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IR Study of Complexation in the System 1,10-Phenanthroline–$LiClO_4$ ($NaClO_4$)–Acetone

A. S. Denisova and M. B. Lysinova

Research Institute of Chemistry, St. Petersburg State University, St. Petersburg, Russia

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Abstract—By *ab initio* calculations, the molecular geometries of 1,10-phenanthroline and its 1 : 1 and 1 : 2 complexes with lithium and sodium ions were optimized, and the frequencies and intensities of normal modes of these species were evaluated. The experimentally observed bands were assigned on the basis of the calculation results. The concentration dependences of the IR spectra of the system 1,10-phenanthroline–$LiClO_4$ ($NaClO_4$)–acetone-d_6 (C_{phen} 0.05, C_{salt} from 0 to 1 M) were interpreted. The formation of the 1 : 1 and 1 : 2 complexes was confirmed spectroscopically.

Interest in complexes of 1,10-phenanthroline and its derivatives with Li^+ and Na^+ ions is due to the possibility of using such ligands in clinical lithium sensors, primarily potentiometric, applicable in media with a large excess of sodium ions [1]. To optimize the sensor selectivity, it is necessary to know the stoichiometry and constants of complexation of the sensor substance with ions in an ion-selective membrane [2, 3].

From the vibration spectra of solutions containing a ligand and a metal salt, it is possible to evaluate the concentration distribution of coexisting species and the step complexation constants, provided that the states of the ligand in complexes of different stoichiometries are spectroscopically discernible; if the spectral characteristics of complexes of different stoichiometries coincide, only the overall complexation constants can be determined. An IR study of complexation involves assignment of the vibration bands of the ligand in the free state and in complexes. With simple ligands like NH_3 or CN^-, or with ligands in which the complexing groups have characteristic bands sensitive to complexation with a metal (e.g., β-diketones, carboxylic acids, primary amines [4]), interpretation of the vibration spectra involves no problems. However, the assignment becomes considerably more difficult when one or several ligand molecules coordinate with the metal in a polydentate mode to form chelates. Such a case is typical for the majority of compounds showing promise as analytical sensors: crown ethers, carboxamides, and aromatic heterocycles, including 1,10-phenanthroline derivatives [5, 6].

Assignment of normal modes in the spectra of multicentered chelates is often made using the isotope shifts of the frequencies in the spectra of the deuterated complexes [7]; however, deuteration can be performed only with a limited set of compounds.

In this work we studied complexation in the system 1,10-phenanthroline–$LiClO_4$ ($NaClO_4$)–acetone by IR spectroscopy. 1,10-Phenanthroline (phen) forms five-membered chelate rings with metal ions [8]. In organic solvents, lithium and sodium ions form 1 : 1 and 1 : 2 complexes with phenanthroline [9], which complicates interpretation of the experimental IR spectra. To analyze the concentration dependences of the IR spectra of solutions containing a free ligand and complexes of different stoichiometries, we used in this work the calculated frequencies and intensities of the spectrum components for the free ligand molecule and its complexes with cations. This approach can also be applied to other classes of organic ligands.

The phen molecule (point group C_{2v}) has 60 normal modes: $\Gamma = 21A_1 + 10A_2 + 20B_2 + 9B_1$. Three types of vibrations are IR-active: in-plane vibrations A_1 and B_2, and out-of-plane vibrations B_1. Out-of-plane vibrations A_2 are forbidden in the IR spectrum (their calculated intensity is zero).

Hartree–Fock calculations of vibration frequencies usually give overestimated values. In this work, the calculated vibration frequencies of each type were correlated with the experimental vibration frequencies of the same type determined in [10] by IR and Raman spectroscopy (mulls of phen in Nujol and hexachlorobutadiene) and assigned using data for the deutero derivatives. We found that, in the entire frequency range, the calculated and experimental frequencies were proportional, with the proportionality factor of 0.89. In what follows, as far as the calculated frequen-

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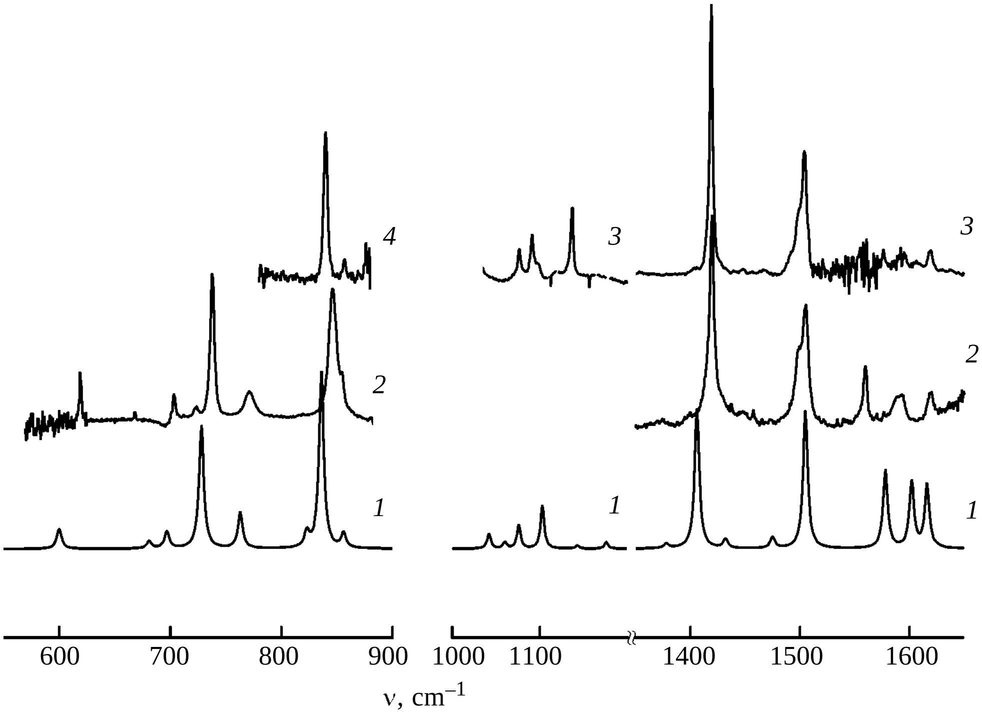


