

CONTRIBUTIONS TO THE CHEMISTRY OF HIGHLY  
CONCENTRATED AQUEOUS ELECTROLYTE SOLUTIONS. XXI.\*

THE DENSIMETRIC STUDY OF AQUO  
AND NITRATO COMPLEXES OF  $\text{Ag}^+$   
AND  $\text{Tl}^+$  IONS IN NITRATE SOLUTIONS

V. JEDINÁKOVÁ and J. ČELEDA

*Department of Nuclear Fuel Technology and Radiochemistry,  
Institute of Chemical Technology, Prague 6*

Received May 22nd, 1970

The densimetric method described formerly has been applied to the study of complexes of univalent thallium and silver in aqueous solutions of  $\text{NaClO}_4$ ,  $\text{NaNO}_3$ ,  $\text{NH}_4\text{NO}_3$  and  $\text{HNO}_3$  (from 0.1 to 6 mol/l). The  $\text{Tl}^+$  ion is present in the perchlorate solutions as a diaquo complex; in nitrate solutions this complex is transformed — without any change of the coordination number — into the electroneutral mononitrate-monoaquo complex with the stability constant of  $0.4 \pm 0.1 \text{ l mol}^{-1}$  (in the concentration range from 1 to 6 mol/l of  $\text{NO}_3^-$ ). The  $\text{Ag}^+$  ion remains in both perchlorate and nitrate solutions and in the whole concentration range studied in the form of the diaquo complex.

The hydration of  $\text{Ag}^+$  and  $\text{Tl}^+$  ions and their association with anions in aqueous solutions has been treated in relatively few studies, most of which, moreover, dealt only with diluted solutions. Very little is known about the distribution of associated anions between the outer and inner coordination spheres of these cations and about their coordination numbers in the solution. Solvation of the  $\text{Ag}^+$  ions in the aqueous solution is unknown (*cf. ref.*<sup>1</sup>). Based on the fact that silver salts do not form crystalline hydrates it is assumed that no stable aquo complexes of  $\text{Ag}^+$  with a well-defined composition exist in the aqueous solution. On the other hand,  $\text{Ag}^+$  forms well-defined complexes  $\text{AgX}_2$  with a linear configuration<sup>1</sup> with ammonia and with other ligands of negligible  $\pi$ -bonding ability. These complexes are very stable and do not attach any other species X even if the latter are present in a considerable excess. This has been explained by Orgel<sup>2</sup> as due to the hybridization of the  $d^{10}$  and  $d^9s^1$  states which are energetically close to each other. The hybridization produces one flat hybrid orbital  $d_{z^2} - s = \psi_1$ , with maximum electron density in the XY plane, and one prolonged orbital  $d_{z^2} + s = \psi_2$ , extended in the direction of the Z-axis. During the addition of ligands, the former orbital is occupied by the non-bonding electron pair of the  $\text{Ag}^+$  cation, while the latter, vacant orbital, hybridizes with the vacant  $5p_z$ -orbital of the same ion thus giving rise to two oppositely directed hybrid orbitals  $\psi_2 + p_z$  and  $\psi_2 - p_z$  which act as acceptors of the donor electron pairs of ligands X. Two  $\sigma$ -bonds directed into two opposite directions are thus formed.

\* Part XX: J. Inorg. Nucl. Chem. 31, 2793 (1969).

