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Synthesis, Vibrational Spectra, and Structure of 4'-(4''-Benzo-15-Crown-5)oxy-2,2':6',2''-Terpyridine (L) and Its Transition Metal Complexes. Extraction and Ion-Selective Properties of L

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Abstract—Complexes of Co(II), Ni(II), Zn(II), and Cu(II) perchlorates and hexafluorophosphates with 4'-(4''-benzo-15-crown-5)oxy-2,2':6',2''-terpyridine (L) $[M(L)_2](ClO_4)_2 \cdot 3H_2O$ and $[M(L)_2](PF_6)_2 \cdot 2H_2O$ were synthesized. The spectral criteria of ligand coordination through the terpyridine nitrogen atoms were established. An assumption concerning the benzo-15-crown-5 conformation in the ligand molecule in the synthesized complexes was made. The extraction and ion-selective properties of L were studied.

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Derivatives of 2,2':6',2''-terpyridine (Tpy) and its metal complexes are currently the subject of keen attention of researchers owing to the wide scope of their practical application caused by their unique physicochemical properties. It is known that Pd(II), Pt(II), and Au(III) complexes with Tpy and its various functional derivatives possess unique luminescence properties, can react with DNA and are biologically active, which is promising for the design of labels in biological assays and in tumor therapy [1, 2]. The Co(II) complex with thio-substituted Tpy exhibits superconductivity owing to the stacking interaction of the pyridine rings and is promising for the design of nanolevel devices, "molecular transistors" [3, 4]. Metal complexes with terpyridines are used as catalysts of organic reactions, for example, in alkene epoxidation and aziridation [5, 6]. The inclusion of terpyridine fragments in polymers is useful for the design of new-generation sensors [7].

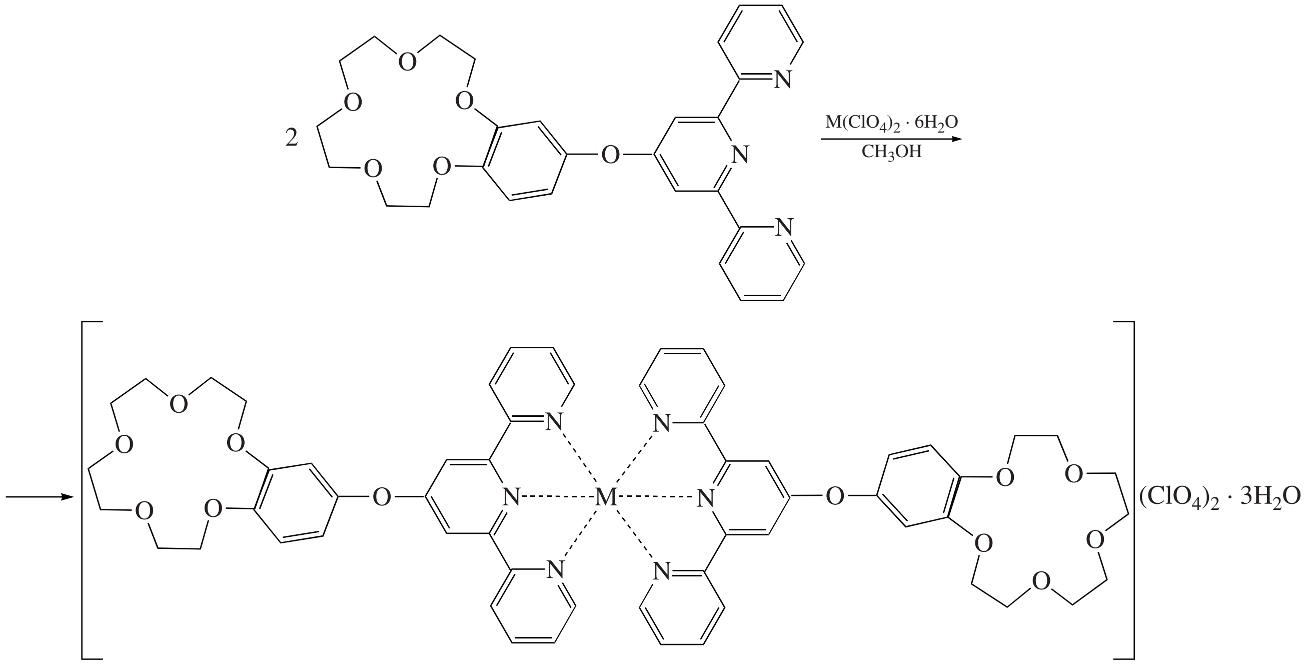
Of particular interest are heterotropic terpyridine ligands comprising coordinating fragments of various compound classes. These can be used to develop supramolecular assemblies. A bisterpyridine cycle and a supramolecular Cu(II) complex obtained from this cycle as a polymeric chain have been reported [8]. The synthesis of crown-substituted terpyridines potentially capable of forming supramolecular assemblies is important as these organic ligands have remained almost uninvestigated before our studies.

