# Physical Chemistry

## *Ab initio* calculations of chloride complexes of Au, Hg, Tl, Pb, and Bi in anomalous oxidation states ($^2S_{1/2}$ electron state)

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*Ab initio* calculations of chloride complexes of Au, Hg, Tl, Pb, and Bi in anomalous oxidation states ($^2S_{1/2}$ electron state) were carried out by the Becke—Lee—Yang—Parr density functional method using the Dunning—Hay LanL2DZ basis set. Optimum geometric parameters and electronic characteristics of $MCl_n(H_2O)_m{}^q$ ($n$ = 1—4 and $m$ = 0, 4, 5) complexes were determined. In each of the considered series the spin population on the central metal atom decreases as its atomic number increases. The energy of transition of the unpaired electron to the lowest unoccupied MO decreases in the same order. The unpaired electron occupies an orbital that is mostly a linear combination of the s-orbital of the metal atom and the p-orbital of the Cl atom (the antibonding σ-orbital of the M—Cl bond). Distinctions in the changes in spectral properties of aquacomplexes and chloride complexes in isoelectronic series, observed as the degree of oxidation of the metal atom increases, were explained. The results of calculations are in agreement with the experimental data obtained by ESR and optical spectroscopy.

**Key words:** *ab initio* calculations; density functional method; chloride complexes of Au, Hg, Tl, Pb, and Bi; anomalous oxidation states.

Experimental studies of the properties of ions of Groups IB—IVB metals in anomalous oxidation states (AOS) in glassy media[1] and aqueous solutions[2] have shown that the ligand environment of the ions in AOS affects their electronic and optical characteristics. The density of the unpaired electron on the metal atom in the $^2S_{1/2}$ electron state decreases as the degree of oxidation in the series of isoelectronic ions increases.[1] At the same time, the energies of optical transitions at the absorption band maxima ($E_{\lambda_{max}}$) for aquacomplexes of ions in AOS regularly increase as the degree of oxidation in the series of isoelectronic ions increases, whereas the reverse is observed for chloride complexes. Attempts were made to explain these phenomena on the basis of analysis of correlation diagrams for similar compounds[1—3]; however, they seem to be unconvincing. Experimental data obtained by ESR and optical spectroscopy and by pulse radiolysis for chloride aquacomplexes in concentrated solutions of hydrochloric acid (6—8 *M* HCl), aqueous solutions, and alkali-metal halide crystals (AHC [4—7]) are summarized in Table 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1049—1055, June, 1999.

**Table 1.** Major results of the studies of chloride complexes of ions in AOS by ESR and optical spectroscopy Group IVB elements

| Ion in AOS | Low-temperature glasses (77 K) | | Aqueous solutions (300 K), | Crystals (77 K) | | | |
|---|---|---|---|---|---|---|---|
| | | | | NaCl | | | KCl |
| ($J$) | $A_{iso}/A^0_{iso}$ | $\lambda_{max}$ | $\lambda_{max}$ | $A_{iso}/A^0_{iso}$ | $\alpha$ | $\beta$ | $\lambda_{max}$ |
| $^{197}Au^0$ | | | | 0.931 | 8.08 | 12.8 | 9.685 |
| (3/2) | | | | | | | 5.461 |
| | | | | | | | 5.209 |
| $^{199}Hg^{1+}$ | 0.661 | 6.198 | 5.060 | 0.817 | 8.28 | 26.3 | 5.123 |
| (1/2) | | 4.592 | 4.132 | | | | 4.959 |
| | | | | | | | 4.592 |
| | | | | | | | 4.305 |
| $^{203}Tl^{2+}$ | 0.462 | 5.903 | | 0.615 | 8.03 | 39.0 | 5.635 |
| (1/2) | | 4.427 | | | | | 4.732 |
| | | | | | | | 4.217 |
| | | | | | | | 3.406 |
| $^{207}Pb^{3+}$ | 0.359 | 5.635 | 4.492 | 0.422 | 6.27 | 31.4 | 5.739 |
| (1/2) | | 4.132 | 3.874 | | | | 4.092 |
| | | 3.646 | 3.262 | | | | 2.665 |
| | | | 2.556 | | | | |
| $^{209}Bi^{4+}$ | | 3.351 | | | | | |
| (9/2) | | 2.638 | | | | | |

*Note.* The $E_{\lambda_{max}}$ values are given in eV; $\alpha = (A_s/A^0_s)_{Cl} \cdot 10^3$, $\beta = (A_p/A^0_p)_{Cl} \cdot 10^3$, $(A^0_s)_{Cl}$ = 204.21 mT, and $(A^0_p)_{Cl}$ = 15.66 mT.