This linear coordination of the  $\text{Ag}^+$  ion has been confirmed by the X-ray structural analysis<sup>3,4</sup> in the case of  $\text{NH}_3$  ligands in crystalline amo-complexes. The distinct covalent character of the two  $\sigma$ -bonds has been determined from the IR spectra of crystalline  $[\text{Ag}(\text{NH}_3)_2]\text{SO}_4$  and  $[\text{Ag}(\text{NH}_3)_2]\text{NO}_3$  and also in the corresponding deuteriated salts<sup>5</sup>, where the values of  $\nu_{\text{sym}} = 380 \text{ cm}^{-1}$ ,  $\nu_{\text{as}} = 460 \text{ cm}^{-1}$  and the force constant of  $1.65 \text{ dyn}/\text{\AA}$  have been found for the  $\text{Ag}-\text{N}$  bonds. Because the  $\text{H}_2\text{O}$  molecule has a very similar electron configuration and similar donor-acceptor properties as the  $\text{NH}_3$  molecule, the conclusion on the non-existence of well-defined aquo complexes, derived from the composition of solid salts, seems rather doubtful. The dehydration of the  $\text{Ag}^+$  ion when entering into the crystal lattice could be caused by water-anion competition. If this competition does not take place, one should suppose — from the analogy with the amo-complexes — that the  $\text{Ag}^+$  ion could also form an analogous linear complex  $[\text{Ag}(\text{H}_2\text{O})_2]^+$  with the  $\text{H}_2\text{O}$  ligands, similarly as it forms a linear anion  $[\text{Ag}(\text{OH})_2]^-$  with  $\text{OH}^-$  ligands in strongly alkaline solutions<sup>1</sup>.

However, even in aqueous solutions the coulombic ion-dipole competition should be taken into account since it has a distinct tendency to turn the dipole of the  $\text{OH}_2$  ligand into the radial direction, which prevents the formation of the donor-type  $\sigma$ -bond  $\text{Me}-\text{OH}_2$ . Therefore it cannot be predicted which of these two possible structures will be more stable in the aqueous solutions.

The degree of association of  $\text{Ag}^+$  ions with  $\text{NO}_3^-$  anions has been determined by measuring the solubility of  $\text{AgNO}_3$  in normal and heavy water<sup>6</sup>. In the  $0.1\text{M}-\text{NO}_3^-$  solution a practically total dissociation has been found whereas in  $1\text{M}$  solution about 25% of  $\text{Ag}^+$  ions has been associated with  $\text{NO}_3^-$  ions;  $pK_{\text{dis}}$  of  $\text{AgNO}_3$  has been estimated to  $-0.2$  (ref.<sup>7</sup>).

For the  $\text{Tl}^+$  ion only the formation of complexes with halide-, oxygen- and sulphur ligands has been reported<sup>1</sup>. These ligands form with  $\text{Tl}^+$  preferably  $\text{TlX}_2$  complexes, sometimes also  $\text{TlX}_4$  (ref.<sup>8</sup>). The same type of complexes can therefore be expected also in the case of  $\text{H}_2\text{O}$  and  $\text{NO}_3^-$  ligands where the coordination bond is formed by oxygen atoms, in spite of the fact that the existence of these complexes has not yet been proved. Only the total association of  $\text{Tl}^+$  ions with  $\text{NO}_3^-$  and  $\text{ClO}_4^-$  (in both inner and outer spheres) has been determined and the values of  $pK_{\text{dis}} = +0.3$  and  $0.0$ , respectively, have been published<sup>7</sup>. The values of  $2.38$  (at  $0^\circ\text{C}$ ),  $2.15$  (at  $25^\circ\text{C}$ ) and  $2.06 \text{ l mol}^{-1}$  (at  $40^\circ\text{C}$ ) for the association constant of  $\text{TlNO}_3$  have been determined from the solubility measurements of  $\text{TlNO}_3$  in aqueous solutions of  $\text{KNO}_3$  and  $\text{NaClO}_4$  at various temperatures<sup>9</sup>. However, it is not known to what extent the  $\text{NO}_3^-$  anion in this associate is bound in the inner coordination sphere and whether it acts as a uni- or bidentate ligand. The Raman spectra can prove the existence of this bond<sup>7</sup> and as a matter of fact they already did so in complexes of  $\text{Tl}^+$  with  $\text{OH}^-$  ions<sup>10</sup> similarly as they proved the existence of the metal-metal bond in the  $\text{Hg}_2^{2+}$  ion<sup>11</sup>. However, in concentrated solutions of  $\text{TlNO}_3$  and  $\text{AgNO}_3$  they could reveal neither the existence of  $\text{Ag}_2^{2+}$  and  $\text{Tl}_2^{2+}$  ions nor the association of the cations with nitrate ions<sup>12</sup>.

