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Nickel(II), Cobalt(II), Copper(II), and Zinc(II) Complexes with 4'-(4'''-Benzo-15-Crown-5)methyloxy-2,2':6',2''-Terpyridine: Syntheses and Vibrational Spectra

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Abstract—Complexes of 4'-(4'''-benzo-15-crown-5)methyloxy-2,2':6',2''-terpyridine (L) with metal perchlorates and hexafluorophosphates, $[ML_2](ClO_4)_2 \cdot nH_2O$ and $[ML_2](PF_6)_2 \cdot nH_2O \cdot mC_2H_5OH$ (M = Ni(II), Co(II), Zn(II), Cu(II); $n = 0–3$; $m = 0–2$), were synthesized. Their vibrational spectra were studied. The spectral criteria for ligand coordination through the terpyridinic nitrogen atoms were established. The conformational structure of the B15C5 macrocycles of a ligand molecule in the synthesized complexes was proposed. The complexes were studied by thermogravimetry.

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INTRODUCTION

2,2'-Bi- and 2,2':6',6''-terpyridines (polypyridines) are among most widely used ligands in coordination and supramolecular chemistry. Polypyridines and, more often, their complexes with transition metals are used as catalysts, analytical reagents, and selective extracting agents. The photophysical properties of the polypyridine ligands and their complexes with transition metal cations are of special interest. For example, 4'-(4-N,N-diphenyl)-2,2':6',2''-terpyridine manifests fluorescence properties and can be used as a sensor to Zn^{2+} cations [1]. The platinum(II) complex with 2,2':6',2''-terpyridine $[Pt(Tpy)OH]BF_4$ exhibits luminescence properties [2] and can undergo the photoinduced electron transfer from a donor to an acceptor, which allows one to use it as a strong oxidant in photochemical reactions. The zinc(II), ruthenium(III), and osmium(III) complexes with 4'-(C_6H_4-*n*-NBu_2)-2,2':6',2''-terpyridine possess nonlinear optical properties [3]. The ruthenium complexes with 2,2':6',2''-terpyridines bearing the acetylenide and cyclopentadienyl moieties as substitients in position 4' are promising for the creation of devices of a new generation for information storage and reading [4]. At present, one of the main problems is the development of methods for the target synthesis of functionalized polypyridine derivatives for the purpose of optimizing their properties.

Great attention is given to the study of crown ethers since the moment of their discovery to the present time. The introduction of various substituents into crown ether molecules makes it possible to vary their spectral, photochemical, complexation, and other properties in a wide range [5, 6].

4'-Crown-ether-substituted 2,2':6',2''-terpyridines are of special interest due to the presence in the same molecule of the terpyridine fragment binding the *d*-metal cations and the crown ether moiety capable of selective binding alkaline and alkaline-earth metal cations. However, these heterotopic ligands remain to be an almost unstudied class of compounds.

The syntheses of 4'-(4'''-benzo-15-crown-5)methyloxy-2,2':6',2''-terpyridine (L) and its complexes $[CoL_2](ClO_4)_2 \cdot 3H_2O$ (**I**) and $[ZnL_2](ClO_4)_2 \cdot 3H_2O$ (**II**) were described [7]. It is found by X-ray diffraction analysis that compounds **I** and **II** are isostructural and consist of the $[ML_2]^{2+}$ complex cations (M = Co, Zn), ClO_4^- anions, and molecules of water of crystallization. In the both complexes, the metal atom is surrounded by six nitrogen atoms of the terpyridine moieties of two organic ligands.