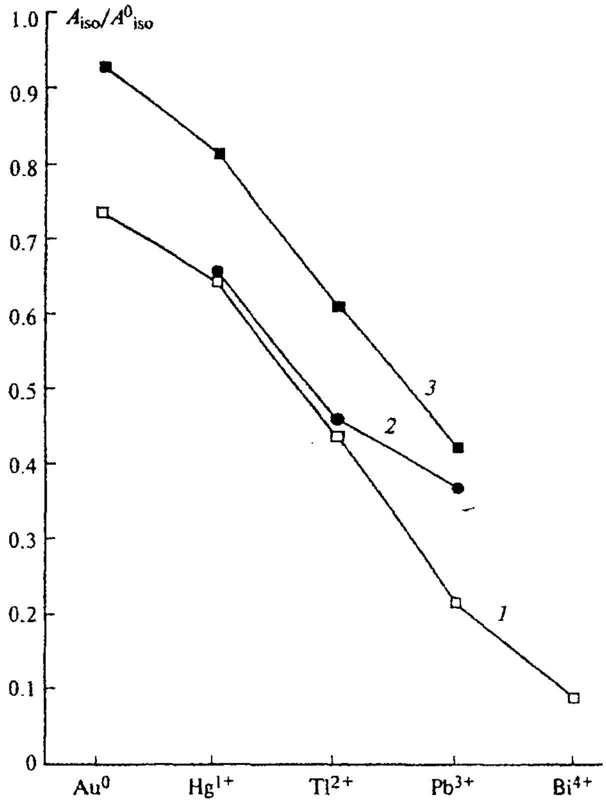

**Fig. 1.** Changes in the calculated (*1*) and experimental spin populations on the ns-AO in the $AuCl^{1-}$, $HgCl(H_2O)_5{}^0$, $TlCl(H_2O)_5{}^{1+}$, $PbCl(H_2O)_5{}^{2+}$, and $BiCl_4$ complexes and the $A_{iso}/A_{iso}{}^0$ ratio from experimental data (at 77 K) for low-temperature glasses (*2*) and for NaCl crystal (*3*).

The ratio of the isotropic hyperfine coupling (IHFC) constant $A_{iso}$ calculated using the Breit—Rabi (B—R) formula[8] using ESR spectroscopy data, to the $A^0_{iso}$ value (the IHFC constant for the free ion[9]) in the $^2S_{1/2}$ electron state is proportional to the spin population of the ns-AO of the metal atom. The spin population of the central metal ion in chloride aquacomplexes regularly decreases as the degree of oxidation increases (Fig. 1, curves *2* and *3*). It is known[10] that preferable formation of AuCl, $HgCl_2$, $TlCl_2{}^+$, $PbCl_4{}^{2-}$, and $BiCl_4{}^-$, from which ions in AOS are generated, is observed in solutions of hydrochloric acid. Capture of thermolyzed electrons[1,2] ($e^-_{therm}$) causes appearance of the $AuCl^-$, $HgCl_2{}^-$, and $TlCl_2$ species, while interaction with the $Cl_2{}^-$ anion leads to $PbCl_4{}^-$ and $BiCl_4$ species. The $HgCl_4{}^{2-}$, $TlCl_6{}^{3-}$, $PbCl_6{}^{2-}$, and $BiCl_6{}^{1-}$ ions,[10] capable of trapping $e^-_{therm}$ to produce $HgCl_4{}^{3-}$, $TlCl_6{}^{4-}$, $PbCl_6{}^{3-}$, and $BiCl_6{}^{2-}$ ions in AOS, are present in concentrated solutions of hydrochloric acid in a smaller amount. Let us denote the chloride complex with the ion in the oxidation state $z$ as $M^{z+}$, *i.e.*, by $Au^0$, $Hg^{1+}$, $Tl^{2+}$, $Pb^{3+}$, and $Bi^{4+}$ ions are meant chloride aquacomplexes with gold, mercury, *etc.* ions in a degree of oxidation of 0, 1, *etc.*

It should be emphasized that the superhyperfine structure (SHFS) for $Cl^-$ ions can be determined using ESR technique only in the case of AHC. From the data in Table 1 it can be seen that the $\alpha$ values change slightly as the degree of oxidation of the central ion in AOS changes, whereas the $\beta$ values increase by almost a factor of 3 in the series of $Au^0$, $Hg^{1+}$, $Tl^{2+}$, and $Pb^{3+}$ ions. Hence it follows that the unpaired electron is delocalized mainly over the p-AO of $Cl^-$ atoms.

The number of $Cl^-$ anions in the coordination sphere also affects optical characteristics of the ion in AOS. In fact, all $E_{\lambda_{max}}$ values for aqueous solutions (previously,[11,12] mercury and lead aquacomplexes containing one $Cl^-$ anion were obtained) are smaller than for chloride complexes of the same ions in concentrated HCl solutions. This tendency persists also for the ions in AOS obtained by irradiating KCl crystals,[4—7] though for this system the dependence of the $E_{\lambda_{max}}$ values of optical absorption bands in the UV region on the nature of the central ion in AOS is nonmonotonic.

It is obvious that these regularities can be explained by peculiarities of the electronic structure of chloride complexes of ions in AOS. This work is dedicated to the interpretation of the peculiarities of optical properties of chloride complexes compared to those of aquacomplexes from the viewpoint of electronic structure of the ions in AOS in the $^2S_{1/2}$ electron state. We performed *ab initio* calculations of chloride complexes of the above ions with different numbers of $Cl^-$ ligands in the coordination sphere. The results of calculations of chloride complexes were compared with the experimental data on low-temperature glasses (aqueous solutions of metal salts in 6 *M* HCl, frozen at 77 K) and AHC (taking NaCl and KCl crystals as examples) in which the above ions are generated under the action of hard radiation.

## Calculation procedure

Currently, energy and thermodynamic characteristics of clusters and metal complexes are determined using theoretical methods developed on the basis of the density functional theory (DFT) based on the Hohenberg—Kohn theorem[13] and the Kohn—Sham equation.[14] 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.

Previously, the $E_{ex}[P]$ functional that includes the Slater exchange and corrections due to the electron density gradients[15] and the Becke—Lee—Yang—Parr (BLYP) electron density functional $E_{corr}[P]$ containing local and nonlocal terms[16,17] were proposed.

