Synthesis of Metal Complexes with 2-[Bis(2-phenylethyl)thiophophorylhydroxymethyl]-1-organilimidazoles. Crystal Structure of ZnCl₂ · 2L

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Abstract—The reactions of Zn(II), Cd(II), Cu(II), Co(II), Pd(II) dichlorides with 2-[bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1-organilimidazoles (L¹–L⁴) were studied. The novel complexes were synthesized and characterized by IR and NMR spectroscopies. Depending on the nature of imidazolephosphinesulfide, both monodentate (at the "pyridine" N(1) atom of heterocycle) and the N,S-bidentate binding of the ligand by a metal can be realized in the above metal complexes. The structure of the complex $ZnCl_2 \cdot 2L^4$ (I) (L⁴ = 2-[bis(2phenylethyl)thiophosphorylhydroxymethyl]-1-ethylbenzimidazole) was studied by X-ray diffraction. One of the two independent L⁴ molecules performs the solvate function, while another one, together with two Cl atoms, is coordinated through the atoms N(1) and S to the Zn atom at the vertices of a slightly distorted tetrahedron. The molecule of the complex is united with the solvate molecule into [ZnCl₂L₄]L⁴ associates by strong intermolecular hydrogen bonds to give nonplanar four-membered H-cycle OH₂N.

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Polydentate ligand systems with N,P,S,O-donor centers are the least studied objects in coordination chemistry. The use of the above bases in the metal complex synthesis is restricted, first of all, by the absence of suitable methods of their preparation. Recently, we developed technologically effective and atom-saving method of synthesizing functionalized azoles, i.e., 2-[bis(2-[phenylethyl)thiophosphorylhydroxymethyl]-1-organilimidazoles, based on nucleophilic addition of available secondary phosphine sulfides to 1-organil-2formylimidazoles [1]. The derivatives of imidazoles with thiophosphoryl and hydroxyl substituents, containing donor centers of different nature, play an important role in developing the concepts of coordination bond, geometry, and structure of complexes, as well as in solving the question of regioselective binding of metal to complexes with polyfunctional ligands. Such imidazolephosphine sulfides with pharmaceutical properties are promising compounds not only in design of biologically active metal complexes [2, 3], but also in the synthesis of the metal complex catalysts of a new generation [4], which are also used in the interface transfer reactions [5].

The complexes based on the tertiary alkyl- and arylphosphine sulfides have been reported in [6-12]; however, the data on the complexes with the tertiary

heterylphosphine sulfides are almost unavailable. Only two complexes of palladium [13] and indium [14] with 4,5-bis(diphenylthiophosphoryl)-1,2,3-triazole are known.

Lately, we have shown that, depending on the acceptor nature, 2-(diorganilphospphorylhydroxymethyl]-1organilimidazoles can compete in reactions with some metal chlorides and give molecular or chelate complexes, where the donor-acceptor bond with a metal involves the heterocyclic N atom and the O atom of the P=O group of imidazolephosphine oxide [15]. In this work, in continuation of the study of the complexation reactions of polydentate imidazolephosphine chalcogenides, we investigated for the first time the reactions of Zn, Cd, Cu, Co, and Pd dichlorides with 2-[bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1-vinylimidazole (L^1) , 2-[bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1-ethylimidazole (L^2), 2-[bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1-vinylbenzimidazole (L^3) , 2-[bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1ethylbenzimidazole (L^4) with the aim to estimate the effect of the nature of the chalcogen donor atom and of the acceptor on the type of coordination of imidazolephosphine sulfides L¹–L⁴ to a metal and determine the properties and structures of the complexes formed:



EXPERIMENTAL

Synthesis of complexes of ZnCl₂ and CdCl₂ with ligands L¹–L⁴. The calculated amounts of the ligand and salt were mixed in acetone at 20–25°C and in 8 h, compounds of the white color were precipitated using the following solvents: ether (Zn complex with L¹ and Cd complexes with L¹–L⁴), hexane (Zn complexes with L²–L⁴). The precipitates were filtered, washed with the corresponding mixture acetone–ether (1 : 1) or acetone–hexane (1 : 1), and dried in vacuum.

Synthesis of PdCl₂ complexes with ligands L^1-L^4 . The calculated amounts of the ligand and salt were mixed in a boiling acetone for 8 h. The complex compounds of the bright brown color were precipitated from the reaction mixture with dry ether, filtered, washed with ether, and dried in vacuum.

Synthesis of CuCl₂ complexes with ligands L¹, L⁴ and CoCl₂ complexes with L¹. The calculated amounts of the ligand and salt were mixed in acetone for 24 h at 20–25°C (Cu and Co complexes with L¹) and in ethanol (Cu complex with L⁴). The complexes of mustard (Cu complexes) and blue (Co complexes) color precipitated with ether from the reaction mixture were filtered, washed with ether, and dried in vacuum.

The results of the elemental analysis and some physicochemical properties of the title metal complexes are given in Table 1.

A single crystal of the complex bis{2-(2-phenylethyl)thiophosphorylhydroxymethyl]-1-ethylbenzimidazole}dichlorozinc, $[ZnCl_2 \cdot 2L_2^4]$ (I) suitable for X-ray diffraction analysis was obtained by recrystallization of $[ZnCl_2 \cdot L^4]$ from ethanol.

The IR spectra of the synthesized complexes were recorded on a IFS 25 Bruker spectrometer using KBr pellets and Nujol.

The ¹H NMR spectra of solutions of complexes in $CDCl_3$ and $DMSO-d_6$ were measured on a DPX-400 Bruker spectrometer at room temperature with HMDS as internal standard.

The quantum-chemical calculations of molecules and their vibration spectra were performed by MP2/6-31G**//HF/6-31G* method using GAUSSIAN-98 program package [16].