Fig. 1. IR spectra of phen: (*1*) spectrum with the calculated frequencies and intensities, plotted assuming the Lorentz line shape with a half-width of 5 cm^{-1}; (*2–4*) experimental spectra taken in acetone-d_6, CCl_4, and $CDCl_3$, respectively.

cies are concerned, they are multiplied by this factor. However, absolute coincidence of the calculated and experimental frequencies cannot be expected, because, firstly, the experimental conditions in this work (acetone solutions) differ from those in [10]; secondly, in calculations, solvation of the ligand and complexes was not taken into account, whereas actually the spectra of compounds in a condensed medium, even incapable of specific interactions, can significantly differ from those in a vacuum [11].

Nevertheless, as seen from Fig. 1, agreement of the calculated frequencies and intensities for phen in a vacuum with the experimental IR spectra of phen in solution is quite satisfactory. Examples of bands exhibiting different sensitivity to the environment are shown in Fig. 1. The positions of in-plane vibrations A_1 and B_2 (1300–1700 cm^{-1}) are weakly sensitive to the solvent polarity. Contrastingly, the B_1 vibration of phen (calculated frequency 836 cm^{-1}) is observed at 840 cm^{-1} in low-polar $CDCl_3$ and at 847 cm^{-1} in polar $(CD_3)_2CO$. Thus, agreement between the calculated and experimental frequencies is the best in low-polar solvents. This is quite natural, because in calculations there is no solvent field, in low-polar solvents this field is symmetrical, and in solvation of phen with polar solvent molecules their preferential orientations are different at different parts of the phen molecule, causing local asymmetry of the solvent field.

However, in the case of phen, the solvent effect is relatively weak, and, on the whole, the calculated spectrum (Fig. 1, *1*) satisfactorily reproduces the experimental IR spectrum of phen in acetone (Fig. 1, *2*). This fact allowed as to assign the experimental IR spectra of phen–$LiClO_4$ ($NaClO_4$) solutions in deuteroacetone on the basis of the calculated spectra of the molecules and complexes in a vacuum.

The complexes M(phen)$^+$ (M = Li, Na) belong to the C_{2v} point group and have the following normal modes: $\Gamma = 22A_1 + 10A_2 + 21B_2 + 10B_1$.

The structural parameters of the M(phen)$_2^+$ complexes were optimized for the D_{2d} symmetry, to which corresponds the following set of normal modes: $\Gamma = 22A_1 + 10A_2 + 22B_2 + 11B_1 + 32E$.

The frequencies and intensities of vibrations, taking into account correlations of irreducible representations of the D_{2d} group and its C_{2v} subgroup [12], are listed in Tables 1 and 2. As seen from these data, complexation with the lithium ion causes somewhat stronger changes in the calculated frequencies than complexation with the sodium ion. We can distinguish a set of normal modes of phen sensitive to formation of 2 : 1 and 1 : 1 complexes (i.e., changing by no less than 5 cm^{-1} upon complexation) (cm^{-1}): 600 (B_2), 682 (A_1), 728 (B_1), 763 (B_1), 823 (A_1), 836 (B_1), 1042 (B_2), 1076 (A_1), 1505 (A_1), and 1602 (A_1). Based on

Table 1. Calculated frequencies and intensities[a] of vibrations of the phen molecule and its complexes with Li^+ and Na^+ ions