**Table 2.** Interatomic distances ($R$/Å), effective charges ($q_i$/au), and spin populations ($\sigma_i$) on the atoms of chloride complexes

| Complex | $R$(M—Cl) | $q_M$ | $q_{Cl}$ | $\sigma_M$ | $\sigma_{Cl}$ |
|---|---|---|---|---|---|
| $AuCl^{1-}$ | 2.635 | −0.572 | −0.428 | 0.737 | 0.263 |
| $HgCl^0$ | 2.665 | 0.309 | −0.309 | 0.592 | 0.408 |
| $HgCl_2^{1-}$ | 2.833 | 0.086 | −0.543 | 0.514 | 0.243 |
| $HgCl_3^{2-}$ | 3.081 | 0.040 | −0.680 | 0.546 | 0.151 |
| $TlCl^{1+}$ | 2.908 | 0.994 | 0.006 | 0.839 | 0.161 |
| $TlCl_2^0$ | 2.705 | 0.693 | −0.347 | 0.235 | 0.382 |
| $TlCl_3^{1-}$ | 2.787 | 0.552 | −0.517 | 0.295 | 0.235 |
| $TlCl_4^{2-}$ | 2.912 | 0.520 | −0.630 | 0.327 | 0.169 |
| $PbCl_3^0$ | 2.570 | 0.875 | −0.292 | 0.162 | 0.279 |
| $PbCl_4^{1-}$ | 2.641 | 0.798 | −0.450 | 0.191 | 0.203 |
| $BiCl_4^0$ | 2.563 | 1.053 | −0.263 | 0.097 | 0.228 |

In this work we report the results of *ab initio* calculations of chloride complexes $MCl_n(H_2O)_m{}^q$ of metals in AOS (the $^2S_{1/2}$ electron state), where M = Au, Hg, Tl, Pb, and Bi (the $n$, $m$, and $q$ values are listed in Tables 2—5), performed by the BLYP functional[15—17] method using the Dunning—Hay basis sets of two-exponential heavy-element atomic functions (LanL2DZ).[18—19] 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.[20]

## Results and Discussion

### *Structure of chloride complexes*

The results of full geometry optimization of chloride metal complexes containing no water molecules show that dichloride, trichloride, and tetrachloride complexes have a linear, a planar (with chlorine atoms forming an equilateral triangle), and a tetrahedral structure, respectively. The calculated geometric parameters of the complexes are listed in Tables 2 and 3. From the results of calculations it follows that $Au^0$ is capable of adding only one $Cl^-$ ion (addition of the second ion is energetically unfavorable), whereas the $Hg^{1+}$ and $Tl^{2+}$ ions can add from one to four $Cl^-$ ions. In Table 2, we present data only for $PbCl_3$ and $PbCl_4^-$, since attempts to calculate $PbCl^{2+}$ and $PbCl_2^{3+}$ failed because of convergence problems of the self-consistent field.

Octahedral structures were calculated for monochloride and dichloride $MCl_n(H_2O)_m{}^q$ aquacomplexes. Water molecules lie in the $xy$ plane and chlorine lie on the $z$ axis. These complexes were calculated using optimization of the M—Cl, M—O, and M—O′[*] interatomic distances ($R$) and the H—O—H bond angles (ω); according to calculations, in all cases the $R$(O—H) distances and ω(H—O—H) bond angles lie in the range (0.990±0.001) Å and (109.3±0.2)°, respectively.

**Table 3.** Interatomic distances ($R$/Å), effective charges ($q_i$/au), and spin populations ($\sigma_i$) on the atoms of aquacomplexes

| Complex | $R$(M—Cl) | $R$(M—O),<br>$R$(M—O′) | $q_M$ | $q_{Cl}$ | $q_O$<br>($q_{O'}$) | $\sigma_M$ | $\sigma_{Cl}$ | $\sigma_O$<br>($\sigma_{O'}$) |
|---|---|---|---|---|---|---|---|---|
| $HgCl(H_2O)_5{}^0$ | 2.756 | 2.973,<br>3.001 | 0.286 | −0.495 | −0.635<br>(−0.634) | 0.645 | 0.238 | 0.005<br>(0.007) |
| $HgCl_2(H_2O)_4{}^{1-}$ | 2.861 | 5.215 | 0.122 | −0.567 | −0.648 | 0.527 | 0.236 | 0.000 |
| $TlCl(H_2O)_5{}^{1+}$ | 2.712 | 2.691,<br>2.638 | 0.862 | −0.319 | −0.689<br>(−0.685) | 0.442 | 0.426 | 0.015<br>(0.027) |
| $TlCl_2(H_2O)_4{}^0$ | 2.781 | 2.771 | 0.693 | −0.474 | −0.663 | 0.348 | 0.297 | 0.006 |
| $PbCl(H_2O)_5{}^{2+}$ | 2.695 | 2.479,<br>2.400 | 1.259 | −0.097 | −0.714<br>(−0.706) | 0.223 | 0.619 | 0.022<br>(0.046) |
| $PbCl_2(H_2O)_4{}^{1+}$ | 2.908 | 2.583 | 1.059 | −0.258 | −0.699 | 0.000 | 0.497 | 0.002 |

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[*] The primed O atoms lie in the $xz$ plane.

