of Zn(II) with RC(S)NHP(O)(O*i*Pr)$_2$ ligands (*R* = Ph, *p*-BrPh, NH_2, *i*PrNH, *t*BuNH, *c*-C_6H_{11}NH, Et_2N, *c*-C_5H_{10}N, *c*-OC_4H_8N, PhNH, *p*-MeOPhNH, *p*-BrPhNH) [1], and interaction of some of these complexes with 2,2′-bipyridine (**bipy**) and 1,10-phenanthroline (**phen**) [2]. The appearance of the hard donor carbonyl or phosphoryl oxygen atoms in the coordination sphere of the central ion makes it coordinatively unsaturated, which, in turn, can lead to the formation of heteroligand or polynuclear complexes with the central atom having the coordination number 5 or 6.

On the other hand a promising strategy for inorganic crystal engineering through combining noncovalent bonds such as van der Waals, π···π stacking and hydrogen bonds with coordination chemistry has attracted increasing attention in recent years [3–5].

In this work, we report on the synthesis of **[Zn(phen)LCl]** and **L–CH_2–L** (L = PhC(S)NP(O)(O*i*Pr)$_2^-$) using the reaction of the starting complex **[Zn(phen)L_2]** with CH_2Cl_2.

N-Phosphorylated thiobenzamide **HL**, and complexes **[ZnL_2]**, **[Zn(bipy)L_2]** and **[Zn(phen)L_2]** were prepared according to previously described methods [2,6,7]. Complex **[Zn(phen)LCl]** and *S,S*′-bis(benzimidothio-*N*-diisopropoxyphosphoryl)methane **L–CH_2–L** were prepared by the following procedure: a suspension of **[Zn(phen)L_2]** in CH_2Cl_2 (10 mL) was stirred for 3 h, and after few days colourless crystals of the complex were isolated (Scheme 1). The solvent from the mother solution was removed in vacuo and a precipitate of **L–CH_2–L** was obtained [8]. Recrystallization of **[Zn(bipy)L_2]** from dichloromethane or acetone solutions, and **[Zn(phen)L_2]** from acetone solution lead to fine crystalline precipitates of the starting complexes. Unfortunately, we were not able to get X-ray suitable crystals of **[Zn(bipy)L_2]** and **[Zn(phen)L_2]**.

It should be noted that **L–CH_2–L** was previously synthesized by the reaction of the potassium salt **KL** with CH_2I_2 in boiling acetonitrile solution [9]. The yield of **L–CH_2–L** was 69%. Reaction of **[Zn(phen)L_2]** with CH_2Cl_2 leads to the yields of 98% and 96% for **[Zn(phen)LCl]** and **L–CH_2–L**, respectively. Using $CHCl_3$ or CCl_4 instead of CH_2Cl_2 does not lead to the formation of chlorine substituted products even under reflux conditions.

In the $^{31}P\{^1H\}$ spectrum of **[Zn(phen)LCl]** a singlet signal, with a chemical shift characteristic for the amidophosphate environment of the phosphorus nucleus [10], was observed at 6.6 ppm. This signal is low-field shifted in comparison to the corresponding resonance of the parent complex **[Zn(phen)L_2]** (δ = 6.1 ppm [2]). There is a singlet at −3.2 ppm in the $^{31}P\{^1H\}$ NMR spectrum of **L–CH_2–L** (δ = −3 ppm in $CCl_4 + CD_3C_6D_5$ [9]).

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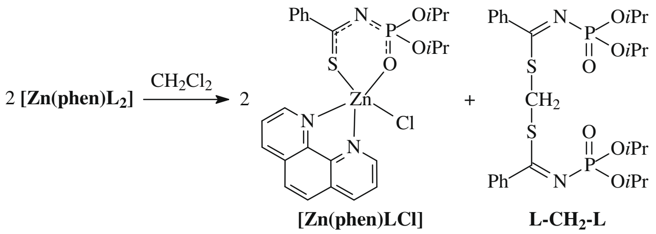

Scheme 1. Preparation of **[Zn(phen)LCl]** and **L–CH$_2$–L**.