phen, C_{2v}		Li(phen)$_2^+$, D_{2d} (C_{2v})		Li(phen)$^+$, C_{2v}		Na(phen)$_2^+$, D_{2d} (C_{2v})		Na(phen)$^+$, C_{2v}	
ν, cm^{-1}	I, D^2/MA^2	ν, cm^{-1}	I, D^2/MA^2	ν, cm^{-1}	I, D^2/MA^2	ν, cm^{-1}	I, D^2/MA^2	ν, cm^{-1}	I, D^2/MA^2
A_1		B_2 (A_1–A_1)		A_1		B_2 (A_1–A_1)		A_2	
225	0.10	248	0.13	254	0.09	240	0.58	210	0.92
389	0.06	384	0.05	370	0.52	247	0.87	244	0.02
		481	4.12	446	2.09	394	0.35	397	0.17
528	0.00	532	0.30	534	0.07	527	0.00	529	0.00
682	0.07	701	1.38	704	0.65	692	0.68	694	0.34
823	0.15	832	1.13	835	0.59	827	0.67	829	0.30
967	0.07	982	0.12	989	0.07	981	0.09	986	0.04
1060	0.07	1062	0.25	1062	0.04	1064	0.19	1063	0.03
1076	0.24	1091	1.18	1095	0.57	1087	0.93	1089	0.42
1143	0.03	1147	0.16	1147	0.04	1146	0.16	1146	0.06
1183	0.00	1192	0.04	1192	0.00	1191	0.00	1190	0.00
1242	0.00	1251	0.17	1254	0.17	1250	0.12	1251	0.09
1320	0.07	1321	0.47	1320	0.10	1319	0.43	1319	0.10
1378	0.05	1384	0.44	1384	0.37	1378	0.31	1378	0.23
1432	0.09	1432	0.11	1433	0.09	1432	0.14	1433	0.08
1505	1.40	1512	4.85	1515	2.45	1511	4.45	1514	2.19
1602	0.68	1596	1.74	1596	0.79	1598	1.56	1599	0.65
1626	0.01	1623	0.32	1625	0.27	1623	0.34	1626	0.25
3006	0.7	3019	0.12	3030	0.28	3018	0.03	3015	0.72
3015	0.69	3027	0.66	3037	0.13	3026	0.00	3035	0.11
3025	1.02	3035	0.98	3043	0.20	3027	2.51	3042	0.27
3041	0.00	3047	0.34	3061	0.01	3045	0.14	3058	0.01
B_2		E (B_2)		B_2		E (B_2)		B_2	
		25	0.00	393	0.98	18	0.00	179	0.36
439	0.01	451	0.01	452	0.04	445	0.02	445	0.01
489	0.01	489	0.02	490	0.04	491	0.02	492	0.02
600	0.20	618	0.30	630	0.41	612	0.22	615	0.22
697	0.17	695	0.39	697	0.61	696	0.33	697	0.39
856	0.15	868	0.00	871	0.01	865	0.02	865	0.01
988	0.01	990	0.01	991	0.05	990	0.00	991	0.02
1042	0.16	1055	0.08	1059	0.09	1053	0.11	1056	0.13
1103	0.44	1110	0.70	1111	0.87	1110	0.63	1110	0.72
1176	0.07	1178	0.13	1174	0.13	1176	0.13	1172	0.13
1216	0.04	1214	0.00	1213	0.00	1215	0.01	1214	0.01
1258	0.01	1263	0.04	1261	0.03	1262	0.02	1261	0.02
1389	0.00	1391	0.10	1391	0.22	1393	0.06	1393	0.06
1406	1.42	1408	1.80	1406	2.21	1408	1.89	1407	2.24
1475	0.11	1473	0.16	1472	0.19	1474	0.15	1473	0.17
1578	0.80	1593	1.44	1594	1.76	1588	1.17	1589	1.25
1616	0.65	1611	0.09	1609	0.07	1611	0.23	1610	0.24
3005	0.37	3011	0.01	3028	0.00	3010	0.01	3015	0.43
3007	0.20	3019	0.08	3030	0.25	3018	0.12	3026	0.01
3016	0.01	3035	0.00	3038	0.00	3027	0.11	3035	0.02
3040	1.60	3047	0.56	3061	0.13	3045	0.58	3058	0.23

Table 1. (Contd.)

phen, C_{2v}		$Li(phen)_2^+$, D_{2d} (C_{2v})		$Li(phen)^+$, C_{2v}		$Na(phen)_2^+$, D_{2d} (C_{2v})		$Na(phen)^+$, C_{2v}	
ν, cm^{-1}	I, D^2/MA^2	ν, cm^{-1}	I, D^2/MA^2	ν, cm^{-1}	I, D^2/MA^2	ν, cm^{-1}	I, D^2/MA^2	ν, cm^{-1}	I, D^2/MA^2
B_1		E (B_1)		B_1		E (B_1)		B_1	
98	0.16	69	0.01	92	0.03	53	0.04	57	0.26
		122	0.13	164	1.78	117	0.10	115	0.51
231	0.11	236	0.10	231	0.08	236	0.08	231	0.12
430	0.00	437	0.01	430	0.00	432	0.00	428	0.00
491	0.02	498	0.01	494	0.00	498	0.02	495	0.01
728	1.26	724	1.17	718	1.54	725	1.16	721	1.42
763	0.37	780	0.20	773	0.22	779	0.23	772	0.27
836	1.80	849	1.84	845	1.88	849	1.86	845	1.88
963	0.01	982	0.02	982	0.01	979	0.02	976	0.01
986	0.01	1000	0.00	996	0.01	999	0.00	995	0.01
		E (B_2 + B_1)				(B_2 + B_1)			
		341	0.67			163	0.37		

[a] 1 D^2/MA^2 = 1 debye^2/(Å^2 amu) = 42.2547 km/mol.

Table 2. Calculated zero-intensity vibration frequencies (ν, cm^{-1}) of the phen molecule and its complexes with Li^+ and Na^+ ions

phen, C_{2v}	$Li(phen)^+$, C_{2v}	$Na(phen)^+$, C_{2v}	$Li(phen)_2^+$, D_{2d} (C_{2v})	$Na(phen)_2^+$, D_{2d} (C_{2v})	$Li(phen)_2^+$, D_{2d} (C_{2v})	$Na(phen)_2^+$, D_{2d} (C_{2v})	$Li(phen)_2^+$, D_{2d} (C_{2v})	$Na(phen)_2^+$, D_{2d} (C_{2v})	$Li(phen)_2^+$, D_{2d} (C_{2v})	$Na(phen)_2^+$, D_{2d} (C_{2v})
A_2			A_1 (A_1 + A_1)		A_1 (A_1 + A_1)		A_2 (A_2 + A_2)		B_1 (A_2–A_2)	
106	128	117	129	174	1248	1249	133	124	45	43
236	241	238	235	256	1320	1315	248	245	135	124
402	403	401	357[a]	348	1385	1379	410	406	250	246
541	533	536	523	521	1436	1429	540	541	407	407
595	597	597	682	671	1515	1515	600	599	540	542
798	802	803	827	825	1602	1598	810	811	601	600
821	824	825	982	981	1623	1623	828	828	811	811
961	976	973	1068	1067	3019	3018	978	976	828	828
974	983	980	1092	1087	3030	3026	986	985	978	977
990	999	998	1144	1147	3039	3035	1003	1002	986	985
			1192	1188	3064	3063			1003	1002

[a] Calculated intensity 0.12, because of participation of the Li^+ ion in the vibration.

the results of preliminary calculations, we chose the spectrum ranges from which the richest information on complexation can be derived, and also the solvent (acetone-d_6) transparent in these ranges. Some of the complexation-sensitive vibrations manifested in the spectrum ranges in which the solvent and anion have no absorption are shown in Fig. 2. The possibility of spectroscopically distinguishing the complexes $Li(phen)_2^+$ and $Li(phen)^+$ is illustrated by Fig. 3a, showing the calculated spectrum as a sum of Lorentzian functions with a half-width of 5 cm^{-1}.

