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Competitive Coordination of 2-[(Diorganylphosphinoyl)-hydroxymethyl)]-1-organylimidazoles with Metal Chlorides

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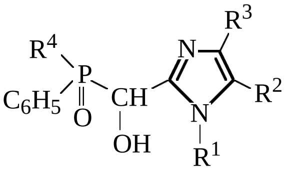
Abstract—The structure of complexes of bivalent cobalt, copper, zinc, cadmium, and palladium chloride and tetravalent tin chlorides with 1-organyl-2- [(diorganylphosphinoyl)hydroxymethyl]imidazoles, synthesized for the first time, was studied by ^{1}H NMR and IR spectroscopy. The formation of two types of metal complexes, molecular (Zn, Cd, Pd, Sn) and chelate (Co, Cu), was established. For crystalline 1 : 1 complexes, the structures with imidazolylphosphine oxide playing the role of an N^3,*O*-bidentate ligand were proposed. In 2L : 1 complexes, these ligands are monodentate and coordinate by the P=O oxygen atom. In DMSO solutions, the molecular complexes undergo dissociation to form coordination compounds in which, depending of the nature of the ligand, either M←N^3 or M←O donor–acceptor bond takes place.

Functionalyzed imidazoles with phosphine oxide and hydroxyl substituents are convenient objects for research into the competitive coordination of metals, associated with the ability of polydentate ligand systems to react by different potential donor centers, depending on the nature of the attacking reagent and the reaction conditions [1]. Synthesis of metal complexes on the basis of polyfunctional tertiary phosphine oxides of the azole series opens up possibilities for widely varying the coordination site of the metal (=N, O=P, HO, and CH_2=CH). Polysubstituted chiral phosphorus- and oxygen-containing polydentate azole ligands play an important role in asymmetric metal-complex catalysis [2]. Metal complexes of such compounds hold much practical promise primarily because azoles and organophosphorus compounds exhibit a strong physiological activity [3–6]. Development of convenient methods of regioselective synthesis of complexes on the basis of imidazolylphosphine oxides is also important for searching among them of effective sorbents, flotation agents, insecticides, and other materials with useful properties [7, 8].

In the present work we have studied for the first time reactions of 2-[(diphenylphosphinoyl)hydroxymethyl]-1-methylimidazole (**I**), 2-[(diphenylphosphinoyl)hydroxymethyl]-1-vinylimidazole (**II**), 1-ethyl-2-[(diphenylphosphinoyl)hydroxymethyl]benzimidazole (**III**), 2-[(diphenylphosphinoyl)hydroxymethyl]-1-vinylbenzimidazole (**IV**), 2-[[ethyl(phenyl)phosphinoyl]hydroxymethyl]-1-methylimidazole (**V**), 1-ethyl-2-[[ethyl(phenyl)phosphinoyl]hydroxymethyl]imidazole (**VI**), and 1-ethyl-2-[[ethyl(phenyl)phosphinoyl]hydroxymethyl]benzimidazole (**VII**) with Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pd^{2+}, and Sn^{4+} chlorides, with the aim to synthesize new metal complexes with phosphorus- and oxygen-containing azole ligands and to correlate the structure of the resulting complexes with the structure of the ligand, the nature of the metal, and reaction conditions.



I–VII

I, R^1 = CH_3; R^2 = R^3 = H; R^4 = C_6H_5. **II**, R^1 = CH=CH_2; R^2 = R^3 = H; R^4 = C_6H_5. **III**, R^1 = C_2H_5; (R^2 + R^3) = $(CH)_4$; R^4 = C_6H_5. **IV**, R^1 = CH=CH_2; (R^2 + R^3) = $(CH)_4$; R^4 = C_6H_5. **V**, R^1 = CH_3; R^2 = R^3 = H; R^4 = C_2H_5. **VI**, R^1 = C_2H_5; R^2 = R^3 = H; R^4 = C_2H_5. **VII**, R^1 = C_2H_5; (R^2 + R^3) = $(CH)_4$; R^4 = C_2H_5.

