Aquacomplexes of ions of Group IB—IVB metals in anomalous oxidation states ($^2S_{1/2}$ electron state): a theoretical study

Yu. A. Borisov[a]* *and A. I. Aleksandrov*[b]

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: yabor@ineos.ac.ru
[b]*Institute of Synthetic Polymer Materials, Russian Academy of Sciences,*
70 ul. Profsoyuznaya, 117393 Moscow, Russian Federation.
Fax: +7 (095) 420 2229. E-mail: aleks@lx.ispm.ac.ru

Ab initio calculations of aquacomplexes of the ions of Group IB—IVB metals in anomalous oxidation states ($^2S_{1/2}$ electron state) were carried out by the Becke—Lee—Yang—Parr (BLYP) density functional method using the Dunning—Hay DZ basis set. Optimum geometric parameters and electronic characteristics were determined of aquacomplexes $M(H_2O)_n^{z+}$, where M^{z+} = Au^0 (n = 2, 4); Ag^0, Cu^0 (n = 2, 4, 6); Zn^{1+}, Cd^{1+}, Hg^{1+} (n = 4, 6); Ga^{2+}, In^{2+}, Tl^{2+} (n = 6); and Ge^{3+}, Sn^{3+}, Pb^{3+} (n = 6). The spin population on the central metal atom decreases as the atomic number increases in the corresponding periods. The energy of transition of the unpaired electron to the first vacant level increases in the same order. The results of calculations are in agreement with experimental data obtained by ESR and optical spectroscopy.

Key words: aquacomplexes of ions of Group IB—IVB metals, anomalous oxidation states, *ab initio* calculations, density functional method.

The efficiency of redox processes with participation of polyvalent metals is associated with the properties of their ions in anomalous oxidation states (AOS) formed as intermediates. These extremely active species can be obtained in aqueous solutions by pulse[1] or low-temperature radiolysis (with subsequent recording of their ESR spectra).[2]

Table 1. Isotropic hyperfine coupling constants (A_{iso}) and positions of absorption maxima (λ_{max}) in optical spectra of aquacomplexes of ions of Group IB—IVB metals in AOS at different temperatures

Ion in AOS	Low-temperature glasses (77 K)		Aqueous solutions (300 K)
	A_{iso} (A^0_{iso})/mT	λ_{max}/nm	λ_{max}/nm
$^{63}Cu^0$	(209.4)		380
$^{67}Zn^{1+}$	(83.5)	290	310
$^{69}Ga^{2+}$	226.0 (503.4)	245	268
Ge^{3+}	(107.7)		
$^{109}Ag^0$	58.0 (70.5)	330	360
$^{111}Cd^{1+}$	325.0 (513.7)	270	300
$^{113}In^{2+}$	(813.9)	235	260
$^{117}Sn^{3+}$	682.5 (1593.5)	215	
$^{197}Au^0$	(108.9)		~260
$^{199}Hg^{1+}$	1135.0 (1445.3)	240	233
$^{203}Tl^{2+}$	4321.0 (6262.2)	225	~215
$^{207}Pb^{3+}$	1600.0 (2779.6)	~200	~200

Properties of ions of Group IB—IVB metals in AOS ($^2S_{1/2}$ electron state), *viz.*, Cu^0, Zn^{1+}, Ga^{2+}, Ge^{3+}, Ag^0, Cd^{1+}, In^{2+}, Sn^{3+}, Au^0, Hg^{1+}, Tl^{2+}, and Pb^{3+}, in frozen (T = 77 K) and standard (T = 300 K) aqueous solutions have long been studied[2—4] and covered in detail in the reviews.[5,6] The major results for aquacomplexes of ions of Group IB—IVB metals in AOS obtained by ESR and optical spectroscopy are summarized in Table 1 (the data were taken from Refs. 5—9). Low-temperature experiments (at 77 K) were carried out using concentrated aqueous solutions of perchloric acid (5.0—8.5 M $HClO_4$), which resulted in the formation of the so-called low-temperature glasses.[7,8] Aqueous solutions of perchlorates of the above metals were studied by pulse radiolysis.[9] It has been shown[5—9] that basic properties of isoelectronic ions of the metals belonging to the same period of the Periodic system monotonically change in the Cu^0—Zn^{1+}—Ga^{2+}—Ge^{3+}, Ag^0—Cd^{1+}—In^{2+}—Sn^{3+}, and Au^0—Hg^{1+}—Tl^{2+}—Pb^{3+} series as the atomic number of the element in the corresponding period increases. The A_{iso}/A^0_{iso} ratio (A^0_{iso} and A_{iso} are the isotropic hyperfine coupling constants for the free ion and for the complex stabilizing this ion, respectively), which is equal to the density of the unpaired electron on the outer ns-AO, decreases as the degree of oxidation of the