In complexation, the shapes of the normal modes are, on the whole, preserved; this is seen from Fig. 2 for phen and its 1 : 2 and 1 : 1 complexes with Li^+. At the same time, the extent of participation of particular atoms in a vibration changes upon complexation, as demonstrated by the example of the two most intense B_1 bands (Table 3) undergoing opposite shifts upon complexation.

Table 3 shows that complexation of phen with a metal ion is accompanied by an appreciable increase

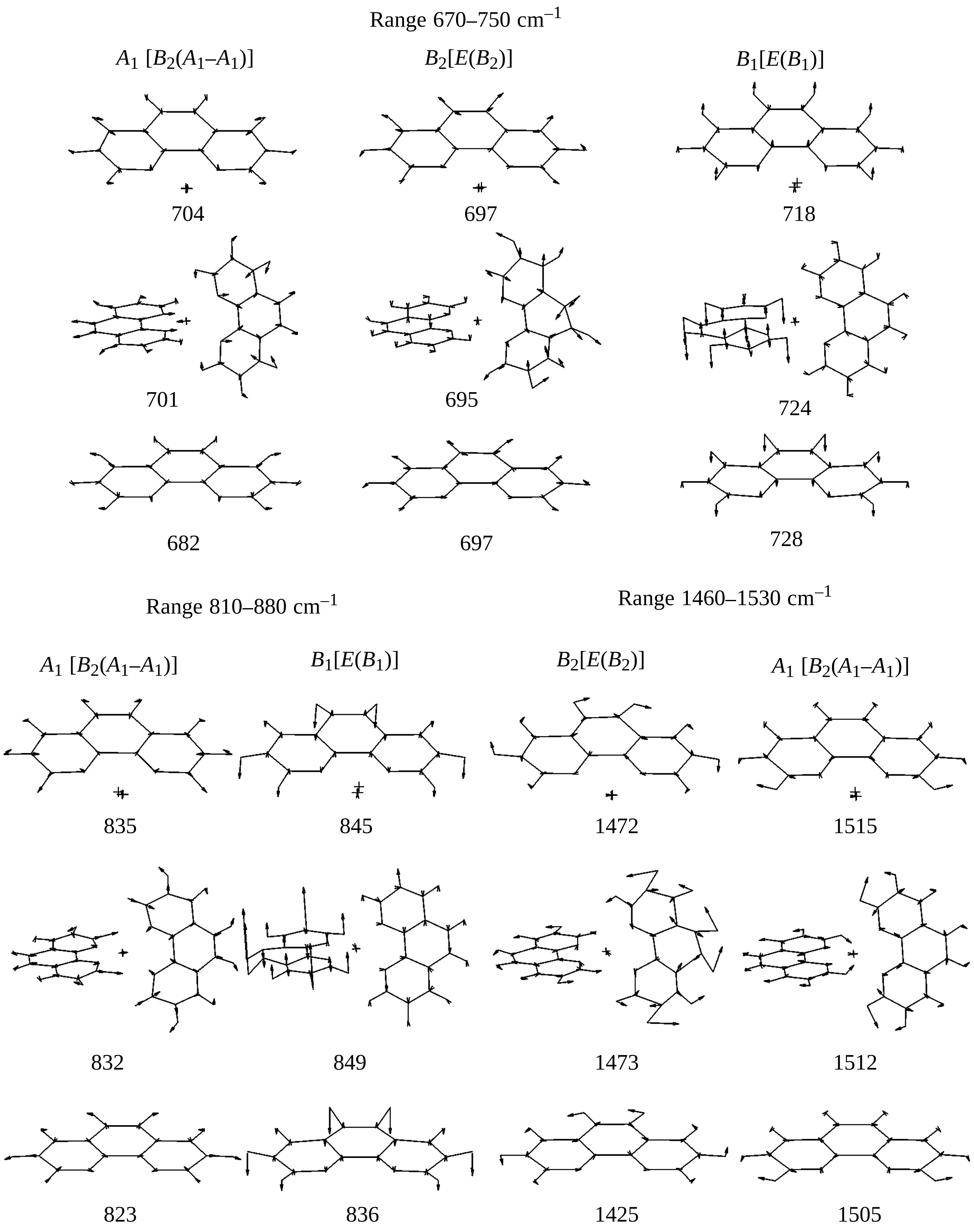


Fig. 2. Shapes of the normal modes of Li(phen)$^+$, Li(phen)$_2^+$, and phen. Frequencies in cm^{-1}.

in the contribution of hydrogen atoms 13 and 14 [coordinate (3)] to the normal mode ν_{49} (B_1) and by a decrease in the contribution of torsional skeleton vibrations [coordinates (6)–(8)]. With the ν_{51} mode (B_1), the pattern is more complex: the contributions of the out-of-plane displacements of hydrogen atoms 21 and 22 [coordinate (1)], 15 and 16 [coordinate (2)], and 17 and 18 [coordinate (4)] decrease, that of hydro-

