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Spectroscopic Characteristics of Dimethylsulfoxide Molecules Coordinated to Mg^{2+} Cation. Structure of Complexes $[Mg(DMSO)_i(CH_3CN)_{6-i}]^{2+}$ from the Data of Quantum-Chemical Calculations and IR Spectra of $Mg(ClO_4)_2$–DMSO–CH_3CN Solutions

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Abstract—By the DFT B3LYP/6-31G** method the geometry was optimized and IR spectra were calculated of complexes $[Mg(DMSO)_i(CH_3CN)_{6-i}]^{2+}$ (i = 1–6). The values of free energy ΔG in the reaction of ligands substitution in the coordination sphere of the cation were determined. A satisfactory agreement between experimental and calculated values of structural parameters and infrared spectra of free molecules and coordinated to the cation DMSO was obtained. The regularities in the changes of the spectroscopic and structural characteristics of $[Mg(DMSO)_i(CH_3CN)_{6-i}]^{2+}$ complexes at varying their composition were revealed. The frequencies and absolute integral intensities of DMSO bands in the IR spectra of pure liquid, solutions in acetonitrile, and in three-component solutions $Mg(ClO_4)_2$–DMSO–CH_3CN were measured. A correspondence between the calculated change of the frequency and absolute intensity of the IR bands ν(C≡N), ν(C–C), ν(S=O), and ν(SC) of the complexes and the corresponding values in the IR spectra of the solutions with different content of components of binary solvent was found.

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The problem of ion solvation is among the leading in the physical chemistry of solutions. Particular interest in recent years is attracted by the study of the preferred solvation of cations in multicomponent systems formed at dissolving an electrolyte in a mixture of aprotic polar solvents [1–12]. The application of the IR spectroscopy for this purpose is very effective, owing to high sensitivity of the frequency and absolute integral intensity of the IR bands of molecules to the changes in the molecular environment. The problem of determining composition of the ion solvation shell from the intensity of infrared absorption bands is complicated by the fact that spectroscopic characteristics of molecules in the coordination sphere of a cation suffer significant changed at varying composition of the ion solvation shell [3, 8, 13]. Analysis of these changes, together with quantum chemical calculations (allowing independent determination of the possible spectrally distinguishable forms, contributing to the overall contour of the IR band), allows the identification of the solvates of different composition and determinating the con-tribution of the corresponding components into the overall contour of the IR band, thus exploring the equilibrium of different solvate forms in the solution [14].

In the present work we performed quantum-chemical calculations of structure and spectroscopic properties of the complexes of magnesium cation $[Mg(DMSO)_i(CH_3CN)_{6-i}]^{2+}$, i = 1–6. The calculation results were compared with the pattern of changes in frequency and absolute integral intensities of the bands in the IR spectra of ternary solutions of $Mg(ClO_4)_2$–DMSO–CH_3CN at a variation of the binary solvent. The $Mg(ClO_4)_2$–DMSO–CH_3CN system is a convenient model for studying the processes of the preferred ion solvation in solutions: a binary solvent components have high values of permittivity and dipole moments, while they are characterized by different solvating ability (the donor numbers of acetonitrile and DMSO are 14.1 and 29.8, respectively [15]). A high electric potential created by the Mg^{2+} cations causes major structural and spectroscopic effects at the coordination of solvent molecules. Due to the fact that the perchlorate anion is a weak Lewis base, the formation of ion pairs in solutions of perchlorate occurs to a lesser extent than in the case of such anions as I^-.

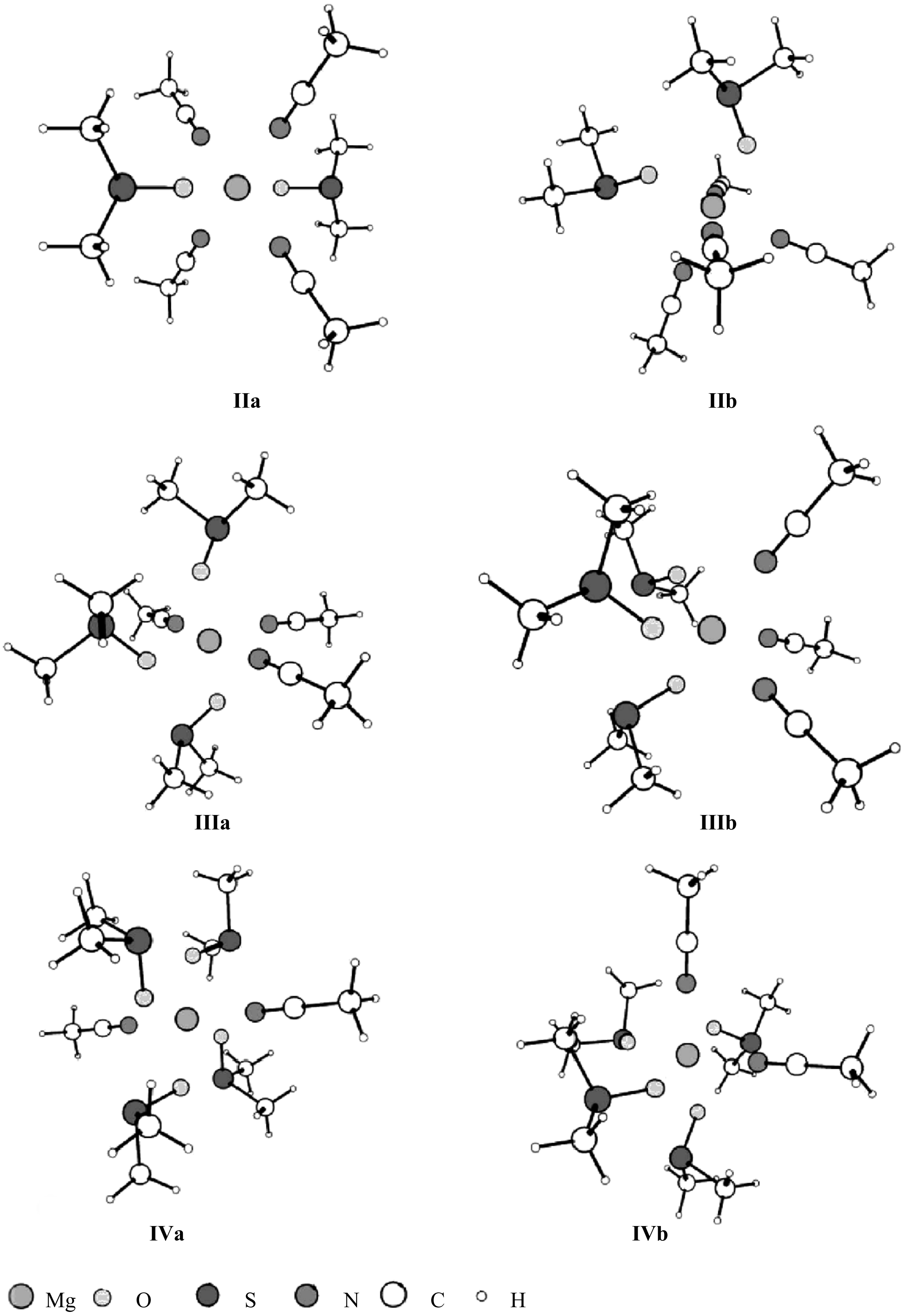
Quantum-Chemical Calculation of Structure and Infrared Spectra of the Complexes $[Mg(DMSO)_i(CH_3CN)_{6-i}]^{2+}$

The geometry optimization and calculation of IR spectra of the complexes $[Mg(DMSO)_i(CH_3CN)_{6-i}]^{2+}$, $i = 1–6$ (structures **I–VI**) was performed by the method of density functional DFT with the B3LYP potential in 6-31G** basis, using Gaussian03 program [16]. For the complexes with $i = 2–4$ calculations were carried out of two structures with different symmetry of the ligands positions (Fig. 1). The choice of the basis and the method of calculation were tested in the calculation of structural parameters and infrared spectra of DMSO molecule and complex **VI**. The calculated values of geometric parameters of DMSO molecule are consistent with the experimental values [17], the deviations do not exceed 0.027 Å and 0.8° (Table 1).