X-ray diffraction analysis. Crystals of complex I, $C_{52}H_{58}Cl_2N_4O_2P_2S_2Zn$ (in the form of colorless needles) belong to monoclinic crystal system. The unit cell parameters: $\underline{a} = 17.726$ (4), b = 18.126 (2), c = 16.458 (3) Å, $\beta = 96.41(6)^\circ$, V = 5254.7(2) Å³, ρ (calcd.) = 1.306 g/cm³, $\mu_{Mo} = 32.3$ cm⁻¹, F(000) = 2160, M = 1033.35, Z = 4, space group $P2_1/c$.

The experimental data set was obtained from a single crystal at room temperature on automated four-circle CAD-4 Enraf-Nonius diffractometer (graphite monochromator, CuK_{α} radiation, ω scan mode, $2\theta_{max} = 120^{\circ}$). The total of 7386 reflections was registered ($R_{int} = 0.035$, $0 \le h \le 19$, $-24 \le k \le 0$, $-12 \le l \le 18$).

The structure was solved by the direct method (SHELXL-97)[17] and refined by the least-squares method in full-matrix anisotropic approximation (on F^2) for non-hydrogen atoms (SHELXL-97) [18]. The hydroxyl hydrogen atoms were localized from the Fourier difference synthesis and refined isotropically. The positions of the hydrogen atoms at the C atoms were calculated geometrically (C-H 0.96 Å) and included in refinement with fixed geometrical and thermal parameters $U_{\rm H}$, which are 0.1–0.3 Å² larger than the U_i parameters of the corresponding C atoms. The final refinement parameters: $R_1 = 0.043$, $wR_2 = 0.077$ for 1541 reflections with $F_0 \ge 4\sigma(F_0)$; $R_1 = 0.385$, $wR_2 = 0.143$ for all reflections; GOOF = 0.918. The maximum and minimum residual densities are 0.118 and 0.017 e Å³, the extinction coefficient is equal to 0.0000(5).

The coordinates and thermal parameters of the atoms in complex I are listed in Table 2, the main bond lengths and bond angles are given in Table 3.

RESULTS AND DISCUSSION

In this work, the reaction of investigated imidazolephosphine sulfides L^1-L^4 with metal dichlorides was performed in anhydrous solvents (acetone, ethanol) at a ratio of the starting components 1: 1, 4L: 1, and 2L: 1. As a result, the complexes of the composition 1 : 1 were obtained, except for the compounds $ZnCl_2 \cdot 2L^2$ and $CuCl_2 \cdot 2L^4$. Complexes based on imidazolephosphine sulfides L^1 , L^2 were formed in 43–98% yield (Table 1). The complexes of Cd with imidazolephosphine sulfides L^1-L^4 were obtained with the maximum yield (~98%), the yield of the complexes of Zn with L^1-L^4 and Co with L^1 was 85–95%, whereas the complexes with the analogous composition 1 : 1 with imidazolephosphine oxides were formed in a lower yield (48–73%) [15]. The $CuCl_2 \cdot L^1$ and $CuCl_2 \cdot 2L^4$ complexes were obtained with the yield 49 and 54%, respectively. The elevation of the reaction temperature to 70-80°C was found to cause the decomposition of imidazolephos-

Table 1. Cor	nplexes based on imidazo	lephosphine sul	fides L ¹ –L ⁴						
Jonnon	Emnirical formula			Content (found	/calculated), %			U° F	Viald 06
Compound		С	Н	Z	CI	S	Р	⁴ mp , C	1 ICIU, /0
[ZnL ¹ Cl ₂]	$C_{22}H_{25}Cl_2N_2OPSZn$	49.52/49.59	4.79/4.70	5.28/5.26	13.25/13.34	6.19/6.01	5.62/5.82	178-180	89
[ZnL ² Cl ₂]	$C_{22}H_{27}Cl_2N_2OPSZn$	48.91/49.40	5.37/5.05	5.31/5.24	13.06/13.29	6.17/5.99	5.76/5.80	142–146	87
$[\operatorname{ZnL}_2^2 \operatorname{LCl}_2]$	$C_{44}H_{54}Cl_2N_4O_2P_2S_2Zn$	56.59/56.63	5.58/5.79	5.81/6.01	7.42/7.61	6.55/6.86	6.57/6.65	62–64	LL
[ZnL ³ Cl ₂]	$C_{26}H_{27}Cl_2N_2OPSZn$	53.27/53.57	4.37/4.64	4.73/4.81	11.94/12.19	5.69/5.49	5.05/5.32	160–164	85
[ZnL ⁴ Cl ₂]	$C_{26}H_{29}Cl_2N_2OPSZn$	53.21/53.39	5.02/4.96	4.98/4.79	12.24/12.15	5.55/5.48	5.23/5.30	169–171	95
$[CdL^{1}Cl_{2}]$	C ₂₂ H ₂₅ CdCl ₂ N ₂ OPS	45.32/45.56	4.44/4.31	5.01/4.83	12.18/12.25	5.71/5.52	5.18/5.35	108-110	98
[CdL ² Cl ₂]	$C_{22}H_{27}CdCl_2N_2OPS$	45.38/45.40	4.78/4.64	4.99/4.81	12.44/12.21	5.36/5.50	5.11/5.33	99–101	66
$[CdL^3Cl_2]$	$C_{26}H_{27}CdCl_2N_2OPS$	49.39/49.57	4.07/4.29	4.45/4.45	11.14/11.28	4.85/5.08	4.71/4.93	155–157	43
[CdL ⁴ Cl ₂]	C ₂₆ H ₂₉ CdCl ₂ N ₂ OPS	49.24/49.41	4.38/4.59	4.51/4.43	11.54/11.24	4.98/5.07	4.76/4.91	152–154	60
[CuL ¹ Cl ₂]	C ₂₂ H ₂₅ Cl ₂ CuN ₂ OPS	49.60/49.76	4.92/4.71	5.47/5.28	13.26/13.38	6.32/6.03	5.94/5.84	115 decomp.	49
$[CuL_2^4Cl_2]$	$C_{52}H_{58}Cl_2CuN_4O_2P_2S_2$	60.32/60.55	5.53/5.63	5.69/5.43	6.54/6.89	5.97/6.21	6.22/6.02	143–146	54
$[CoL^1Cl_2]$	C ₂₂ H ₂₅ Cl ₂ CoN ₂ OPS	50.04/50.19	4.93/4.75	5.24/5.32	13.17/13.50	6.27/6.08	5.71/5.89	169–172	86
[PdL ¹ Cl ₂]	$C_{22}H_{25}Cl_2N_2OPSPd$	46.16/46.04	4.21/4.36	4.81/4.88	12.45/12.38	5.31/5.58	5.27/5.41	66-76	58
[PdL ² Cl ₂]	$C_{22}H_{27}Cl_2N_2OPSPd$	45.62/45.88	4.66/4.69	5.05/4.87	12.06/12.34	5.38/5.56	5.26/5.39	88 decomp.	67
[PdL ³ Cl ₂]	$C_{26}H_{27}Cl_2N_2OPSPd$	49.95/50.05	4.14/4.33	4.34/4.49	11.14/11.39	5.01/5.13	5.13/4.97	124–129	73
[PdL ⁴ Cl ₂]	$C_{26}H_{29}Cl_2N_2OPSPd$	49.51/49.89	4.73/4.64	4.31/4.48	11.16/11.35	4.96/5.12	5.02/4.96	115-118	54