Previously [9, 10], we reported the synthesis and structure of transition metal complexes with 4'-(4'''-benzo-15-crown-5)methyloxy-2,2':6',2''-terpyridine (L'). As a continuation of the research into the complexing and ion-selective properties of crown terpyridine derivatives, we synthesized a new ligand, 4'-(4'''-benzo-15-crown-5)oxy-2,2'-terpyridine (L) and Ni(II), Co(II), Cu(II), and Zn(II) perchlorate and hexafluorophosphate complexes based on this ligand. The vibrational spectra of these compounds were studied, the spectral criteria for ligand coordination through nitrogen heteroatoms were established, and an assumption was made concerning the benzo-15-crown-5 (B15C5) macrocycle conformation in the complexes. The extraction and ion-selective properties of L were studied.

EXPERIMENTAL

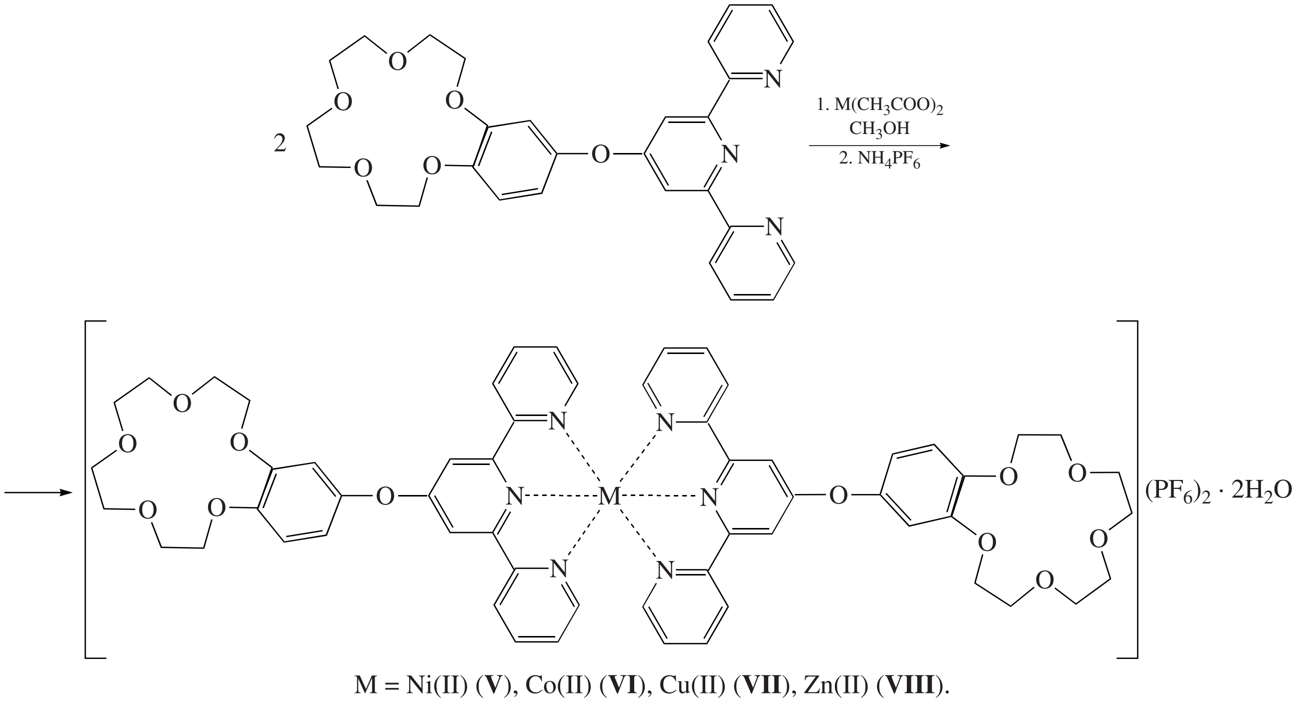
Commercial chromatography grade methanol (LabScan), Reagent ACS acetonitrile (Acros Organics), 99% ammonium hexafluorophosphate (Acros Organics), and nickel(II), cobalt(II), copper(II), and zinc(II) perchlorate hexahydrates and acetate hydrates (Aldrich) were used.