For the "rigid" ions O-type coordination of DMSO molecules is preferred [18], in particular, this type of coordination is found at the X-ray study of solid solutions of $Mg(ClO_4)_2$–DMSO [19]. The calculated structural characteristics of complexes **I–VI** containing O-coordinated DMSO molecules of C_1 symmetry (with the exception of **IIa**, **IVa**, **VI**), are shown in Table 2. At the coordination to a cation, the DMSO molecule exhibits the properties of σ-ligand: the bonds S=O are lengthened (by 0.043 Å), while the S–C bonds, on the contrary, are shortened (by 0.020 Å); the CSC bond angle is increased by 2.8°, while the OSC decreased by 1.7°–3.2°; the increase in SCN angle is less than 1°. Structure **VI** is a slightly distorted octahedron, the OMgO angle deviates from 90° by 1.9°. The calculated MgO bond length in the complex **VI** is 0.05 Å longer than the value derived from crystallographic study [19], the MgOS angles are smaller than the experimental ones. The calculated values are close to the X-ray diffraction parameters of $[Zn(DMSO)_6]\cdot(ClO_4)_2$ [20].

The calculations indicate a significant change in some geometric parameters of the complexes **I–VI** with an increase in the number of DMSO molecules in their composition. The introduction of each subsequent DMSO molecule into the ion coordination sphere increases the Mg–N and Mg–O bond lengths (by 0.09 Å in the series), causes the distortion of collinearity of the ion–ligand bonds and coplanarity of structural fragments MgOS/MgO'S' in the *trans*-position relatively to the cation in the mixed complexes (except for **IVa**), due to the steric factors. The angle MgOS increases in the series **I–VI** by 10°, similar effect in the change of MgOC angles at the coordination of DMF molecules was observed in [13]. Based on the values of MgOSC dihedral angles, the complexes **I–IIIa** can be assigned to the *trans-trans*-coordinated [19], **IIIb**, **VI** to the *trans-cis*-coordinated, and **IV, V,** to partially *trans-trans*-, partially *trans-cis*-coordinated. In the **IIb–VI** complexes nonequivalence of the methyl groups in the coordinated DMSO molecule is observed, which is seen as the difference of SC bond lengths, OSC angles, and MgOSC dihedral angles in axial and equatorial groups. The changes in structural parameters of the coordinated DMSO molecules in the series of complexes are by an order of magnitude smaller than the changes at the coordination of the molecules to the cation, the maximum change in SO bond length is 0.006 Å. The values of structural parameters of coor-dinated CH_3CN molecules correspond to those calcu-lated for the complexes $[Mg(DMF)_i(CH_3CN)_{6-i}]^{2+}$ [13].

Population analysis by the method of natural bond orbitals (NBO, [21]) shows (Table 3) that at the coordination of DMSO molecule the negative charge on the oxygen atom gains 0.15 electron charge on the average, a positive charge on the sulfur atom increases by 0.05 e; charge on the carbon atoms decreases (by 0.012–0.014 e), and on the H atom increases (by 0.014–0.028 e). This observation, as well as a decrease in the order and elongation of SO bond, is consistent with the conclusion [18] on the increase in the contribution of the resonance form $(CH_3)_2S^+–O^-$ to the coordinated DMSO molecule. The charge on the cation remains unchanged in the series **I–VI** ($\Delta q^{NBO} \le 0.03$ e). At the same time, the calculation of the charge distribution by the method of atomic polar tensors (APT) indicates a decrease in the effective charge of the cation Mg^{2+} in this series ($\Delta q^{APT} \le 0.34$ e), which can be explained by the deformation of the charge $\partial q_{Mg}/\partial Q$ at the Mg–O bond vibration. The values of charges on the atoms of the coordinated DMSO molecules are markedly changed in the series (decrease in the charge on the oxygen atom Δq^{NBO} is 0.014 e, on sulfur 0.008 e) and show a tendency to get



IIa **IIb**

IIIa **IIIb**

IVa **IVb**

Fig. 1. Structure of the complexes $[Mg(DMSO)_i(CH_3CN)_{6-i}]^{2+}$, $i = 2–4$.

Table 1. Selected structural parameters (Å, deg) of DMSO molecules in the complexes $[Mg(DMSO)_i(CH_3CN)_{6-i}]^{2+}$, $i = 1–6$, according to the DFT B3LYP/6-31G** calculations

Parameter	DMSO		I	IIa	IIb	IIIa	IIIb	IVa	IVb	V	VI
	calculation	experimental[a]									
SO	1.512	1.485	1.553	1.552	1.555	1.555	1.556	1.558	1.557	1.556	1.555
SC_1	1.837	1.799	1.817	1.817	1.816	1.816	1.816	1.816	1.816	1.817	1.817
SC_2	1.837	1.799	1.817	1.817	1.817	1.817	1.818	1.817	1.818	1.818	1.819
OSC_1	107.5	106.7	104.7	104.8	104.4	104.2	103.8	104.0	104.0	104.2	104.3
OSC_2	107.5	106.7	104.7	104.8	105.1	105.3	105.9	105.6	105.8	105.6	105.8
CSC	95.9	96.6	98.7	98.6	98.9	98.9	98.8	98.8	98.9	98.9	98.7

[a] Determined by the method of microwave spectroscopy [17].