Previously we found [9, 10] that the reactions of 2-[[bis(phenylethyl)phosphinoyl]hydroxymethyl]-1-vinylimidazole (**VIII**) with methyl iodide and 1-ethyl-2-[(diphenylphosphinoyl)hydroxymethyl]imidazole (**IX**) with camphorsulfonic acid involve the heteroring N^3 atom and gives rise to complex compounds of the ionic type. At the same time, ambident imidazoles **I**–**VII** can act as monodentate ligands coordinating via the P=O oxygen atom or via the heteroring N^3

Table 1. Complexes of 2-[(diorganylphosphinoyl)hydroxymethyl)-1-organylimidazoles **I**–**VII**

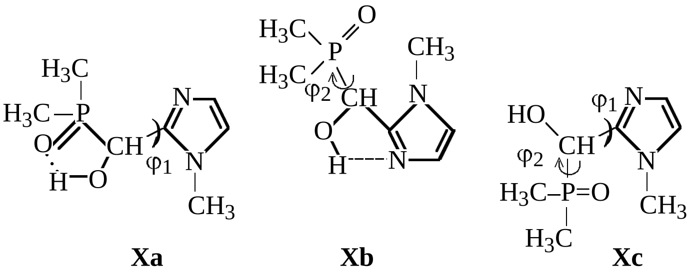
Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	Cl		C	H	Cl
$ZnCl_2 \cdot$ **II**	74	160 (decomp.)	47.15	3.97	15.22	$C_{18}H_{17}Cl_2N_2O_2PZn$	46.94	3.72	15.39
$ZnCl_2 \cdot$ **III**	73	192–195	51.28	4.16	13.23	$C_{22}H_{21}Cl_2N_2O_2PZn$	51.52	4.10	13.36
$ZnCl_2 \cdot$ **IV**	17	210–212	51.48	3.76	14.20	$C_{22}H_{19}Cl_2N_2O_2PZn$	51.76	3.73	13.92
$ZnCl_2 \cdot$ **V**	53	128 (decomp.)	39.31	4.56	17.39	$C_{13}H_{17}Cl_2N_2O_2PZn$	38.96	4.25	17.73
$ZnCl_2 \cdot 2$**VI**	39	110 (decomp.)	48.05	5.35	10.66	$C_{28}H_{38}Cl_2N_4O_4P_2Zn$	48.55	5.49	10.26
$CdCl_2 \cdot 2$**I**	33	170 (decomp.)	50.07	4.16	8.54	$C_{34}H_{34}CdCl_2N_4O_4P_2$	50.53	4.21	8.79
$CdCl_2 \cdot$ **II**	48	123–125	43.01	3.53	13.73	$C_{18}H_{17}CdCl_2N_2O_2P$	42.60	3.33	14.00
$CdCl_2 \cdot 2$**III**	80	185–187	55.87	4.70	7.40	$C_{44}H_{42}CdCl_2N_4O_4P_2$	56.15	4.49	7.59
$CdCl_2 \cdot 2$**IV**	80	190 (decomp.)	56.50	4.08	7.75	$C_{44}H_{38}CdCl_2N_4O_4P_2$	56.71	4.08	7.62
$CdCl_2 \cdot$ **V**	59	158–160	35.03	4.17	15.76	$C_{13}H_{17}CdCl_2N_2O_2P$	34.89	3.83	15.58
$CdCl_2 \cdot$ **VII**	64	175–177	41.92	4.28	14.16	$C_{18}H_{21}CdCl_2N_2O_2P$	42.27	4.11	13.89
$CuCl_2 \cdot$ (**I**-H)	55	122–124	49.57	4.15	8.76	$C_{17}H_{16}ClCuN_2O_2P$	49.76	3.90	8.66
$SnCl_4 \cdot 2$**II**	71	144–147	43.26	3.09	14.43	$C_{36}H_{34}Cl_4N_4O_4P_2Sn$	43.26	3.40	14.22
$CoCl_2 \cdot$ (**IV**-H)	42	117–119	56.57	4.05	7.45	$C_{22}H_{18}ClCoN_2O_2P$	56.47	3.85	7.59
$PdCl_2 \cdot$ **V**	80	162–163	35.23	4.10	15.84	$C_{13}H_{17}Cl_2N_2O_2PPd$	35.37	3.85	16.10
$PdCl_2 \cdot 2$**VII**	87	149–151	51.54	4.95	8.96	$C_{36}H_{42}Cl_2N_4O_4P_2Pd$	51.86	5.04	8.52