On the other hand, the ion pair should manifest itself in the Raman spectrum by its specific frequency because in ion pairs in which the ions are attracted by purely electrostatic forces the polarizability of the system could somewhat vary with vibrational changes of the interatomic distance. However, from theoretical considerations<sup>13</sup> it turns out that in the case of aqueous solutions the intensity should be about  $10^{-2}$  times lower than in the case of a donor bond so that it seems impossible to detect the formation of ion pairs by this method.

In our previous studies<sup>14-19</sup> it has been shown that information on the ligand bonds in the inner coordination sphere of the ion can be obtained by measuring the apparent molar volumes of their salts in solutions. The method is based on a comparison of the measured values with those calculated using the simplified model of the solution structure for various assumed compositions of the complex. This

method is applicable up to high concentrations of the electrolyte in which the molar volume of the added sample is measured (up to 5 mol/l and even higher). It also identifies the bonding of electroneutral ligands; inclusive of  $\text{H}_2\text{O}$ . In the present study this method has been used as an independent method contributing to the elucidation of questions which remain unsolved after previous studies on the  $\text{Ag}^+$  and  $\text{Tl}^+$  ions.

### EXPERIMENTAL

The apparent molar volumes have been measured using anhydrous (freshly dried) samples of  $\text{AgNO}_3$  and  $\text{TlNO}_3$  of controlled composition. The apparent molar volumes  $V_i'$  of these samples were measured in solutions containing an excess of the base electrolyte ( $\text{NaClO}_4$ ,  $\text{NaNO}_3$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{HNO}_3$ ) by the differential float method<sup>16</sup>. Samples of weight of the order of  $10^{-3}$  moles per 100 ml of the base-electrolyte solution have been used. All chemicals used were of the analytical grade and were used without further purification. The preparation of solutions, the procedure of the measurement of the apparent molar volumes of samples and the evaluation of experimental data have been the same as in the previous studies<sup>16-19</sup>. The molar volumes of electrolytes in solutions without any other additional electrolyte were determined from the published densities<sup>20</sup> using the formula derived formerly<sup>21</sup>

$$V_i = [1 - (\Delta d / \Delta p) \cdot (100 - p) / d] \cdot (M / d), \quad (1)$$

where  $M$  is the molecular mass of the electrolyte under study,  $p$  is its concentration in the solution (%),  $d$  is the solution density and  $\Delta d$  and  $\Delta p$  are the differences of  $d$  and  $p$ , respectively, taken between the values for the given solution and the nearest higher value given in the tables.

The extrapolated concentrations  $c^0$  of the base electrolytes ( $\text{NaClO}_4$ ,  $\text{NaNO}_3$ ,  $\text{NH}_4\text{NO}_3$  and  $\text{HNO}_3$ ), corresponding to the "water-free" solution, were determined using the potassium chloride as an electrolyte which — with the exception of electrostatically bound hydrate shells — does not contain any firmly bound water molecules on its ions. Moreover, its apparent molar volume  $V_i^0$  in the "water-free" state is known from the previous studies<sup>14,15</sup> with sufficient reliability. The

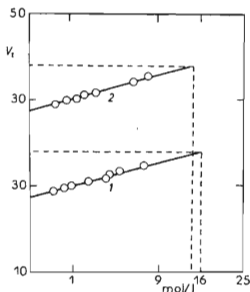


FIG. 1

Determination of the Concentration of the Base Electrolyte  $c^0$ , Corresponding to the "Water-free" State of Ions