Table 2. Selected structural parameters (Å, deg) of the complexes $[Mg(DMSO)_i(CH_3CN)_{6-i}]^{2+}$, $i = 1–6$

Parameter	I	IIa	IIb	IIIa	IIIb	IVa	IVb	V	VI	VI[a]	$[Zn(DMSO)_6](ClO_4)_2$[b]
MgO	2.019	2.037	2.022–2.069	2.036–2.061	2.059–2.065	2.071–2.073	2.070–2.091	2.089–2.103	2.111	2.051, 2.063, 2.084	2.096, 2.111
MgN	2.197–2.217	2.229	2.111–2.240	2.232–2.272	2.240–2.246	2.273	2.261–2.266	2.284	–	–	–
MgOS	134.8	132.5	129.0–130.7	126.3–129.5	127.0–127.2	124.8–125.6	124.2–127.6	123.0–125.7	124.3	127.5, 130.2, 139.8	116.4, 120.3
φ_{OMgO}, *cis*[c]	–	–	1.3	0.4	4.1	0.1	4.0	4.2	1.9		3.6, 1.1
trans-[d]	–	0.0	–	0.1	–	0.0	0.1	6.9	0.0		4.1
θ_{OMgN}, *cis*[c]	2.6	2.0	2.5	1.9	3.9	0.1	2.0	4.4	–		
trans-[d]	1.9	–	4.2	2.3	8.0	–	8.4	–	–		
χ_{MgOSC}	128.3	128.3–128.4	94.9 –161.5 –134.1 122.4	165.1 –91.3 –124.0 132.5 161.9 –94.4	169.6 –86.9 170.8 –85.6 170.6 –86.0	85.1 –171.4 –97.3 159.2	163.5 –92.7 165.0 –91.4 179.9 –76.7 –153.0 103.3	157.9, –98.5 –156.2, 99.9 152.1, –104.3 169.6 –86.9 –148.7 107.8	168.6 –87.8		
$\Psi_{SOO'S'}$, *trans*-	–	179.8	–	–125.6	–	180.0	–57.0 –134.8	–123.6 154.3	180.0		
$\Psi_{SOO'S'}$, *cis*-	–	–	76.6	–89.5 –76.2	–66.2 –66.8 –67.0	89.4 146.4	–138.3 –108.1 –98.3 160.3	–92.2 –162.0 119.1 –70.5	±72.4 ±97.8		

[a] X-ray data for $[Mg(DMSO)_6](ClO_4)_2$ [19]. [b] X-ray data [20]. [c] Average deviation from 90.0° of OMgX angle in *cis* position. [d] Deviation from 180.0° of OMgX angle in *trans* position.

Table 3. Atomic charges[a] (au) and dipole moments of the complexes $[Mg(DMSO)_i(CH_3CN)_{6-i}]^{2+}$, $i = 1–6$, calculated by DFT B3LYP/6-31G** method

Atom	**I**	**IIa**	**IIb**	**IIIa**	**IIIb**	**IVa**	**IVb**	**V**	**VI**	DMSO molecule
Mg	1.67	1.68	1.68	1.69	1.68	1.69	1.70	1.70	1.70	
	(0.75)	(0.78)	(0.77)	(0.80)	(0.75)	(0.82)	(0.80)	(0.82)	(0.80)	
	2.08	*2.05*	*2.02*	*1.96*	*1.94*	*1.88*	*1.89*	*1.85*	*1.77*	
O	–1.09	–1.08	–1.08	–1.08	–1.08	–1.09	–1.07	–1.08	–1.07	–0.93
	–1.01	*–0.99*	*–0.98*	*–0.98*	*–0.96*	*–0.97*	*–0.96*	*–0.94*	*–0.92*	*–0.66*
S	1.28	1.27	1.27	1.28	1.27	1.28	1.24	1.28	1.27	1.22
	0.89	*0.89*	*0.89*	*0.90*	*0.89*	*0.91*	*0.90*	*0.90*	*0.89*	*0.85*
$C_{1,2}$	–0.89	–0.89	–0.89	–0.89	–0.88	–0.89	–0.88	–0.89	–0.89	–0.90
	–0.09	*–0.09*	*–0.08*	*–0.08*	*–0.08*	*–0.10*	*–0.08*	*–0.08*	*–0.08*	*–0.12*
	–0.09	*–0.09*	*–0.10*	*–0.10*	*–0.10*	*–0.08*	*–0.11*	*–0.11*	*–0.10*	*–0.12*
H	0.28	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.25
	0.05	*0.04*	*0.05*	*0.05*	*0.05*	*0.05*	*0.04*	*0.04*	*0.04*	*0.01*
μ	2.89	0.00	3.68	2.44	4.20	0.00	3.05	1.75	0.00	3.93
μ_{exp}										3.96 [22]

[a] The results of the analysis of natural populations, in parentheses by Mulliken, italics APT.

closer to the parameters of free DMSO molecule, which causes the relevant patterns in the variation of intensity of IR bands. In **IIb**–**VI** the charge nonequivalence on the carbon atoms of methyl groups $C_{1,2}$ in DMSO Δq^{NBO} is 0.005 e.

The calculation of the vibration spectrum of DMSO with B3LYP potential, in general, gives better agreement with experiment than at the use of the BLYP (standard deviation of the calculated vibration frequencies from the experimental values falls to 16 cm^{-1} compared with 26 cm^{-1} with BLYP), including better match of the vibration frequencies ν(SO) (deviation from the experimental value is 1 cm^{-1}, compared with 50 cm^{-1}), as well as vibrations ν_s(SC) and ν_{as}(SC) (30 cm^{-1} compared with 100 cm^{-1}). Due to the proximity of these groups to the center of coordination, these vibrations are most susceptible to the changes owing to the influence of ion-molecular interactions, and, therefore, are the most interesting. The influence of intermolecular interactions in solutions on the spectral characteristics of DMSO molecule was carried out in the framework of the polarized continuum model (PCM [23]).

The results of calculation of the spectroscopic characteristics of DMSO molecules, the dimer $(DMSO)_2$, and the complexes **I** and **VI** are compared in Tables 4 and 5 with the experimental values obtained from the spectra of gaseous [24, 25] and liquid DMSO solutions CH_3CN–DMSO , CH_3CN–$Mg(ClO_4)_2$, DMSO–$Mg(ClO_4)_2$ and $Mg(ClO_4)_2$–DMSO–CH_3CN. There is a good correlation between the calculated and experimental values of frequency and the respective values of absolute intensity of the bands. The maximum deviation (160 cm^{-1}) is observed for the stretching vibrations of C–H bonds due to the high anharmonicity of these vibrations.

The calculation of structure and vibration spectrum of the dimer $(DMSO)_2$ executed by us (Table 4) confirms an assumption [27] that some components of the complex contour of stretching vibrations bands ν (SO), ν_s(SC), and ν_{as}(SC) in the spectrum of a solution of DMSO in acetonitrile can be assigned to the vibrations of the dimer. According to the calculation, a strong band at 1046 cm^{-1} in the IR spectrum of the dimer [absolute integral intensity 9.2, the experimental value 12.3 $(D/Å)^2$] shifted to low frequency compared with the vibration of DMSO molecule (1054 cm^{-1}) corresponds to asymmetric vibration of the dimer. Vibrations of the dimer SC bond are shifted to higher frequencies and are of higher intensity compared with the vibrations of free molecule: The calculated intensity of the dimer IR bands A_s(SC) is 0.33 and A_{as}(SC) is 1.1 $(D/Å)^2$.