The synthesis procedure and X-ray diffraction data for L were described previously [11]. Transition metal perchlorate complexes with L: $[CoL_2](ClO_4)_2 \cdot 3H_2O$ (**I**), $[ZnL_2](ClO_4)_2 \cdot 3H_2O$, (**II**) $[NiL_2](ClO_4)_2 \cdot H_2O$ (**III**), and $[CuL_2](ClO_4)_2 \cdot 3H_2O$ (**IV**) were prepared as shown in the Scheme [9]:



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

Synthesis of [ML$_2$](PF$_6$)$_2$ · 2H$_2$O complexes (M = Ni (V), Co (VI), Cu (VII), and Zn (VIII)). Methanol solutions of the corresponding metal acetate and L (M : L = 1 : 2) were mixed at room temperature. A 40-fold molar excess of ammonium hexafluorophosphate was added to the mixture to precipitate the corresponding complex. The precipitate was filtered off, washed with methanol and diethyl ether, dried in a vacuum, and recrystallized from an ethanol–acetonitrile mixture (3 : 1 by volume).



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

Table 1. Results of elemental analysis of Co(II), Ni(II), Zn(II), and Cu(II) complexes with L ($C_{29}O_6N_3H_{29}$)

Compound	Content (found/calculated), %		
	C	H	N
$Ni(ClO_4)_2 \cdot 2(C_{29}O_6N_3H_{29}) \cdot H_2O$	49.71/51.88	6.19/6.26	3.77/4.37
$Co(ClO_4)_2 \cdot 2(C_{29}O_6N_3H_{29}) \cdot 3H_2O$	51.62/51.87	6.52/6.26	4.19/4.80
$Cu(ClO_4)_2 \cdot 2(C_{29}O_6N_3H_{29}) \cdot 3H_2O$	50.26/51.69	6.26/6.24	4.26/4.79
$Zn(ClO_4)_2 \cdot 2(C_{29}O_6N_3H_{29}) \cdot 3H_2O$	51.67/51.62	6.47/6.23	5.66/4.78
$Ni(PF_6)_2 \cdot 2(C_{29}O_6N_3H_{29}) \cdot 2H_2O$	49.17/49.20	6.04/5.94	4.04/4.41
$Co(PF_6)_2 \cdot 2(C_{29}O_6N_3H_{29}) \cdot 2H_2O$	48.43/49.20	5.94/5.94	3.64/4.41
$Cu(PF_6)_2 \cdot 2(C_{29}O_6N_3H_{29}) \cdot 2H_2O$	49.51/49.04	6.13/5.92	4.43/4.40
$Zn(PF_6)_2 \cdot 2(C_{29}O_6N_3H_{29}) \cdot 2H_2O$	47.96/48.97	5.96/5.91	3.77/4.39

The results of elemental analysis are summarized in Table 1.

The IR absorption spectra were recorded on a Vertex 70 Bruker spectrometer in the 4000–400 cm^{-1} range for mineral oil mulls.

For extraction experiments, 10^{-2} M solutions of ligands in chloroform and aqueous solutions of nitrates of all elements to be determined with a 10^{-3} mol/l concentration in relation to each element were prepared from exact weight portions. To 0.5 ml of each aqueous solution, 0.1 or 1 M HNO_3 (1.5 ml) was added (the experiments were carried out at pH 1 and 0).

Extraction experiments were carried out in ground-stoppered test tubes at room temperature with 1 : 1 volume ratio of organic and aqueous phases. The solutions were stirred on a stirring device at 60 rpm for 1 h, which was sufficient for invariable distribution ratios to be attained. The contents of elements in the equilibrated aqueous solutions were determined by inductively coupled plasma mass spectrometry (ICP-MS). After extraction prior to the MS determination, aliquots of the starting solutions in the aqueous phase were diluted 40-fold with a 2% solution of HNO_3, and 0.1 ml of a 10^{-6} M solution of $CsNO_3$ was added to the resulting solution as an internal standard. Determination was carried out on a Plasma Quard VG mass spectrometer (UK) at the Institute of Solid State Physics of the RAS. The limit of metal determination was 0.03 μg/l.

The plasticized polymeric membranes containing L and L' were prepared by a eported procedure [12] (a solution of the active component in the organic plasticizing solvent was introduced into a polyvinyl chloride matrix). The membranes had the following composition (wt. %): neutral carrier, 1; polyvinyl chloride, 33; plasticizer, 66. As the plasticizer, *o*-nitrophenyl octyl ether (ε = 23) was used. Polyvinyl chloride was dissolved in cyclohexanone. The resulting mixture was poured into a glass Petri dish and left in air until it was completely dry (5 to 7 days). Discs 5 to 7 mm in diameter were cut out of the resulting membrane and glued to the end of the polyvinyl chloride tube by a special adhesive (composition of the membrane). The electrode thus obtained was soaked for 24 h in a 10^{-2} M solution of KCl for L and 10^{-2} M solution of $CuCl_2$ for L'. An OP-082OP (Radelkis) silver chloride electrode was used as the reference electrode.