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Table 2. Geometric parameters (interatomic distances (*R*) and bond angles (ω)) of aquacomplexes

Complex	*R*/Å				ω/deg	
	M—O	M—O′	O—H	O′—H′	H—O—H	H′—O′—H′
$Cu(H_2O)_6$	2.321	2.098	1.000	0.985	109.0	113.3
$Zn(H_2O)_6{}^{1+}$	2.196	1.190	1.004	0.992	110.8	111.4
$Ga(H_2O)_6{}^{2+}$	2.229	2.167	0.995	0.992	108.8	110.6
$Ge(H_2O)_6{}^{3+}$	2.172	2.128	0.996	0.995	108.3	110.5
$Ag(H_2O)_6$	2.508	2.466	0.996	0.987	109.9	112.1
$Cd(H_2O)_6{}^{1+}$	2.461	2.436	0.998	0.993	109.6	110.5
$In(H_2O)_6{}^{2+}$	2.346	2.302	0.994	0.992	108.6	110.0
$Sn(H_2O)_6{}^{3+}$	2.291	2.254	0.996	0.996	107.9	109.6
$Hg(H_2O)_6{}^{1+}$	2.762	2.680	0.990	0.989	109.1	110.0
$Tl(H_2O)_6{}^{2+}$	2.550	2.500	0.990	0.989	109.1	110.4
$Pb(H_2O)_6{}^{3+}$	2.364	2.327	0.995	0.995	108.8	110.5
$Cu(H_2O)_4$	2.160	—	1.005	—	110.6	—
$Zn(H_2O)_4{}^{1+}$	2.191	—	0.994	—	110.3	—
$Ag(H_2O)_4$	2.544	—	0.998	—	110.1	—
$Cd(H_2O)_4{}^{1+}$	2.438	—	0.991	—	109.9	—
$Au(H_2O)_4$	3.242	—	0.990	—	109.3	—
$Hg(H_2O)_4{}^{1+}$	2.616	—	0.989	—	110.0	—
$Cu(H_2O)_2$	2.028	—	1.003	—	111.9	—
$Ag(H_2O)_2$	2.497	—	0.994	—	110.5	—
$Au(H_2O)_2$	2.521	—	0.990	—	111.4	—

metal (z) increases. The energies of optical transitions corresponding to the absorption band maxima ($E_{\lambda_{max}}$) increase as z increases for both the ions formed in low-temperature glasses upon γ-irradiation at 77 K and the ions generated in aqueous solutions at 300 K exposed to a high-energy electron beam (see Table 1).

Calculation procedure

Currently, energy and thermodynamic characteristics of clusters and metal complexes are determined[11—15] using theoretical methods developed on the basis of the density functional theory (DFT), based on the Hohenberg—Kohn theorem,[16] and the Kohn—Sham equation.[17] The latter is analogous to the Hartree—Fock equation; however, it includes electron exchange and correlation. The Kohn—Sham energy functional has the form

$$E_{KS}[P] = V + \langle hP \rangle + 1/2 \cdot \langle PJ(P) \rangle + E_{ex}[P] + E_{corr}[P],$$

where $E_{ex}[P]$ and $E_{corr}[P]$ are the exchange and correlation energy functionals, respectively; V is the energy of internuclear interaction; $\langle hP \rangle$ is the one-electron energy; $1/2 \cdot \langle PJ(P) \rangle$ is the quasi-classical repulsive energy of electrons; and P is the density matrix. The $E_{ex}[P]$ functional includes the Slater exchange and corrections due to the electron density gradients[18] and the $E_{corr}[P]$ functional for the correlation energy includes local and nonlocal terms.[19,20]

In this work we report the results of *ab initio* calculations of $M(H_2O)_n{}^{z+}$ aquacomplexes, where M^{z+} is the ion of IB—IVB Group metals in AOS (the $^2S_{1/2}$ electron state)* (M^{z+} = Cu^0, Ag^0, Au^0; Zn^{1+}, Cd^{1+}, Hg^{1+}; Ga^{2+}, In^{2+}, Tl^{2+}; Ge^{3+}, Sn^{3+}, Pb^{3+}),* performed by the Becke—Lee—Yang—Parr (BLYP) electron density functional method[18—20] using the Dunning—Hay basis sets of two-exponential heavy-element atomic functions (LanL2DZ).[21,22] Calculations were carried out with full geometry optimization of the complexes on a CRAY J-90 supercomputer (Berkeley, California, USA) using the GAUSSIAN-94 program.[23]

Most of the calculations were performed for octahedral (n = 6) hexacoordinated aquacomplexes. Additional calculations were carried out for Ag^0 and Au^0 (n = 2, 4) and for aquacomplexes of Zn^{1+}, Cd^{1+}, and Hg^{1+} (n = 4).