Table 1
Crystal data, data collection and refinement details for **[Zn(phen)LCl]**.

Empirical formula	$C_{25}H_{27}ClN_3O_3PSZn$
Formula weight	581.38
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	7.8780(16)
b (Å)	10.525(2)
c (Å)	17.167(3)
α (°)	99.61(3)
β (°)	93.51(3)
γ (°)	108.20(3)
V (Å^3)	1323.4(5)
Z	2
D_{calc} (Mg m^{-3})	1.459
T (K)	293(2)
μ (mm^{-1})	1.200
F(0 0 0)	600
$\theta_{min-max}$ (°)	2.2–28.0
Reflections collected	11,923
Unique reflections	6208
Observed reflections [$I > 2.0\sigma(I)$]	4261 (R_{int} = 0.039)
R indices (all data)	R_1 = 0.0395, wR_2 = 0.0984

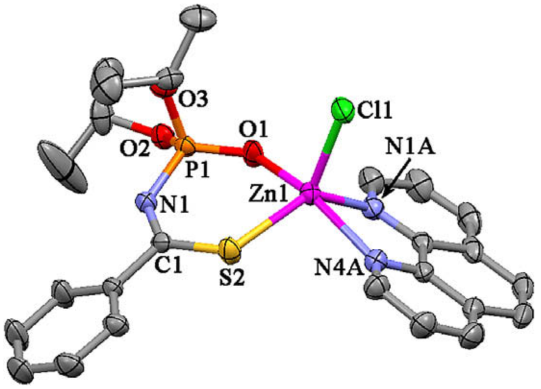

Fig. 1. Molecular structure of the complex **[Zn(phen)LCl]**. Hydrogen atoms were omitted for clarity.

The ^{1}H NMR spectrum of **[Zn(phen)LCl]** contains a set of signals for the (iPrO)$_2$P(O) and Ph protons. There are also signals corresponding to the polyaromatic chelate ligand. Analysis of the integral intensities of the proton signals testifies the suggested complex structure of **[Zn(phen)LCl]**, which was also proved by the elemental analysis. In the ^{1}H NMR spectrum of **L–CH$_2$–L** besides a set of signals for the (iPrO)$_2$P(O) and Ph protons there is a singlet for the CH$_2$ protons at 4.49 ppm.

According to the X-ray data the complex **[Zn(phen)LCl]** crystallizes in the triclinic space group $P\bar{1}$ (Table 1) [11]. It contains a distorted tetragonal-pyramidal ZnClN$_2$OS core (Fig. 1). The selected bond lengths and angles are given in Table 2.

Table 2
Selected bond lengths (Å) and bond angles (°) for **[Zn(1,10-phen)LCl]**.