The electroanalytical parameters were measured by placing the tested electrode coupled with the standard reference electrode into the tested solution and measuring the emf (mV).

The measuring circuit for L was as follows:

Ag, AgCl | KCl (1 M)| tested solution | membrane | KCl (10^{-2} M) | AgCl, Ag

The measuring circuit for L' was as follows:

Ag, AgCl | KCl (1 M)| tested solution | membrane | $CuCl_2$ (10^{-2} M) | AgCl, Ag

The emf was measured by an OP-300 pH ion meter (Radelkis, BHP). The electroanalytical parameters of ion selective electrodes were determined according to IUPAC recommendations [13] at pH 5–7 and the selectivity coefficients were determined by the method of bionic potentials.

RESULTS AND DISCUSSION

According to powder X-ray diffraction data [11], the structural units of ligand L are isolated non-planar molecules.

When assigning the vibration frequencies in the IR spectra of ligand L, we proceeded from the fact that L is a more rigid analog of ligand L' [10]. The difference between the structures of L and L' is only the presence of the CH_2 group between the terpyridine and crown ether fragments in L'. Therefore, all assignments of the principal IR vibration frequencies carried out for L' were considered to be also valid for L (the assignment for some IR vibration frequencies of L is given in Table 2).

We will consider only the vibration frequencies that allow one to draw conclusions about the coordination mode of the ligand and also the vibration frequencies in the conformationally sensitive regions, which can be used to determine the conformation of the ethylene glycol units in the macrocycle.

It was found [10] that incorporation of the $–H_2C–O–$ fragment between the terpyridine and crown-ether moieties in L' gives rise to two new bands in the IR spectrum as compared with the spectra of Tpy and B15C5 (~1352 and 1197 cm^{-1}). When establishing the coordination of L' through the nitrogen heteroatoms, the band at 1197 cm^{-1} was considered as analytical. Upon coordination of L' by transition metals, this band shifts by ~8 cm^{-1} to higher frequencies. These regions of the spectrum of L also exhibit two bands (1358 and 1195 cm^{-1}), their positions and intensity ratio being retained almost invariable on passing from L' to L. Also, a new strong band appears in the IR spectrum of L at about 1229 cm^{-1}. These three bands (1358, 1229, and 1195 cm^{-1}) correspond to the Py–O–Ph fragment in L molecule and are probably due to symmetric and antisymmetric vibrations of the $C_{Py}–O–C_{Ph}$ group.

According to X-ray diffraction data, the conformation of the B15C5 macrocycle in L is described by the formula: TCT T_GS_+ T_G_G S_+TG_+ SG_+T. In conformity with the conformational nonuniformity of B15C5, the conformationally sensitive ν_{as}(COC) and ν(CO) + ν(CC) + $\rho(CH_2)$ regions of the IR spectrum of L contain a large number of bands. A similar situation was observed for L'. This allowed us to assume, on the basis of spectral data, conformational nonuniformity of the B15C5 macrocycle in L' and to suggest its conformational structure [10]. The conformation of B15C5 in the uncoordinated L' molecule can be represented as TCT TGT TGG TGS TGT. When comparing the conformational formulas of B15C5 in L and L', one can see that the macrocycles differ by the conformational composition of the ethylene glycol units. This fact confirms the influence of substituents in the benzene ring of B15C5 on the macrocycle conformation.

The conformationally sensitive ν_{as}(COC) region of the IR spectrum of L shows two bands: a strong band at 1127 cm^{-1} corresponding, according to structural data, to the TGG unit, and a weaker band at 1090 cm^{-1} corresponding to the TGS_+ unit. In the range of 950–800 cm^{-1}, note bands for the T_GS_+ T_G_G fragment (938 cm^{-1}) and the T_GS_+ unit (854 and 840 cm^{-1}). The band at 867 cm^{-1} can be assigned to the STG unit according to reported correlations [14].

The complexation of L with transition metals results in pronounced changes in the IR spectrum (Table 2). Irrespective of the nature of the metal and the anion, the spectra of the complexes are similar over the whole spectral range including the conformationally sensitive region. Generally, the spectra of these complexes are simpler and smoother not only than the spectrum of L but also than the spectra of analogous complexes with L'. This fact suggests a different structure for these compounds compared to the complexes with L' and higher conformational uniformity of the B15C5 macrocycles in the coordinated ligands. One can also assume that the macrocycles in the complexes with L we studied are closely similar in the conformational structure.