Results and Discussion

The structure of aquacomplexes

We considered aquacomplexes with octahedral coordination of the oxygen atoms of water molecules to the central metal ion. In this structure four water molecules are in the xy plane and the remaining two water molecules are in the xz plane. The full symmetry group of such an aquacomplex is D_{2h}. Calculations of octahedral clusters were performed with energy optimization over the M—O, M—O′, O—H, and O′—H′ interatomic distances (R) and the H—O—H and H′—O′—H′ bond angles (ω).** The results of calculations are listed in Table 2.

Comparison of geometric parameters (R(O—H) = 0.99 Å, ω(H—O—H) = 108.6°) of the free and coordinated water molecules calculated by the same

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* Previously,[7] analogous calculations were performed at the semiempirical level of theory. Positions of optical absorption bands were analyzed using the modified Balmer formula that makes it possible to take into account the medium effect.[10]

* Hereafter we will denote $M(H_2O)_n{}^{z+}$ as M^{z+} ($M(H_2O)_n{}^{z+} \equiv M^{z+}$).

** The primed atoms (H′ and O′) lie in the xz plane.

(BLYP/LanL2DZ) method shows that the bond lengths and bond angles in the four H_2O molecules lying in the equatorial plane of the octahedral complex are slightly distorted. Changes in the geometry of the water molecules lying in the *xz* plane are more appreciable. This particularly concerns the H′—O′—H′ bond angles.

For all aquacomplexes considered, the M—O distances are somewhat longer than the M—O′ distances, *i.e.*, the octahedron is "compressed" along the *z* axis; the maximum difference (0.223 Å) is observed for Cu^0 aquacomplex. Optimization of geometric parameters for Au^0 does not result in an octahedral complex, *i.e.*, the gold ion can not coordinate six H_2O molecules simultaneously. For octahedral clusters of Cu^0, Zn^{1+}, Ga^{2+}, and Ge^{3+}, a tendency for the M—O bond lengths to be shortened in the above order is observed, except for the Zn^{1+} complex, in which the Zn—O distance is shorter than the Ga—O distance in the Ga^{2+} complex. For aquacomplexes of Ag^0, Cd^{1+}, In^{2+}, and Sn^{3+} the M—O bond lengths decrease monotonically. The same dependence is also observed for Hg^{1+}, Tl^{2+}, and Pb^{3+} complexes. Comparison of the M—O interatomic distances for the elements of the same groups of the Periodic system shows that they regularly increase as the atomic number of the metal atom increases.

It has been reported[24] that the formation of linear aquacomplexes with the coordination number (*CN*) equal to 2 is characteristic of the elements of the copper subgroup; however, tetrahedral complexes with *CN* = 4 can also be formed as in the case of zinc subgroup elements. We have performed theoretical investigations of aquacomplexes of the metals of these subgroups with the above *CN* values. The results of calculations are also listed in Table 2.

The structure of different aquacomplexes of the elements of the copper subgroup is characterized by the following features. The Cu—O bond length nearly linearly depends on the coordination number, *viz.*, on going from complexes with *CN* = 2 to the complexes with *CN* = 4 and further to those with *CN* = 6, the Cu—O bond is lengthened by 0.132 and by 0.161 Å, respectively. For Ag^0 aquacomplexes, the *CN* increase from 2 to 4 results in the lengthening of the Ag—O interatomic distance by 0.047 Å; however, it is shortened by 0.036 Å as the *CN* increases from 4 to 6. Analogous dependences are also characteristic of aquacomplexes of the elements of the zinc subgroup (z = 1+): transformation of the tetrahedral configuration of the complex into the octahedral one causes lengthening of the M—O distance by 0.005, 0.023, and 0.146 Å for Zn^{1+}, Cd^{1+}, and Hg^{1+}, respectively.

Relative stability of aquacomplexes

Using the calculated values of the total energies of aquacomplexes of Group IB—IVB elements, one can analyze their relative stability at different *CN*. To this end, it is sufficient to determine the changes in the total energies (E_{tot}) of the systems for the following processes: $M(H_2O)_n{}^{z+} = M(H_2O)_m{}^{z+} + (n - m)\ H_2O + \Delta E_{tot}$.