Bond lengths			
Zn(1)–Cl(1)	2.2579(10)	P(1)–O(1)	1.4805(19)
Zn(1)–S(2)	2.3869(9)	P(1)–O(2)	1.5577(18)
Zn(1)–O(1)	2.0734(18)	P(1)–O(3)	1.5582(18)
Zn(1)–N(1A)	2.121(2)	P(1)–N(1)	1.629(2)
Zn(1)–N(4A)	2.229(2)	N(1)–C(1)	1.291(3)
S(2)–C(1)	1.723(2)		
Bond angles			
Cl(1)–Zn(1)–S(2)	117.13(4)	Zn(1)–S(2)–C(1)	112.21(8)
Cl(1)–Zn(1)–O(1)	100.72(7)	O(1)–P(1)–O(2)	107.40(10)
Cl(1)–Zn(1)–N(1A)	107.00(7)	O(1)–P(1)–O(3)	114.26(12)
Cl(1)–Zn(1)–N(4A)	98.58(7)	O(1)–P(1)–N(1)	117.34(12)
S(2)–Zn(1)–O(1)	93.28(6)	O(2)–P(1)–O(3)	102.49(10)
S(2)–Zn(1)–N(1A)	134.90(7)	O(2)–P(1)–N(1)	106.92(11)
S(2)–Zn(1)–N(4A)	88.07(6)	O(3)–P(1)–N(1)	107.18(11)
O(1)–Zn(1)–N(1A)	87.11(8)	Zn(1)–O(1)–P(1)	128.60(11)
O(1)–Zn(1)–N(4A)	157.53(10)	P(1)–N(1)–C(1)	129.53(18)
N(1A)–Zn(1)–N(4A)	76.27(9)	S(2)–C(1)–N(1)	129.37(18)
Torsion angles			
C(1)–S(2)–Zn(1)–Cl(1)	108.20(10)	Zn(1)–O(1)–P(1)–O(2)	−159.33(15)
C(1)–S(2)–Zn(1)–O(1)	4.39(12)	Zn(1)–O(1)–P(1)–O(3)	87.73(18)
C(1)–S(2)–Zn(1)–N(1A)	−84.79(13)	Zn(1)–O(1)–P(1)–N(1)	−39.0(2)
C(1)–S(2)–Zn(1)–N(4A)	−153.15(12)	C(1)–N(1)–P(1)–O(1)	28.3(3)
P(1)–O(1)–Zn(1)–Cl(1)	−96.97(17)	C(1)–N(1)–P(1)–O(2)	148.9(2)
P(1)–O(1)–Zn(1)–S(2)	21.44(18)	C(1)–N(1)–P(1)–O(3)	−101.8(3)
P(1)–O(1)–Zn(1)–N(1A)	156.27(19)	N(1)–C(1)–S(2)–Zn(1)	−14.8(3)
P(1)–O(1)–Zn(1)–N(4A)	114.3(2)	S(2)–C(1)–N(1)–P(1)	0.4(4)

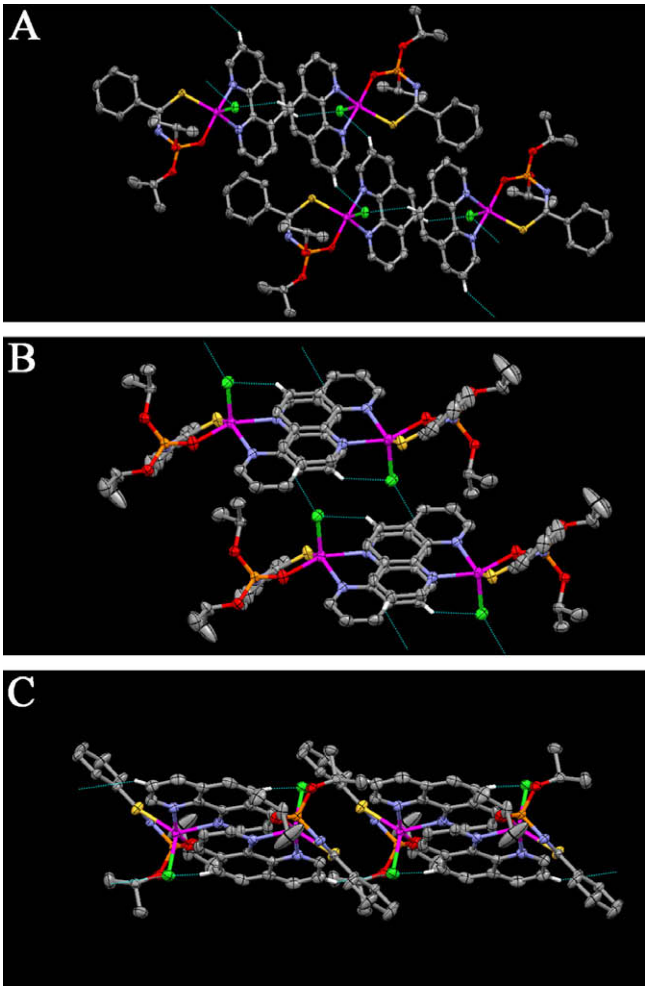

Fig. 2. Packing and hydrogen bonding in the crystal of **[Zn(phen)LCl]** along the *a* axis (**A**), *b* axis (**B**) and *c* axis (**C**). H-atoms, not involved in hydrogen bonding, are omitted for clarity.