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SYNTHESIS OF METAL COMPLEXES

Atom	x	У	Z	$U_{\rm eq}$, Å ²	Atom	x	У	Z	$U_{\rm eq}$, Å ²
Zn(1)	0.7813(1)	0.1596(1)	0.9700(1)	0.0544(5)	C(26)	0.9875(6)	0.2519(6)	1.3048(6)	0.075(4)
Cl(1)	0.7961(2)	0.2362(2)	0.8674(2)	0.085(1)	P(1B)	0.7585(2)	-0.4385(2)	1.1761(2)	0.061(1)
Cl 2)	0.7933(2)	0.0405(2)	0.9335(2)	0.081(1)	S(1B)	0.8081(2)	-0.3527(2)	1.1365(2)	0.073(1)
P(1)	0.7147(2)	0.1938(2)	1.1418(2)	0.0452(9)	O(1B)	0.7915(4)	-0.5700(4)	1.2477(4)	0.078(3)
S (1)	0.6679(2)	0.1758(2)	1.0286(2)	0.63(1)	H(1B)	0.786	-0.597	1.214	0.17(3)
O(1)	0.7671(3)	0.3148(3)	1.0902(4)	0.054(2)	N(1B)	0.8687(5)	-0.5773(5)	1.1061(6)	0.048(3)
H(1)	0.795(3)	0.368(4)	1.085(3)	0.02(2)	N(2B)	0.9576(6)	-0.5055(5)	1.1707(5)	0.042(3)
N(1)	0.8678(5)	0.1807(5)	1.0573(5)	0.045(3)	C(1B)	0.8837(7)	-0.5294(6)	1.1640(7)	0.044(3)
N(2)	0.9352(6)	0.2395(5)	1.1602(5)	0.041(3)	C(2B)	0.9937(8)	-0.5435(6)	1.1112(6)	0.039(3)
C(1)	0.8655(7)	0.2245(6)	1.1206(8)	0.039(3)	C(3B)	0.9510(7)	-0.6314(6)	1.0090(7)	0.052(4)
C(2)	0.9870(7)	0.2019(6)	1.1179(8)	0.042(3)	C(4B)	1.0244(8)	-0.6338(6)	0.9900(7)	0.060(4)
C(3)	1.0653(7)	0.1966(6)	1.1299(7)	0.062(4)	C(5B)	1.0811(7)	-0.5897(7)	1.0282(7)	0.060(4)
C(4)	1.0978(7)	0.1532(7)	1.0738(8)	0.068(4)	C(6B)	1.0679(6)	-0.5421(6)	1.0899(7)	0.054(4)
C(5)	1.0548(8)	0.1168(7)	1.0107(7)	0.073(4)	C(7B)	0.9360(8)	-0.5867(6)	1.0718(7)	0.040(3)
C(6)	0.9785(7)	0.1225(6)	0.9998(6)	0.056(4)	C(8B)	0.8293(6)	-0.5062(6)	1.2238(7)	0.058(4)
C(7)	0.9439(7)	0.1657(6)	1.0555(7)	0.40(3)	C(9B)	0.6922(6)	-0.4869(6)	1.1044(7)	0.081(4)
C(8)	0.7938(5)	0.2591(5)	1.1455(6)	0.036(3)	C(10B)	0.7064(8)	-0.4856(7)	1.0175(9)	0.105(5)
C(9)	0.7516(5)	0.1117(5)	1.1926(5)	0.050(3)	C(11B)	0.6470(1)	-0.530(2)	0.9628(9)	0.099(6)
C(10)	0.6910(6)	0.0502(7)	1.1969(7)	0.093(4)	C(12B)	0.6450(1)	-0.603(1)	0.951(1)	0.113(7)
C(11)	0.7261(6)	-0.0239(7)	1.2060(1)	0.059(4)	C(13B)	0.5900(1)	-0.6380(9)	0.9000(1)	0.113(6)
C(12)	0.7401(8)	-0.061(1)	1.1390(1)	0.099(5)	C(14B)	0.5374(9)	-0.597(2)	0.8560(9)	0.106(7)
C(13)	0.7710(1)	-0.1310(1)	1.1400(1)	0.110(6)	C(15B)	0.5340(1)	-0.522(1)	0.864(1)	0.122(9)
C(14)	0.7905(9)	-0.1590(1)	1.2170(2)	0.113(7)	C(16B)	0.5890(1)	-0.4891(9)	0.917(1)	0.117(7)
C(15)	0.7810(1)	-0.1260(1)	1.2880(1)	0.124(7)	C(17B)	0.7077(7)	-0.4194(6)	1.2635(7)	0.103(6)
C(16)	0.7484(9)	-0.0570(1)	1.2820(1)	0.094(5)	C(18B)	0.6747(9)	-0.3550(8)	1.2714(9)	0.168(8)
C(17)	0.6464(5)	0.2334(5)	1.2042(5)	0.044(3)	C(19B)	0.6422(9)	-0.3329(9)	1.3500(9)	0.084(5)
C(18)	0.6141(6)	0.3082(6)	1.1756(6)	0.065(4)	C(20B)	0.6747(8)	-0.2796(8)	1.3990(1)	0.099(5)
C(19)	0.5644(8)	0.3396(6)	1.2353(8)	0.053(4)	C(21B)	0.6400(1)	-0.258(1)	1.4660(1)	0.126(7)
C(20)	0.4882(8)	0.3274(6)	1.2279(7)	0.076(4)	C(22B)	0.5770(1)	-0.294(1)	1.4850(1)	0.13(1)
C(21)	0.4435(8)	0.3587(8)	1.2840(1)	0.095(5)	C(23B)	0.5469(8)	-0.348(1)	1.4360(1)	0.108(6)
C(22)	0.4780(1)	0.3998(9)	1.3442(9)	0.090(6)	C(24B)	0.5780(1)	-0.3676(7)	1.3680(9)	0.103(5)
C(23)	0.5530(1)	0.4160(7)	1.3556(8)	0.086(5)	C(25B)	0.9980(6)	-0.4589(6)	1.2329(8)	0.064(4)
C(24)	0.5966(7)	0.3824(7)	1.2977(9)	0.070(4)	C(26B)	1.0358(7)	-0.4993(6)	1.3058(7)	0.102(5)
C(25)	0.9579(6)	0.2902(6)	1.2288(8)	0.067(4)					