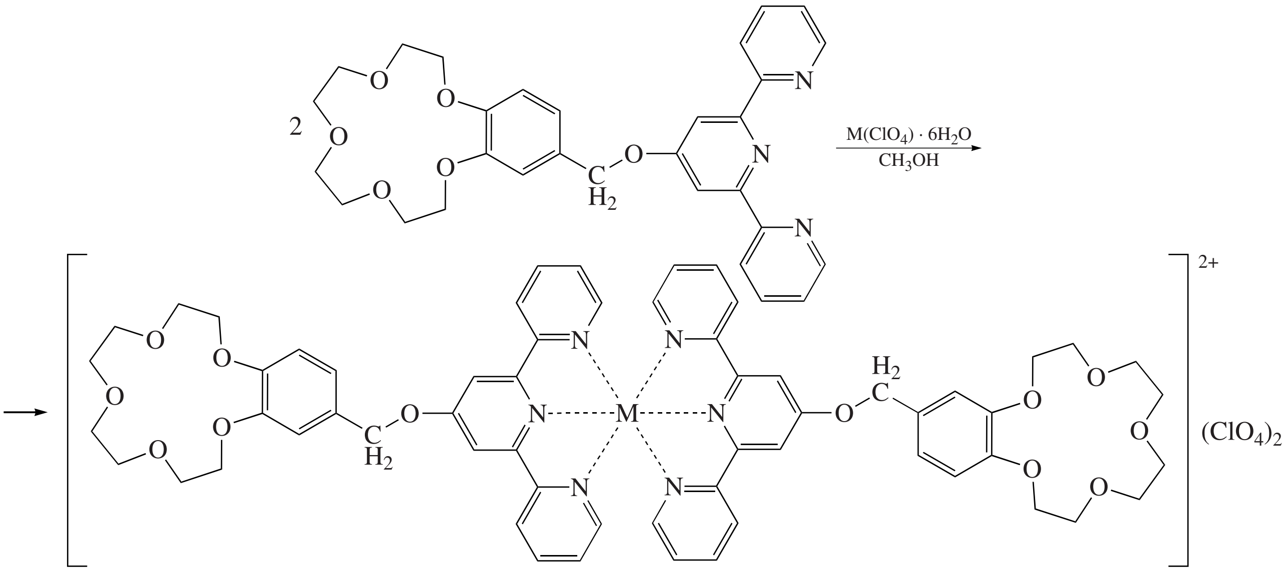
Continuing the studies of the complexation properties of L, we synthesized the complexes of Ni(II) and Cu(II) perchlorates and the complexes of Zn(II), Ni(II), Co(II), and Cu(II) hexafluorophosphates with L, studied their vibrational spectra, established the spectral criteria for ligand coordination through the nitrogen heteroatoms, and proposed the conformational structures of the macrocycles of the ligand molecule in the complexes that were not structurally studied.

EXPERIMENTAL

Commercially available methanol (Lab-Scan, chromatographically pure), acetonitrile (Reagent ACS, Acros Organics), and 99% ammonium hexafluorophosphate (Acros Organics) were used.

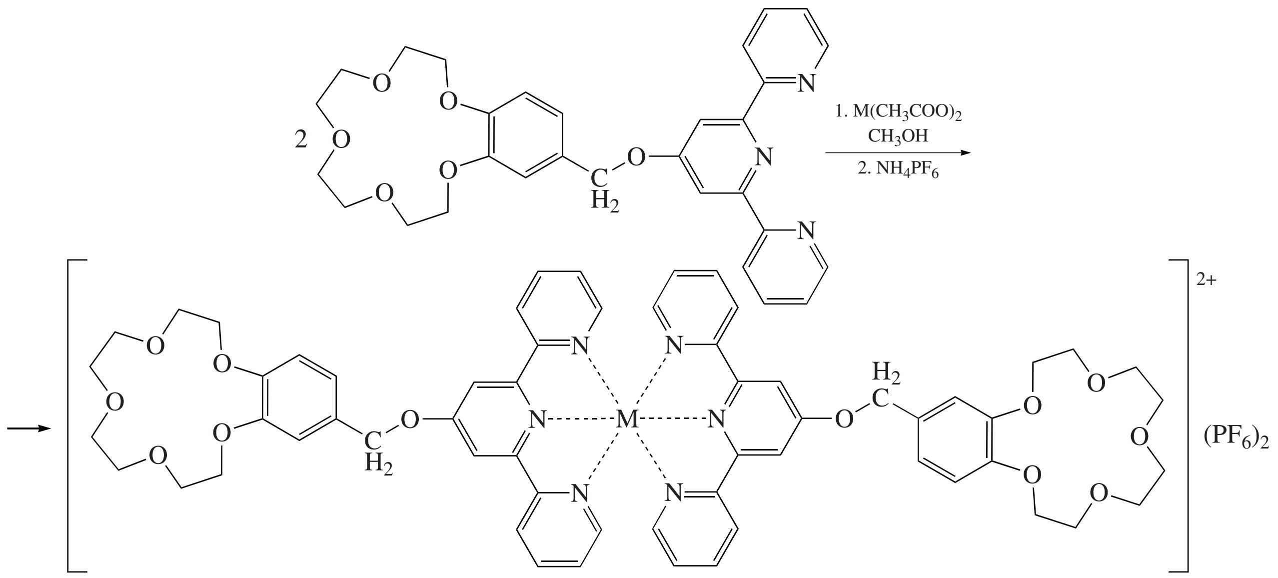
Nickel(II), cobalt(II), copper(II), and zinc(II) perchlorate hexahydrates and acetate hydrates (Aldrich) were used for the syntheses of the complexes.