atom, depending on the nature of the acceptor. Moreover, bidentate ligation, as well as chelate formation are also possible.

The reactions of imidazoles **I**–**VII** with metal chlorides were carried out at room temperature or at 70°C in ethanol or acetone at 1:1 and 1:2 salt:ligand ratios (Table 1). As a result, complexes with the composition corresponding mostly to the starting reagent ratio were isolated, except for the adducts $ZnCl_2 \cdot L$ (L = **III**–**V**), $CdCl_2 \cdot$ **II**, and $CoCl_2 \cdot$ **IV**, in which the salt:ligand ratio is higher than that taken in reaction (1:2). The complex $PdCl_2 \cdot 2$**VII** was obtained at an equimolar salt:ligand ratio in the reaction mixture (Table 1). The preferred site of coordination of metals to polydentate imidazolylphosphine oxides was determined by comparative analysis of the IR and ^1H NMR spectra of free and coordinated ligands **I**–**VII**.

In [10], by means of IR and ^1H and ^{31}P NMR spectroscopy we showed that compounds **I**–**IV** contain both intra- and intermolecular hydrogen bonds, mainly of the OH···O=P type.

In the present work, to establish the mutual location of electron-donor centers in ligands **I**–**VII**, we performed quantum-chemical calculations of the model 2-[(dimethoxyphosphinoyl)hydroxymethyl]-1-methylimidazole (**X**) at the HF/6-31G* level with full geometry optimization. As a result, it was established that imidazolylphosphine oxide **X** has three energetically stable forms with intramolecular hydrogen bonds OH···O=P (**Xa**) and OH···N (**Xb**), and with a free OH group (**Xc**) (see scheme bellow).

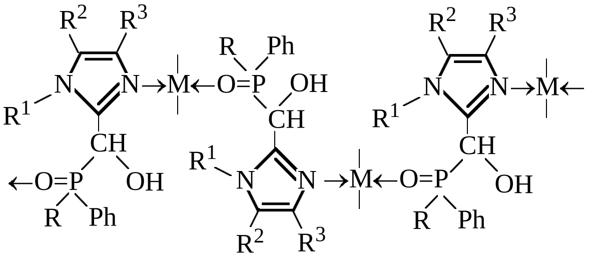


Xa	**Xb**	**Xc**
φ1 113°	φ2 177°	φ1 132°, φ2 71°
θ 83°	θ 134°	θ 130°
μ 4.99 D	μ 1.09 D	μ 2.11 D
Δ*E* –21.4 kJ mol^{-1}	Δ*E* 0 kJ mol^{-1}	Δ*E* –19.3 kJ mol^{-1}

The φ^1 and φ^2 dihedral angles in structures **Xa**–**Xc** relate to rotation of the azole ring or the phosphine oxide group with respect to the plane defined by the C–OH group. The θ angle determines the mutual position of the planes defined by the P=O group and the heteroring. The calculations show that these planes are almost orthogonal to each other: The θ angle is 83° in form **Xa** and 134° and 130° in forms **Xb** and **Xc**, respectively. Under real conditions, the effects of the medium and coordinating agent can shift the equilibrium between forms **Xa**–**Xc** that have much different calculated dipole moments (see scheme).