Table 2. The atomic coordinates and thermal parameters U_{eq} in structure I

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Deni	Molecule L ^{4C} Molecule L ^{4S}		A	(i) dag		
Bond	<i>d</i> ,	Å	Angle	w, deg		
Zn(1)-Cl(1)	2.224(3)		C(9)P(1)C(17)	107.4(4)	105.5(5)	
Zn(1)-Cl(2)	2.258(3)		Zn(1) S(1)P(1)	97.1(1)		
Zn(1)-S(1)	2.343(3)		H(1)O(1)C(8)	124(3)	111(3)	
Zn(1)–N(1)	2.017(9)		Zn(1)N(1)C(1)	126.3(8)		
P(1)–S(1)	1.977(4)	1.935(4)	Zn(1)N(1)C(7)	127.9(7)		
P(1)–C(8)	1.84(1)	1.87(1)	C(1)N(1)C(7)	104.6(9)	105.5(9)	
P(1)–C(9)	1.798(9)	1.80(1)	C(1)N(2)C(2)	106.0(1)	107.1(9)	
P(1)–C(17)	1.813(9)	1.81(1)	C(1)N(2)C(25)	130.0(1)	129.0(1)	
P(1)–C(8)	1.41(1)	1.41(1)	C(2)N(2)C(25)	123.3(9)	123.2(9)	
N(1)–C(1)	1.31(2)	1.29(2)	N(1)C(1)N(2)	113.0(1)	113.0(1)	
N(1)–C(7)	1.38(2)	1.39(2)	N(1)C(1)C(8)	124.0(1)	125.0(1)	
N(2)–C(1)	1.36(2)	1.37(2)	N(2)C(1)C(8)	122.0(1)	122.0(1)	
N(2)–C(2)	1.39(2)	1.41(2)	N(2)C(2)C(3)	132.0(1)	133.0(1)	
N(2)-C(25)	1.48(2)	1.45(2)	N(2)C(2)C(7)	105.0(1)	103.0(1)	
C(1)–C(8)	1.51(2)	1.51(2)	C(3)C(2)C(7)	123.0(1)	124.0(1)	
C(2)–C(3)	1.38(2)	1.40(2)	C(2)C(3)C(4)	115.0(1)	116.0(1)	
C(2)–C(7)	1.38(2)	1.39(2)	C(3)C(4)C(5)	122.0(1)	124.0(1)	
C(6)–C(7)	1.40(2)	1.39(2)	C(4)C(5)C(6)	122.0(1)	122.0(1)	
C(9)–C(10)	1.56(2)	1.48(2)	C(5)C(6)C(7)	118.0(1)	115.0(1)	
C(10)–C(11)	1.48(3)	1.54(3)	N(1)C(7) C(2)	111.0(1)	111.0(1)	
C(17)–C(18)	1.52(1)	1.32(1)	N(1)C(7) C(6)	129.0(1)	129.0(1)	
C(18)–C(19)	1.50(2)	1.53(2)	C(2)C(7)C(6)	121.0(1)	120.0(1)	
C(25)–C(26)	1.48(2)	1.50(2)	P(1)C(8)O(1)	103.8(6)	109.7(7)	
Angle	ω,	deg	P(1)C(8)C(1)	113.0(7)	110.9(8)	
Cl(1)Zn(1)Cl(2)	111.8(1)		O(1)C(8)C(1)	110.7(8)	108.0(9)	
Cl(1)Zn(1) S(1)	114.4(1)		P(1)C(9)C(10)	113.2(7)	117.2(9)	
Cl(1)Zn(1)N(1)	106.1(3)		C(9)C(10)C(11)	112.0(1)	112.0(1)	
Cl(2)Zn(1)S(1)	109.9(1)		C(10)C(11)C(12)	119.0(1)	127.0(2)	
Cl(2)Zn(1)N(1)	106.5(3)		C(10)C(11)C(16)	124.0(1)	116.0(2)	
S(1)Zn(1)N(1)	107.6(3)		P(1)C(17)C(18)	115.2(7)	121.0(1)	
S(1)P(1)C(8)	112.0(3)	111.2(4)	C(17)C(18)C(19)	111.3(9)	122.0(1)	
S(1)P(1)C(9)	113.2(3)	117.4(4)	C(18)C(19)C(20)	122.0(1)	121.0(1)	
S(1)P(1)C(17)	111.6(3)	113.4(4)	C(18)C(19)C(24)	119.0(1)	118.0(1)	
C(8)P(1)C(9)	105.9(4)	108.4(5)	N(2)C(25)C(26)	113.4(9)	114.9(9)	
C(8)P(1)C(17)	106.3(4)	99.4(5)				