The procedure of the synthesis of L and its electronic absorption and NMR spectra were described [7]. The complexes of L with the metal cations and perchlorate ion, namely, $[CoL_2](ClO_4)_2 \cdot 3H_2O$, $[ZnL_2](ClO_4)_2 \cdot 3H_2O$), $[NiL_2](ClO_4)_2 \cdot H_2O$ (**III**), and $[CuL_2](ClO_4)_2 \cdot 3H_2O$ (**IV**), were synthesized according to the scheme



M = Co(II) (**I**), Zn(II) (**II**), Ni(II) (**III**), Cu(II) (**IV**).

The metal hexafluorophosphate complexes with L, namely, $[NiL_2](PF_6)_2 \cdot 2(C_2H_5OH) \cdot H_2O$ (**V**), $[CoL_2](PF_6)_2 \cdot 3H_2O$ (**VI**), $[CuL_2](PF_6)_2$ (**VII**), and $[ZnL_2](PF_6)_2 \cdot 3H_2O$ (**VIII**), were synthesized according to the scheme



M = Ni(II) (**V**), Co(II) (**VI**), Cu(II) (**VII**), Zn(II) (**VIII**).

Table 1. Elemental analysis results for the Co(II), Ni(II), Zn(II), and Cu(II) complexes with L ($C_{30}O_6N_3H_{31}$)

Compound	Content (found/calculated), %		
	C	H	N
$Ni(ClO_4)_2 \cdot 2(C_{30}O_6N_3H_{31}) \cdot H_2O$	54.70/53.97	6.53/6.29	3.88/4.79
$Cu(ClO_4)_2 \cdot 2(C_{30}O_6N_3H_{31}) \cdot 3H_2O$	52.11/52.40	6.77/6.11	3.84/4.95
$Co(PF_6)_2 \cdot 2(C_{30}O_6N_3H_{31}) \cdot 3H_2O$	48.11/49.28	6.35/5.54	5.26/5.01
$Ni(PF_6)_2 \cdot 2(C_{30}O_6N_3H_{31}) \cdot 2(C_2H_5OH) \cdot H_2O$	51.26/50.62	6.35/5.54	5.26/5.01
$Zn(PF_6)_2 \cdot 2(C_{30}O_6N_3H_{31}) \cdot 3H_2O$	47.71/49.07	5.91/5.72	5.02/4.64
$Cu(PF_6)_2 \cdot 2(C_{30}O_6N_3H_{31})$	53.30/51.08	6.64/5.95	5.47/4.39

The synthesis was carried out by the mixing of methanolic solutions of the corresponding metal acetate (1 equiv) and L (2 equiv) at room temperature. The subsequent addition of a 40-fold molar excess of ammonium hexafluorophosphate resulted in the precipitation of complexes **V**–**VIII**. The precipitates were filtered off, washed with methanol and diethyl ether, dried in vacuo, and recrystallized from an ethanol–acetonitrile (3 : 1, vol/vol) mixture.

The elemental analysis data for the synthesized compounds are given in Table 1.

IR spectra were recorded on a Vertex 70 spectrometer (Bruker) in the 4000–400 cm^{-1} range (suspensions in Nujol).

Thermogravimetry was carried out on a Q derivatograph (MOM, Hungary) in the temperature interval from 20 to 700°C in platinum crucibles with a heating rate of 10 K/min.

RESULTS AND DISCUSSION

The bands in the IR spectrum of L in the 1700–400 cm^{-1} region were assigned by the comparison of the vibrational spectra of 4'-chloroterpyridine (CTP), 4'-hydroxymethylbenzo-15-crown (HMB15C5), and benzo-15-crown-5 (B15C5) and published data [8, 9] for pyridine (Py). The main vibrational frequencies in the IR spectra of L and the complexes synthesized from L are given in Table 2.