**Table 4.** Enthalpies of conversions (Δ*H*) of complexes of metals in AOS

| Initial complex | Final complex | Δ*H* /kcal mol$^{-1}$ |
|---|---|---|
| $Au(H_2O)_2$ | $AuCl^{1-}$ | −38.4 |
| $HgCl(H_2O)_5{}^0$ | $HgCl_2{}^{1-}$ | −19.0 |
| $HgCl_2{}^{1-}$ | $HgCl_3{}^{2-}$ | +39.3 |
| $HgCl_2{}^{1-}$ | $HgCl_4{}^{3-}$ | +141.2 |
| $Hg(H_2O)_6{}^{1+}$ | $HgCl(H_2O)_5{}^0$ | −86.4 |
| $HgCl$ | $HgCl(H_2O)_5{}^0$ | −12.2 |
| $HgCl_2{}^{1-}$ | $HgCl_2(H_2O)_4{}^{1-}$ | 0.0 |
| $TlCl_2(H_2O)_4$ | $TlCl_3{}^{1-}$ | −34.3 |
| $TlCl_2{}^0$ | $TlCl_3{}^{1-}$ | −67.6 |
| $TlCl_2(H_2O)_4$ | $TlCl_4{}^{2-}$ | −11.4 |
| $TlCl^{1+}$ | $TlCl(H_2O)_5{}^{1+}$ | −104.5 |
| $Tl(H_2O)_6{}^{2+}$ | $TlCl(H_2O)_5{}^{1+}$ | −187.4 |
| $TlCl_2{}^0$ | $TlCl_2(H_2O)_4{}^0$ | −33.4 |
| $TlCl(H_2O)_5{}^{1+}$ | $TlCl_2(H_2O)_4{}^0$ | −109.2 |
| $PbCl_2(H_2O)_4{}^{1+}$ | $PbCl_3{}^0$ | −100.0 |
| $PbCl_2(H_2O)_4{}^{1+}$ | $PbCl_4{}^{1-}$ | −184.7 |
| $Pb(H_2O)_6{}^{3+}$ | $PbCl(H_2O)_5{}^{2+}$ | −300.1 |
| $PbCl(H_2O)_5{}^{2+}$ | $PbCl_2(H_2O)_4{}^{1+}$ | −196.8 |

As was shown by calculations of aquacomplexes of gold monochloride, the $AuCl^-$ anion is incapable of forming complexes with water molecules. The bonds with water molecules in complex $HgCl_2(H_2O)_4{}^{1-}$ are so weak that the equilibrium distance from the metal atom to the ligand exceeds 5 Å (see Table 3). This means that the $HgCl_2(H_2O)_4{}^{1-}$ complex is a chloride $HgCl_2{}^{1-}$ complex surrounded by widely separated water molecules. The Hg—Cl interatomic distances in the latter complex and in the aquacomplex considered differ by less than 1%.

The dependence of *R*(M—Cl) on the degree of oxidation for monochloride complexes has an extremum, the longest *R*(M—Cl) distance being observed in the $TlCl(H_2O)_5{}^{1+}$ complex. The analogous dependence for dichloride complexes also has an extremum; however, a minimum corresponding to $TlCl_2(H_2O)_4{}^0$ is observed in this case. The *R*(M—Cl) values in tri- and tetrachloride complexes monotonically decrease as the degree of oxidation of the metal ion in AOS increases.

### *Relative stability of chloride complexes*

Based on the calculated total energies of metal complexes, the water molecule, and the $Cl^{1-}$ ion, we calculated the enthalpy of conversion of one complex into another one occurring with change in the coordination of the chloride ions and water molecules. These data are summarized in Table 4, where the enthalpies of conversions of chloride complexes refer to the zero temperature without considering zero-point vibrational energy corrections. The enthalpies were determined using the results of calculations of aquacomplexes reported earlier.[19]

A general tendency is the increase in the energy of the M—Cl bond as the degree of oxidation increases (see Table 4). The enthalpies of substitution reactions of water molecules by chloride ions in aquacomplexes are also shown in Table 4; their values monotonically decrease from −38.4 to −300.1 kcal mol$^{-1}$ on going from gold to lead. According to calculations, the $AuCl^{1-}$, $HgCl_2{}^{1-}$, $TlCl_3{}^{1-}$, and $PbCl_4{}^{1-}$ ions should be the most stable in HCl solutions; however, complexes $HgCl(H_2O)_5{}^0$, $TlCl_2(H_2O)_4$, $PbCl_2(H_2O)_4{}^{1+}$, *etc.* can coexist with the former (see Tables 2—5).

### *Electronic structure of chloride complexes*

As was mentioned above, interpretation of experimentally established regularities requires a detailed analysis of the data on the electronic structure of chloride complexes of metals in AOS. Let us consider the charge and spin population distributions in this type of aquacomplexes (see Tables 2 and 3) using two series of

**Table 5.** Energies of occupied and unoccupied levels ($E_{OMO}$ and $E_{UMO}$) (symmetry indicated) and possible electronic transitions (Δ*E*)