Testing substance  $\text{KCl}$ ,  $V_{\text{KCl}}^0 = 38.0 \text{ ml} \cdot \text{mol}^{-1}$ <sup>15</sup>,  
 1  $\text{NaNO}_3$ , 2  $\text{NH}_4\text{NO}_3$ , at  $25^\circ\text{C}$ . The apparent volume  $V_{\pm}$  given in ml/mol.

extrapolation has been done using the empirical Masson rule: the measured values of  $V_{KCl}^0$  were plotted against the square root of the base-electrolyte molarity (Fig. 1), similarly as in the previous studies. The following values have been found:

$$(c_{NaClO_4}^0)^{1/2} = 3.6 \text{ mol}^{1/2} \text{ l}^{-1/2} \text{ (cf.}^{16} \text{)} .$$

$$(c_{NaNO_3}^0)^{1/2} = 4.0 \text{ mol}^{1/2} \text{ l}^{-1/2} ,$$

$$(c_{NH_4NO_3}^0)^{1/2} = 3.8 \text{ mol}^{1/2} \text{ l}^{-1/2} ,$$

$$(c_{HNO_3}^0)^{1/2} = 3.85 \text{ mol}^{1/2} \text{ l}^{-1/2} \text{ (cf.}^{15} \text{)} .$$

For  $AgNO_3$  as the base electrolyte the average value of  $3.9 \text{ mol}^{1/2} \text{ l}^{-1/2}$  has been adopted because of the low differences between individual nitrates. The error in the determination of apparent molar volumes  $V_{\pm}$  did not exceed  $\pm 1.0 \text{ ml/mol}$  for the sample weights used.

Theoretical values of apparent molar volumes  $V_{\pm}$  of the electrolytes have been calculated for the anhydrous form of the samples as the difference of volumes of the presumably formed entities,  $V_i$ , and those of the consumed components of the solution,  $V_j$ :

$$V_{\pm} = \sum_i V_i - \sum_j V_j . \quad (2)$$

The values  $V_i$  and  $V_j$ , used in these calculations, for both limits ("water-free" state  $V^0$  and the infinite dilution  $V^\infty$ ) are given in Table I. All the measurements were performed at  $25.00 \pm 0.05^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### The $Ag^+$ Ion

The nature of the  $Ag^+$  ion in the solution has been determined by the measurement of the apparent molar volume of the silver nitrate in anhydrous samples of  $AgNO_3$  dissolved in solutions of  $NaClO_4$ ,  $NaNO_3$  and  $HNO_3$  (cf. Fig. 2). Along with these experimental data the partial molar volumes of  $AgNO_3$  in its own solutions have been calculated using Eq. (1) and the published densities of  $AgNO_3$  solutions.

In all the above cases the experimental values of  $V_{\pm}$  are in agreement with the straight line calculated for the diaquo silver cation  $[Ag(H_2O)_2]^+$  in the whole concentration range studied. The straight line calculated for the nitrate with an anhydrous cation lies by about 10–12 ml/mol higher. On the other hand, the molar volumes of the tetra-aquo complex, calculated for the given weight of the anhydrous sample, i.e. assuming consumption of four molecules of free water in the solution and their transfer into the complex according to Eq. (2), lead to values by about 10 ml/mol lower. The differences in  $V_{\pm}$  values between these forms exceed the experimental error by about one order of magnitude so that this result can be accepted as sufficiently convincing. From the published data quoted above it can be assumed that the diaquo complex has a linear configuration with the two  $H_2O$  ligands bound to the central  $Ag^+$  ion by the hybrid orbitals ( $d_{z^2}s$ )  $p_z$ . The fact that in excess of water (as is the case

in aqueous solutions) the  $\text{Ag}^+$  ion forms the complex of the  $\text{MeX}_2$  type even with such a weak donor as the ligand  $\text{H}_2\text{O}$ , manifests the high stability of the axially symmetric divalent state of this ion<sup>2,22</sup>.