Table 4. Experimental and calculated (DFT B3LYP/6-31G**) values of vibration frequencies (cm^{-1}) of DMSO molecules and the dimer (DMSO)$_2$

Vibration symmetry	Assignment	DMSO							(DMSO)$_2$
		experiment				calculation			calculation
		gas[a]	solution[b]	solution[c]	liquid	gas[d]	gas	RSM[e]	RSM[e]
A"	$\tau(\mathrm{CH_3})$	178				173	184	191	205, 206
A'	$\tau(\mathrm{CH_3})$	258				219	231	236	262, 271
A'	$\delta(\mathrm{CSC})$	305				269	283	287	289, 296
A"	$\delta(\mathrm{CSO})$	334				278	297	305	313, 318
A'	$\gamma\mathrm{SO}$, $r_\perp(\mathrm{CH_3})$	384	376			342	359	363	365, 366
A'	$\nu(\mathrm{CS})$	667	661	664	664	570	633	646	648, 649
				668[f]	668[f]				
A"	$\nu(\mathrm{CS})$	697	692	693	693	596	663	679	682, 683
				698[f]	698[f]				
A"	$r_{\|}(\mathrm{CH_3})$	820	881	893	896	859	896	907	917, 919
A"	$r_\perp(\mathrm{CH_3})$	900	915	927	930	895	936	946	950, 951
A'	$r_\perp(\mathrm{CH_3})$, $\nu(\mathrm{SO})$	935	926	951	954	922	965	964	964, 968
A'	$r_{\|}(\mathrm{CH_3})$	955	1004	1016	v str	987	1030	1034	1042, 1046
				1029					
				1048[f]					
A'	$\nu(\mathrm{SO})$, δ_s	1102	1101	1060		1055	1101	1054	1049, 1052
A"	δ_s	1300	1293	1293	1292	1278	1332	1337	1337, 1339
A'	δ_s	1310	1310	1310	1310	1303	1356	1358	1359, 1361
				1331	1332				
				1397	1394				
A"	δ'_s	1400	1404	1407	1407	1420	1456	1450	1451, 1451
A'	δ'_s	1410	1419	1419	1419	1433	1469	1460	1460, 1461
A"	δ'_{as}	1420	1440	1438	1438	1437	1473	1463	1470, 1470
A'	δ'_{as}	1435			2818	1455	1492	1480	1496, 1503
A"	$\nu_s(\mathrm{CH_3})$			2871	2873	2979	3054	3050	3049, 3045
A'	$\nu_s(\mathrm{CH_3})$		2922	2930	2912	2981	3056	3051	3051, 3051
A"	$\nu_{as}(\mathrm{CH_3})$			2993	2994	3079	3155	3152	3149, 3149
A'	$\nu_{as}(\mathrm{CH_3})$					3083	3159	3156	3154, 3154
A"	$\nu_{as}(\mathrm{CH_3})$		3001	3083	3063	3091	3167	3162	3162, 3162
A'	$\nu_{as}(\mathrm{CH_3})$					3092	3168	3163	3165, 3168
	r					0.9995	0.9998	0.9999	
	sd					26	16	15	

[a] [24]. [b] [25]. [c] Solution of DMSO in CH$_3$CN, C_{DMSO} = 1.329 mol l^{-1}. [d] DFT BLYP/6-31G**. [e] Solvents CH$_3$CN and DMSO. The DMSO vibration frequencies calculated by the RSM method for these solvents are identical within 1 cm^{-1}. [f] The component of the band corresponding to the vibrations of the DMSO dimer [26]. The absolute intensities of the dimer vibration bands: ν_{668} = 0.54, ν_{698} = 1.80, ν_{1048} = 12.3 (D/Å)^2.

Table 5. Experimental and calculated (B3LYP/6-31G**) frequencies and absolute integral intensities of absorption bands of DMSO molecules dissolved in acetonitrile and the complexes $[Mg(DMSO)_i(CH_3CN)_{6-i}]^{2+}$ (**I**) and $[Mg(DMSO)_6]^{2+}$ (**VI**) in the middle IR region

Assignment in the spectrum of complex **I**	Experiment						Calculation							
	frequency, cm^{-1}			intensity of bands (D/Å)^2			frequency[a], cm^{-1}				intensity of bands[b] (D/Å)^2		
	molecule[c]	**I**	**VI**	molecule[c]	**I**	**VI**	molecule[c]	**I**	**VI**	Δν[d]	molecule[c]	**I**	**VI**
νMgO(N), φ(MgOS), φ(OSC), $r_{\parallel}$ and $r_{\perp}(CH_3)$								458	440	42		3.54	1.61
ν(CS)	664[e]	682	679	0.09[f]	0.05	0.06	646	660	660	1.4	0.20	0.011	0.031
ν(CS)	693[e]	718	715	0.12[f]	0.18	0.34	679	698	700	0.6	0.53	0.12	0.15
$r_{\parallel}(CH_3)$	893	904	906	0.05	0.20	0.09	907	925	927	0.7	0.08	0.05	0.08
$r_{\perp}(CH_3)$	927		944	0.22		0.45	946	964	*953*	8.2	0.24	0.12	*2.98*
$r_{\perp}(CH_3)$, ν(SO)	950	971	967	0.40	1.1	1.2	964	*985*	966	8.6	1.20	*3.36*	0.63
$r_{\perp}(CH_3)$, ν(SO)	1016	1023		0.50	2.5		1034	*1027*	1023	14.6	0.83	*3.29*	1.63
$r_{\parallel}(CH_3)$	1060[e]			5.1[e]			*1054*	1055	1055	7.4	*4.50*	0.84	0.59
δ_s	1293		1295	0.02		0.05	1337	1352	1352	1.8	0.02	0.026	0.019
δ_s	1310		1312	0.55		0.09	1358	1377	1375	1.2	0.17	0.18	0.23
	1331		1319			0.25							
δ'_s	1397		1353			0.15	1450	1452	1453	0.4	0.32	0.30	0.20
δ'_s	1407		1406	0.24		0.26	1460	1464	1464	3.0	0.15	0.24	0.08
δ'_{as}	1419		1422	0.22		0.80	1463	1466	1467	3.6	0.00	0.78	0.11
δ'_{as}	1438		1437	0.55		0.39	1480	1484	1485	1.7	0.58	0.68	0.74
	2871												
$\nu_s(CH_3)$	2930		2918	0.91		0.32	3050	3069	3067[g]	0.1	0.02	0.000	0.024
$\nu_s(CH_3)$							3051	3069	3069[g]	0.01	0.04		
$\nu_{as}(CH_3)$	2993		3007	0.74		0.68	3152	3172	3170[g]	0.15	0.00	0.018	0.021
$\nu_{as}(CH_3)$							3156	3172	3173[g]	0.04	0.10		
$\nu_{as}(CH_3)$	3083			0.10			3162	3184	3182[g]	0.02	0.03	0.003	0.046
$\nu_{as}(CH_3)$							3163	3184	3191[g]	0.18	0.02		
r							0.9999		0.9999		0.94	0.90	0.73
sd							15		10		0.4	1.0	0.7

[a] These frequencies correspond to a position of the maximum of the envelope of a complex band consisting of *i* components. [b] The total intensity of the band divided by the number of molecules of DMSO in the complex. [c] In DMSO dissolved in CH_3CN, Experiment: C_{DMSO} = 1.329 mol l^{-1} ; calculation RSM, solvent CH_3CN. [d] Frequency splitting of individual vibrations of the complex. [e] Characteristics of the vibration band fluctuations of the monomer, the position of the components corresponds to the data [26]. [f] Finding characteristics of the band in the absorption spectrum of the DMSO–$Mg(ClO_4)_2$ binary mixture is difficult even in thin layers (15 μm) due to the overlap by strong absorption bands of vibrations ν_3 of perchlorate anion and ν(SO) of DMSO molecules. [g] Degeneracy is deleted owing to the difference of axial and equatorial CH_3 groups.