| Complex | $E_{OMO}$ /eV | $E_{UMO}$ /eV | Possible transitions | Δ*E* /eV |
|---|---|---|---|---|
| $AuCl^{1-}$ | −0.82 ($\sigma_g$) | 3.65 ($\pi$) | $\sigma_g$—$\pi$ | 3.11 |
| | 0.54 ($\sigma_g$) | 7.21 ($\pi$) | $\sigma_g$—$\pi$ | 6.67 |
| $HgCl^0$ | −7.84 ($\sigma_g$) | −1.20 ($\pi$) | $\sigma_g$—$\pi$ | 2.51 |
| | −3.71 ($\sigma_g$) | 4.73 ($\pi$) | $\sigma_g$—$\pi$ | 8.43 |
| $HgCl_2{}^{1-}$ | −2.83 ($\sigma_g$) | 3.26 ($\pi_u$) | $\sigma_g$—$\pi_u$ | 3.02 |
| | 0.24 ($\sigma_g$) | 9.03 ($\pi_u$) | $\sigma_g$—$\pi_u$ | 8.79 |
| $HgCl_3{}^{2-}$ | 12.27 ($a_1'$) | 6.91 ($a_2'$) | $a_1'$—$a_2'$ | 4.08 |
| | 2.83 ($a_1'$) | 8.33 ($e'$) | $a_1'$—$e'$ | 5.50 |
| $HgCl(H_2O)_5{}^0$ | −4.41 ($a_1$) | 0.33 ($b_2$) | $a_1$—$b_2$ | 1.66 |
| | −1.33 ($a_1$) | 0.38 ($b_1$) | $a_1$—$b_1$ | 1.71 |
| | | 2.91 ($b_2$) | $a_1$—$b_2$ | 4.24 |
| $HgCl_2(H_2O)_4{}^{1-}$ | −1.98 ($a_{1g}$) | 3.02 ($e_u$) | $a_{1g}$—$e_u$ | 2.26 |
| | 0.76 ($a_{1g}$) | 4.38 ($e_u$) | $a_{1g}$—$e_u$ | 3.62 |
| $TlCl^{1+}$ | −15.67 ($\sigma_g$) | −7.75 ($\pi$) | $\sigma_g$—$\pi$ | 1.12 |
| | −8.87 ($\sigma_g$) | −0.49 ($\pi$) | $\sigma_g$—$\pi$ | 8.38 |
| $TlCl_2{}^0$ | −10.36 ($\sigma_g$) | −2.53 ($\pi_u$) | $\sigma_g$—$\pi_u$ | 1.52 |
| | −7.97 ($\sigma_u$) | 3.73 ($\pi_u$) | $\sigma_g$—$\pi_u$ | 7.78 |
| | −4.05 ($\sigma_g$) | | | |
| $TlCl_3{}^{1-}$ | −5.55 ($a_1'$) | 2.01 ($a_2'$) | $a_1'$—$a_2'$ | 2.69 |
| | −0.68 ($a_1'$) | 3.86 ($e'$) | $a_1'$—$e'$ | 4.54 |
| $TlCl_4{}^{2-}$ | 2.09 ($a_1$) | 7.56 (e) | $a_1$—e | 5.47 |
| | | 12.08 (e) | $a_1$—e | 9.99 |
| $TlCl(H_2O)_5{}^{1+}$ | −10.12 ($a_1$) | −3.92 ($b_2$) | $a_1$—$b_2$ | 1.33 |
| | −2.25 ($a_1$) | −3.81 ($b_1$) | $a_1$—$b_1$ | 1.44 |
| | | −1.03 ($b_2$) | $a_1$—$b_2$ | 4.22 |
| $TlCl_2(H_2O)_4{}^0$ | −6.58 ($a_{1g}$) | −0.4 ($e_u$) | $a_{1g}$—$e_u$ | 1.88 |
| | −2.28 ($a_{1g}$) | 0.79 ($b_{1g}$) | $a_{1g}$—$b_{1g}$ | 3.07 |
| | | 2.28 ($b_{2g}$) | $a_{1g}$—$b_{2g}$ | 4.56 |
| $PbCl_3{}^0$ | −13.93 ($a_1'$) | −4.30 ($a_2'$) | $a_1'$—$a_2'$ | 0.22 |
| | −4.52 ($a_1'$) | −1.72 ($e'$) | $a_1'$—$e'$ | 2.80 |
| $PbCl_4{}^{1-}$ | −1.20 ($a_1$) | 2.66 (e) | $a_1$—e | 3.86 |
| | | 9.09 (e) | $a_1$—e | 10.29 |
| $PbCl(H_2O)_5{}^{2+}$ | −15.64 ($a_1$) | −9.03 ($b_2$) | $a_1$—$b_2$ | 0.35 |
| | −9.38 ($a_1$) | −8.87 ($b_1$) | $a_1$—$b_1$ | 0.51 |
| | | −6.07 ($b_2$) | $a_1$—$b_2$ | 3.31 |
| $PbCl_2(H_2O)_4{}^{1+}$ | −12.46 ($a_{1g}$) | −5.33 ($e_u$) | $a_{1g}$—$e_u$ | 1.12 |
| | −6.45 ($a_{1g}$) | −4.41 ($a_{2u}$) | $a_{1g}$—$a_{2u}$ | 2.04 |
| | | −2.94 ($b_{1g}$) | $a_{1g}$—$b_{1g}$ | 3.51 |
| $BiCl_4{}^0$ | −4.98 ($a_1$) | −3.59 (e) | $a_1$—e | 1.39 |

monochloride compounds, *viz.*, $AuCl^{1-}$, $HgCl^0$, and $TlCl^{1+}$ and $Hg(H_2O)_5{}^0$, $TlCl(H_2O)_5{}^{1+}$, and $PbCl(H_2O)_5{}^{2+}$, respectively. In these series the charges on the metal atoms monotonically increase, the spin populations on the metal atoms decrease, and that on the Cl atom increases (except for $TlCl^{1+}$). The spin populations on the O atoms of water molecules are rather low. It should be noted that only p-AO are responsible for the spin populations on Cl atoms, whereas the s-AO make rather small contributions.

Analogous dependences are also observed for the series of dichloride complexes $HgCl_2{}^{1-}$, $TlCl_2{}^0$, $HgCl_2(H_2O)_4{}^{1-}$, $TlCl_2(H_2O)_4{}^0$, $PbCl_2(H_2O)_4{}^{1+}$ and for tri- and tetrachloride complexes in which the charges on the metal atoms also monotonically increase while those on the Cl atoms decrease. In this case the spin population on the metal atom decreases, whereas that on the Cl atom increases. The dependence of the spin population on the metal atom (see Tables 2, 3) on the number of ligands in its coordination sphere is more complex, *viz.*, in some instances its values decrease (*e.g.*, in the series of mono- and dichloride aquacomplexes) while in some other cases they increase (*e.g.*, in lead chloride complexes) or this dependence has an extremum (in the series of thallium chloride complexes).