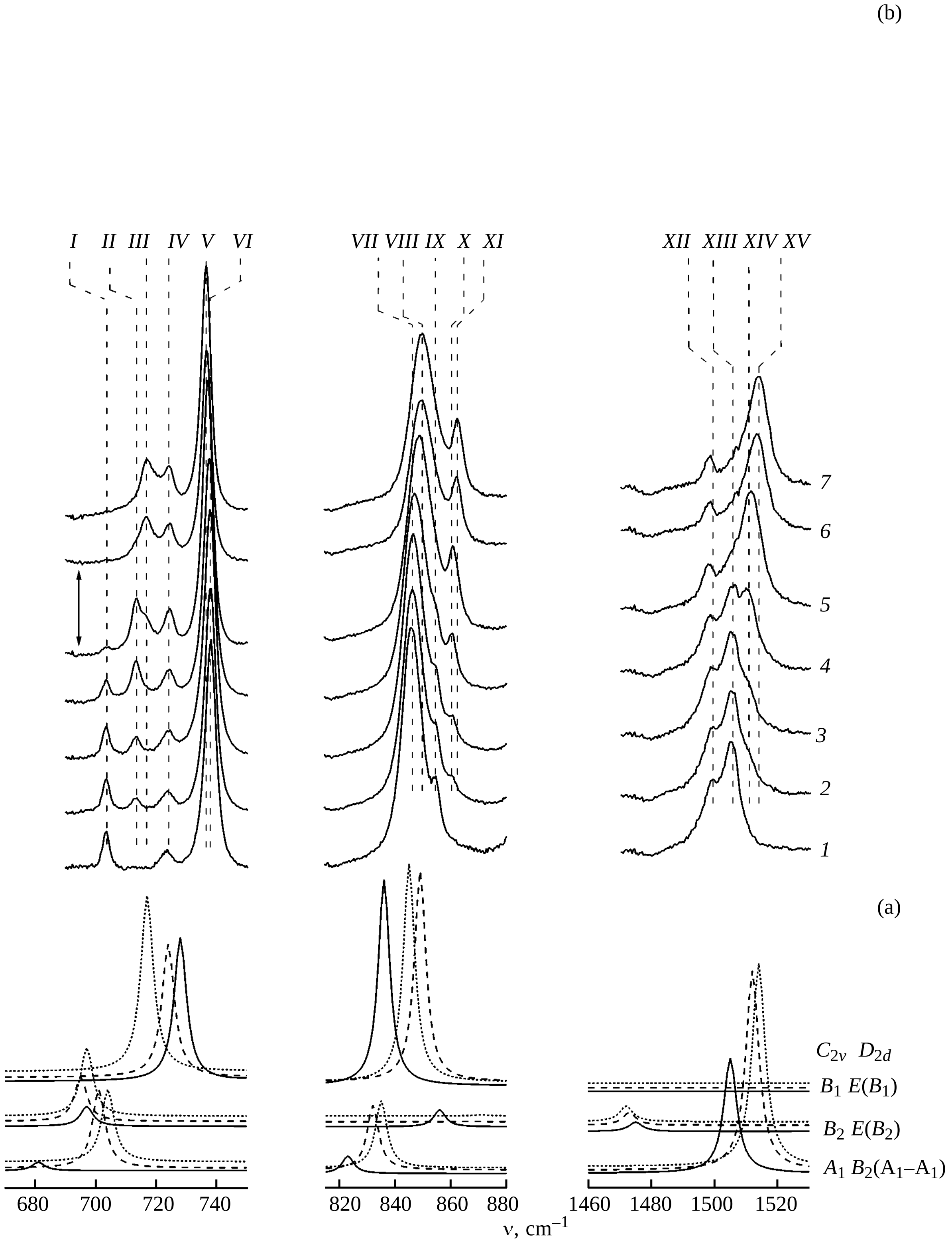
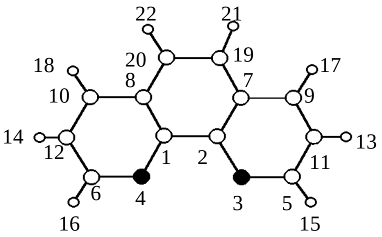


Fig. 3. Assignment, based on the calculation results, of the spectrum components in the experimental IR spectra of the system phen–$LiClO_4$– $(CD_3)_2CO$: (a) calculated spectra of phen, Li(phen)$_2^+$, and Li(phen)$^+$; (solid line) phen, (dashed line) Li(phen)$_2^+$, and (dotted line) Li(phen)$^+$; the vibration types, taking into account correlations between the irreducible representations of the C_{2v} and D_{2d} groups, are given to the right of the spectra; (b) experimental IR spectra of 0.05 M solutions of phen in $(CD_3)_2CO$ at $LiClO_4$ concentration (M) of (*1*) 0, (*2*) 0.005, (*3*) 0.008, (*4*) 0.014, (*5*) 0.027, (*6*) 0.035, and (*7*) 0.101; the vertical lines denote the positions of the assigned components.

Table 3. Nonzero changes in the internal coordinates[a] for the most intense normal modes B_1[b] of the phen molecule and the complexes Na(phen)$^+$ and Li(phen)$^+$. The distribution of the potential energy of vibrations throughout the internal coordinates is given in parentheses



Vibration	ν_{49} (B_1)			ν_{51} (B_1)		
	phen, 836 cm^{-1}	Na(phen)$^+$, 845 cm^{-1}	Li(phen)$^+$, 845 cm^{-1}	phen, 728 cm^{-1}	Na(phen)$^+$, 721 cm^{-1}	Li(phen)$^+$, 718 cm^{-1}
OPBE[c] 22 20 8 19 (1)	0.283 (0.224)	0.284 (0.222)	0.281 (0.222)	0.123 (0.062)	0.093 (0.039)	0.087 (0.034)
OPBE 16 6 4 12 (2)	0.120 (0.035)	0.125 (0.037)	0.121 (0.037)	0.046 (0.000)	0.037 (0.000)	0.032 (0.000)
OPBE 14 12 6 10 (3)	0.159 (0.106)	0.166 (0.119)	0.171 (0.119)	0.107 (0.000)	0.119 (0.006)	0.123 (0.008)
OPBE 18 10 12 8 (4)	0.114 (0.018)	0.111 (0.020)	0.114 (0.020)	0.018 (0.000)	0.008 (0.000)	0.004 (0.000)
TORS[d] 2 3 5 11 (5)	0.058 (0.009)	0.055 (0.008)	0.054 (0.008)	0.202 (0.180)	0.204 (0.188)	0.203 (0.189)
TORS 5 11 9 7 (6)	0.071 (0.026)	0.067 (0.024)	0.066 (0.024)	0.136 (0.094)	0.133 (0.082)	0.132 (0.080)
TORS 9 7 2 3 (7)	0.130 (0.070)	0.121 (0.060)	0.121 (0.060)	0.206 (0.128)	0.210 (0.141)	0.211 (0.145)
TORS 2 1 8 20 (8)	0.119 (0.000)	0.115 (0.000)	0.113 (0.000)	0.090 (0.039)	0.098 (0.040)	0.098 (0.037)
TORS 4 1 8 20 (9)	0.044 (0.020)	0.046 (0.020)	0.044 (0.020)	0.074 (0.019)	0.070 (0.013)	0.072 (0.010)

