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Abstract

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ON THE QUESTION OF THE STABILITY OF COMPLEX COMPOUNDS OF DIVALENT PLATINUM OF THE MONO- AND TRIAMMINE TYPE

In our previous works we investigated the stability of a number of platinates (^1), as well as compounds of the tetrammine (^2) and diammine (^3) types. The present article gives the corresponding data for the remaining members of the Werner–Miolati transition series, namely: compounds of the monoammine type (Cossa salts), as well as of the triammine type (Cleve salts).

Experimental part

The synthesis of the potassium Cossa salt $K[\mathrm{PtNH_3Cl_3}]$ and of Cleve chloride $[\mathrm{Pt(NH_3)_3Cl}]Cl$ was carried out by the methods described in the literature. The composition of the compounds obtained was checked by chemical analysis for platinum and chlorine. The measurement procedure was described in previous articles. A definite concentration of ammonia and chlorine ions in solution was produced by dissolving NH_4Cl and adding NH_4OH. The values of the overall instability constants were calculated by the formula:

$$K^c = \frac{[\mathrm{Pt}^{2+}][\mathrm{NH_3}][\mathrm{Cl}^-]^3}{[\mathrm{PtNH_3Cl_3}^-]}$$

for the monoammine, and by the formula:

$$K^c = \frac{[\mathrm{Pt}^{2+}][\mathrm{NH_3}]^3[\mathrm{Cl}^-]}{[\mathrm{Pt(NH_3)_3Cl}^+]}$$

for the triammine. Experimental data and the calculation of the values of pK^c are given in Table 1.

(Figure: Fig. 1. Stability diagram of chloro derivatives forming the Werner–Miolati transition series. 1 –A = NH_3; 2 –A = CH_3NH_2)

Fig. 1. Stability diagram of chloro derivatives forming the Werner–Miolati transition series. 1 –$A = NH_3$; 2 –$A = CH_3NH_2$

On the basis of the data obtained and the results of earlier investigations, a graph was constructed on which the values of the overall instability constants for all members of the Werner–Miolati transition series are compared (Fig. 1).

Figure 2 presents the available data for iodo derivatives containing coordinated molecules of ammonia and methylamine. From the graphs presented it is evident that the values of the instability constants decrease regularly as coordinated chlorine and iodine ions are replaced by ammonia and methylamine molecules.

Discussion of the Results

It can be seen that the introduction of one ammonia molecule into the complex entails a sharp increase in stability ($\Delta pK^c = 7.5$). On going from the monoamine to the diamine there is a further increase in stability, but it is already less pronounced ($\Delta pK^c = 4.3$). On going from the trans-diamine to the triamine, $\Delta pK^c = 4.4$, and from the triamine to the tetramine, $\Delta pK^c = 2.5$.

It is very interesting to compare the values we obtained for the instability constants of the ammine and methylammine complexes of divalent platinum with the data of Chatt and Gamlen (^{4}) concerning the constants corresponding to the elimination of ammonia or methylamine from salts

(Figure: Fig. 2. Stability diagram of iododerivatives forming the Werner-Miolati transition series; 1 –A = NH3; 2 –A = CH3NH3)

Fig. 2. Stability diagram of iododerivatives forming the Werner-Miolati transition series;
$1 - A = \mathrm{NH_3}$; $2 - A = \mathrm{CH_3NH_3}$

$$\left[\begin{matrix}\mathrm{C_2H_4} & \mathrm{Cl} \\ \mathrm{Cl} & \mathrm{NH_3}\end{matrix}\mathrm{Pt}\right]$$

and

$$\left[\begin{matrix}\mathrm{C_2H_4} & \mathrm{Cl} \\ \mathrm{Cl} & \mathrm{CH_3NH_2}\end{matrix}\mathrm{Pt}\right].$$

For the first of these compounds the equilibrium constant corresponding to the process:

$$\text{trans-}[\mathrm{PtCl_2NH_3C_2H_4}] + \mathrm{H_2O} \rightleftarrows \text{trans-}[\mathrm{PtCl_2H_2OC_2H_4}] + \mathrm{NH_3}$$

is equal to $1.6 \cdot 10^{-8}$. The equilibrium constant for the methylamine derivative is equal to $2.5 \cdot 10^{-9}$.

Taking into account the strong trans influence of coordinated ethylene and the composition of the inner sphere of the Zeise-salt derivatives, it is natural to consider that the constants found correspond to the fourth instability constants of the tetramines. Under this assumption one can calculate the values of the remaining instability constants of the tetramines using J. Bjerrum' s formula.

According to J. Bjerrum, when only the statistical effect is present, the ratio of successive stability constants is given by the expression:

$$\frac{k_n}{k_{n+1}} = \frac{(N-n+1)\cdot(n+1)}{(N-n)\cdot n},$$

where k_n and k_{n+1} are successive stability constants, N is the maximum coordination number, and n is the number of already attached ligands of the given composition.