Table 3. The bond lengths and bond angles in structure I

phine sulfides $L^{1}-L^{4}$ to the starting fragments, i.e., imidazolecarbaldehydes and phosphine sulfides. The reaction products also contained complexes with the corresponding 1-ethyl(vinyl)imidazolecarbaldehydes. The analogous reaction of CuCl₂ with the ligands L^{2} , L^{3} occurs even without heating.

The types of coordination of polydentate imidazolephosphine oxides to the metal atoms were proposed by us on the basis of the spectral data (IR, ¹H NMR) and theoretical calculations of free and coordinated molecules L^1-L^4 and the model calculations—2-[bis(2-methyl)-thiophosphorylhydroxymethyl]-1-methylimidazole (L) and 1-vinyl-2-hydroxymethylimidazole (L⁵).

To determine the conformations of L^1-L^4 molecules, the model ligand L was calculated and the minima on the potential energy surface were found to correspond to three conformation isomers: with intramolecular hydrogen bonds (**IHB**) OH···N (**L**_a), OH···S=P (**L**_b), and with a free HO group (**L**_c):



As in the case with the oxygen analog of imidazolephosphine oxide [15], the most stable among conformers $L_{a,b,c}$, according to the calculation data, is the L_a conformer with a strong IHB O–H···N between the hydroxyl group and the "pyridine" N atom of imidazole ring. The conformer L_b with the IHB OH···S=P is energetically less favorable than the isomer L_a (by 4.00 kcal/mol). The minimum stability ($\Delta E =$ 8.74 kcal/mol) is shown by the L_c conformer with a free hydroxyl group.

The calculation of the normal vibrations of isomers L and their complexes with ZnCl₂ was performed with the aim to qualitatively estimate the change in the vibration frequencies of the functional groups, which can participate in the formation of the coordination or hydrogen bonds. It was shown that the stretching vibrations of free OH and P=S groups in the L ligand are characterized by the calculated frequencies 4076 and 625 cm⁻¹, respectively, while the stretching vibrations of the azole ring, by the frequencies 1740, 1680 cm^{-1} . For L conformers with IHB OH---N=C and OH---S=P, the frequency of the stretching vibration of the O–H bond is 60 and 75 cm⁻¹ lower than v(OH) of a free hydroxyl group, respectively. The value v(P=S) also decreases (by 18 cm⁻¹), while the stretching vibration of a heterocycle undergo shifts, both a long-wave shift by 8 cm⁻¹ (the high-frequency vibration 1740 cm⁻¹) and a short-wave shift by 10 cm⁻¹ (the low-frequency vibration 1680 cm⁻¹). The coordination with the participation of the S atom in zinc chloride complexes with all L isomers reduces the value v(P=S) by 18 cm⁻¹, while that with the participation of the N atom increases the frequency of the stretching vibration of the azole ring by ~10 cm⁻¹. When the Zn atom forms the chelate ring closed by the coordination bonds $S \longrightarrow Zn \longleftarrow N$ (the 1 : 1 complex), the value v(P=S) also decreases by 17 cm⁻¹ at insignificantly changing frequency ($\Delta v = 4 \text{ cm}^{-1}$) of the stretching vibrations of the heterocycle. The above change in the vibration frequencies agrees with the observed shifts of IR bands of the synthesized complexes as compared with free imidazolephosphine sulfides L¹–L⁴.

Thus, in IR spectra of Zn, Cd, Cu, and Co complexes with 1-vinyl- and 1-ethylimidazolephosphine sulfides (L^1, L^2) and Pd complexes with benzimidazole ligands L^3 , L^4 , a short-wave shift (by 15–20 cm⁻¹) of the absorption bands due to the stretching vibrations of imidazole ring was observed at 1480-1520 cm⁻¹ as compared to the ligands themselves, as in the case of hydrochloride molecules L^1-L^4 [1], which suggests the formation of the $N \longrightarrow M$ bond in the above compounds. However, the heterocycle vibration frequencies in the complexes of Zn, Cd with benzimidazolephosphine sulfides L^3 , L^4 and copper with L^4 remain unchanged (1478, 1483, 1496, 1520 cm⁻¹). At the same time, in the spectra of the above complexes, the maximum of a doublet band (550-568 cm⁻¹) due to the stretching vibrations of the P=S group is lowered by 6–17 cm⁻¹, while in the spectra of the Zn and Cd compounds with imidazolephosphine sulfide L^3 , the indicated absorption band position remains almost unchanged. A small shift of the band v(P=S) is caused, in our opinion, by the formation of the OH...S bond upon the change in the ligand conformation in a complex, which agrees with the calculated data. Note that the coordination of the tertiary alkyl- and arylphosphine sulfides and of imidazolidine-2-thiones to Lewis acids is attended by the formation of the molecular complexes with the S \longrightarrow M coordination bond, whose spectra exhibit considerable lowering of the stretching vibrations due to the P=S group from 20 to 60 cm⁻¹ [10, 19].