Table 3
Hydrogen bond lengths (Å) and angles (°) for **[Zn(1,10-phen)LCl]**[a].

D–H···A	D–H	H···A	D···A	D–H···A
C(6A)–H(6A)···Cl(1)$^{\#1}$	0.93	2.64	3.041(2)	107
C(10A)–H(10A)···Cl(1)$^{\#2}$	0.93	2.74	3.561(4)	147

[a] Symmetry codes: #1 $2-x, 1-y, 2-z$; #2 $1-x, -y, 2-z$.

Table 4
Selected π···π interactions for **[Zn(1,10-phen)LCl]**[a].

Cg(*I*)[b]	Cg(*J*)	Cg–Cg[c] (Å)	Dihedral angles (°)	*β*[d] (°)
Cg(3)	Cg(3)$^{\#1}$	5.289(2)	0	49.09
Cg(3)	Cg(6)$^{\#1}$	3.8687(19)	0.79(15)	26.15
Cg(6)	Cg(6)$^{\#1}$	3.679(2)	0	18.71

[a] Symmetry codes: #1 $1-x, -y, 2-z$.

[b] Cg(3): N(4A)–C(3A)–C(8A)–C(7A)–C(6A)–C(5A), Cg(6): N(1A)–C(2A)–C(3A)–C(8A)–C(9A)–C(10A)–C(11A)–C(12A)–C(13A)–C(14A), where Cg refers to the ring center of gravity and the numbers represent the rings involved in the interactions.

[c] Cg–Cg: distance between ring centroids.

[D] *β*: angle Cg(*I*) → Cg(J) vector and normal to plane I.

Bond lengths (S)C–N ($\Delta d \approx -0.07$ Å) and P–N ($\Delta d \approx -0.04$ Å) are shortened (Table 2) and the C═S ($\Delta d \approx 0.08$ Å) and P═O ($\Delta d \approx 0.02$ Å) distances are considerably lengthened in comparison with the corresponding interatomic distances reported for **HL** [10]. The vice versa situation is observed for the same interatomic distances in comparison with the complex **[ZnL$_2$]** [7]. The bond lengths distribution in the ligand **L** confirms the superiority of *S*-enolic tautomeric form S–C═N–P═O.

The six-membered Zn–O–P–N–C–S cycle has the asymmetrical boat conformation. The maximal deviation of atoms from the least square plane (LSP) of the cycle is observed for the oxygen (−0.178(2) Å) and phosphorus (0.2051(9) Å) atoms. The five-membered Zn–N–C–C–N cycle is almost planar. The maximal deviation of atoms from LSP of the cycle is observed for the zinc (0.0628(10) Å) and the nitrogen (−0.057(2) and −0.045(2) Å) atoms.

There are intermolecular hydrogen bonds of the type C–H···Cl–Zn in the crystal of **[Zn(phen)LCl]** (Fig. 2 and Table 3). These bonds are formed between the two H-atoms of the phenanthroline ligand of a molecule, and the chlorine atoms of two neighboring molecules, while the Cl-atom forms two intermolecular hydrogen bonds with protons of the polyaromatic ligands, corresponding to the same two neighboring molecules. Additionally to the intermolecular H-bonds π···π stacking interactions between the phenanthroline rings (Table 4) produce centrosymmetric dimers in the crystal structure of **[Zn(phen)LCl]** (Fig. 2).