In the complexes with L, the ν_{Py} and ν_{Ph} vibrations of the benzocrown ether occur approximately in the same spectral range (1602–1510 cm^{-1}) as in the case of complexes with L' [10]. The lowest-frequency band corresponding to the ν_{Ph} mode of the B15C5 benzene ring is somewhat shifted (5–8 cm^{-1}) to lower frequency with respect to its position in the spectrum of free L. The other band frequencies in the spectra of all complexes in this region, assigned mainly to the stretching vibrations of heterocycles, occur at higher frequencies than these bands of the free ligand. This increase in the ν_{Py} frequency is indicative of coordination of L through nitrogen heteroatoms, as was established for complexes with L' and confirmed by X-ray diffraction for a number of complexes [9].

The ν_s(PhO) and ν_{as}(PhO) bands barely change their positions (Table 2), indicating that the anisole oxygen atoms are not involved in the coordination.

The IR spectra of complexes with L exhibit a shift of bands assigned to ν(PyO) + ν(PhO): the band at 1195 cm^{-1} shifts to higher frequency and the band at 1229 cm^{-1} shifts to lower frequency. As a result, a new weaker broad band appears in the spectra of complexes at 1213–1208 cm^{-1}.

In the case of complexes with L', the shift of the ν(PyO) + $\nu(H_2CO)$ band (1197 cm^{-1}) by 5–8 cm^{-1} to higher frequency was indicative of ligand coordination through nitrogen atoms, which was confirmed by X-ray diffraction data. Thus, the band in the range of 1213–1208 cm^{-1} in the spectra of complexes with L was considered as an analytical band indicative of coordination through nitrogen atoms.

The complexation also induces pronounced changes in the conformationally sensitive spectral regions. Thus in the ν_{as}(COC) region, the spectra of metal hexafluoro-

Table 2. Assignment of the key IR vibration frequencies (cm^{-1}) of nickel, cobalt, and copper perchlorate and hexafluorophosphate complexes

Assignment	L	$[Ni(L)_2](ClO_4)_2 \cdot H_2O$	$[Co(L)_2](ClO_4)_2 \cdot 3H_2O$	$[Cu(L)_2](ClO_4)_2 \cdot 3H_2O$	$[Zn(L)_2](ClO_4)_2 \cdot 3H_2O$	$[Ni(L)_2](PF_6)_2 \cdot 2H_2O$	$[Co(L)_2](PF_6)_2 \cdot 2H_2O$	$[Cu(L)_2](PF_6)_2 \cdot 2H_2O$	$[Zn(L_1)_2](PF_6)_2 \cdot 2H_2O$
ν(PyO) +	1358	1367	1365	1365	1365	1376	1367	1366	1376
ν(PhO)									
$\delta(CH)_{Py}$	1337	1300	1302	1302	1297	1303	1303	1303	1301
$\delta(CH)_{Ph}$	1295								
$\delta(CH_2)$	1281								
ν_s(PhO),	1263	1262	1260	1261	1263	1262	1262	1260	1262
δ(NCH)									
$\tau(CH_2)$	1248	1249	1249	1250	1250	1251	1249	1251	1246
ν_{as}(PhO)	1246								
ν(PyO) +	1229								
ν(PhO)		1209	1209	1212	1211	1210	1209	1214	1210
	1195								
$\delta(CH)_{Ph}$	1157	1160	1162	1162	1163	1163	1163	1163	1163
	1140						1145		
	1127	1127	1131	1129	1129	1128			
ν_{as}(COC)	1141								
	1127	1127	1131	1129	1129	1128	1126	1126	1127
$\nu(ClO_4^-)$	1090								
		1083	1083	1086	1086				
ν_s(COC)						1080	1072	1079	1078
ν(CC)	1054	1055	1056	1057	1055	1054	1053	1054	1053
		1033	1027	1033	1026	1034	1027	1033	1033
$\delta(CH)_{Ph}$	999	1017	1015	1016	1014	1017	1016	1013	1015
$\delta(Cç)_{Py}$	988	991	988	989	990	991	988	991	991
	971	977							
ν(CO) +	938	944	943	944	943	944	945	946	944
ν(CC) +		932	932 sh	933	932 sh				
$\rho(CH_2)$,									
$\delta(CH)_{Ph}$	882	885	885	886	887				
$\rho(CH_2)$ +	867	866	857	861	858	875	874	873	874
ν(CO)	855	850							
	846								
	840								
	829								
$\nu(PF_6^-)$						840	837	838	840
ν_{resp}	808								
$\delta(CH)^{np}_{Ph}$	794	795	794	795	797	794	792	796	792
$\delta(CH)^{np}_{Py}$	732	748	745	745	748	749	740	743	748
		726	727	726	726	727	724	727	725
	699								
δ(CCO) +	665								
δ(COC) +	657	655	656	655	658	657	657	656	656
δ(NCC)	628	642	639		640	641	641	635	640
δ(CCC)	622								
δ(CNC)	614					612	612	616	614
	585								
	559								
	543								
$\delta(ClO_4^-)$		621	624	621	622				
$\delta(PF_6^-)$						557	557	558	554