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Table 4. The chemical shisfts (δ , ppm) of the protons in ¹H NMR spectra (CDCl₃) of free and coordinated imidazolephosphine sulfides L¹-L⁴, Het-CH_X=C H_{A} *

Compound	H _X (q)	H _A (d)	H _B (d)	H _{CH(OH)} (s)	H _{CH₂} (m)	H _{CH₃} (t)	H _{4,5}
L ¹ **	7.46	4.87	5.42	5.36			7.70, 7.02
[PdL ¹ Cl ₂]**	7.62 (-0.17)	5.39 (-0.52)	5.94 (-0.52)	6.13 (-0.77)			8.33, 7.87 (-0.63, 0.85)
L ²				4.94	4.16	1.38	6.98, 6.92
$[\operatorname{Zn} \operatorname{L}_2^2 \operatorname{Cl}_2]$				5.92 (-0.98)	4.36 (-0.20)	1.42 (-0.04)	7.11, 6.93 (-0.13, 0.01)
[PdL ² Cl ₂]				5.61 (-0.67)	4.38 (-0.22)	1.42 (-0.04)	7.41, 6.98 (-0.43, 0.06)
L ² **				5.17	4.09	1.33	6.98, 6.92
$[ZnL^2Cl_2]^{**}$				5.44(-0.27)	4.22 (-0.13)	1.31(+0.02)	7.32, 6.99 (-0.34, -0.07)
[CdL ² Cl ₂]**				5.39(-0.22)	4.25 (-0.66)	1.31(+0.02)	7.32, 6.99 (-0.34, -0.07)
L ³	7.45	5.33	5.53	5.16			
[ZnL ³ Cl ₂]	7.47 (-0.02)	5.57 (-0.24)	5.61 (-0.08)	5.54 (-0.38)			
[PdL ³ Cl ₂]	7.73 (-0.28)	5.69 (-0.36)	5.95 (-0.42)	5.84 (-0.68)			
L^4				5.08	4.38	1.31	
[PdL ⁴ Cl ₂]				5.57 (-0.49)	4.53 (-0.15)	1.51 (-0.20)	
L ⁵ **	7.24	4.88	5.43	4.54			7.61, 6.90
$[\operatorname{Zn} L_2^5 \operatorname{Cl}_2]^{**}$	7.28 (-0.04)	5.07 (-0.19)	5.63 (-0.20)	4.73 (-0.19)			7.82, 7.06
							(-0.21, -0.16)

Note: *The direction and value of the shift of a proton signal in the complexes against the corresponding ligand are given in parentheses: (-) downfield shift, (+) upfield shift.

**The spectra of compounds were recorded in DMSO-d₆.



Fig. 1. The structure of molecules $ZnCl_2L^{4C}$ and L^{4S} in complex I.

The comparative analysis of the stretching vibrations of the OH groups in IR spectra of imidazolephosphine sulfides L^1-L^4 and their complexes indicates also the change in the type of hydrogen bonds in imidazolephosphine sulfides on their binding with the electronacceptor. In the spectra of the complexes, the absorption bands v(OH) of the hydroxyl group associated with the N atom of a heterocycle undergo a high-frequency shift (3150–3300 cm⁻¹) as compared with the bands in the spectra of free ligands (3130–3150 cm⁻¹). The highest shift (up to 3326 cm⁻¹) was observed for the Zn complexes, which indicates association of the OH…OH type. The analogous absorption band in the spectra of the Cd, Cu, Co, and Pd complexes lies within 3150-3240 cm⁻¹, which can be explained by the formation of intermolecular hydrogen bond OH...S. IR spectra of solutions of the Pd and Zn complexes of imidazolephosphine sulfides L^1 and L^2 (in CHCl₃, CCl₄) contain a broad absorption band with maxima at 3200 and $3607 \text{ cm}^{-1} (\text{PdCl}_2 \cdot \text{L}^1)$ and 3270, 3490, and 3608 cm^{-1} $(ZnCl_2 \cdot L^2)$. In the spectra of strongly diluted solutions of these complexes, the low-frequency components $(3200 \text{ and } 3270 \text{ cm}^{-1})$ disappear, while the bands due to the IHB $v(OH \dots S)$ and a free v(OH) with the corresponding frequencies 3490 and ~3610 cm⁻¹ remain unchanged.

The indicated changes in the characteristic absorption frequencies of the functional groups in IR spectra of the synthesized complexes with account of the calculated vibration spectra of the conformation isomers L and their complexes suggest that the coordination of imidazolephosphine sulfides L^1-L^4 with a metal gives the complexes with the donor-acceptor bond at the N atom of a heterocycle and leads to the change in the ligand molecule conformation resulting in the formation of intramoleular and intermolecular hydrogen bonds OH…S and OH…OH, respectively. The experimental and calculation data for the Zn, Cd, Cu complexes based on the ligands L^3 and L^4 do not exclude also the formation of the chelate complex with N,S-bidentate binding of a metal. The calculations revealed that both chelate with the distances N \rightarrow Zn 2.160 and S \rightarrow Zn 2.567 Å and the molecular complex with the coordination center at the N atom (N \rightarrow Zn 2.041 Å) have equal energy of formation.

The ¹H NMR structural study of complexes based on imidazolephosphine sulfides L^1-L^4 also showed the possibility of formation of compounds with both monodentate (at the N atom of a heterocycle) and N,S-bidentate metal coordination. Thus, the analysis of the ¹H NMR spectra of solutions of the Zn, Cd, Pd complexes, measured due to the limited solubility not only in CDCl₃ but also in DMSO-d₆, indicated essential changes as compared to the spectra of free molecules L^1-L^4 (Table 4). The exceptions were the adducts of zinc with imidazolephosphine sulfides L^1 , L^4 and of cadmium with L^1 , L^3 , L^4 (in DMSO-d₆), whose spectra are similar to those of unbonded ligand molecules, which suggests their complete dissociation in a solution. As compared to ¹H NMR spectra of free ligands, the spectra of the remaining complexes exhibit downfield shifts of the proton signals of a heterocycle and substituents in positions 1 and 2 of the azole ring (Table 4). The shift of a signal of the proton CH of the hydroxymethyl group in different compounds differs considerably. In the spectra of $[ZnL^2Cl_2]$, $[CdL^2Cl_2]$, and [PdL³Cl₂], this shift ($\Delta\delta$) lies in the interval