The intense bands at 1600–1524 cm^{-1} correspond to the stretching vibrations of the benzene rings of the terpyridine and crown ether, and the intense bands at 1467–1405 cm^{-1} are attributed to the bending vibrations of the CH and CH_2 groups.

Theν_s(PhO) and ν_{as}(PhO) vibrations of B15C5 appear in the IR spectrum of L as an intense doublet band with maxima at 1271 and 1250 cm^{-1}. Two new (compared to those of CTP and HMB15C5) narrow intense bands appear in the spectrum of L at 1352 and 1197 cm^{-1}. They can be assigned to the vibrations of the new fragment formed due to the attachment of the CTP and HMB15C5 molecules, namely, Ph–H_2C–O–Py.

The ν_{as}(COC) and ν_s(COC) vibrations appear at 1150–1050 cm^{-1} in the spectra of the crown ethers. The IR spectrum of L contains two bands: an intense band at 1144 cm^{-1} and a medium-intensity band at 1119 cm^{-1}. According to the correlations [10, 11], in the case of benzocrown ethers and their azomethine derivatives, the frequency ν_{as}(COC) ~1120 cm^{-1} is ascribed to the vibrations of the ethylene glycol unit with a conformation close to TGG. The band at 1144 cm^{-1} is attributed to the $\delta(CH)_{Ph}$ bending vibrations. The corresponding band in the spectra of HMB15C5 and CTP appears at 1138 and 1143 cm^{-1}, respectively.

However, the most informative (from the viewpoint of the conformational structure of the B15C5 macrocycle) is a region of 1000–700 cm^{-1}, where the ν_{resp} pulsation vibration of the macrocycle and the mixed stretching–bending vibrations $\rho(CH_2) + \nu(CO) + \nu(CC)$ of particular ethylene glycol units appear [12]. Since the IR spectrum of CTP in the region from 993 to 780 cm^{-1} contains only two bands at 882 and 816 cm^{-1}, we can propose the conformational structure of the macrocycle in free L.

The spectral conformational analysis was performed for B15C5 and related complexes [10]. The introduction of various substituents into the benzene ring of B15C5 was shown [11] to change the macrocycle conformation and to deviate the torsion angles from their ideal values (T-180, S-120, G-60, and C-180). The frequency–conformation correlation of the ethylene glycol unit for some azomethine derivatives of B15C5, nitrobenzo-15C5, and their complexes was determined on the basis of the X-ray diffraction [13–16] and spectral [11, 17, 18] data. Based on the results of these studies, we determined the macrocycle conformation in free L.

According to [10, 11], the band at 932 cm^{-1} in the IR spectrum of L correlates to the fragment of two units (TGT TGG) in the macrocycle, the low-intensity band at 953 cm^{-1} correlates to the TGT unit, and the band at 920 cm^{-1} is attributed to the vibration of the unit with a conformation close to TGG. The doublet of a medium-intensity band with a maximum at 855 cm^{-1} and a less intense band at 845 cm^{-1} is assigned to the vibration of the TGT unit. The band at 870 cm^{-1}, as well as the band at 829 cm^{-1}, is due to the vibration of the unit with a conformation close to TGS. The band at 766 cm^{-1} is attributed to the ν_{resp} pulsation vibration of the macrocycle.

Table 2. Assignment of selected vibrational frequencies (cm^{-1}) in the IR spectra of L and its complexes with zinc, nickel, cobalt, and copper perchlorates and hexafluorophosphates