Table 3. Changes in the total energies of aquacomplexes (ΔE_{tot}) depending on changes in the *CN* of the metal

M	*z*	*n*	*m*	ΔE_{tot}* /kcal mol^{-1}
Cu	0	6	4	3.1
Cu	0	4	2	2.1
Zn	1+	6	4	22.3
Ag	0	6	4	−8.4
Ag	0	4	2	−0.8
Cd	1+	6	4	19.1
Au	0	4	2	−8.0
Hg	1+	6	4	15.3
Ga	2+	6	4	48.3
Ge	3+	6	4	108.3

* Here *n* and *m* are the *CN* of the initial and final state of the complex, respectively, and *z* is the charge of the complex.

If the ΔE_{tot} values are positive, the *CN* decrease of the metal ion is energetically unfavorable; otherwise, the removal of water molecules from its coordination sphere leads to a decrease in the total energy. In this work we only consider changes in the total energies of the systems under study that depend on the *CN* of the metal atom despite a certain role played by entropy contributions and zero-point vibrational energy corrections. Selected calculated ΔE_{tot} values corresponding to the change in the *CN* from 6 to 4 (transformation of octahedron into tetrahedron) and from 4 to 2 (change of the tetrahedral environment of the metal atom to that consisting of two H_2O molecules) are listed in Table 3.

The results of calculations show that the octahedral configuration of aquacomplexes is the most preferable for Cu^0. At the same time, the change in the energy of the octahedral aquacomplex of Cu^0 after the loss of two water molecules and transformation into a complex with *CN* = 4 is small (3 kcal mol^{-1}). After removal of two more water molecules, which corresponds to the change in the *CN* of the copper atom from 4 to 2, the energy of the complex increases by only 2 kcal mol^{-1}. The configuration with *CN* = 2 is the most favorable for aquacomplexes of Ag^0 ions. At the same time, transformation of a complex with *CN* = 4 into a configuration with *CN* = 2 occurs with an insignificant gain in energy, whereas transformation of a complex with *CN* = 4 into a configuration with *CN* = 6 requires an energy expenditure of 8 kcal mol^{-1}. This tendency is more pronounced for aquacomplexes of Au^0. According to our calculations, there are no aquacomplexes of Au^0 with *CN* = 6, whereas transformation of a complex with *CN* = 2 into a complex with *CN* = 4 requires an energy expenditure of 8 kcal mol^{-1}. Aquacomplexes with *CN* = 6 are the most stable complexes of the zinc subgroup ions in AOS. The removal of two H_2O molecules requires an energy of 22.3, 19.1, and 15.3 kcal mol^{-1} for Zn^{1+}, Cd^{1+}, and Hg^{1+} complexes, respectively. For

Table 4. Effective charges (q_i/au) and spin populations (σ_i/au) on the atoms of aquacomplexes

Complex	q_{M}	q_{O}	q_{H}	$q_{\mathrm{O}^\cdot}$	$q_{\mathrm{H}^\cdot}$	σ_{M}	σ_{O}	$\sigma_{\mathrm{O}^\cdot}$
$Cu(H_2O)_6$	−0.450	−0.610	0.312	−0.635	0.383	0.776	−0.002	0.006
$Zn(H_2O)_6{}^{1+}$	0.918	−0.681	0.331	−0.678	0.377	0.237	−0.022	−0.008
$Ga(H_2O)_6{}^{2+}$	1.092	−0.691	0.414	−0.679	0.428	0.705	−0.002	0.002
$Ge(H_2O)_6{}^{3+}$	1.417	−0.710	0.482	−0.689	0.487	0.664	0.041	0.054
$Ag(H_2O)_6$	−0.428	−0.623	0.339	−0.635	0.369	0.782	−0.004	0.004
$Cd(H_2O)_6{}^{1+}$	0.753	−0.672	0.349	−0.671	0.371	0.501	−0.011	−0.005
$In(H_2O)_6{}^{2+}$	1.208	−0.715	0.419	−0.708	0.430	0.718	0.001	0.005
$Sn(H_2O)_6{}^{3+}$	1.600	−0.735	0.480	−0.720	0.485	0.707	0.033	0.042
$Hg(H_2O)_6{}^{1+}$	0.548	−0.661	0.366	−0.659	0.372	0.797	0.007	0.012
$Tl(H_2O)_6{}^{2+}$	1.148	−0.707	0.421	−0.699	0.427	0.687	0.036	0.045
$Pb(H_2O)_6{}^{3+}$	1.543	−0.720	0.476	−0.702	0.482	0.524	0.064	0.083
$Cu(H_2O)_4$	−0.046	−0.602	0.307	—	—	0.516	−0.023	—
$Zn(H_2O)_4{}^{1+}$	0.640	−0.690	0.390	—	—	0.733	−0.004	—
$Ag(H_2O)_4$	−0.148	−0.609	0.323	—	—	0.717	−0.014	—
$Cd(H_2O)_4{}^{1+}$	0.618	−0.685	0.390	—	—	0.825	0.005	—
$Au(H_2O)_4$	−0.177	−0.629	0.336	—	—	0.952	0.004	—
$Hg(H_2O)_4{}^{1+}$	0.581	−0.674	0.390	—	—	0.837	0.020	—
$Cu(H_2O)_2$	−0.132	−0.615	0.341	—	—	0.719	−0.018	—
$Ag(H_2O)_2$	−0.150	−0.621	0.348	—	—	0.874	−0.001	—
$Au(H_2O)_2$	−0.225	−0.610	0.361	—	—	0.850	0.027	—