TABLE I  
Apparent Molar Volumes in the "Water-free" State of the Solution,  $V^\circ$ , and in the Infinite Dilution at 25°C,  $V_{25}^\infty$ , ml mol<sup>-1</sup>

Species	$V^\circ$	$V_{25}^\infty$	Species	$V^\circ$	$V_{25}^\infty$
$\text{Ag}^+$	9.3	4.0	$\text{Tl}^+$	14.3	10.0
$[\text{Ag}(\text{H}_2\text{O})_2]^+$	37.2	33.0	$[\text{Tl}(\text{H}_2\text{O})_2]^+$	40.7	36.5
$[\text{Ag}(\text{H}_2\text{O})(\text{NO}_3)]^\circ$	58.8	58.8	$[\text{Tl}(\text{H}_2\text{O})(\text{NO}_3)]^\circ$	63.0	63.0
$[\text{Ag}(\text{NO}_3)_2]^-$	79.2	76.0	$[\text{Tl}(\text{NO}_3)_2]^-$	83.5	80.5
$[\text{Ag}(\text{H}_2\text{O})_4]^+$	62.5	59.0	$[\text{Tl}(\text{H}_2\text{O})_4]^+$	66.8	63.0
$[\text{Ag}(\text{H}_2\text{O})_3(\text{NO}_3)]^\circ$	83.5	83.5	$[\text{Tl}(\text{H}_2\text{O})_3(\text{NO}_3)]^\circ$	88.6	88.6
$[\text{Ag}(\text{H}_2\text{O})_2(\text{NO}_3)_2]^-$	103.5	100.5	$[\text{Tl}(\text{H}_2\text{O})_2(\text{NO}_3)_2]^-$	108.0	105.5
$\text{NO}_3^-^a$	36.3	31.0	$[\text{Tl}(\text{H}_2\text{O})_6]^+$	91.5	88.5
$\text{H}_2\text{O}^a$	18.06	18.06	$[\text{Tl}(\text{H}_2\text{O})_5(\text{NO}_3)]^\circ$	111.5	111.5

<sup>a</sup> These values are experimental data evaluated from published densities of solutions<sup>15</sup>, all other values were calculated from the model using a method described elsewhere<sup>17,18</sup>.

TABLE II  
Concentration Stability Constants of the  $[\text{Tl}(\text{H}_2\text{O})(\text{NO}_3)]^\circ$  Complex, Evaluated from the Experimental Apparent Molar Volumes  $V_\pm$  (Fig. 3) using Eq. (3), at 25°C

$c_{\text{NaNO}_3}$ mol/l	$V_{\text{TlNO}_3}$ ml/mol	$K_{\text{TlNO}_3}$ l mol <sup>-1</sup>	$c_{\text{NH}_4\text{NO}_3}$ mol/l	$V_{\text{TlNO}_3}$ ml/mol	$K_{\text{TlNO}_3}$ l mol <sup>-1</sup>
0.0	34.2	—	0.13	34.2	—
0.12	33.3	—	0.27	35.5	—
0.25	33.3	—	0.64	36.7	—
0.49	34.7	0.34	0.99	37.3	0.45
0.64	35.2	0.29	1.30	38.4	0.48
0.96	37.0	0.44	1.69	36.6	0.39
1.13	38.2	0.53	2.68	41.3	0.51
2.61	40.4	0.42	3.88	41.0	0.34
3.84	41.6	0.40	5.16	42.8	0.44
5.12	42.2	0.46	6.42	43.5	0.51
6.39	42.4	0.34	—	—	—