Comparison of experimental and calculated IR spectral parameters of the complex **VI** shows that for the vibrations localized near the coordination site the calculation predicts correctly a shift of the bands of solvent molecules at their location in the cation coordination sphere: an increase in the vibration frequency ν(SC), ν(CH) and a decrease in the frequency ν(SO). The calculated shifts of the ν(SC) vibration bands of DMSO molecules in the composition of the complex **VI** compared to the DMSO dissolved in acetonitrile agrees quantitatively with the experimentally measured values [$\Delta\nu_s$(SC): calculated 15, experimental 14 cm^{-1}; $\Delta\nu_{as}$(SC): calculated 22, experimental 21 cm^{-1}]. Thus, calculations with DFT B3LYP/6-31G** gives an adequate description of the spectral properties of DMSO molecules and complex **VI**.

In complexes **I**–**VI** due to the significant value of the metal–ligand force constant the coordinated molecules are interacting, and that alters the shape of generalized normal vibrations. The natural vibration coordinates maximally contributing to the normal vibration of the complex **I** are shown in Table 5. In the IR spectra of the complexes (similar to $[Mg(DMF)_i\cdot(CH_3CN)_{6-i}]^{2+}$ [13]) in the region of 500–400 cm^{-1} besides the vibration bands γ(CCN) of acetonitrile (404–416 cm^{-1}) there are strong bands (Fig. 2a), which can be assigned to the metal–ligand bond vibrations. The shape of these normal-mode vibrations include the contribution of the vibration coordinates q(MgH), φ(MgOS), φ(OSC), φ(HMgO), and γ(HMgH), X = O, N, as well as and $r_{\|,\perp}(CH_3)$, γ(MgNC), and γ(CCN). In complex **VI** the splitting of vibration frequencies in this region is 42 cm^{-1}, in the mixed complexes the splitting is larger; position and absolute intensity of the component is determined by the number of coordinated DMSO molecules and positional symmetry of the ligands. According to the calculation, the most intense bands to be expected in the spectra of the complexes **IVa**, **V,** and **VI** that contain two pairs of DMSO molecules in the *trans*-position relative to the central ion. A significant difference in the position, shape, and intensity of the bands in the considered region can be used for identification of some solvates. The total absorption intensity in the region of 400–500 cm^{-1} increases in the series **I**–**VI** due to the greater values of the dipole moment μ_k and the derivative $\partial\mu_k/\partial q_k$ of Mg–O bond as compared with Mg–N. The higher value of the absorption intensity in this region of complex **VI** compared with $[Mg(DMF)_6]^{2+}$ {ν_{max} 402 cm^{-1}, A_{total} 6.2 $(D/Å)^2$ [13]} indicates 1.5-fold increase in polarity of Mg–O bond in **VI**, which is consistent with estimates of the charges on the O atoms.

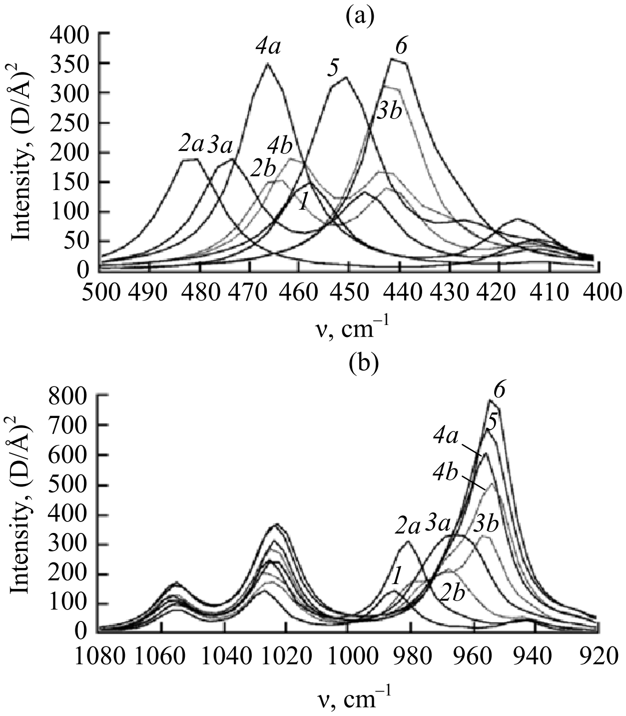


Fig. 2. Calculated IR spectra of the complexes $[Mg(DMSO)_i\cdot(CH_3CN)_{6-i}]^{2+}$ in the regions of vibration (a) ν(MgO) and (b) ν(CO), the Lorentz contour, $\Delta\nu_{1/2}$ = 15 cm^{-1}.

Some of the normal DMSO vibrations in the region of 1100–900 cm^{-1} contains contributions of SO bond stretching vibrations and torsional vibrations of methyl groups. These normal-mode vibrations are retained in the complexes **I**–**VI**, but due to the interaction of these vibration coordinates with the coordinates of the bonds Mg–O and Mg–N the shape of vibrations in the series suffers changes in such a way that an increase in the number of coordinated DMSO molecules with the largest contribution of SO bond is shifted to lower frequencies (Table 5, indicated in italics). In the considered spectral region, the greatest splitting of vibration frequencies due to the interaction of different ligands is 15 cm^{-1} for the band at 1023 cm^{-1} and 8 cm^{-1} for other vibrations. For other normal-mode vibrations of complexes in the middle IR region the mixing of vibration coordinates of molecules is small, and the assignment of bands in the spectrum is the same as in the spectrum of DMSO molecule [25].

The spectral characteristics of the ligand molecules in the mixed complexes **I**–**VI** vary appreciably. Inasmuch as the regularity in the intensity variation