[a] Each of the natural coordinates given in the table has a mirror-symmetrical pair. [b] Assignment for phen [10]. [c] Deviation of the atom denoted by the first figure from the plane of atoms denoted by the next three figures. [d] Variation of the torsion angle formed by the atoms denoted by the given sequence of four figures. In parentheses is the number of the internal coordinate.

gen atoms 13 and 14 [coordinate (3)] increases, and the contributions of out-of-plane displacements of the carbon and nitrogen atoms [coordinates (7) and (8)] increase. Changes in the extent of participation of the light and heavy atoms in the vibrations may be one of the causes of different trends in shifts of vibration bands of the same class upon complexation; some other factors may also be operative, such as, e.g., changes in the force field upon complexation.

When assigning the bands in the experimental spectra (Fig. 3b, Roman figures), we primarily took into account the band intensities and the directions of their shifts, comparing these data with the calculated spectra (Fig. 3a). In some cases, inversion of the relative arrangement of certain components as compared to the calculated spectrum was admitted. For example, the experimental band at 721–723 cm^{-1} was assigned to a B_2 vibration (calculated frequency 697 cm^{-1}) on the basis of the fact that its position and intensity vary only slightly upon complexation (Fig. 3b, *IV*). At the same time, the band observed at 701–717 cm^{-1} was assigned to the A_1 vibration (calculated frequency 682–704 cm^{-1}), as with increasing concentration of the salt, in compliance with the calculation results (Fig. 3a), it underwent a high-frequency shift with an increase in the intensity (Fig. 3b). Another example of inversion of the relative arrangement of the bands

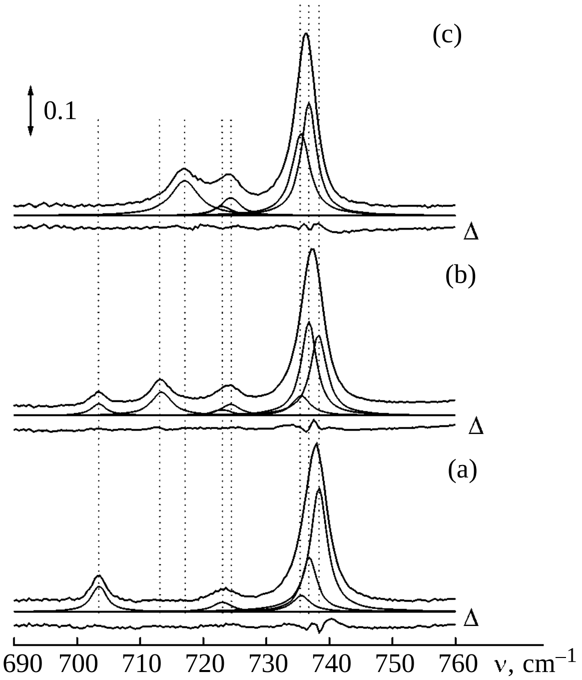


Fig. 4. Results of joint treatment by the Löwenberg–Marraquard algorithm of the experimental spectra of 0.05 M solutions of phen in $(CD_3)_2CO$. $LiClO_4$ concentration, M: (a) 0, (b) 0.014, and (c) 0.101. (Δ) Difference between the experimental spectrum and the spectrum fitted by the sum of the Lorentz functions.

is as follows: the component shifting upon complexation from 854 to 862 cm^{-1} was assigned to the A_1 vibration (Fig. 3b, *IX*–*XI*), whereas the component with a maximum at 845–854 cm^{-1} was assigned to the B_1 vibration (Fig. 3b, *VII*, *VIII*). This assignment was based on the fact that the B_1 vibration band, according to calculations, should be stronger. The calculated shifts of some bands upon complexation [682–704 (A_1), 728–718 (B_1), 836–845 (B_1), 1505–1515 cm^{-1} (A_1); Fig. 3a] agree with the experimentally observed shifts in the direction (701–717, 738–735, 845–851, 1505–1514 cm^{-1}; Fig. 3b), but in most cases are overestimated in the value.

By a similar procedure, we assigned the bands in the IR spectra of the system $(CD_3)_2CO$–phen–$NaClO_4$.

Using the assignments made for the 1 : 1 and 1 : 2 complexes of Li^+ and Na^+ with phen, we resolved the experimental spectra into components belonging to the free ligand and to the ligand moiety in complexes of different stoichiometries.

The initial set of parameters for fitting the experimental spectrum by the sum of Lorentz functions included the required number of components and preliminary values of their frequencies (±2 cm^{-1}) and half-widths (3–7 cm^{-1}). The positions of the maxima and the half-widths were refined in the course of joint treatment by the Löwenberg–Marraquard algorithm [13] of the spectra of solutions with a constant (0.05 M) phen concentration and different (zero, “middle,” and maximal) concentrations of the salt. Apparently, when resolving a single spectrum, a better fitting can be attained, but only joint treatment of several spectra allows evaluation of common frequencies and half-widths of the components, optimized over the whole series. In this work, the component frequencies and half-widths optimized by joint treatment of four and more spectra virtually coincided with the results of treatment of three spectra.