Table 3. Distribution ratios for various elements with L and L' used as extractants (c_{HNO_3} = 0.1 and 1 mol/l)

Element	L		L'	
	c_{HNO_3} = 0.1 mol/l	c_{HNO_3} = 1 mol/l	c_{HNO_3} = 0.1 mol/l	c_{HNO_3} = 1 mol/l
Na(I)	0.26	0.27	0.31	0.34
K(I)	0.20	0.42	0.40	0.42
Mg(II)	0.27	0.36	0.29	0.32
Ca(II)	0.35		0.08	0.08
Al(III)	0.13	0.26	0.39	0.23
Cr(III)	0.33	0.39	0.38	0.32
Fe(III)	0.25	0.35	0.28	0.28
Ni(II)	3.33	1.12	20.92	3.71
Cu(II)	2.00	0.81	5.80	2.94
Zn(II)	3.22	0.51	6.94	0.34
Cd(II)	2.05	0.42	1.08	0.30
Zr(IV)	0.14	0.16	0.13	0.09
Nb(V)	0.35	0.19	0.26	0.26
La(III)	0.22	0.20	0.22	0.15
Eu(III)	0.18	0.21	0.21	0.16
Gd(III)	0.38	0.20	0.41	0.22
Hf(IV)	0.34	0.18	0.34	0.13
W(VI)	0.17	0.07	0.44	0.13
Pb(II)	0.39	0.50	0.42	0.45
Bi(III)	0.31	0.14	0.66	0.09
Th(IV)	0.30	0.19	0.31	0.13
U(VI)	0.36	0.17	0.34	0.13

phosphate complexes **V–VIII** exhibit only one band in the range of 1128–1125 cm^{-1} (Table 2), whereas the spectrum of L has three bands: 1141, 1127, and 1090 cm^{-1}. The same region in the IR spectra of metal perchlorate complexes **I–IV** shows a strong broad band (with a maximum at 1086–1082 cm^{-1} corresponding to $\nu(ClO_4^-)$), which masks the ν_{as}(COC) band.

In another conformationally sensitive region (870–800 cm^{-1}), the spectral pattern is also markedly simpler for any of the complexes than for free L. In the spectra of **I–IV**, note a broad asymmetric medium-intensity band with maxima at 944 and 932 cm^{-1} and a weaker band with a maximum at 857 cm^{-1}. An exception is the nickel perchlorate complex whose spectrum exhibits, apart from the band at 944 cm^{-1}, two bands at lower frequencies (866 and 850 cm^{-1}).

In the IR spectra of **V–VIII**, the region in question shows a strong $\nu(PF_6^-)$ band. Nevertheless, the spectra of all of these compounds also show a medium-intensity band at 945 cm^{-1}.

According to spectral and X-ray diffraction data for complexes with L' and reported correlations [14], the bands in the range of 944–932 cm^{-1} can be attributed to the presence of a B15C5 fragment with a conformation close to TGT TGG, while the band at 857 cm^{-1} can be assigned to a nearly-TGT unit. These results suggest that in all of the complexes with L, the B15C5 macrocycle in the ligand is composed of units with conformations close to those listed above (TGG, TGT).

Note that the band recorded at 867 cm^{-1} in the spectrum of free L, which was assigned to an STG unit of B15C5, is absent in the spectra of all synthesized complexes. Apparently, upon coordination, this ethylene glycol unit changes the conformation. An exception is the nickel perchlorate complex **I**, for which a medium-intensity band is retained in the spectrum at 866 cm^{-1}.

Generally, the spectral data point to a higher conformational uniformity of B15C5 macrocycles in transition metal complexes than in free L.

The narrow rather strong bands at ~622 and ~557 cm^{-1} correspond to bending vibrations of the perchlorate and hexafluorophosphate ions, respectively.

All perchlorate (**I–IV**) and hexafluorophosphate (**V–VIII**) complexes with L contain water. The presence of outer-sphere water molecules in these complexes follows from the medium-intensity broad band at 3583–3190 cm^{-1}.