Assignment	L	$Zn[PF_6]_2 \cdot 2L \cdot 3H_2O$	$Ni[PF_6]_2 \cdot 2L \cdot 2(C_2H_5OH) \cdot H_2O$	$Co[PF_6]_2 \cdot 2L \cdot 3H_2O$	$Cu[PF_6]_2 \cdot 2L$	$Zn[ClO_4]_2 \cdot 2L \cdot 3H_2O$	$Ni[ClO_4]_2 \cdot 2L \cdot H_2O$	$Co[ClO_4]_2 \cdot 2L \cdot 3H_2O$	$Cu[ClO_4]_2 \cdot 2L \cdot 3H_2O$
$\nu(PyO) + \nu(H_2CO)$	1352	1354	1355	1365	1360	1360	1364	1362	1362
$\delta(CH)_{Py}$, $\delta(CH)_{Ph}$		1304		1294 Ô	1305		1338	1303	1341
$\delta(CH_2)$		1290					1298		1303
$\nu_s(PhO)$, $\delta(NCH)$	1271	1272	1271	1268	1275	1273	1268	1271	1270
$\tau(CH_2)$, $\nu_{as}(PhO)$					1260				
	1250	1251	1248	1249	1248	1252	1253	1254	1254
		1243	1242		1236	1240			
$\nu(PyO) + \nu(H_2CO)$	1197	1215	1215	1216	1218	1216	1219	1219	1219
$\delta(CH)_{Ph}$	1177	1179	1182		1176	1181		1180	
		1163	1164	1166	1165	1168	1165	1162	1165
					1159	1161			
	1144	1138	1138	1135		1138	1140	1139	1139
$\nu_{as}(COC)$, $\nu(ClO_4^-)$	1144	1138	1138	1135	1129	1138	1140	1139	1139
	1119	1119	1118						
		1112	1111						
			1100	1106					
		1099		1095	1095	1098	1093	1097	1096
$\nu_s(COC)$, $\nu(CC)$	1087				1085				
		1079	1077	1075	1073	1075			
	1055	1053	1052	1055	1052	1056	1056	1055	1056
				1041	1037		1033	1033	1034
	1030	1026	1030	1032	1026	1023			
$\delta(CH)_{Ph}$, $\delta(CH)_{Py}$	1003		1015	1014	1012		1014	1015	1013
	982	990	991	991	993	987	987	985	986
	975	973	971	978	972	972	974	972	975

Table 2. (Contd.)

Assignment	L	$Zn[PF_6]_2 \cdot 2L \cdot 3H_2O$	$Ni[PF_6]_2 \cdot 2L \cdot 2(C_2H_5OH) \cdot H_2O$	$Co[PF_6]_2 \cdot 2L \cdot 3H_2O$	$Cu[PF_6]_2 \cdot 2L$	$Zn[ClO_4]_2 \cdot 2L \cdot 3H_2O$	$Ni[ClO_4]_2 \cdot 2L \cdot H_2O$	$Co[ClO_4]_2 \cdot 2L \cdot 3H_2O$	$Cu[ClO_4]_2 \cdot 2L \cdot 3H_2O$
$\nu_s(COC) + \nu(CC) + \rho(CH_2)$	953				953		960		
	932	933	936	937	942	932	932	932	932
	920	910		904	911				
					901				
	890				890	893	887	889	895
$\rho(CH_2) + \nu(CO), \nu(PF_6^-)$	870	875	876		874				865
	855				868	862		865	
	845	846	840	838	839	845	845	844	845
	828	833							
		814	811			816 Ô			
	808					801	801	798	798
$\nu_{resp}, \delta(CH)^{нп}_{Ph}, \delta(CH)^{нп}_{Py}$							801		
	791	794	795	793	792	793		798	
	766	765	766		764	765		767	766
					752		751		
	741	747	748	749	744	746		747	746
				740 Ô					
		727	727	728	727	728	726	727	729
$\delta(CCO) + \delta(COC) + \delta(NCC), \delta(CCC), \delta(CNC)$	697	701	701	698	699	700	701	700	700
	660	661	660	661	661	661	662	661	661
	648		642			638 Ô	642		
	630	638	632	629	633				
	622								
	607	611	612		613				
	589		594		577	591		589	593
									546
$\delta(PF_6^-)$		555	558	558	566				
$\delta(ClO_4^-)$						623	624	622	623

According to these data, the macrocycle conformation in a molecule of uncoordinated L can be presented as follows: TCT TGT TGG TGS TGT.

The characteristic, rather intense doublet bands at 808, 791 and 741, 730 cm^{-1}, which are related to the nonplanar bending vibrations of the benzene rings in the terpyridine moiety (816, 788 and 741, 732 cm^{-1} in the spectrum of CTP), almost retain their position in the spectrum of L. The band at 791 cm^{-1}is maximally intense due to the contribution of the bending vibrations of the benzene ring of the macrocycle.