The change of this diaquo complex into the nitrate complexes, which should be followed by a substantial increase of  $V_{\pm}$  values (cf. Fig. 2), has not been observed even at highest concentrations of  $\text{NO}_3^-$  (5–6 mol/l). This is in agreement with the results obtained from Raman spectra<sup>12</sup>, which proved that the  $\text{NO}_3^-$  ion does not enter into the inner coordination sphere of the  $\text{Ag}^+$  ion even at highest concentrations, otherwise it would be observable in the Raman spectra because of the high covalent character of bonds in  $\text{Ag(I)}$  complexes. The association of silver nitrate determined electrometrically and by the measurements of solubility, according to which the 50% association of  $\text{Ag}^+$  ions with  $\text{NO}_3^-$  ions is achieved already at concentrations of about 1.6 mol/l of  $\text{NO}_3^-$  (ref.<sup>6,7</sup>), relates evidently only to the formation of ion pairs (the association in the outer sphere), which does not manifest itself in the values of apparent molar volumes<sup>15</sup>.

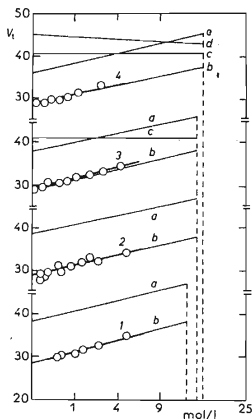


FIG. 2

The Apparent Volume of  $\text{AgNO}_3$ ,  $V_{\pm}$  (ml/mol, at 25°C) in the Various Base Electrolytes

1  $\text{NaClO}_4$ , 2  $\text{AgNO}_3$  (calculated from the published densities of solutions<sup>20</sup>), 3  $\text{HNO}_3$ , 4  $\text{NaNO}_3$ . Values calculated from the model: a  $\text{Ag}^+$ , b  $[\text{Ag}(\text{H}_2\text{O})_2]^+$ , c  $[\text{Ag}(\text{H}_2\text{O})(\text{NO}_3)]^0$ , d  $[\text{Ag}(\text{NO}_3)_2]^-$ .

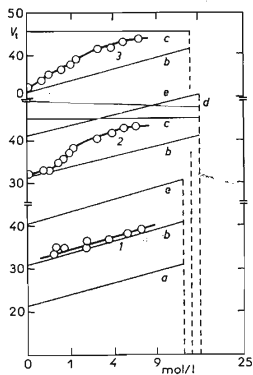


FIG. 3

The Apparent Volume of  $\text{TiNO}_3$ ,  $V_{\pm}$  (ml/mol, at 25°C) in the Various Base Electrolytes

1  $\text{NaClO}_4$ , 2  $\text{NaNO}_3$ , 3  $\text{NH}_4\text{NO}_3$ . Straight lines calculated from the model: a  $[\text{Ti}(\text{H}_2\text{O})_4]^+$ , b  $[\text{Ti}(\text{H}_2\text{O})_2]^+$ , c  $[\text{Ti}(\text{H}_2\text{O})(\text{NO}_3)]^0$ , d  $[\text{Ti}(\text{NO}_3)_2]^-$ , e  $\text{Ti}^+$ .

*The Tl<sup>+</sup> Ion*

In solutions of NaClO<sub>4</sub> the apparent volumes of TlNO<sub>3</sub> indicate the formation of a diaquo complex, similarly as in the case of AgNO<sub>3</sub> (cf. Fig. 3). No indications of the formation of complexes with the anion ClO<sub>4</sub><sup>-</sup> in the inner coordination sphere of the Tl<sup>+</sup> cation have been observed in the molar volumes up to the highest concentration of NaClO<sub>4</sub> (8 M). The published value of the association constant of TlClO<sub>4</sub>, about 1.0 l mol<sup>-1</sup>, as measured by thermodynamic methods<sup>7</sup>, according to which about 50% of the Tl<sup>+</sup> ions in the 1M perchlorate solution are already associated with ClO<sub>4</sub><sup>-</sup> anions, is due only to the formation of ion pairs in which the ions preserve the same hydration shells as in the free state.