In the IR spectra of the metal complexes of imidazoles **I**–**VII**, the P=O bands are shifted red by 30–50 cm^{-1} compared with the respective bands of the free ligands, unlike what is observed with ionic complexes of imidazolylphosphine oxides **VIII** and **IX** [9, 10] whose P=O absorption band is in the same place as in the spectra of the free ligands (Table 2). The bands of stretching vibrations of the azole ring (1410–1510 cm^{-1}) of free ligands **I**–**VII** are shifted slightly blue in going to the 1 : 1 complexes and remain unchanged in going to the 2L : 1 complexes (Table 2). Note that the monodentate coordination of a ligand to an electron acceptor, involving the oxygen atom in phosphine oxides [11, 12] or the pyridine nitrogen atom in azole derivatives [9, 10, 13, 14] (Table 2) is accompanied by a stronger shift of the P=O and heteroring absorption bands (by 80–100 and 10–30 cm^{-1}, respectively), whereas formation of chelate complexes most frequently produces a red shift of the stretching vibration frequencies of the heteroring [15].

In the IR spectra of the complexes of $ZnCl_2$, $CdCl_2$, $PdCl_2$, and $SnCl_4$ with imidazolylphosphine oxides **I**–**VII**, there are stretching vibration bands of the hydroxymethyl group: C–O (1030–1050 cm^{-1}) and OH (3070–3300 cm^{-1}), implying intramolecular hydrogen bonding of the coordinated ligands. The absorption band of the associated OH group of the free ligands (ν 3000–3100 cm^{-1}) in the spectra of the corresponding complexes increases to 3250–3300 cm^{-1} for $MCl_n \cdot L$ and to 3070–3180 cm^{-1} for $MCl_n \cdot 2L$ (Table 2). Such a blue shift of the ν(OH) band may be associated both with the weakening of intramolecular hydrogen bonding due to formation of an additional O→M bond [16, 18] and with a change in the type of association [10]. Thus, analysis of the IR spectra of coordinated and free ligands **I**–**VII**, as well as the ortogonal mutual location of the donor centers in the ligands in hand (*trans* conformation), proposed on the basis of calculations, allows the 1 : 1 complexes to be assigned the structure of polymeric chains with both heteroatoms being coordination centers and the ligand playing the role of a bridge between the central atoms of complex **A**. We do not also exclude formation of an OH···OH hydrogen bond in complexes **A**. Evidence for this suggestion is provided by a considerable shift of the ν(OH) band (to 3250–3300 cm^{-1}) compared with the free ligand (Table 2).



A

M = Zn, Cd, Pd, Sn.

Note that the complex formation gives rise to additional interactions and may be attended with a transition of the imidazolylphosphine oxides to the *cisoid* conformation. At such a location of the N and O centers, molecules **I**–**VII** can, playing the role of a double bridge between the metal atoms, form dimeric 2 : 2 complexes **B**. For example, by X-ray diffraction we revealed a similar structure in bis(μ-1,1'-divinyl-2,2'-biimidazolyl)tetrachlorodicobalt; therewith, the coordinated 1,1'-divinyl-2,2'-biimidazolyl ligand had the same *cisoid* conformation as the free ligand [18, 19].

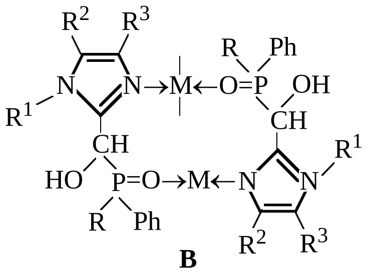
In the 2L : 1 complexes, imidazolylphosphine

Table 2. IR (KBr) and ^{1}H NMR[a] (DMSO-d_6) spectral parameters of free and coordinated 2-[diorganylphosphinoyl)-hydroxymethyl]-1-organylimidazoles **I**–**IX**