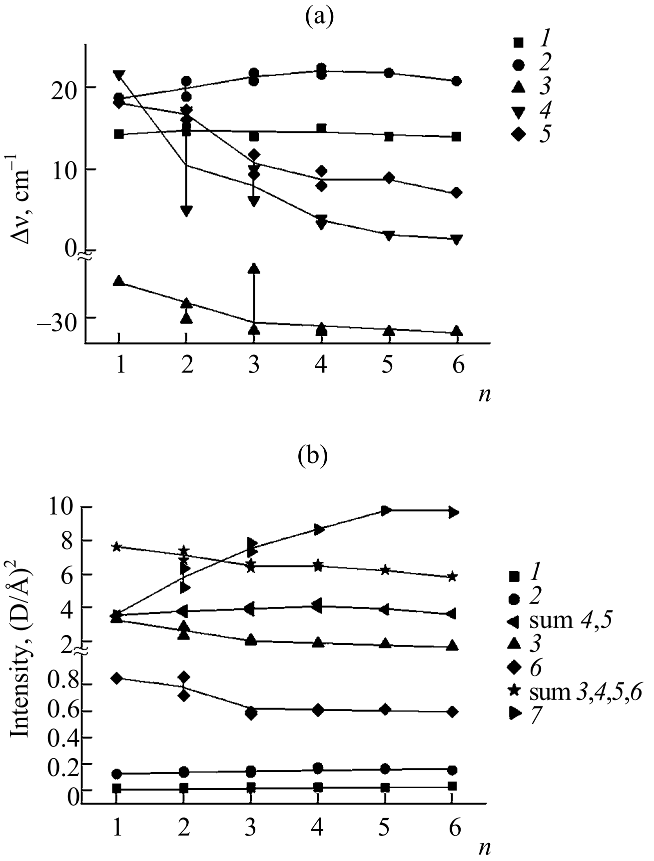


Fig. 3. Parameters of DMSO molecules IR absorption bands of the $[Mg(DMSO)_i(CH_3CN)_{6-i}]^{2+}$ complexes vs. the number of DMSO molecules in their composition. (a) Frequency shift of IR absorption bands of DMSO molecules in the mixed complexes as compared with solution of DMSO in acetonitrile and (b) intensity of IR bands per 1 molecule of DMSO: (*1*) $\nu_s(SC)$, (*2*) $\nu_{as}(SC)$, (*3*) 1023 cm^{-1}, (*4*) 966 cm^{-1}, (*5*) 953 cm^{-1}, (*6*) 904 cm^{-1}, and (*7*) the total intensity of absorption in the region of Mg–O vibrations.

and in the shift of vibration bands of the CH_3CN molecules in the $[Mg(DMSO)_i(CH_3CN)_{6-i}]^{2+}$ complexes reproduce the dependences found in the study of DMF-containing magnesium complexes [13], in this study we examined only the effects associated with the changes in the spectroscopic characteristics of the coordinated DMSO molecules. The respective dependence for the vibration most sensitive to the composition of the solvate are shown in Fig. 3. The greatest changes in the absolute intensities and shifts of absorption bands in the mid-IR region are observed for the vibrations at 1050–950 cm^{-1}: the shift of the band vibrations ν_{966} of **VI** reaches 19 cm^{-1} in the series, the intensity of the bands ν_{1055} and ν_{1023} suffer 1.5–2-fold changes, respectively. The intensity of the band $\nu_s(SC)$ is changed 3-fold. The absolute magnitude and the direction of the effect is determined by the nature of the normal vibrations. For most of the vibrations (as in the case of $\{[Mg(DMF)_i(CH_3CN)_{6-i}]^{2+}$complexes [13]} at the increase in the number of molecules in the DMSO solvate a trend is observed to smaller shift and change in intensity of vibrations of ligand DMSO in comparison with the same characteristics of free molecule. The difference between the steric structure of the complexes of the same composition in most cases only slightly affects the position and intensity of the bands in the IR spectrum (Fig. 2b).

Calculated values of the energy of formation ΔG_0 of complexes (Table 6) indicate their high stability, while ΔG_0 of **VI** by 15 kJ mol^{-1} exceeds the ΔG_0 of $[Mg(DMF)_6]^{2+}$ [13]. The values of free energies ΔG_i of substitution reactions of ligands in the coordination sphere of ion indicate that DMSO molecule is more prone to coordination to the cation compared with CH_3CN.

$$[Mg(DMSO)_i(CH_3CN)_{6-i}]^{2+} + DMSO$$
$$\rightleftarrows [Mg(DMSO)_{i+1}(CH_3CN)_{6-i}]^{2+} + CH_3CN.$$

Structure of complexes **IIIa** and **IVa** with *trans*-arrangement of the DMSO ligand is energetically preferable. In general, in the series **I**–**VI** there is a tendency of decrease in ΔG_i, but the formation of 1:2 complexes is more advantageous. The values of ΔG_i characterizing the process of the ion transsolvation in the $CH_3CN–Mg(ClO_4)_2–DMSO$ system are compared with the values calculated for the same complexes containing DMF: energy ΔG_i coincides within ±3 kJ mol^{-1}, except for the value ΔG_4 (in the system $CH_3CN–Mg(ClO_4)_2–DMSO$ this parameter is by 11 kJ mol^{-1} larger and is comparable with the ΔG_2).

Analysis of the IR Sectra of $CH_3CN–Mg(ClO_4)_2–DMSO$ Slutions

While in the spectra of solutions of alkali metal salts the shift of the bands of coordinated DMSO gives a “shoulder” on the main band corresponding to vibrations of molecules not included in the cation solvation shell [27], addition of anhydrous magnesium perchlorate to DMSO leads to appearance in the IR spectrum of new absorption bands (Figs. 4 and 5). As can be seen from Table 5, the action of the Mg^{2+} cation on the DMSO molecules leads to a shift of the bands of SO and SC bonds vibrations and a significant change in their intensity (≥200%). The bands of DMSO CH_3 groups stretching and bending vibrations of the molecules in the solvation shell of Mg^{2+} cation

Table 6. Free energy of formation ΔG_0 and the energy of the ligand substitution reaction ΔG_i in the coordination sphere of the complexes $[MgX_i(CH_3CN)_{6-i}]^{2+}$, X = DMSO, DMF, according to the calculation by the method of density functional (kJ mol^{-1})

Comp. no.	$[Mg(DMSO)_i(CH_3CN)_{6-i}]^{2+}$				$[Mg(DMF)_i(CH_3CN)_{6-i}]^{2+}$
	$-\Delta G_o$, kJ mol^{-1}		$-\Delta G_i$, kJ mol^{-1}		$-\Delta G_i$, kJ mol^{-1} [13]
	B3LYP	BLYP	B3LYP	BLYP	BLYP
I	1406	1389	42	34	36
IIa	1457	1426	51	37	40
IIb	1463	1430	56	42	
IIIa	1496	1458	34	28	28
IIIb	1488	1449	25	18	
IVa	1536	1501	39	43	32
IVb	1530	1494	34	35	
V	1570	1526	34	25	21
VI	1597	1549	28	23	22

are less shifted. Their characteristics were defined from the differential absorption spectra with compensation of the absorption of pure solvent (Figs. 5b, 5c).

Spectral characteristics of DMSO molecules in the solvates of mixed composition are markedly changed compared with the corresponding characteristics of the DMSO molecules in the $[Mg(DMSO)_6]^{2+}$ solvate, as evidenced by the spectra of ternary solutions $Mg(ClO_4)_2$–DMSO–CH_3CN [C(DMSO) 0.26–2.27 mol l^{-1}] shown in Figs. 4 and 5. Dimethyl sulfoxide is a more active solvating component of the binary solvent, in accordance with its higher donor number. At the concentration ratio of DMSO and the cation ≤ 4.5, in the IR spectra of ternary systems there are no bands of the DMSO vibrations of the molecules not included in the cation solvation shell. Thus, the concentration of DMSO molecules in the cation coordination sphere becomes equal to the total concentration of this component, which significantly simplifies the interpretation of the spectra and determination of the absolute integral intensities.