In nitrate solutions (Fig. 3) the experimental points at concentrations higher than 1 mol l<sup>-1</sup> of NO<sub>3</sub><sup>-</sup> distinctly deviate from the diaquo complex line and are shifted towards the line calculated for the neutral mononitrato-monoaquo complex. We may conclude that in this region one ligand H<sub>2</sub>O is being substituted by one ligand NO<sub>3</sub><sup>-</sup> forming thus the complex [Tl(H<sub>2</sub>O)(NO<sub>3</sub>)<sup>0</sup> without any change of the coordination number. The concentration stability constant of this mononitrato complex at one particular concentration can be calculated from the measured values of  $V_{\pm}$ :

$$K'_{\text{TlNO}_3} = (V_{\pm} - V_{\text{Tl}^+}) / [(V_{\text{TlNO}_3} - V_{\pm}) \cdot c_{\text{NO}_3^-}], \quad (3)$$

where  $V_{\text{Tl}^+}$  and  $V_{\text{TlNO}_3}$  are the apparent molar volumes of the diaquo complex and of the mononitrato-monoaquo complex, respectively, which were determined from the straight lines for the corresponding complexes at the given value of NO<sub>3</sub><sup>-</sup> concentration,  $c_{\text{NO}_3^-}$  is the analytical concentration of the nitrate used as the base electrolyte (Table II). The average value of  $K'_{\text{TlNO}_3}$  determined by this procedure in nitrate solutions in the concentration range from 2 to 6 mol/l of NO<sub>3</sub><sup>-</sup> is  $0.4 \pm 0.1$  l mol<sup>-1</sup>, which is about one fifth of the value determined by thermodynamic methods<sup>7,9</sup>. This would indicate that only about 20% of nitrate ions associated with the Tl<sup>+</sup> cation are coordinated in the inner coordination sphere, the remaining fraction being formed by ion pairs.

The structure of these complexes can be estimated recalling that water is a unidentate ligand so that the formation of the diaquo complex requires the formation of two  $\sigma$ -bonds. There is no reason to assume any change of the number of bonds due to the coordination of the NO<sub>3</sub><sup>-</sup> ligands in the inner coordination sphere so that we may assume that thallium is forming two bonds also in the [Tl(H<sub>2</sub>O)(NO<sub>3</sub>)<sup>0</sup> complex. The NO<sub>3</sub><sup>-</sup> anion in this complex would therefore be also a unidentate ligand.

Since there is already one occupied non-bonding s-orbital in the valence sphere of the Tl<sup>+</sup> ion, the  $sp^2$  hybridization with a valence angle of about 120° (ref.<sup>23</sup>), should be expected when two purely covalent  $\sigma$ -bonds are formed. This effect on the valence angle of the "inert" s-pair has been observed for Sn(II), Pb(II), As(III),

Sb(III), and Bi(III) in SnO, PbO, SnCl<sub>2</sub>·2 H<sub>2</sub>O, K<sub>2</sub>SnCl<sub>4</sub>·H<sub>2</sub>O, KSbF<sub>6</sub>, (NH<sub>4</sub>)<sub>2</sub>SbCl<sub>5</sub>, Bi<sub>2</sub>O<sub>3</sub>, etc., where the degree of the covalent character is high<sup>23</sup>. On the other hand, the purely electrostatic character of the ion–ligand interaction would lead to the linear configuration X—Tl—X, in which the electrostatic potential energy is minimum. From the experimental values of the association constant the Bjerrum-Fuoss theory of ion association gives the closest-approach distance *a* for the Tl(I) complexes substantially shorter than the sum of the crystallographic radii<sup>24</sup> and it is therefore assumed by the authors that the bonds have a highly covalent character<sup>25</sup>. On the other hand, the shift of the NMR signal of <sup>205</sup>Tl, as measured relatively to metallic thallium, is equal to 21·5 (p.p.m.) for solid TlI, 11·0 for TlBr, 6·3 for TlCl and 1·7 for TlNO<sub>3</sub>, respectively, which means that there is a rather low covalent character of the bond: about 10% in TlI and only 1% in TlNO<sub>3</sub> (ref.<sup>23</sup>). Raman spectra agree with these results in that they do not show any appreciable vibration either for the Tl—OH<sub>2</sub> bonds or for the Tl—O<sub>3</sub>N bonds.