In summary, the novel Zn(II) complex **[Zn(phen)LCl]** was successfully synthesized from the precursor **[Zn(phen)L$_2$]** and CH_2Cl_2. It was established that both chlorine atoms are substituted by **L** with formation of **[Zn(phen)LCl]** and **L–CH$_2$–L**. Using $CHCl_3$ or CCl_4 instead of CH_2Cl_2 does not lead to the formation of chlorine substituted products even under reflux conditions. Also, the similar complex **[Zn(bipy)L$_2$]** did not show this type of reaction under the same conditions.

To date we can only speculate on the quite selective character of this reaction and why the very similar **bipy**-containing complex does not show the same reaction. The latter might be explained by the rigidity of the **phen** ligand compared to **bipy** and will be further explored in the future by applying other α-diimine ligands. Future work will be devoted to the application of the C–Cl bond cleavage reaction to other substrates and the elucidation of the reaction mechanism.

Acknowledgments

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Appendix A. Supplementary material

CCDC 730812 contains the supplementary crystallographic data for **[Zn(phen)LCl]**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.07.019.

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[8] *Physical measurements:* NMR spectra were obtained on a Bruker Avance 300 MHz spectrometer at 25 °C. ^1H and ^{31}P NMR spectra ($CDCl_3$) were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to $SiMe_4$ (^1H) and 85% H_3PO_4 ($^{31}P\{^1H\}$). Elemental analyses were performed on a CHNS HEKAtech EuroEA 3000 analyzer. *Synthesis of* ***[Zn(phen)L$_2$]*** *and* ***L–CH$_2$–L***: A suspension of **[Zn(phen)L$_2$]** (0.1 g, 0.12 mmol) in CH_2Cl_2 (10 mL) was stirred for 3 h. After 2 days colourless crystals of **[Zn(phen)LCl]** appeared. The mixture was left for 2 days more. Then the solution was decantated. Crystals of complex were isolated, washed by *n*-hexane and dried in vacuo. **[Zn(phen)LCl]**. Yield: 0.067 g (98%). M.p. 163–165 °C. ^1H NMR: $\delta = 1.18$ (d, $^3J_{H,H} = 6.1$ Hz, 12H, CH_3), 4.66 (d sept, $^3J_{POCH} = 7.7$ Hz, $^3J_{H,H} = 6.2$ Hz, 2H, OCH), 7.32–7.50, 7.87–8.04, 8.23–8.37, 8.46–8.60, 9.45–9.57 (m, 13H, Ph + phen) ppm. $^{31}P\{^1H\}$ NMR: $\delta = 6.6$ ppm. *Anal.* Calcd. for $C_{25}H_{27}ClN_3O_3PSZn$ (581.37): C, 51.65; H, 4.68; N, 7.23. Found: C, 51.84; H, 4.49; N, 7.38%. The solvent from the mother solution was removed in vacuo and the resulting precipitate of **L–CH$_2$–L** was washed by *n*-hexane. **L–CH$_2$–L**. Yield: 0.070 g (96%). M.p. 126–127 °C (126 °C [4]). ^1H NMR: $\delta = 1.12$ (d, $^3J_{H,H} = 6.3$ Hz, 24H, CH_3), 4.74 (m, 4H, OCH), 4.49 (s, 2H, CH_2), 7.06–7.18, 7.25–7.49, 7.61–8.04 (m, 10H, Ph) ppm. $^{31}P\{^1H\}$ NMR: $\delta = -3.2$ ppm (−3 ppm in $CCl_4 + CD_3C_6D_5$ [4]). *Anal.* Calcd. for $C_{27}H_{40}N_2O_6P_2S_2$ (614.69): C, 52.76; H, 6.56; N, 4.56. Found: C, 52.89; H, 6.47; N, 4.45%.

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[11] The X-ray data for **[Zn(phen)LCl]** were collected on a Bruker Smart Apex II diffractometer. Data were corrected for absorption using SADABS [12] program. The structure was solved by direct method using the SHELXS97 [13] program and refined by the full matrix least-squares using SHELXL97 [13]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located on difference map and refined isotropically.

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