Let us consider resolution of the experimental spectrum for the system $(CD_3)_2CO$–phen–$LiClO_4$ in the range 670–750 cm^{-1} as example.

As seen from Figs. 2 and 3a, there should be nine components in the range 670–750 cm^{-1} and six components in each of the ranges 800–900 and 1450–1550 cm^{-1}. However, for the first range, the number of functions fitting the experimental spectrum can be decreased to eight by describing the B_2 components (belonging to different complexes but having close positions and intensities) by a single Lorentz function. The positions of the maxima and the half-widths, determined by joint treatment of three experimental spectra (Fig. 4), were used for resolving the other spectra of the series, with the component intensities being the only varied parameters.

By resolving the experimental spectra in the ranges 650–750, 800–900, and 1450–1550 cm^{-1}, we obtained the dependences of the integral intensities of the spectrum components on the salt concentration. Figure 5 shows such dependences for the system with lithium perchlorate. The components belonging to the free ligand give monotonically descending curves (Fig. 5a); those belonging to the 2 : 1 complex give curves with a maximum (Fig. 5b); and those belonging to the 1 : 1 complex give ascending sigmoid (S-shaped) curves (Fig. 5c). When the bands belonging to different complexes strongly overlap (e.g., in the range of strong B_1 bands), it appears impossible to reliably determine the intensities of separate components, although, on the whole, the shape of dependences *1* and *4* in Fig. 5d resembles the pattern in Fig. 5b, and the shape of dependences *2* and *5* resembles the pattern in Fig. 5c. For these cases, we plotted the dependences of the total intensities of the components corresponding to both components vs. the salt concentration (Fig. 5d, curves *3* and *6*).

Figure 6 shows as an example the concentration

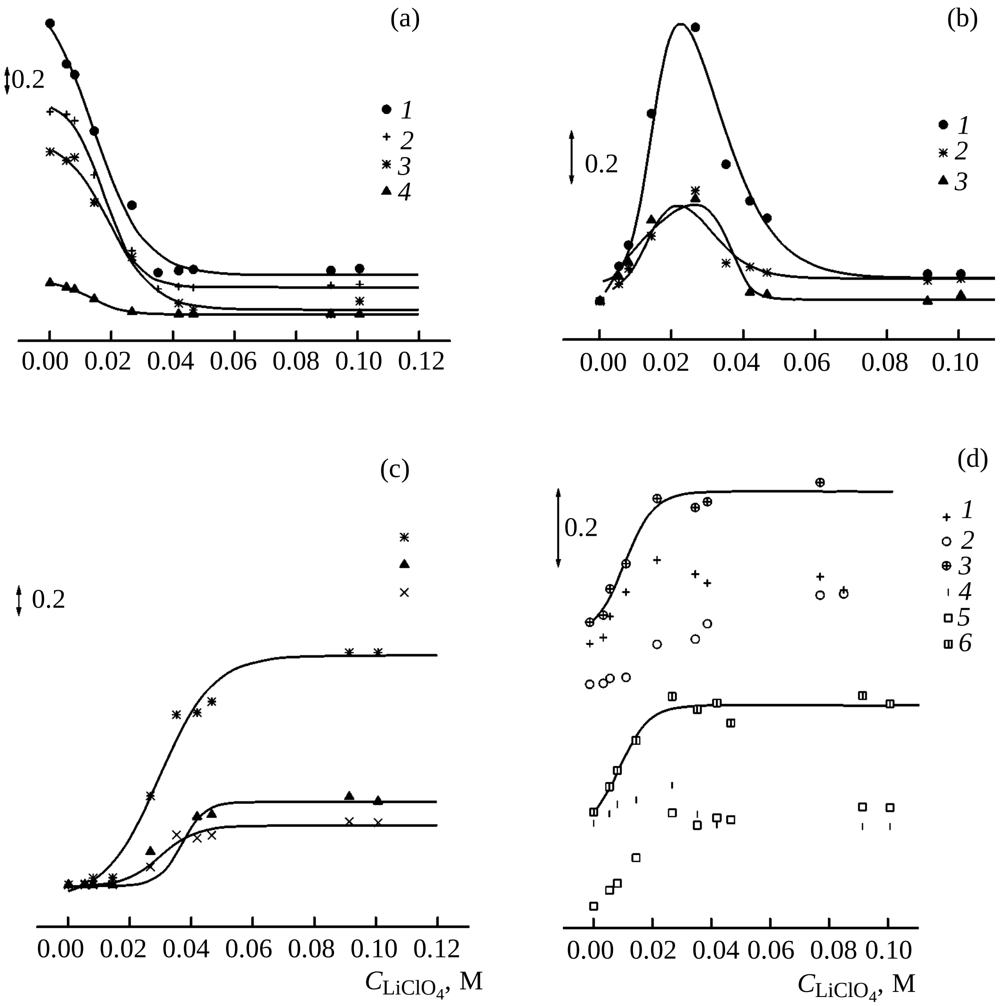


Fig. 5. Integral intensities of particular components of the IR spectra of the system phen–$LiClO_4$–$(CD_3)_2CO$ as functions of salt concentration (layer thickness 140 μm). (a) Components belonging to the free ligand: (*1*) 845, (*2*) 1505, (*3*) 738, and (*4*) 703 cm^{-1}; (b) components belonging to the complex $Li(phen)_2^+$: (*1*) 1511, (*2*) 861, and (*3*) 713 cm^{-1}; (c) components belonging to the complex $Li(phen)^+$: (*1*) 1514, (*2*) 717, and (*3*) 862 cm^{-1}; and (d) components [(*1*) 735, (*2*) 737, (*4*) 848, (*5*) 851 cm^{-1}] and curves (*3, 6*) corresponding to the sum of the complexes $Li(phen)_2^+$ and $Li(phen)^+$.

dependences of the integral intensity of the A_1 component in the spectra of the systems of phen with $LiClO_4$ and $NaClO_4$. The calculated frequency of this vibration is 682 cm^{-1} for the free ligand, and upon complexation it increases (Tables 1 and 2; Fig. 3a).