aquacomplexes of Ga^{2+} and Ge^{3+}, the energy expenditure in the case of the *CN* change from 6 to 4 is so large (48.6 and 108.3 kcal mol^{-1}, respectively) that these processes cannot occur in practice.

Thus, the calculated total energies of aquacomplexes of ions of Group IB—IVB elements with different *CN* indicate that aquacomplexes of Cu^0 can form structures with *CN* = 2, 4, and 6; those of Ag^0 and Au^0 can form structures with *CN* = 2 and 4; and those of Zn^{1+}, Cd^{1+}, and Hg^{1+} can form structures with *CN* = 6. For the latter, structures with *CN* = 4 can be formed under specific conditions. The remaining ions in AOS (Ga^{2+}, Ge^{3+}, In^{2+}, Sn^{3+}, Tl^{2+}, Pb^{3+}) always form only octahedral aquacomplexes (*CN* = 6).

Electronic structure of aquacomplexes

Table 4 lists the major characteristics of the electronic structure of the aquacomplexes of ions in AOS of Group IB—IVB elements, *viz.*, effective charges on the central (q_{M}), oxygen (q_{O}, $q_{\mathrm{O}^\cdot}$), and hydrogen (q_{H}, $q_{\mathrm{H}^\cdot}$) atoms and corresponding spin populations (σ_{M}, σ_{O}, $\sigma_{\mathrm{O}^\cdot}$). The energies of several occupied and vacant MOs for two directions of the electron spin (ε_α and ε_β) are listed in Table 5.

A clearly seen dependence between formal and effective charges on the metal atoms is observed for the three series of aquacomplexes considered.

The effective charges on the metal atoms in the octahedral complexes of Cu^0 and Ag^0 are negative. In all aquacomplexes considered, the total effective charges on the water molecules (ligands) are positive and vary over a rather wide range (0.01—0.24 au). A tendency is observed for the spin population on the central atom (σ_{M}) to decrease as the formal charge of aquacomplex increases. Departures from this rule are observed for complexes of Zn^{1+} and Cd^{1+} with the octahedral coordination of ions to water molecules (see Table 4); these complexes are characterized by rather high negative spin populations of the O atoms and positive spin populations of the H atoms of the ligands.

The calculated and experimental spin populations on the metal atoms in aquacomplexes of two series, Ag^0—Sn^{3+} and Au^0—Pb^{3+}, are compared in Figs. 1, *a* and *b*. For the Ag^0 ion in AOS (see Fig. 1, *a*) the values calculated for *CN* = 2 and 4 are given. The corresponding aquacomplexes differ slightly in relative stability (the difference in their total energies is 0.8 kcal mol^{-1}). For the Cd^{1+} ion in AOS, the values calculated for *CN* = 4 and 6 are shown. The relative stabilities of aquacomplexes of this ion at different *CN* differ more substantially (by 19.1 kcal mol^{-1}). The spin populations for the Au^0 ion in AOS obtained for *CN* = 2 and 4 and for the Hg^{1+} ion for *CN* = 4 and 6 are given in Fig. 1, *b*. The general tendency to change the calculated spin populations in both series is in agreement with experimental data. Thus, the spin population of the central metal atom in the isoelectronic series decreases as the charge of the aquacomplex increases.