The lower-frequency region in the spectrum of CTP exhibits four distinct medium-intensity bands at 680, 657, 623, and 572 cm^{-1}, which are due to the bending vibrations of the NCC, CCC, and CNC angles. In the spectrum of L, these bands are retained and appear at 697, 660, 629, and 622 cm^{-1}.

The complex formation of L through the nitrogen atoms of the terpyridine fragment results in certain changes in the IR spectrum.

Note that the vibrational spectra of all the synthesized complexes are analogous, except for the regions of the conformationally sensitive stretching–bending vibrations of the macrocycle (975–800 cm^{-1}). Some exception is the IR spectrum of the copper hexafluorophosphate complex in which many bands are split.

The ν_{Py} vibrations of terpyridine and ν_{Ph} of benzocrown ether appear in both the IR spectra of structurally studied complexes **I** and **II** and the spectra of other complexes in an interval of 1622–1514 cm^{-1}. The lowest-frequency band is assigned to the ν_{Ph} vibrations of the benzene ring of the crown ether. This band is somewhat shifted to the low-frequency region (7–10 cm^{-1}) compared to its position in the spectrum of the free ligand. The other frequencies in the spectra of all complexes in this region, assigned predominantly to the stretching vibrations of the heterocycles, are higher than similar frequencies of the free ligand. This increase in ν_{Py} upon coordination agrees with published data [19], where it was shown for nicotineamide that the coordination through the nitrogen heteroatom resulted in an increase in ν_{Py}.

The bands due to the ν_s(PhO) and ν_{as}(PhO) vibrations of the crown ether part of the L molecule do not almost change their position (Table 2), which confirms that the anisolic oxygen atoms are not involved in the coordination.

The IR spectra of the complexes exhibit the shift of the band at 1197 cm^{-1} (assigned to ν(Py–O) + ν(H_2CO)) by 8–10 cm^{-1} to the high-frequency region compared to its position in the spectrum of free L. Since in the spectra of L and its complexes this vibration appears as a narrow intense band, it can be considered as an analytical one for the determination of the coordination mode of L through the terpyridinic nitrogen atoms.

The 1150–1050 cm^{-1} region contains the ν_{as}(COC) and ν_s(COC) vibrations. In the IR spectra of the perchlorate complexes, this region exhibits the very intense band with a maximum at 1098–1093 cm^{-1} due to the stretching vibrations of the outer-sphere ClO_4^- anion, which overlaps the ν_{as}(COC) band. The $\delta(\mathrm{ClO}_4^-)$ bending vibrations appear as a medium-intensity band at 622–624 cm^{-1}.

The conformational structure of the macrocycles in the complexes can be judged about by an analysis of the spectral pattern in a region of 1000–700 cm^{-1}. According to the X-ray diffraction data [7], the conformation of the macrocycles in complex **II** can be described as T$_-$CT$_-$T$_-$GT TGG S$_-$G$_+$T$_-$TGT$_-$. According to the described correlations [10, 11] and X-ray diffraction data, the band at 932 cm^{-1} in the spectrum of this complex is caused by the T$_-$GT TGG fragment, the band at 862 cm^{-1} is related to the presence of the S$_-$G$_+$T$_-$ unit, and the band at 845 cm^{-1} is due to the ethylene glycol unit with the TGT conformation.

The conformation of the macrocycles in complex **I** is somewhat different: TCT T$_-$GT TGG SGT SGT. However, the macrocycles also contain the attachment of the T$_-$GT TGG units and, hence, the IR spectrum of the complex exhibits a band at 932 cm^{-1}. The band at 843 cm^{-1} corresponds to the TGT unit, and the band at 865 cm^{-1} corresponds to the units with the SGT conformation. Some difference in the wavelengths is due to the deviation of the torsion angles from ideality by different values.

An analysis of the discussed region in the spectral pattern of the structurally unstudied Ni(II) and Cu(II) perchlorate complexes shows that the macrocycles of the B15C5 ligand also contain the TGT TGG units of the fragments, because the spectra of the both complexes exhibit the band at 932 cm^{-1}. The unit of the TGT conformation with the corresponding band at 845 cm^{-1} and the unit close to SGT in conformation, and the bands at 866 and 865 cm^{-1} (the Ni(II) and Cu(II) complexes, respectively) are also observed. In addition, the spectrum of the nickel complex at 960 cm^{-1} contains the medium-intensity band due to the TGT unit.