Compound	IR, ν, cm^{-1}			NMR, δ, ppm				
	P=O	OH	heteroring	H_A (d.d)[b]	H_B (d.d)[b]	CH_{OH}, d	H^4, d	H^5, d
I	1180	3100	1485, 1440, 1405	–	–	5.78	7.04	6.70
$CdCl_2\cdot$ 2**I**	1150	3180	1485, 1440	–	–	5.99 (–0.21)	7.10 (–0.06)	6.87 (–0.17)
$CuCl_2\cdot$ **I**	1130	–	1495, 1440, 1415	–	–	–	–	–
II	1200	3000	1480, 1435	4.74	5.33	5.91	7.44	6.80
$ZnCl_2\cdot$ **II**	1150	3300	1485, 1438	4.81 (–0.07)	5.37 (–0.04)	6.05 (–0.14)	7.45 (–0.01)	6.90 (–0.10)
$CdCl_2\cdot$ **II**	1150	3250	1485, 1435	4.81 (–0.07)	5.34 (–0.01)	6.01 (–0.10)	7.45 (–0.01)	6.87 (–0.07)
$SnCl_4\cdot$ 2**II**	1160	3120	1480, 1435	4.92 (–0.18)	5.49 (–0.16)	6.14 (–0.23)	7.47 (–0.03)	7.17 (–0.37)
III	1200	3000	1475, 1435, 1410	–	–	6.05	–	–
$ZnCl_2\cdot$ **III**	1145	3300	1485, 1440, 1435	–	–	6.08	–	–
$CdCl_2\cdot$ 2**III**	1170	3120	1475, 1437, 1410	–	–	6.19	–	–
IV	1190	3080	1470, 1450, 1430	5.13	5.56	6.10	–	–
$ZnCl_2\cdot$ **IV**	1140	3280	1480, 1465, 1435	–	–	–	–	–
CdCl2 · 2**IV**	1165	3100	1470, 1450, 1430	5.16	5.55	6.14	–	–
CoCl2 · **IV**	1135	–	1485, 1460, 1430	–	–			
V	1180	3100	1480, 1460, 1435	–	–	5.88	7.58	7.39
$ZnCl_2\cdot$ **V**	1160	3300	1500, 1465, 1445	–	–	5.57 (+0.31)	7.24 (+0.34)	7.00 (+0.39)
$ZnCl_2\cdot$ **V**[c]	–	–	–	–	–	5.51, 5.39	7.16, 7.11	6.95, 6.92
$CdCl_2\cdot$ **V**	1150	3250	1495, 1460, 1440	–	–	5.55 (+0.33)	7.15 (+0.43)	7.00 (+0.39)
$CdCl_2\cdot$ **V**[c]	–	–	–	–	–	5.46, 5.37	7.10, 7.07	6.94, 6.92
$PdCl_2\cdot$ **V**	1150	3250	1495, 1460, 1440	–	–	5.24 (+0.64)		
VI	1180	3095	1490, 1460, 1440	–	–	5.81, 5.80	7.53, 7.49	7.27, 7.23
$ZnCl_2\cdot$ 2**VI**	1155	3120	1490, 1460, 1440	–	–	5.57, 5.40 (+0.24), (+0.40)	7.32, 7.12 (+0.21), (+0.37)	7.00, 6.92 (+0.27), (+0.31)
VII	1190	3070	1480, 1455, 1430	–	–	6.17, 5.97	–	–
$CdCl_2\cdot$ **VII**	1150	3250	1485, 1460, 1435	–	–	5.87, 5.65 (+0.30), (+0.32)	–	–
$PdCl_2\cdot$ 2**VII**	1160	3050–3150	1480, 1455, 1430	–	–	5.52, 5.40 (+0.65), (+0.57)	–	–
VIII	1157	3105	1521, 1495, 1483	4.85	5.41	5.23	7.20	7.01
$CH_3I\cdot$ **VIII**	1155	3110	1542, 1517, 1496	5.33 (–0.48)	5.63 (–0.22)	6.19 (–0.96)	7.23 (–0.03)	7.12 (–0.11)
IX	1200	3100	1490, 1445	–	–	5.70	6.83	6.83
CSA[d] · **IX**	1200	3140	1518, 1445	–	–	6.52 (–0.82)	7.29 (–0.46)	7.01 (–0.18)