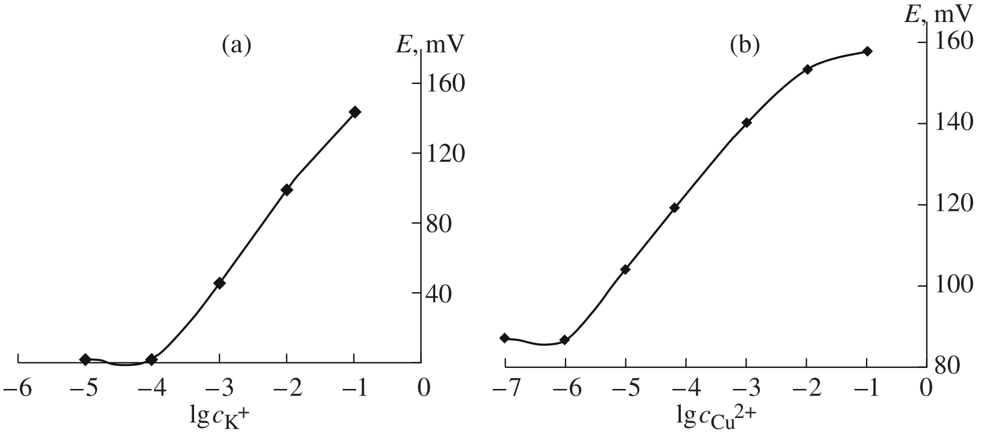


Fig. 1. Electrode functions of (a) K^+-selective electrode based on L and (b) Cu^+-selective electrode based on L'.

We studied the extraction ability of L in comparison with L' toward alkali, alkaline earth, transition, and rare earth metal cations. In the study of extraction processes, the distribution ratio (D) was defined as the ratio of the metal concentration in the organic phase to the metal concentration in the aqueous phase in the presence of nitric acid. Table 3 presents the D values determined at two different concentrations of HNO_3 (0.1 and 1 mol/l).

The bisfunctional ligands L and L' possess coordinating fragments of different nature (N-donor and O-donor), each making its own contribution to the extraction properties. As the nitric acid concentration increases, the nitrogen atoms of the pyridine rings are protonated, which results in the loss of their donor properties.

The experiments demonstrated that in the extraction of transition and rare earth metals in the presence of L and L', an increase in the nitric acid concentration results in a decrease in the distribution ratios D for these ligands and, as a consequence, in a decrease in the extraction efficiency. This fact indicates that the major contribution to the extraction ability of L and L' is made by their N-donor terpyridine fragments. The extraction of alkali and alkaline earth metals almost does not depend on the HNO_3 concentration.

The distribution ratios for L do not exceed 3.3, which is too low for the possible use of L as an extractant for transition and alkali metal cations.

At low nitric acid concentration, L' is an efficient extractant for transition metals such as Cu(II), Zn(II), Ni(II) (D = 5.80, 6.94, and 21, respectively). The extraction ability of L' with respect to other metal cations (alkali and alkaline earth cations) is low, which attests to a low degree of participation of the donor oxygen atoms of the crown-ether fragment in the extraction interactions.

The potentiometric selectivity of organic ligands is known to be in good agreement with their extraction and complexing properties [15]. Therefore, we carried out studies in which L and L' served as active components of the plasticized polymeric (polyvinyl chloride) membranes.

Characteristics of a K^+-selective electrode based on L are presented in Fig. 1a. The linear response of the electrode potential was found in the pK^+ range of 1.0 to 4.0, the slope of the electrode function was 48.0 ± 0.5 mV/pK^+ at 20°C in aqueous solutions of KCl.

Characteristics of a Cu^{2+}-selective electrode based on L' are presented in Fig. 1b. The linear response of the electrode potential was found in the pCu^{2+} range of 2.0 to 6.0, the slope of the electrode function was 19.1 ± 0.5 mV/pCu^{2+} at 20°C in aqueous solutions of $CuCl_2$.

Logarithms of the selectivity coefficients of the electrodes $\log K^{pot}_{K^+/M^{z+}}$ (for L) and $\log K^{pot}_{Cu^{2+}/M^{z+}}$ (for L') with respect to most of interfering ions are in the range of –2 to –3 (Fig. 2a, 2b). For comparison, the logarithms of the selectivity coefficients of a Pb^{2+}-selective electrode based on B15C5 are also given (Fig. 2c) [16]. Characteristics of the electrodes based on L and L' are comparable with those of the previously developed electrodes based on benzo-15-crown-5 and other crown compounds [16–19].

The results of extraction experiments with L and L' show that minor changes in the composition and structure of the ligand result in considerable changes in extraction properties. Thus ligand L' is more flexible and conformationally mobile compound than L, which must affect the extraction properties.