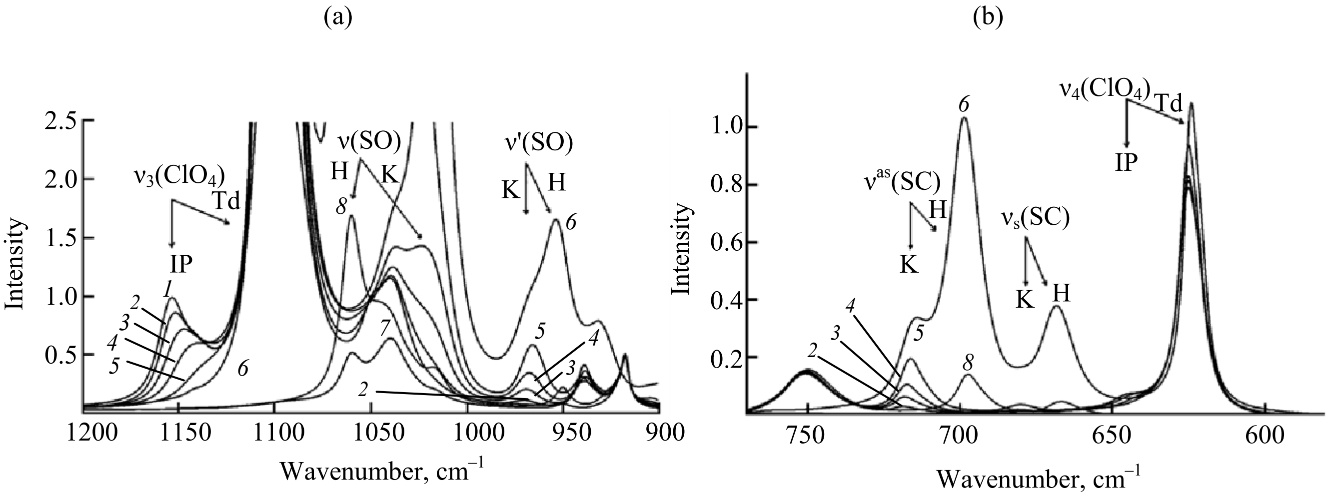

(a) (b)

Fig. 4. IR spectra of solutions $Mg(ClO_4)_2$–DMSO–CH_3CN in a 29–30 μm layer: (a) 1200–900 cm^{-1} and (b) 780–580 cm^{-1}. Curves (*1*–*6*): $C[Mg(ClO_4)_2]$ = 0.500±0.001, C(DMSO) = 0.0, 0.265, 0.707, 1.306, 2.272, 13.545 mol l^{-1}, curves (*7*–*8*): $C[Mg(ClO_4)_2]$ = 0.0, C(DMSO) = 0.271, 1.329 mol l^{-1}.

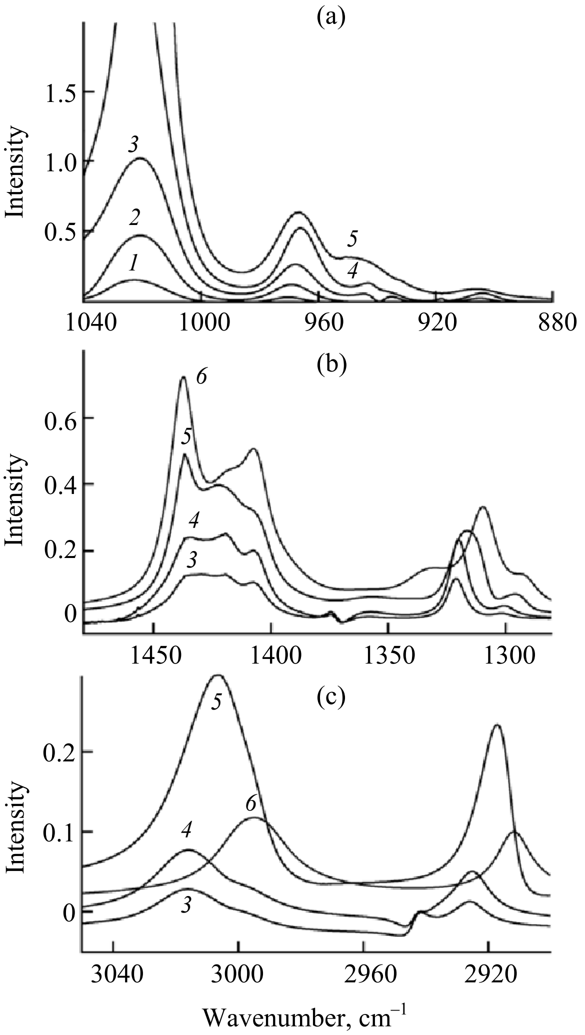


Fig. 5. Differential spectra of $Mg(ClO_4)_2$–DMSO–CH_3CN solutions characterizing absorption of DMSO molecules in the cation solvation shell in the regions: (a) 1050–880 cm^{-1}, (b) 1500–1300 cm^{-1} and (c) 3050–2900 cm^{-1}. Curves (*1*–*5*): $C[Mg(ClO_4)_2]$ = 0.500, *C*(DMSO) = 0.265, 0.707, 1.306, 2.272, 13.545 mol l^{-1}, (*6*) spectrum of DMSO, reduced (b)2.5 times and (c) 10 times.

The concentrations of the solvent molecules included in the solvation shells of the Mg^{2+} cation were calculated with the equations given in [8] taking into account the concentrations of the formed ion pairs. In the spectra of $Mg(ClO_4)_2$–DMSO binary solutions the formation of ion pairs is not observed that might be indicated by the separation of stretching and bending vibrations (ν_3 and ν_4, respectively) of ClO_4^- anion, degenerate in the case of the ion in a free state. However, in the spectra of ternary systems the corresponding splitting of the bands is observed (Figs. 4a, 4b). The concentrations of magnesium ions involved in the formation of ion pairs were identified by analyzing the relative intensities of the split components of vibrations ν_3 (1154, 1142 cm^{-1}) and ν_4 (646 cm^{-1}) of the anion.

In accordance with the calculation results and taking into account the splitting of vibration band ν(CO) of DMF molecules coordinated to the cation observed in the spectra of a similar system CH_3CN–$Mg(ClO_4)_2$–DMF [8, 13], it is expectable to find a significant shift and change in the contour of the band of normal-mode vibration involving the valence coordinate of SO bond directly connected to the coordination center. Quantitative analysis of the IR absorption spectra of binary solutions $Mg(ClO_4)_2$–DMSO in the region of 1060–1000 cm^{-1} is difficult due to the extremely strong ν(SO) vibrations of DMSO molecules, as well as strong absorption of the close by frequency ν_3 vibration of perchlorate anion. However, in the differential spectra of ternary solutions with the compensation of acetonitrile absorption[1] the determination of position and absolute integral intensity of the ν(SO) band becomes possible (Fig. 5a). We found that involvement of DMSO molecules into the solvation shell of the Mg^{2+} cation leads to a shift of the band at 38 cm^{-1} to the low-frequency region, and the band intensity decreases in comparison with the intensity of this band in the spectra of noncoordinated molecules. No significant shift of this band or its splitting due to interaction of the ligands vibrations was detected at the changing composition of the binary solvent.