Let us consider the calculated energies of some levels for the compounds under study. The energies of the levels occupied by an electron pair and preceding the level filled with the unpaired electron, and those of the unoccupied levels to which electron transition is allowed according to selection rules, are shown in Table 5. Analysis of the one-electron energies of the levels and possible transitions makes it possible to point out some regularities for isoelectronic series. The energy of transition of the an unpaired electron from a MO to the lowest unoccupied MO (LUMO) decreases as the degree of oxidation of the metal in the series of monochloride complexes ($AuCl^{1-}$, $HgCl^0$, and $TlCl^{1+}$ and $HgCl(H_2O)_5{}^0$, $TlCl(H_2O)_5{}^{1+}$, and $PbCl(H_2O)_5{}^{2+}$) and in di-, tri-, and tetrachloride compounds increases (see Table 5). This transition corresponds to the optical absorption bands in the near UV and visible spectral regions.

Closest to the experimental data that reflect the dependences of the density of the unpaired electron on the *ns*-AO and the energy at the optical band maximum on the degree of oxidation of the ion in AOS, are the calculated values for the following series of complexes: $AuCl^{1-}$, $HgCl(H_2O)_5{}^0$, $TlCl(H_2O)_5{}^{1+}$, $PbCl(H_2O)_5{}^{2+}$, and $BiCl_4$ (Figs. 1 and 2).

The found regularities of the behavior of the energies of optical transitions substantially differ from those es-

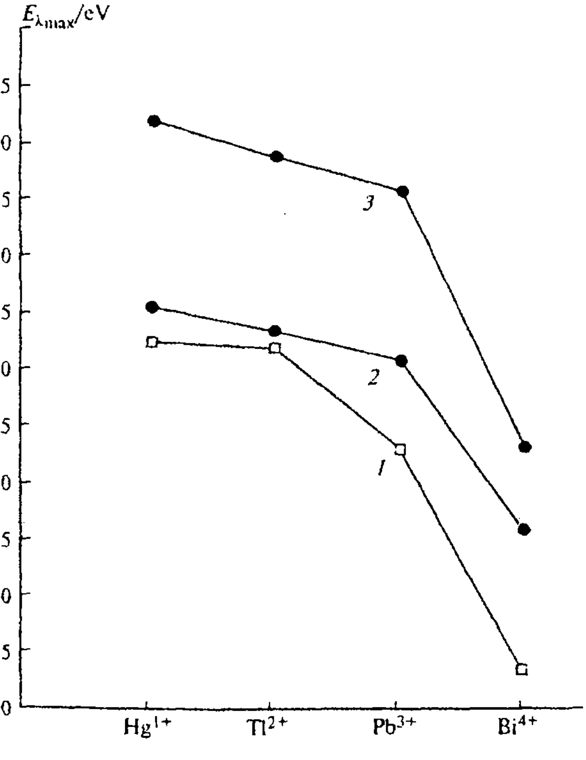

**Fig. 2.** Calculated (*1*) transition energies ($\Delta E$) for chloride complexes $AuCl^{1-}$, $HgCl(H_2O)_5{}^0$, $TlCl(H_2O)^{1+}$, $PbCl(H_2O)_5{}^{2+}$, and $BiCl_4$; experimental transition energies $E_{\lambda_{max}}$ for low-temperature glasses at 77 K (*2*, *3*).