To determine the step stability constants, it is appropriate to choose the concentration ranges in which all the absorbing species coexist in comparable amounts, despite the fact that, under these conditions, the spectrum is the most complex. From data in Figs. 5 and 6, it is possible to evaluate the stability constants of the complex species.

Calculation of the concentrations of particular species from the component intensities is a separate problem whose solution requires determination of the integral absorption coefficients (D_∞/l, where l is the absorbing layer thickness) of these species. For the system with $LiClO_4$, the D_∞/l values for components belonging to phen and $Li(phen)^+$ can readily be determined from the spectra of solutions of free phen (0.05 M) and of solutions in which the 1 : 1 complex prevails (0.05 M phen + 0.1 M $LiClO_4$), respectively; for the system with $NaClO_4$, the 1 : 1 complex prevails at $C_{salt} > 0.15$ M. The system with $NaClO_4$ is a homogeneous solution in the entire examined concentration range, whereas in the system with $LiClO_4$ a solid phase is formed in the region of concentrations close to 2 : 1. In this case, to calculate the speciation and step complexation constants, it is necessary to determine the total ligand concentration in solution.

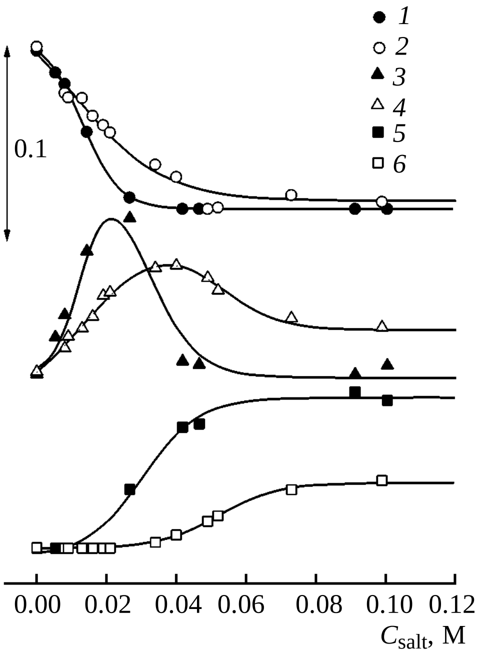


Fig. 6. Intensity of the A_1 component (calculated frequency 682 cm^{-1} for free phen) as a function of the (*1, 3, 5*) $LiClO_4$ and (*2, 4, 6*) $NaClO_4$ concentrations: (*1, 2*) component with a maximum at 703 cm^{-1} corresponding to the free ligand; (*3, 4*) components corresponding to the complexes M(phen)_2^+, maximum at (*3*) 713 and (*4*) 711 cm^{-1}; and (*5, 6*) components corresponding to the complexes M(phen)^+, maximum at (*5*) 717 and (*6*) 712 cm^{-1}.

Thus, we have suggested a procedure for interpreting the concentration dependences of the IR spectra of the systems phen–$LiClO_4$ ($NaClO_4$)–acetone, involving preliminary ab initio calculations of the vibration frequencies and intensities for the free ligand molecule and its complexes of the expected stoichiometry. Based on the results of quantum-chemical calculations for phen, Li(phen)^+, Li(phen)_2^+, Na(phen)^+, and Na(phen)_2^+, we chose the spectrum intervals in which the patterns given by different species are the best discernible. We suggested the parameters for resolving the experimental spectra, proved the formation of the 1 : 1 and 1 : 2 complexes in the systems, and obtained the concentration dependences of the intensities of the spectrum components belonging to the free ligand and its 1 : 1 and 1 : 2 complexes with Li^+ and Na^+.

EXPERIMENTAL

The optimized geometries and harmonic frequencies of the phen molecule and its 1 : 1 and 1 : 2 complexes with Li^+ and Na^+ in a vacuum were calculated by the RHF method using the GAMESS program package [14, 15], assuming the C_{2v} symmetry for free phen and the 1 : 1 complex and the D_{2d} symmetry for the 2 : 1 complex. We used the DZV set of basis functions with one *d*-polarization function on the carbon and nitrogen atoms of the ligand, and for the lithium and sodium ions we used the TZV set with one *d*-polarization function. The displacements of atoms were visualized using the Molden 3.6 program [16]. The spectra were fitted by a sum of Lorentz components with a half-width of 5 cm^{-1}.

Anhydrous $LiClO_4$ and $NaClO_4$ were prepared by a common procedure [17]. Anhydrous phenanthroline was prepared from phenanthroline monohydrate by vacuum sublimation (10^{-2} mm). Deuterated acetone was stored over 4 Å molecular sieves (Institute of Silicate Chemistry, Russian Academy of Sciences) in a hermetically sealed glove box. All manipulations (preparing solutions, filling cells and ampules) were performed in a dry box using plastic and glass vessels. The quality of the chemicals used and the moisture content in solutions were monitored by IR (range of H_2O stretching vibrations, 3800–3400 cm^{-1}) and ^{1}H NMR (δ 1–10 ppm) spectroscopy.

The IR spectra were recorded with a Specord M-80 diffraction spectrophotometer equipped with an IBM-compatible interface, in the ranges 3800–3400 (step 0.8 cm^{-1}, slit 2.5 cm^{-1}), 1660–1300, and 950–570 cm^{-1} (step 0.4 cm^{-1}, slit 1.5 cm^{-1}). A 140-μm NaCl cell was used.

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