The calculation shows that contribution of the SO bond valence coordinate to the ν_{950} cm^{-1} vibration of DMSO molecule is also significant. This conclusion is confirmed by the high sensitivity of this vibration to the coordination of DMSO molecule to the cation: there is a 17 cm^{-1} short-wavelength shift of this band in the spectrum of the $Mg(ClO_4)_2$–DMSO binary solution compared with the DMSO solution in acetonitrile. The shift of this band in the ternary solution increases with a decrease in the number of molecules in the DMSO solvate (Δν 4 cm^{-1}). It should

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[1] The compensation of the absorption of acetonitrile molecules in the Mg^{2+} solvation shell and free was carried out by subtracting from the spectrum of the ternary system the spectrum of pure acetonitrile, as well as the differential spectrum of solution of $Mg(ClO_4)_2$–CH_3CN relative to pure acetonitrile. The coefficients of normalization were selected taking into account the concentration of acetonitrile free molecules and “perturbed” by the cation, and the layer thicknesses in the respective measurements.

be noted that in the calculated spectra of the complexes in this area there is a strong band that experiences the greatest shift in the series of solvates. In the experimental spectra, the absolute intensity of this band is much smaller.

In the spectra of ternary solutions at low DMSO concentrations {providing preferential formation of solvates of $[Mg(DMSO)_1(CH_3CN)_5]^{2+}$ composition} the absolute intensity of the band in the region of 1020 cm^{-1} is 5 times stronger than the intensity of the vibration band of free DMSO molecule. Upon filling the solvation shell with DMSO molecules the band intensity decreases similar to the change in intensity of acetonitrile vibration bands and some of DMF bands [13]. In the region of 1000–900 cm^{-1} in the differential spectra of ternary solutions also there is a band at 944 cm^{-1} (this band strongly overlaps with the vibration band ν(CC) of acetonitrile in the solvation shell) and a weak band at 904 cm^{-1}. By decomposition of the contour into the individual bands we determined the frequencies and integral intensities of the DMSO molecule absorption bands in the solvates of mixed composition. The variations of these values versus the system composition are shown in Fig. 6.

Analysis of the experimental spectra of ternary solutions CH_3CN–$Mg(ClO_4)_2$–DMSO together with the results of quantum-chemical calculation of infrared spectra of the complexes **I**–**VI** show a significant change in the spectroscopic characteristics (ν, *A*) of coordinated DMSO and acetonitrile molecules, depending on the complex composition. In the series of the complexes an increase in the cation–ligand distance at the same charge of the central ion leads to a decrease in the strength of the cation electrostatic field acting on the coordinated DMSO molecules. This results in a significant change in the electrooptic parameters of the bonds at a relatively small change in force constants leading to regular change in the parameters of the bands in the vibration spectra of the complexes.

On the basis of quantum-chemical calculation of IR spectra of the complexes we found that the most promising for the determining the composition of solvates (and possibly spatial arrangement of the ligands) is the study of the vibration spectra of multicomponent solutions in the region of the low-frequency vibrations 300–500 cm^{-1}, where the number of bands, their position, and absolute intensity in the series of complexes change most significantly. By the analysis of the IR spectra of ternary solutions CH_3CN–$Mg(ClO_4)_2$–DMSO we showed that for the determining the composition of solvates absorption bands of the vibrations ν_{966}, ν_{1023} and $\nu_{as}(SC)$ of DMSO can be used, which are the most sensitive to the ion-molecular interactions .

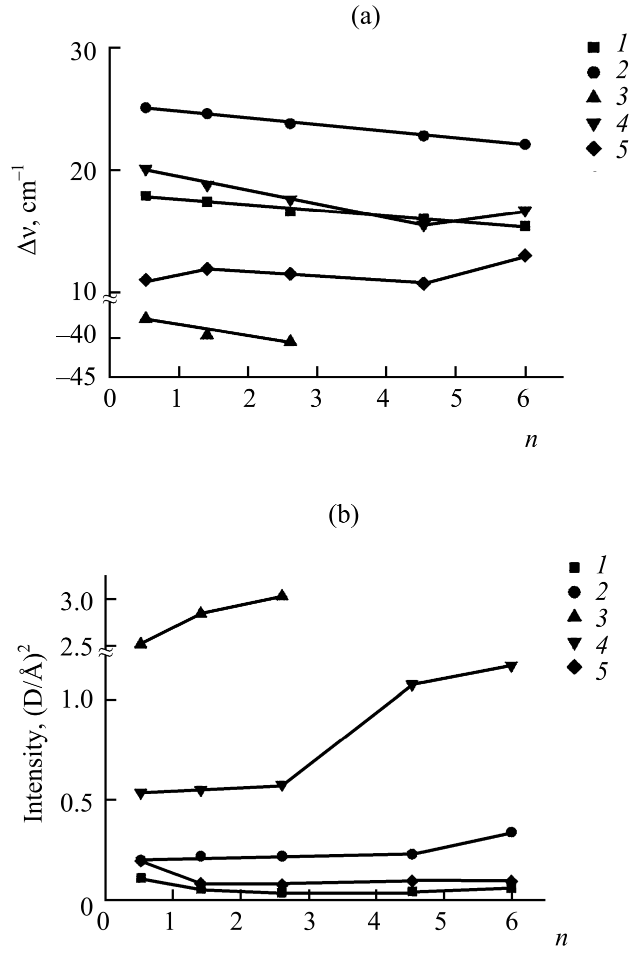

Fig. 6. Parameters of the IR absorption bands of coordinated DMSO molecules in $Mg(ClO_4)_2$–DMSO–CH_3CN solutions vs. average number of DMSO molecules in the solvation shell: (a) frequency shift of IR absorption bands of DMSO molecules in the mixed complexes as compared with solution of DMSO in acetonitrile, (b) absolute intensities of DMSO IR bands. (*1*) $\nu_s(SC)$, (*2*) $\nu_{as}(SC)$, (*3*–*5*) vibrations involving SO bond at 1023, 966, and 904 cm^{-1}.

EXPERIMENTAL

Magnesium perchlorate $Mg(ClO_4)_2 \cdot 6H_2O$ (Fluka) was calcined in a vacuum at *T* = 250° C for several days. Anhydrous DMSO (Aldrich) and acetonitrile (Merck) were kept in a dry box over calcined zeolites (4 Å). Three-component CH_3CN–$Mg(ClO_4)_2$–DMSO solutions with constant concentration of magnesium perchlorate {C[Mg(ClO_4)$_2$] 0.500 mol l^{-1}} and a variable composition of the binary solvent [C(DMSO) 0.265–2.272 mol l^{-1}] were prepared in a dry box by volume–weight method. Monitoring of water content (< 0.001 mol l^{-1}) was carried out spectroscopically. The IR spectra were measured in a flow of nitrogen at 25°C on a Bruker IFS 66v/S FTIR spectrometer in the region of 4000–500 cm^{-1}. We used a cell with NaCl windows, the thickness of the layer (14, 18, 30 and 60 μm) was determined by the interference mehod. Resolving of overlapping bands was carried out using the program OPUS. Reproducibility of the wave number corresponding to the position of maximum of a component of complex contour in 5 independent measurements was 0.2–0.5 cm^{-1}, the intensity reproducibility was 5–20% depending on the intensity ratio of the complex band components.

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