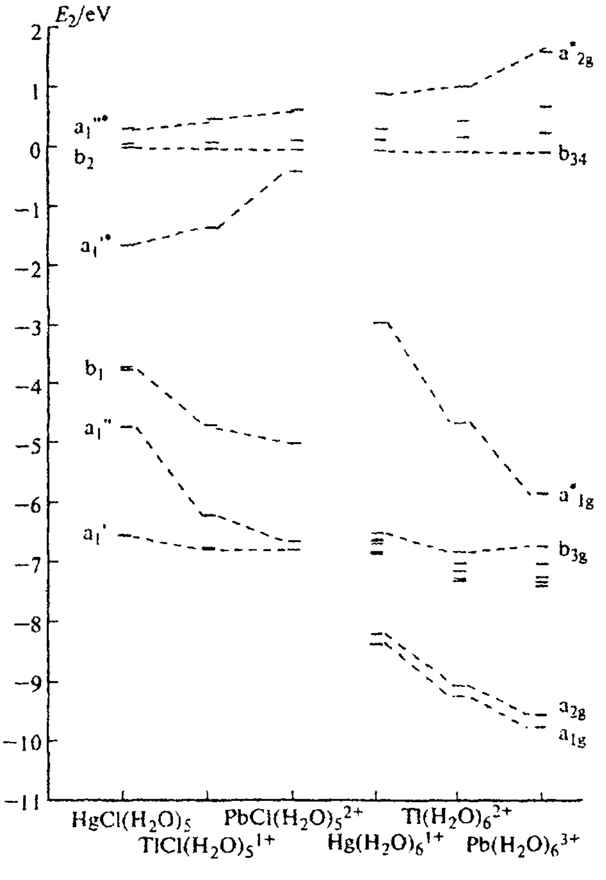

**Fig. 3.** Calculated MO energy levels for $MCl(H_2O)_5{}^{z+}$ and $M(H_2O)_6{}^{z+}$ (M = Hg, Tl, Pb) complexes.

**Table 6.** Energy levels (eV) and energies of electron transitions (Δ/eV) for aquacomplexes

| Energy level | $HgCl(H_2O)_5{}^0$ | $TlCl(H_2O)_5{}^{1+}$ | $PbCl(H_2O)_5{}^{2+}$ | Energy level | $Hg(H_2O)_6{}^{1+}$ | $Tl(H_2O)_6{}^{2+}$ | $Pb(H_2O)_6{}^{3+}$ |
|---|---|---|---|---|---|---|---|
| $a_1''^*$ | 0.64 | −3.42 | −8.35 | $a_{2g}{}^*$ | −2.25 | −6.74 | −11.70 |
| $b_1$ | 0.39 | −3.82 | −8.87 | $b_{1u}$ | −2.84 | −7.32 | −12.61 |
| $b_2$ | 0.32 | −3.93 | −9.03 | $b_{2u}$ | −3.03 | −7.60 | −13.05 |
| $a_1'^*$ | −1.33 | −5.25 | −9.40 | $b_{3u}$ | −3.22 | −7.84 | −13.39 |
| $b_1$ | −3.44 | −8.60 | −14.00 | $a_{1g}{}^*$ | −6.13 | −12.44 | −19.16 |
| $b_2$ | −3.44 | −8.60 | −14.00 | $b_{3g}$ | −9.68 | −14.61 | −20.05 |
| $a_1''$ | −4.40 | −10.11 | −15.64 | $b_{2u}$ | −9.78 | −14.79 | −20.34 |
| $b_1$ | −6.20 | −10.65 | −15.64 | $b_{1u}$ | −9.81 | −14.80 | −20.34 |
| $a_1'$ | −6.21 | −10.68 | −15.77 | $b_{3g}$ | −9.85 | −14.92 | −20.56 |
| | | | | $b_{2g}$ | −9.99 | −15.05 | −20.64 |
| | | | | $b_{1u}$ | −10.02 | −15.09 | −20.71 |
| | | | | $a_{2g}$ | −11.36 | −16.84 | −22.87 |
| | | | | $a_{1g}$ | −11.53 | −17.02 | −23.09 |
| Transition | | | | Transition | | | |
| $\Delta_1$ | 3.76 | 4.67 | 4.96 | $\Delta_1$ | 6.46 | 6.77 | 6.58 |
| $\Delta_2$ | 5.04 | 6.69 | 7.29 | $\Delta_2$ | 9.11 | 10.09 | 11.18 |
| $\Delta_3$ | 4.88 | 5.42 | 6.38 | $\Delta_3$ | 5.40 | 4.58 | 3.92 |
| $(a_1''^*—a_1'')^*$ | −1.88 | −6.77 | −12.00 | $(a_{2g}{}^*—a_{2g})^*$ | −6.81 | −11.79 | −17.28 |
| $(a_1'^*—a_1')^*$ | −3.77 | −7.97 | −12.59 | $(a_{1g}{}^*—a_{1g})^*$ | −8.83 | −14.73 | −21.12 |
| $(b_2—b_1)^*$ | −1.56 | −6.26 | −11.51 | $(b_{3u}—b_{3g})^*$ | −6.45 | −11.22 | −16.72 |
| $\Delta_4$ | 1.89 | 1.20 | 0.60 | $\Delta_4$ | 2.02 | 2.94 | 3.84 |
| $\Delta_5$ | 2.21 | 1.70 | 1.08 | $\Delta_5$ | 2.38 | 3.51 | 4.40 |
| $\Delta_6$ | 0.32 | 0.51 | 0.48 | $\Delta_6$ | 0.36 | 0.57 | 0.56 |

* Center of gravity.

tablished for aquacomplexes[19] (in this case an increase in the energy of optical transition is observed in the series of isoelectronic ions as the degree of oxidation of the metal ion in AOS increases).

Such a distinction in the properties of chloride and aquacomplexes is associated with specific features of the structure of their molecular orbitals between which the electron transitions occur. In fact, in both aquacomplexes and chloride complexes the unpaired electron is localized on the MO composed mostly of the s-AO of the metal and σ(s,p) orbitals of ligands (the O atoms of water molecules and Cl atoms). The unoccupied MO of chloride complexes and aquacomplexes to which the electron is transferred are mostly composed of p-AO of the metal and the $p_x$- and $p_y$-AO of the $Cl^-$ ion (or O atoms in aquacomplexes). The energies of the $M—Cl^-$ and M—O bonds in chloride and aquacomplexes in the isoelectronic series increase (see Table 3 and Ref. 21).

In Table 6, for monochloride complexes $MCl(H_2O)_5{}^{(z-1)+}$ ($z$ = 0, 1, 2) and aquacomplexes $M(H_2O)_6{}^{z+}$ ($z$ = 1, 2, 3) we present (1) the energies for the MO from $a_1'$ ($a_{1g}$) to $a_1''^*$ ($a_{2g}{}^*$); (2) the differences $(b_2 - b_1)$, $(b_{3u} - b_{3g}) = \Delta_1$, $(a_1''^* - a_1'')$, $(a_{2g}{}^* - a_{2g}) = \Delta_2$, and $(a_1'^* - a_1)$, $(a_{1g}{}^* - a_{1g}) = \Delta_3$ between the MO energies; (3) the energies of the "centers of gravity" of these levels, *i.e.*, the $[(b_2 + b_1)/2]$, $[(b_{3u} + b_{3g})/2] = E_{1CG}$, $[(a_1''^* + a_1)/2]$, $[(a_{2g}{}^* + a_{2g})/2] = E_{2CG}$, and $[(a_1'^* + a_1)/2]$, $[(a_{1g}{}^* + a_{1g})/2] = E_{3CG}$ values; and (4) the values of the $\Delta_4 = E_{2CG} - E_{3CG}$, $\Delta_5 = E_{1CG} - E_{3CG}$, and $\Delta_6 = E_{1CG} - E_{2CG}$ energy intervals. As can be seen, the $\Delta_1$ and $\Delta_2$ values increase, while the $\Delta_3$ values increase for chloride complexes and decrease for aquacomplexes as the degree of oxidation of the metal ion in AOS increases. At the same time, the $\Delta_6$ values remain virtually unchanged, while the $\Delta_4$ and $\Delta_5$ values decrease for chloride complexes and increase for aquacomplexes as the degree of oxidation of the ion in AOS increases.