Our studies of ion-selective properties showed that, first, compounds L and L' have rather high potentiometric selectivity with respect to the K^+ and Cu^{2+} cations, respectively. Second, the introduction of substituents into a benzo-15-crown-5 molecule changes considerably the ion-selective properties. The changes may be due, on the one hand, to geometric difference between these molecules and, in the other hand, to the difference between the macrocycle conformations in L and L'.

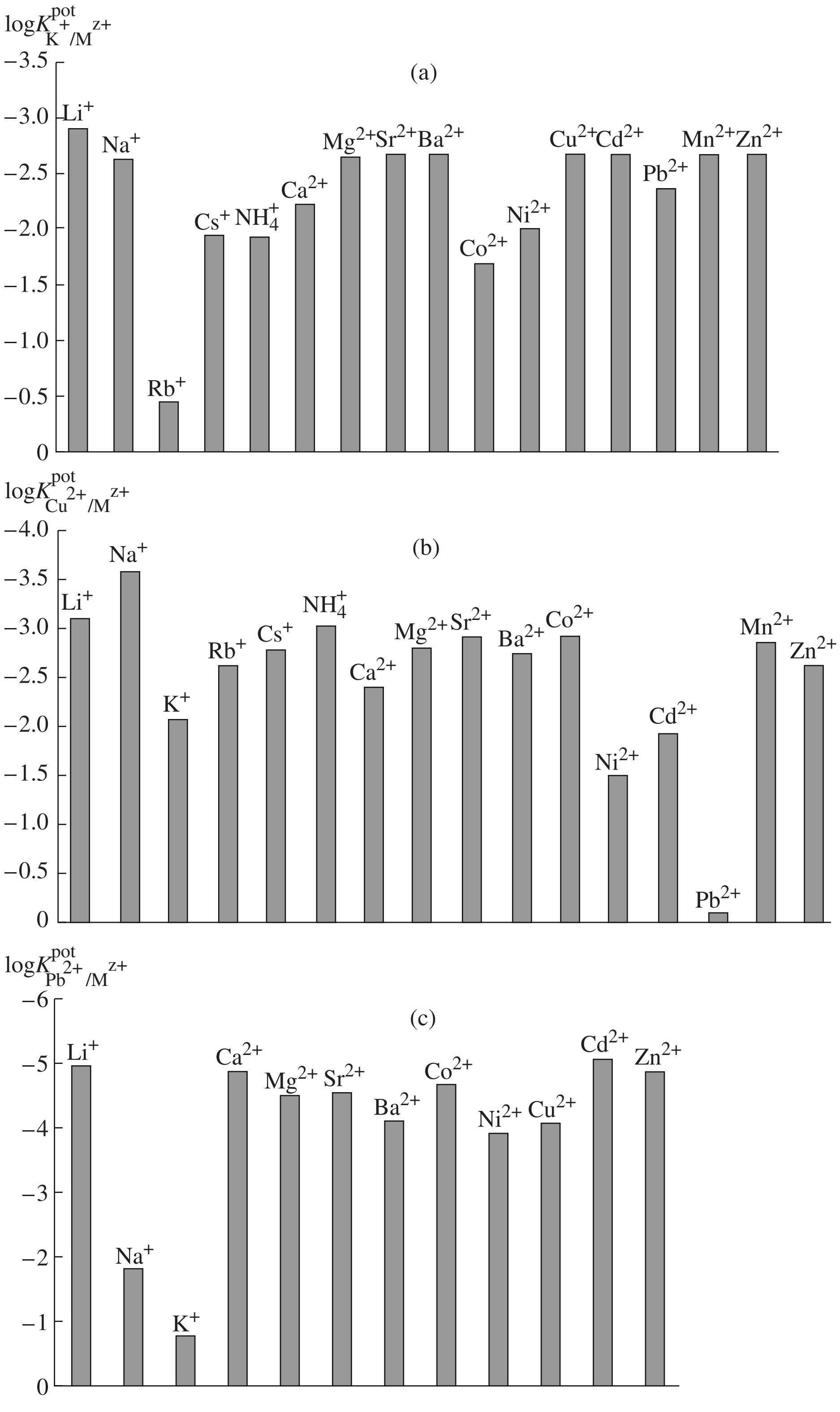


Fig. 2. Potentiometric selectivity coefficients of (a) K^+-selective electrode based on L, (b) Cu^+-selective electrode based on L', and (c) Pb^{2+}-selective electrode based on B125C5 [16]

Data from IR spectroscopy allowed us to suggest that transition metal complexes with L are closely similar in structure, which does not depend on the nature of the metal or the anion. The possibility of polymeric structure cannot be ruled out. The B15C5 macrocycles of molecule L in all of these complexes have similar conformations and the conformational composition of the ethylene glycol units is more uniform than that in free L.

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