A tendency for the energy of transition of the unpaired electron to the nearest vacant level satisfying selection rules to increase as the degree of oxidation *z* of metal in an isoelectronic series increases is observed for aquacomplexes of ions in AOS with *CN* corresponding to the most stable conformations (see Table 5). The dependences of the transition energies on the degree of metal oxidation for the three isoelectronic series are shown in Figs. 2, *a*—*c*. The correlation between the calculated transition energies and spin populations of

Table 5. Energies of occupied and vacant MOs ($E_{\rm OMO}$ and $E_{\rm VMO}$) for electron subsystems with spins α and β (symmetry is indicated in parentheses) and possible transitions (ΔE)

Complex	Spin α		Possible transitions	ΔE /eV	Spin β		Possible transitions	ΔE /eV
	$E_{\rm OMO}$	$E_{\rm VMO}$			$E_{\rm OMO}$	$E_{\rm VMO}$		
$Cu(H_2O)_6$	−0.058 (a_g) −0.034 (b_{3u})	−0.027 (b_{2u}) −0.020 (b_{1u}) −0.017 (a_g)	b_{3u}—a_g a_g—b_{2u}	0.46 0.84	−0.059 (a_g)	−0.028 (b_{2u}) −0.023 (b_{3u})	a_g—b_{2u}	0.84
$Zn(H_2O)_6{}^{1+}$	−0.376 (b_{3g}) −0.175 (a_g)	−0.152 (b_{3u}) −0.143 (b_{2u})	a_g—b_{3u} b_{3g}—b_{3u}	0.63 6.10	−0.375 (b_{3g})	−0.168 (a_g) −0.146 (b_{3u})	b_{3g}—b_{3u}	6.23
$Ga(H_2O)_6{}^{2+}$	−0.560 (b_{3g}) −0.383 (a_g)	−0.292 (b_{3u}) −0.281 (b_{2u})	a_g—b_{3u} b_{3g}—b_{3u}	2.48 7.29	−0.558 (b_{3g})	−0.358 (a_g) −0.286 (b_{3u})	b_{3g}—b_{3u}	7.40
$Ge(H_2O)_6{}^{3+}$	−0.753 (b_{3g}) −0.675 (a_g)	−0.510 (b_{3u}) −0.495 (b_{2u})	a_g—b_{3u} b_{3g}—b_{3u}	4.49 6.61	−0.750 (b_{3g})	−0.644 (a_g) −0.493 (b_{3u})	b_{3g}—b_{3u}	6.99
$Ag(H_2O)_6$	−0.133 (a_g) −0.025 (b_{3u})	−0.024 (b_{2u}) −0.022 (b_{1u}) −0.013 (a_g)	b_{3u}—a_g a_g—b_{2u}	0.33 2.97	−0.133 (a_g)	−0.023 (b_{2u}) −0.023 (b_{3u})	a_g—b_{2u}	2.99
$Cd(H_2O)_6{}^{1+}$	−0.369 (b_{3g}) −0.180 (a_g)	−0.134 (b_{3u}) −0.126 (b_{2u})	a_g—b_{3u} b_{3g}—b_{3u}	1.25 6.39	−0.367 (b_{3g})	−0.173 (a_g) −0.130 (b_{3u})	b_{2g}—b_{3u}	6.45
$In(H_2O)_6{}^{2+}$	−0.551 (b_{3g}) −0.389 (a_g)	−0.298 (b_{3u}) −0.287 (b_{2u})	a_g—b_{3u} b_{3g}—b_{3u}	2.48 6.88	−0.549 (b_{3g})	−0.365 (a_g) −0.292 (b_{3u})	b_{3g}—b_{3u}	6.99