Thus, the energy levels of the $a_1'^*$ and $a_1'$ MO are "pushed apart" as the $z$ values increase and their "center of gravity" approaches those of the ($b_2$, $b_1$) and ($a_1''^*$, $a_1''$) levels for chloride compounds. A different picture is observed for aquacomplexes, *viz.*, the energy interval between the $a_{1g}{}^*$ and $a_{1g}$ levels decreases, whereas the difference between the energies of the "centers of gravity" ($a_{1g}{}^*$, $a_{1g}$) and ($b_{3u}$, $b_{3g}$), ($a_{2g}{}^*$, $a_{2g}$) increases. This is illustrated in Fig. 3, in which the MO energy levels for monochloride complexes and aquacomplexes of $Hg^{1+}$, $Tl^{2+}$, and $Pb^{3+}$ (scaled with respect to the $b_2$ ($b_{3u}$) level, whose energy was taken to be zero) are shown.

The answer as to why such shifts of the energy levels in chloride and aquacomplexes are observed is most likely associated with the fact that, on the one hand, the difference between the s-AO and p-AO energies of the $Cl^-$ ion (or O atom) is rather small (0.99 and 1.218 eV, respectively, as calculated using Tables[22]), whereas, on the other hand, the difference in the electronegativity of the ions in $M^{z+}—Cl^-$ and $M^{z+}—O^{\delta+}$ pairs ($\delta \cong 0$) is rather large. If the energy difference between the s-AO and p-AO of ligands is small, the MO ($a_1'$ and $a_1'^*$ or $a_{1g}$ and $a_{1g}{}^*$, respectively) in complexes that formed are combinations of s-AO and p-AO of both the ligands and the central atom, which results in their additional stabilization. At the same time, the $b_1$ and $b_2$ ($b_{3g}$ and

$b_{3u}$) MO become destabilized and acquire an s-type character in part.[23] This leads to different stabilities of the $a_1'$ and $a_1''^{*}$ ($a_{1g}$ and $a_{1g}^{*}$) MO and the $b_1$ and $b_2$ ($b_{3g}$ and $b_{3u}$) MO in chloride and aquacomplexes of ions in AOS, respectively, and, correspondingly, to different energies. In addition, chloride aquacomplexes are characterized by a substantial contribution of the $p_z$-AO of the $Cl^-$ ion to the $a'$ and $a''^{*}$ ($a_{1g}$ and $a_{1g}^{*}$) MO. This manifests itself in positions of the absorption band maxima, *i.e.*, in the values of the energies of transitions from the $a_1''^{*}$ ($a_{1g}^{*}$) MO to the higher-lying unoccupied MO.

The authors express their gratitude to the Pacific Northwest National Laboratories of the U.S. Department of Energy for providing time on the CRAY J-90 supercomputer (Contract No. DE-AC06-76RLO 1830).

## References

1. A. I. Aleksandrov, A. I. Prokof'ev, and N. N. Bubnov, *Usp. Khim.*, 1996, **65**, 519 [*Russ. Chem. Rev.*, 1996, **65**, 479 (Engl. Transl.)].
2. B. G. Ershov, *Usp. Khim.*, 1997, **66**, 103 [*Russ. Chem. Rev.*, 1997, **66** (Engl. Transl.)].
3. A. I. Aleksandrov, B. G. Ershov, and V. I. Spitsyn, *Dokl. Akad. Nauk SSSR*, 1980, **254**, 907 [*Dokl. Chem.*, 1980 (Engl. Transl.)].
4. P. G. Baranov, R. A. Zhitnikov, and V. A. Khramtsov, *Fiz. Tverd. Tela* [*Solid State Phys.*], 1977, **19**, 3603 (in Russian).
5. P. G. Baranov, R. A. Zhitnikov, and V. A. Khramtsov, *Phys. Stat. Sol. (b)*, 1976, **76**, K109.
6. N. I. Mel'nikov, R. A. Zhitnikov, and V. A. Khramtsov, *Fiz. Tverd. Tela* [*Solid State Phys.*], 1975, **17**, 3234 (in Russian).
7. W. Dreybrodt and D. Sibber, *Phys. Stat. Sol.*, 1967, **20**, 337.
8. G. Breit and I. I. Rabi, *Phys. Rev.*, 1931, **38**, 2082.
9. B. G. Ershov and A. I. Aleksandrov, *Teor. Eksp. Khim.*, 1978, **14**, 679 [*Theor. Exp. Chem.*, 1978, **14** (Engl. Transl)].
10. F. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, J. Wiley and Sons, New York, 1965.
11. N. B. Nazhat and K.-D. Asmus, *J. Phys. Chem.*, 1977, **77**, 614.
12. N. L. Sukhov and B. G. Ershov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 716 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, **33**, 671 (Engl. Transl.)].
13. P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, 136, **3B**, 864.
14. W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, 140 A, 1133.
15. A. D. Beche, *J. Chem. Phys.*, 1993, **98**, 5648.
16. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev.*, 1988, **B37**, 785.
17. B. Miehlich, A. Savin, and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200.
18. T. H. Dunning, Jr., and P. J. Hay, in *Modern Theoretical Chemistry*, Ed. H. F. Schaefer III, Plenum, New York, 1976, 1.
19. P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270, 284, 299.
20. M. J. Frisch, A. Frisch, and J. B. Foresman, *Gaussian 94*, Gaussian Inc., Pittsburgh (PA), 1994.
21. Yu. A. Borisov and A. I. Aleksandrov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 858 [*Russ. Chem. Bull.*, 1999, **48**, No. 5 (Engl. Transl.)].
22. C. E. Moore, *Atomic Energy Levels*, Washington, NBS USA, 1971, **1**, **2**, **3**.
23. H. B. Gray, *Electrons and Chemical Bonding*, W. A. Benjamin NC, New York—Amsterdam, 1965, 317 pp.

*Received September 4, 1998;*
*in revised form November 13, 1998*