This means that the electron configuration on the central Tl<sup>+</sup> cation under these conditions will be similar to the configuration of the free Tl<sup>+</sup> ion, with the inert *s*-pair, the spherically symmetric orbital of which is perturbed only negligibly by the ligand field. Hence it may be inferred that the structure of the [Tl(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> and [Tl(H<sub>2</sub>O)(NO<sub>3</sub>)<sub>2</sub>]<sup>0</sup> complexes is approaching the linear configuration in which the ligands are bound to the central ion by bonds having predominantly ionic (or ion-dipole) character.

## REFERENCES

1. Cotton F. A., Wilkinson G.: *Anorganische Chemie*, 2. Ausg. Deutscher Verlag der Wissenschaften, Berlin 1968.
2. Orgel L.: *J. Chem. Soc.* 1958, 4186.
3. Corey R. B., Wyckoff R. W. G.: *Z. Krist.* 87, 264 (1934).
4. Bertin E. P., Nakagawa I., Mizushima S., Lane T. J., Quagliano J. V.: *J. Am. Chem. Soc.* 86, 525 (1958).
5. Geddes A. L., Bottger G. L.: *Inorg. Chem.* 8, 802 (1969).
6. Ramette R. W., Spencer J. B.: *J. Phys. Chem.* 67, 944 (1963).
7. Davies C. W.: *Ion Association*, p. 69, 169. Butterworths, London 1962.
8. Curtice R. E., Scott A. B.: *Inorg. Chem.* 3, 1383 (1964).
9. Nair V. S., Nancollas G. H.: *J. Chem. Soc.* 1957, 318.
10. George J. H. B., Rolfe J. A., Woodward L. A.: *Trans. Faraday Soc.* 49, 375 (1953).
11. Woodward L. A.: *Phil. Mag.* 18, 823 (1934).
12. Waters D. N., Woodward L. A.: *J. Chem. Soc.* 1954, 3250.
13. Bell R. P., Prue J. E.: *J. Chem. Soc.* 1949, 362.
14. Čeleda J.: *Sci. Papers of the Institute of Chemical Technology, Prague FAT and FOT* 3, Part I, 15 (1959).
15. Čeleda J.: *Sci. Papers of the Institute of Chemical Technology, Prague, Inorg. Technol.* 5, 17 (1964).
16. Čeleda J., Jedináková V.: *This Journal* 32, 271 (1967).
17. Jedináková V., Čeleda J.: *This Journal* 32, 1679 (1967).



18. Jedináková V., Čeleda J.: *J. Inorg. Nucl. Chem.* *30*, 555 (1968).
19. Jedináková V., Čeleda J.: *J. Inorg. Nucl. Chem.* *31*, 2793 (1969).
20. *International Critical Tables* III, p. 60. (1928).
21. Čeleda J., Jedináková V.: *Sci. Papers of the Institute of Chemical Technology, Prague, B 12*, 167 (1968).
22. Vlček A. A.: *Struktura a vlastnosti koordinačních sloučenin* p. 369. Academia, Prague 1966.
23. Phillips C. S. G., Williams R. J. P.: *Inorganic Chemistry*, Vol. 2, *Metals*. Clarendon Press, Oxford 1966.
24. Davies C. W., James J. C.: *Proc. Roy. Soc. A* *195*, 116 (1962).
25. Nancollas G. H.: *Interactions in Electrolyte Solutions*. Elsevier, Amsterdam 1966.

Translated by Z. Prášil.