[a] Parenthesized are the direction and magnitude of the signal shift in going from the starting ligand to the complex: (–) downfield shift and (+) upfield shift. [b] Signals of the vinyl group Het–CH_x=CH_AH_B. [c] At 80°C. [d] CSA is camphorsulfonic acid.

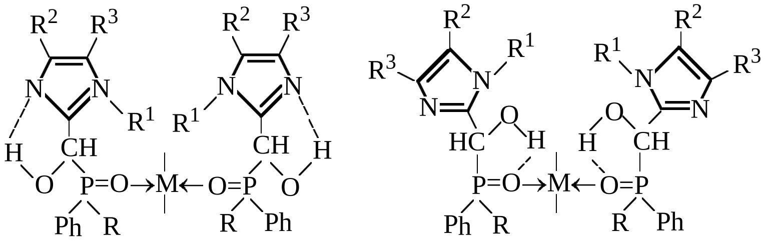
oxides act as monodentate ligands coordinating via the P=O oxygen atom. In complexes **C**, either an OH···N hydrogen bond may form or the OH···O=P hydrogen bond may be preserved with simultaneous involvement of the oxygen atom in coordination with metal, which is evidently confirmed by the smaller blue shift (to 3070–3180 cm^{-1}) of the ν(OH) band (Table 2).



B

M = Zn, Cd, Pd, Sn.

Abundant X-ray diffraction evidence is available

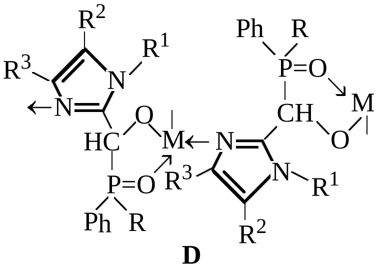


C

M = Zn, Cd, Pd, Sn.

for the simultaneous involvement of oxygen in an intramolecular hydrogen bond and a donor–acceptor bond [1, 20, 21].

The reactions of imidazolylphosphine oxides **I** and **IV** with copper and cobalt dichlorides provide chelates **D**.



D

M = Co, Cu.

The IR spectra of the $CuCl_2$ and $CoCl_2$ complexes contain no absorption bands due to stretching and deformation vibrations of the OH group. The largest shift of the P=O band (50–55 cm^{-1}) is observed, and the blue shift of the heteroring ν band reaches 15 cm^{-1} compared to free ligands **I** and **IV** (Table 2). Unlike what is observed with mixed-ligand chelate compounds on the basis of 2-(hydroxymethyl)-1-vinylimidazoles [22], the evolving HCl enters into donor–acceptor interaction with the lone electron pair of the N^3 atom of the azole ring, which is confirmed by the elemental analyses (Table 1) and IR spectra (lack of the characteristic NH^+ band in the range 2600–3000 cm^{-1}). Evidently, both in the Cu and in the Co chelate compounds with ligands **I** and **IV**, the simultaneous coordination of two acoplanar donor centers, P=O oxygen and heteroring N^3, too, is realized via formation of polymeric structures in which the corresponding imidazolohosphine oxide plays the role of a bridging *N,O*-bidentate ligand.