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Bond X_HY		Distance, Å		Angle (XHV) deg	Equivalent posi-	
Done A-11 ¹¹	Х–Н	Н…Ү	Х…Ү	Aligie (AIII), deg	tion of atom Y	
O(1B)–H(1B)····O(1)	0.74(3)	2.58(2)	3.319(9)	175(3)	<i>x</i> , 1 + <i>y</i> , z	
O(1B)-H(1B)···N(1B)	0.74(3)	2.47(3)	2.833(9)	114(2)	<i>x</i> , <i>y</i> , <i>z</i>	
O(1)-H(1)····N(1B)	1.09(3)	1.65(3)	2.652(9)	151(2)	<i>x</i> , 1 + <i>y</i> , <i>z</i>	

Table 5. The geometric parameters of hydrogen bonds between the molecules L^{4C} and L^{4S} in structure I

0.38–0.22 ppm and is close to the shift ($\Delta \delta \approx 0.2$ ppm) (Table 4) in the spectrum of a model compound $[ZnL_2^5Cl_2]$ (L⁵ = 1-vinyl-2-hydroxymethylimidazole) with coordination exactly at the N³ atom of a heterocycle [20, 21]. On the contrary, in the spectra of $[PdL^{1}Cl_{2}], [ZnL_{2}^{2}Cl_{2}], [PdL^{2}Cl_{2}], [PdL^{3}Cl_{2}], and$ [PdL⁴Cl₂], a signal of the CH(OH) proton shows more substantial shift ($\Delta \delta = 0.98-0.49$ ppm) (Table 4). The observed downfield shift of a signal of the CH(OH) proton in the given complexes can be explained by the formation of the chelate rings in the structure with the participation of heteroatoms S and N. In this case, the additional downfield shift of a signal of the proton $\Delta \delta_{CH(OH)}$ is due to both the effect of the metal coordination with the S atom and the effect of a central atom on the CH proton.

The structure of complex I was determined by X-ray diffraction (Fig. 1) and is peculiar in the presence of two independent molecules L^4 ; one of them (L^{4C}) is involved in the coordination sphere of the Zn atom and another one (L^{4S}) performs the solvate function in the

Table 6. The main torsion angles in structure I

Angle	φ deg				
Aligie	molecule L ^{4C}	molecule L ^{4S}			
S(1)P(1)C(8)O(1)	43.4	-176.6			
S(1)P(1)C(8)C(1)	-76.6	-57.3			
C(19)C(18)C(17)P(1)	-179.7	-170.4			
C(11)C(10)C(9)P(1)	156.5	179.0			
O(1)C(8)C(1)N(1)	-71.8	41.3			
O(1)C(8)C(1)N(2)	104.6	-133.1			
S(1)P(1)C(17)C(18)	-61.4	33.2			
C(2)N(2)C(25)C(26)	-73.6	-81.7			

complex $[ZnCl_2L^{4C}] \cdot L^{4S}$. Both donor centers of imidazolephosphine sulfide L^{4C} (the "pyridine" nitrogen atom N(1) and the S atom) participate in a metal coordination. The L^{4C} ligand in the complex is bidentatechelate and its addition closes a six-membered metalloring.

The Zn atom is coordinated at the vertices of a slightly distorted tetrahedron by the N(1) and S(1) atoms of the ligand L^{4C} and by two chlorine atoms (Cl(1) and Cl(2)). The smallest angles in the tetrahedron are the endocyclic angle SZnN (107.6(3)°) and the angles ClZnN (106.3(3)° ± 0.2°), while the angles ClZnS (112.2(1)° ± 2.3°) have the largest values. The bonds Zn–S 2.343(3), Zn–Cl (1) 2.224(3) and Zn–N 2.017(9) Å have common lengths. The bond Zn–Cl(2) 2.258(3) Å is slightly elongated, possibly, due to the short intermolecular contact (Cl(2)···H(17B) 2.93, Cl(2)···C(17B) 3.742 Å; the angle Cl(2)H(17B)C(17B) 141°).

The chelate cycle ZnSPC₂N is noticeably nonplanar ($\Delta_{av} = \pm 0.152$ Å), the maximum deviations from its mean plane being observed for the atoms P(1) (-0.452 Å) and C(8) (+0.462 Å). the conformation of the above six-membered metallocycle can be most adequately described as a strongly distorted asymmetric boat: the atoms N(10 and P(1) deviate toward one side by 0.318 and 0.792 Å, respectively, from the mean plane of the atoms Zn(1)S(1)C(1)C(8) ($\Delta_{av} = -0.13$ Å).

The independent molecules L^{4C} and L^{4S} in complex I have substantially different conformations. The solvate molecule L^{4S} is in the *cis*-form (L_a) with a strong intramolecular hydrogen bond O(1B)–H(1B)···N(1B) Table 5. The O(1B) atom is *cis* to the N(1B) atom and *trans* to the S(1B) atom (the corresponding torsion angles are equal to 41.3° and –176.6°) (Table 6). In the process of complex formation, the molecule L⁴ conformation changes noticeably: when the N(1) atom enters the coordination sphere of Zn atom, the intramolecular hydrogen bond OH···N in L^{4S} is ruptured, while the 1-ethyl-2-hydroxymethylbenzimidazole fragment in the L^{4C} ligand is rotated through ~130° about the P(1)–C(8) bond as compared with the solvate molecule



Fig. 2. The overlap of molecules L^{4C} (solid line) and L^{4S} (dashed line) with coinciding benzimidazole fragments in structure I.