$Sn(H_2O)_6{}^{3+}$	−0.744 (b_{3g}) −0.653 (a_g)	−0.498 (b_{3u}) −0.484 (b_{2u})	a_g—b_{3u} b_{3g}—b_{3u}	4.22 6.69	−0.741 (b_{3g})	−0.624 (a_g) −0.483 (b_{3u})	b_{3g}—b_{3u}	7.02
$Hg(H_2O)_6{}^{1+}$	−0.356 (b_{3g}) −0.225 (a_g)	−0.118 (b_{3u}) −0.112 (b_{2u})	a_g—b_{3u} b_{3g}—b_{3u}	2.91 6.48	0.354 (b_{3g})	−0.211 (a_g) −0.116 (b_{3u})	b_{3g}—b_{3u}	6.48
$Tl(H_2O)_6{}^{2+}$	−0.537 (b_{3g}) −0.457 (a_g)	−0.288 (b_{3u}) −0.279 (b_{2u})	a_g—b_{3u} b_{3g}—b_{3u}	4.60 6.78	−0.535 (b_{3g})	−0.442 (a_g) −0.285 (b_{3u})	b_{3g}—b_{3u}	6.80
$Pb(H_2O)_6{}^{3+}$	−0.737 (b_{3g}) −0.704 (a_g)	−0.492 (b_{3u}) −0.480 (b_{2u})	a_g—b_{3u} b_{3g}—b_{4u}	5.77 6.67	−0.734 (b_{3g})	−0.679 (a_g) −0.481 (b_{3u})	b_{3g}—b_{3u}	6.88
$Cu(H_2O)_4$	−0.069 (a'') −0.025 (a')	−0.017 (a') −0.013 (a'')	a'—a'' a''—a'	0.33 1.41	−0.068 (a')	−0.017 (a') −0.013 (a') −0.009 (a'')	a'—a''	1.61
$Zn(H_2O)_4{}^{1+}$	−0.418 (a'') −0.229 (a')	−0.165 (a') −0.153 (a') −0.149 (a'')	a'—a'' a''—a'	2.18 6.88	−0.416 (a'')	−0.212 (a') −0.158 (a')	a''—a'	5.55
$Ag(H_2O)_4$	−0.149 (a'') −0.037 (a')	−0.010 (a') −0.005 (a'')	a'—a'' a''—a'	0.87 3.78	−0.146 (a'')	−0.029 (a') −0.008 (a')	a''—a'	3.18
$Cd(H_2O)_4{}^{1+}$	−0.406 (a'') −0.243 (a')	−0.157 (a') −0.144 (a') −0.139 (a'')	a'—a'' a''—a'	2.83 6.77	−0.404 (a'')	−0.226 (a') −0.151 (a')	a''—a'	4.84
$Au(H_2O)_4$	−0.154 (a') −0.113 (a')	0.008 (a') 0.009 (a') 0.011 (a'')	a'—a'' a'—a''	3.37 4.49	−0.147 (a'')	−0.097 (a') −0.097 (a')	a''—a'	1.36
$Hg(H_2O)_4{}^{1+}$	−0.395 (a'') −0.278 (a')	−0.142 (a') −0.135 (a'')	a'—a'' a''—a'	3.89 6.88	−0.393 (a'')	−0.262 (a') −0.138 (a')	a''—a'	3.56
$Cu(H_2O)_2$	−0.141 (b_{2g}) −0.062 (a_g)	−0.041 (b_{1u}) −0.005 (b_{2u})	a_g—b_{1u} b_{2g}—b_{1u}	0.57 2.72	−0.133 (a_g)	−0.050 (a_g) −0.036 (b_{1u})	a_g—b_{1u}	2.64
$Ag(H_2O)_2$	−0.125 (b_{2g}) −0.085 (a_g)	−0.031 (b_{1u}) −0.001 (b_{2u})	a_g—b_{1u} b_{2g}—b_{1u}	1.47 2.56	−0.118 (a_g)	−0.071 (a_g) −0.029 (b_{1u})	a_g—b_{1u}	2.42
$Au(H_2O)_2$	−0.186 (a_g) −0.118 (a_g)	−0.027 (b_{1u}) 0.001 (b_{2u})	a_g—b_{1u} a_g—b_{1u}	2.48 4.33	−0.175 (a_g)	−0.102 (a_g) −0.026 (b_{1u})	a_g—b_{1u}	4.05