The ^1H NMR spectra of imidazolylphosphine oxides **I, II**, and **V**–**VII** in DMSO differ considerably from the spectra of their Zn, Cd, Sn, and Pd complexes. The adducts of ligands **III** and **IV** are an exception, because the proton chemical shifts of the free azoles and their complexes with $ZnCl_2$ and $CdCl_2$ are identical (Table 2). This fact suggests that the latter complexes are completely dissociated in DMSO solutions. The considerable downfield shifts of the vinyl (H_A and H_B) and heteroring (H_4 and H_5) signals in the ^1H NMR spectra of the complexes of imidazoles **I** and **II** compared to the respective signals of the free ligands are indicative of donor–acceptor interaction of the metals with, primarily, N^3 [13, 14]. Appreciable shifts of these proton signals (Δδ 0.16–0.37 ppm) are observed for the complex $SnCl_4 \cdot 2$**II** that comprises the strongest acceptor in the series of metal chlorides in hand (Table 2). In the ^1H NMR spectra of stronger ionic complexes of imidazolylphosphine oxides **VIII** and **IX** with CH_3I and camphorsulfonic acid, in which the acceptors are coordinated in the monodentate fashion by the "pyridine" nitrogen atom of the heteroring [9, 10], the downfield shift of the respective signals reaches more significant values than in the spectra of the adducts under study (Table 2). Evidently, the electrostatic repulsion of the phenyl π system in compounds **I** and **II** and electrons of the central metal atom renders the coordination bond of the latter with the P=O oxygen atom in DMSO solutions weaker than the $N^3 \rightarrow M$ bond and makes it to dissociate.

We found a strong upfield shift of the heteroring and CH signals in the ^1H NMR spectra of the complexes of 2-(ethylphenylphosphinoyl)imidazoles **V**–**VII** compared with the respective signals of the free ligands, which has never been observed in the case of coordination by the nitrogen atom [23]. Such an upfield shift is evidently produced by the shielding effect of the aryl ring through space, which becomes possible if the azole and aryl rings are strongly acoplanar. In this case, the ^1H NMR spectra of the adducts with ligands **V**–**VII** provide indirect evidence for preservation of the coordination by the oxygen atom, because on coordination by N^3 substitution of the phenyl substituent by ethyl should not such significantly affect the strength of the $N^3 \to M$ donor–acceptor bond. Note that in the ^1H NMR spectra of the complexes with ligands **V**–**VII**, the signal of the CH proton of the hydroxymethyl group is shifted stongly upfield compared with the respective signal of the free donors, which can be considered one more evidence for coordination by the P=O oxygen atom.

According to ^1H and ^{31}P NMR data in [9], phosphine oxides with two asymmetric centers (carbon and phosphorus) exhibit diastereomerism. In the spectra of their complexes, most signals are split, which is explained by preservation of two diastereomers of ligands **V**–**VII** in the molecules of the corresponding metal complexes (Table 2).

In conclusion it may be said that unambiguous conclusions as to the structure of the synthesized complexes and their coordination centers may be made by means of X-ray analysis.

EXPERIMENTAL

The IR spectra were recorded on a Bruker IFS-25 instrument in KBr pellets. The NMR spectra were obtained on a Bruker DPX-400 instrument in DMSO-d_6 solutions at room temperature and at 80°C against internal HMDS. Quantum-chemical calculations with full geometry optimization were carried out using the GAUSSIAN-98 program package [24].

The complexes of metal chlorides with ligands **I, II**, and **IV**–**VII** were obtained by stirring ligand and metal salt in absolute ethanol at 60°C for 8–15 h and subsequent precipitation of the products with ether and drying. The complexes of $CdCl_2$ with ligand **I** and of metal chlorides with ligand **III** were obtained at room temperature.

The complexes of $PdCl_2$ with ligands **III, V**, and **VII** were obtained by adding ligands in aqueous $K_2[PdCl_4]$. The precipitates that formed were filtered off, washed with acetone, and dried in a vacuum.

The complex of $PdCl_2$ with ligand **IV** was obtained in acetone at 56°C for 21 h. The product was then filtered off, washed with acetone, and dried.

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