Broad bands with two maxima at ~3580 and ~3446 cm^{-1} correspond to the stretching vibrations of the molecules of water of crystallization in the IR spectra of the structurally studied zinc and cobalt perchlorate complexes. Since the ν(H_2O) bands manifest themselves analogously in the spectra of the nickel and copper perchlorate complexes, water in these complexes is also outer-sphere.

The results of the gravimetric analysis of the complexes bearing the perchlorate ion are given in Table 3. The low temperature of water removal indicates in favor of its outer-sphere character.

Comparing the vibrational spectra of all the complexes containing the ClO_4^- anion, we can conclude that the Co, Zn, and Cu complexes are isostructural, most likely, and macrocycles of the ligands in all perchlorate complexes are similar by the conformational structure.

Table 3. Results of the thermogravimetric analysis of the $[ML_2](ClO_4)_2 \cdot nH_2O$ and $[ML_2](PF_6)_2 \cdot nH_2O \cdot mC_2H_5OH$ (M = Zn, Ni, Cu) complexes

Compound	Temperature of removal of water molecules, °C	Decomposition temperature, °C*
$[ZnL_2](ClO_4)_2 \cdot 3H_2O$	60 (two molecules), 100 (one molecule)	320
$[NiL_2](ClO_4)_2 \cdot H_2O$	100	390
$[CuL_2](ClO_4)_2 \cdot 3H_2O$	65 (one molecule), 130 (two molecules)	380
$[CoL_2](PF_6)_2 \cdot 3H_2O$	70 (one molecule), 150 (two molecules)	260, 350
$[ZnL_2](PF_6)_2 \cdot 3H_2O$	60 (one molecule), 180 (two molecules)	235, 380
$[NiL_2](PF_6)_2 \cdot 2(C_2H_5OH) \cdot H_2O$**	240	282, 365
$[CuL_2](PF_6)_2$		330

Notes: * The Co(II), Ni(II), and Zn(II) complexes decompose in two stages that cannot be separated.
** The temperature of removal of ethanol molecules is 50 and 160°C.

Since the nickel complex contains only one water molecule, its structure is probably somewhat different.

The region of ν_{as}(COC) and ν_s(COC) in the IR spectra of the complexes bearing the PF_6^- anion is free and, therefore, the changes caused by complex formation can be seen in this region. Two bands at 1143 and 1119 cm^{-1} were observed in this region of the IR spectrum of uncoordinated L, whereas the spectrum of the Zn complex contains the following bands: an intense band at 1138 cm^{-1}, low-intensity bands at 1119 and 1112 cm^{-1}, and a medium-intensity band at 1099 cm^{-1}1. According to the known correlations [10, 11], the band at 1119 cm^{-1} can be assigned to the vibration of the T_GG_+ unit, the band at 1112 cm^{-1} is ascribed to the TGS unit, and the band at 1099 cm^{-1} is attributed to the unit with the $T\_GT\_$ conformation.

A broad and very intense band at 845–833 cm^{-1} appears in a lower-frequency range of 950–800 cm^{-1} in the spectra of all hexafluorophosphate complexes. This band is due to the stretching vibrations of the PF_6^- anion and overlaps the most part of the bands of the stretching–bending vibrations of the macrocycle. Nevertheless, the spectrum of the zinc complex contains a medium-intensity band at 933 cm^{-1} (932 cm^{-1} in spectrum of L), which can be ascribed to the TGT TGG fragment. The low-intensity band at 910 cm^{-1} is due to the vibration of the unit in the TGG conformation.

In the spectra of all complexes, the PF_6^- bending vibrations of the anion appear in the interval from 558 to 555 cm^{-1} as a narrow intense band.

Well resolved bands at 3637, 3535, and 3435 cm^{-1} correspond to the stretching vibrations of the water molecules in the spectrum of the zinc complex. The IR spectrum of the cobalt complex exhibits the $\nu(H_2O)$ bands in almost the same regions. As in the case of the structurally studied Zn(II) and Co(II) perchlorate complexes, the $\nu(H_2O)$ bands are due to the stretching vibrations of molecules of the outer-sphere water involving in hydrogen bonding.

The results of the thermogravimetric analysis of the complexes bearing the hexafluorophosphate ion are presented in Table 3.