 L^{4C} . As a result, the L^{4C} molecule becomes the *trans*isomer (L_b). The atom O(1) transforms from the *cis*- to the *trans*-position relative to the atom N(1) (the torsion angle O(1)C(8)C(1)N(1) in the ligand L^{4C} increases to -71.8° and changes its sign) and, conversely, from the *trans*- to the *cis*-position relative to the S(1) atom (the torsion angle S(1)O(1)C(8)O(1) in the ligand L^{4C} decreases with the change in the sign as compared to the L^{4C} molecule from -176.6° to 43.4°) (Table 6).

In addition, two L⁴ molecules have significantly different orientation of benzene rings, obviously due to intermolecular π – π -, d– π -interactions between the L^{4C} and L^{4S} molecules in crystal I. As a result, the dihedral angles between the planes of benzimidazole (**A**) and aromatic rings C(11)–C(16) (**B**), C(19)–C(24) (**B**') in the molecule L^{4S} (A/B 20°, A/B' 116°, and B/B 97°) and in the ligand L^{4C} (A/B 13°, A/B' 64°, and B/B' 75°) differ considerably. The ethyl substituents retain their positions relative to the benzimidazole fragment on the rotation of the latter. The changes observed in the L⁴ molecule during complex formation are shown in Fig. 2, where the ligands L^{4C} and L^{4S} are superimposed, provided that the C atom of benzimidazole fragments coincide.

The molecule of the $[ZnCl_2L^{4C}]$ complex (x, y, z)and the solvate molecule $L^{4S}(x, 1 + y, z)$ in compound I are united by strong intermolecular hydrogen bonds between the N and O atoms into $[ZnCl_2L^{4C}] \cdot L^{4S}$ associates (Fig. 3). The atoms O(1) (x, y, z) and O(1B)(x, 1 + y, z) form three intermolecular hydrogen bonds, i.e., $O(1)-H(1)\cdots N(1B)$, $O(1B)-H(1B)\cdots O(1)$ and $O(1B)-H(1B)\cdots N(1B)$ bonds (Table 5). As a result of the above interactions, two nonplanar H cycles conjugated at the bond N(1BA)-H(1B) are closed: the fourmembered OH₂N with the distance between the atoms H 2.24 Å and the five-membered OHNC₂ cycles. The deviations of the atoms from the mean plane of the first cycle O(1)H(1)H(1B)N(1B) ($\Delta = \pm 0.107^{\circ}$) are: O(1) 0.129, H(1) -0.21, H(1B) -0.01, and N(1B) 0.08 Å. the five-membered H-cycle is distorted almost to the same extent ($\Delta = \pm 0.110$ Å); the atomic deviations from the mean plane O(1B)H(1B)N(1B)C(1B)C(8B) are: O(1B)0.09, H(1B) 0.02, N(1B) 0.091, C(1B) 0.180, C(8B) 0.169 Å. the five-membered cycle has a strongly distorted sofa conformation: the atoms C(1B) and O(1B)deviate to one side from the plane N(1B)C(8B)H(1B)by 0.347 and 0.154 Å, respectively.

The majority of analogous bond lengths in the molecules L^{4C} and L^{4S} are almost equal (Table 4), but in the L^{4C} ligand, as a rule, the bonds to the atoms coordinated

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Fig. 3. The structure of associate $[ZnCl_2L^{4C}] \cdot L^{4S}$ in complex I.

with a metal are slightly elongated. In particular, the bond P–S bond in the L^{4C} molecule (1.977(4) Å) is noticeably (by 0.042 Å) longer than the analogous bond in L^{4S} (1.935(4) Å). Also, the N(1)–C(1) bond in the L^{4C} ligand is somewhat elongated (1.31(2) Å) as compared to the L^{4S} molecule (1.29(2) Å). The P(1)–C(9) and P(1)–C(17) bond lengths in the molecule L^{4C} (av. (1.806(9) ± 0.011 Å)) almost did not change as compared to the analogous bonds in L^{4S} (1.805(10) ± 0.005 Å). The bonds C-OH in the carboxyl groups of L^{4C} and L^{4S} have equal lengths (1.41(1) Å) close to the standard value [22].

In the structural units of crystal I, which are the bulky molecular associates $[ZnCl_2L^{4C}] \cdot L^{4S}$ (Fig. 3), the periphery space is formed on one side by two benzimidazole fragments, and on the other side, by three phenyl rings. The fourth phenyl cycle of the associate is almost perpendicular to its extension. The associate packing in crystals (projection on the plane *xz*) is shown in Fig. 4. The associates are extended between two inversion centers (0, 0, 0) and (1/2, 0, 1/2). In the same direction, along the diagonal (1, 0, 1/2), the columns of associates are formed due to the π - π -stacking interaction of the PD (parallel-displaced) type [23] between the plane-parallel aromatic cycles of benzimidazole fragments C(2B)–C(7B) of the L^{4S} molecule at the inversion center (0, 0, 0) on one side and between the C(19)–C(24) cycles in L^{4C} at the inversion center (1/2, 0, 1/2) on the other side. The extent of overlap of the contacting plane-parallel cycles at the inversion center (0, 0, 0) is shown in Fig. 5. The cycles at the other inversion center show almost the same overlap; the distances between their planes (3.30 and 3.50 Å) are typical of such interactions [24]. The phenyl cycles B and B' that are perpendicular to the extension of associates (at the inversion center (1/2, 0, 0) do not participate in the interaction; the distance between their planes >4 Å. The shortened contacts Cl(2)···O(1B) (3.101 Å) are formed between the columns.

Thus, the results obtained indicate that the investigated 2-[bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1-organilimidazoles L^1-L^4 exhibit the ambidentate nature and can form with Zn, Cd, Cu, Co, and Pd dichlorides both the molecular complexes with the coordination center at the heterocyclic N atom and the chelate complexes with the coordination N \leftarrow M \longrightarrow S bonds.

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Fig. 4. The structural unit packing in crystal I (projection on the plane *xz*).



Fig. 5. The overlap of plane-parallel benzimidazole fragments at the inversion center (0, 0, 0) in structure I.

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