the central metal atom in aquacomplexes suggests that, in frozen aqueous solutions, the Zn^{1+} and Cd^{1+} ions form tetrahedral rather than octahedral structures, as follows from the "gas-phase" calculations of corresponding aquacomplexes. It would be interesting to test this hypothesis by calculating Zn^{1+} and Cd^{1+} aquacomplexes in the framework of continual or discrete models for a tetrahedral environment of water molecules taking into account medium (solvent) effects.

From comparing the results of our theoretical study and the experimental data obtained by ESR and optical spectroscopy one can make some inferences about the geometry and electronic states of the systems considered. It is likely that the Cu^0 aquacomplex has an octahedral structure, whereas the structure with *CN* = 2 is characteristic of complexes of Ag^0 and Au^0. Both the calculated and experimental data indicate that *CN* = 4 is more characteristic of aquacomplexes of Zn^{1+} and

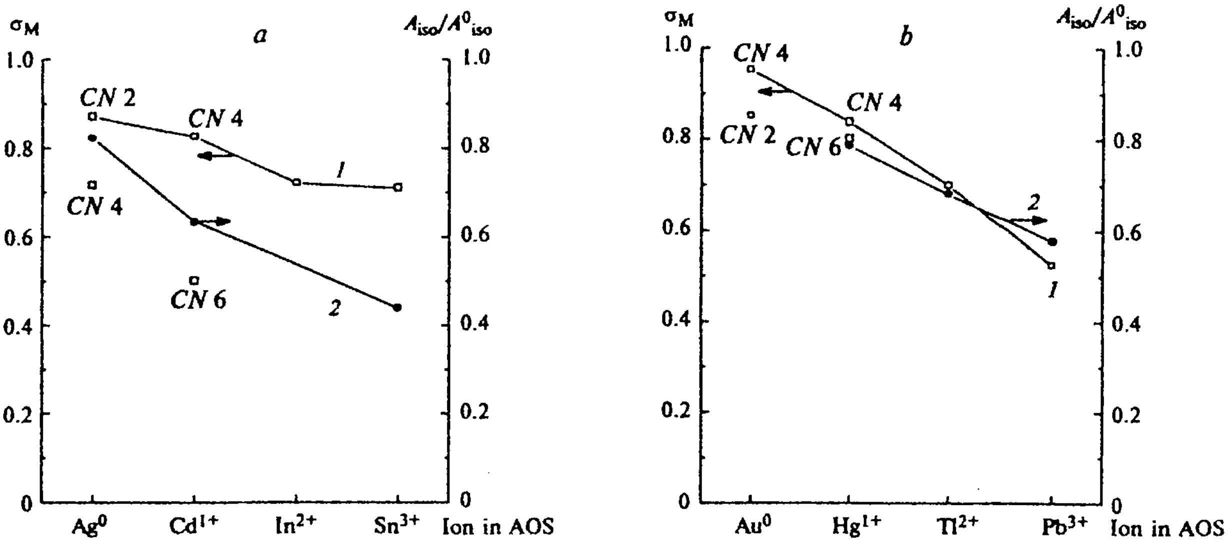

Fig. 1. Calculated spin populations (σ_M) on the ns-AO of the metal in aquacomplexes of the ions of metals of the V (*a*) and VI (*b*) periods in AOS (*1*) and the A_{iso}/A^0_{iso} ratios according to experimental data for low-temperature glasses at 77 K (*2*).

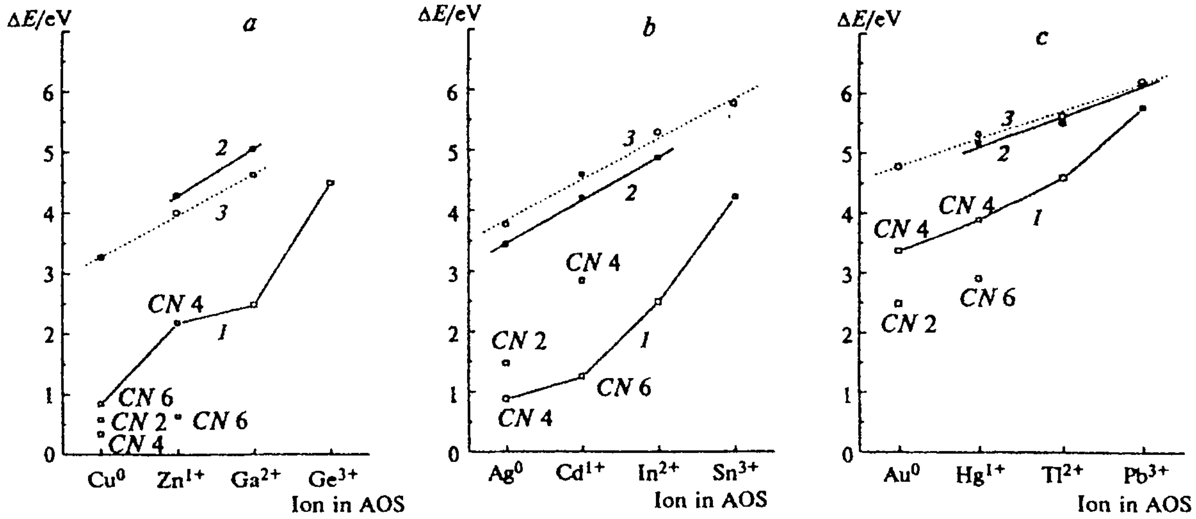

Fig. 2. Calculated transition energies ΔE (*1*) in aquacomplexes of ions of metals of the IV (*a*), V (*b*), and VI (*c*) periods in AOS; experimental transition energies $E_{\lambda_{max}}$ for low-temperature glasses (*2*) and aqueous solutions (*3*).

Cd^{1+}. The remaining ions are coordinated by water molecules to form octahedral complexes. The increase in the formal charge of the ion causes a monotonic decrease in the spin population of the ns-AO of the metal atom in the complexes due to the increase in the spin population on the ligand molecules. Very low spin populations in octahedral complexes of zinc and cadmium correlate with high spin populations on the hydrogen atoms of H_2O molecules. In principle, if such forms exist, the spin density delocalization over an aquacomplex should manifest itself in the hyperfine structure of the ESR spectrum. Since no expected peculiarities are observed in the ESR spectra of zinc and cadmium aquacomplexes, it can be concluded that these ions form tetrahedral structures characterized by spin density localization on the central atom.

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