The IR spectrum of the nickel hexafluorophosphate complex is analogous to that of the zinc hexafluorophosphate complex in the whole spectral range including the conformationally sensitive regions (Table 2). The spectrum of the nickel complex in the ν_{as}(COC) and ν_s(COC) regions also contains three bands at 1118, 1111, and 1100 cm^{-1} attributed to the TGG, TGS, and TGT ethylene glycol units, respectively. Another conformationally sensitive region exhibits a band at 936 cm^{-1} attributed, most likely, to the TGT TGG fragment and a band at 912 cm^{-1}, which is related, in our opinion, to the unit close in conformation to TGG or SGG. Thus, the analysis of the vibrational spectra suggests that in the nickel and zinc complexes the B15C5 macrocycles have a very similar conformation.

The spectrum of the cobalt hexafluorophosphate complex somewhat differs from those of the above-mentioned compounds: this spectrum is smoother and, hence, the macrocycle of the ligand molecule is conformationally more uniform, because only bands related to the ethylene glycol units of the TGT and TGG conformations can be distinguished in the IR spectrum (TGT, 1103 and 1095 cm^{-1}; TGG, 904 cm^{-1}; TGT TGG, 937 cm^{-1}).

More considerable differences are observed in the IR spectrum of the copper hexafluorophosphate complex. In spite of the fact that the general character of the spectrum is retained, many its bands are split. Three bands are detected in the ν_{as}(COC) region of the IR spectrum: an intense band at 1128 cm^{-1} related, according to the correlations [10, 11], to a unit similar in conformation to TGG or SGG; a medium-intensity band at 1112 cm^{-1} attributed to the TGS unit; low-intensity band at 1095 cm^{-1} due to the TGT unit. The 950–800 cm^{-1} region contains bands related to the units with conformations close to those mentioned above: 953 (TGT), 942 (TGT TGS or TGT SGG fragment, and 911 (TGG or TGS).

A new (compared to the spectrum of the free ligand and those of other metal hexafluorophosphate complexes) medium-intensity band appears at 868 cm^{-1} in the IR spectrum of the copper complex. This band can be attributed to the fact that the macrocycles contain a unit in another conformation compared to those discussed above. Taking into account the correlations [10, 11] and the fact that the bands at 869–880 cm^{-1} in the spectra of the crown–azomethine complexes [11–14] were attributed to the vibrations of the units with the *trans*-conformation at the C–C bond (STT, STS, STG, GTT), we can conclude that in the copper hexafluorophosphate complexes at least one ethylene glycol unit has a conformation similar to those listed above.

The copper complex contains no water molecules, which can be a reason for the different crystal structure of this compound. In addition, it was structurally found for the formation of the intracomplex copper salt $\mathrm{CuL'_2}$ with the azomethine derivative B15C5 (L' is 4'-[2-(tosylamino)benzylideneamino]-2,3-benzo-15-crown-5) that the both macrocycles in the composition of the compound had different conformations, unlike the zinc salt with analogous composition [7]. Perhaps, in the copper hexafluorophosphate complex the B15C5 macrocycles also have different conformations, resulting in a more complicated spectrum of the complex compared to the spectra of other complexes.

In the IR spectra of all the synthesized complexes, the bands attributed to the bending vibrations of the NCC, CCC, and CNC angles of the terpyridine moiety are somewhat shifted to the high-frequency region compared to their position in the spectrum of free L (Table 2), which also confirms the coordination of the nitrogen atoms by the complexing metal atom and agrees with published data [19].

The studies showed that the transition metals coordinate L to the nitrogen heteroatoms accompanied by a change in the conformation of the B15C5 macrocycles. The change depends on both the complexing metal and the nature of the anion. The coordination by the cobalt cation results in a more symmetrical conformation of the B15C5 macrocycles regardless of the anion nature. The strongest changes in the conformational respect occur in the B15C5 macrocycles of the L molecule in the copper hexafluorophosphate complex.

In the case of the perchlorate complexes, the compounds similar in structure and conformation of the macrocycles are formed. It is most likely that the hexafluorophosphate complexes are of different structures.

The difference in the conformation of the B15C5 macrocycles of the L molecule in the complexes and in the free ligand can be a reason for different selectivities of these compounds when they are used as active components of plasticized membranes of ion-selective electrodes. The study of their properties is the subject of our further research.

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