In the case of the platinum(II) tetramines considered by us, $N = 4$. Then

$$k_3 = \frac{8}{3}k_4;$$

$$k_2 = 6k_4; \qquad k_1 = 16k_4.$$

On passing to the instability constants, respectively, we have

$$k_3^{-1} = \frac{3}{8}k_4^{-1}; \qquad k_2^{-1} = \frac{1}{6}k_4^{-1}; \qquad k_1^{-1} = \frac{1}{16}k_4^{-1}.$$

Taking the Chatt and Gamlen constant, accepted as k_4^{-1}, we find:

$$k_4^{-1} = 1.6\cdot 10^{-8}, \quad k_3^{-1} = 6\cdot 10^{-9}, \quad k_2^{-1} = 2.7\cdot 10^{-9}, \quad k_1^{-1} = 1\cdot 10^{-9}.$$

Multiplying the values of the successive constants, we must obtain the value of the overall instability constant of the ion $[\mathrm{Pt(NH_3)_4}]^{2+}$, corresponding to the process:

$$[\mathrm{Pt(NH_3)_4}]^{2+} \rightleftarrows \mathrm{Pt}^{2+} + 4\mathrm{NH_3}.$$

When the sequential constants just calculated are multiplied, we obtain:

$$K_{\text{overall}}^{-1} = 16\cdot 10^{-9}\cdot 6\cdot 10^{-9}\cdot 2.7\cdot 10^{-9}\cdot 1\cdot 10^{-9} = 2.59\cdot 10^{-34}\ (25^\circ).$$

The data of our measurements give, on the average, $K_{\text{overall}}^{-1} = 5\cdot 10^{-36}$ (18°). The value of the overall instability constant of the ion $[\mathrm{Pt(NH_3)_4}]^{2+}$, calculated by Bjerrum' s formula from the constant of Chatt and Gamlen, is 52 times greater than the value found by us with the aid of a platinum electrode. If one takes into account that the constant of Chatt and Gamlen was determined at 25°, and ours at 18°, and also the decrease in the values of the constants with decreasing temperature, then the degree of agreement of both values of the overall constant will be still greater.

Even leaving aside the temperature correction, we can draw two conclusions: 1) the difference in the stepwise instability constants of the individual ammonia molecules is mainly determined by a statistical effect; the excess of the overall constant found by us ($5 \cdot 10^{-36}$) over that calculated taking account only of the statistical effect can, without great error, be explained by the increased strength of the bond of the first two NH_3 molecules. According to Bjerrum’ s formula,

$$k_1^{-1} \cdot k_2^{-1} = 2.7 \cdot 10^{-18}.$$

If we proceed from the value of the constant found by us, then it may be assumed that

$$k_1^{-1} \cdot k_2^{-1} = 2.7 \cdot 10^{-18} \cdot \frac{5 \cdot 10^{-36}}{2.5 \cdot 10^{-34}} = 5.4 \cdot 10^{-20}.$$

2) Since the constant of Chatt and Gamlen was determined with the aid of a glass electrode, and our constant with the aid of a platinum electrode, it may be assumed that the potential of the system Pt^0—Pt^{2+}, calculated by Latimer and equal to 1.2 V, does not differ greatly from the true value.

Table 1

Determination of the instability constant

Complex concentration, mol/l	$[Cl^-]$, mol/l	pC_{NH3}	$E = E_{Pt} - E_{cal}$, mV	E_{Pt}, mV	$-\lg[Pt^{2+}]$	pK_c
$[PtNH_3Cl]^-$						
0.0124	0.1	5.8	437	685	17.8	24.7
0.0089	1.0	5.3	385	633	19.6	23.1
0.0051	0.1	5.5	428	676	18.1	24.3
0.008	0.1	5.5	466	714	16.8	23.2
0.005	1.0	5.1	337	585	21.2	24.0
0.0044	1.0	6.0	374	622	19.9	23.5
0.0058	0.1	5.7	437	685	17.8	24.3
0.0035	1.0	4.8	339	587	21.1	23.4
0.0043	0.1	4.9	387	635	19.5	25.0
0.0057	0.1	4.3	365	613	20.2	25.3
0.0364	1.0	5.3	370	618	20.1	24.0
0.157	1.0	5.5	377	625	19.8	24.5
Average . . .						24.1
$[Pt(NH_3)_3Cl]^+$						
0.0040	0.1	4.5	312	560	22.1	34.2
0.0071	1.0	3.3	226	474	25.0	32.7
0.0050	0.1	3.7	281	529	23.2	33.0
0.0080	1.0	4.3	324	572	21.7	32.5

Complex concentration, mol/l	$[Cl^-]$, mol/l	pC_{NH3}	$E = E_{Pt} - E_{cal}$, mV	E_{Pt}, mV	$-\lg[Pt^{2+}]$	pK_c
0.0029	1.0	2.5	168	416	27.0	32.0
0.0512	1.0	5.3	402	650	19.0	33.6
0.0389	1.0	4.5	341	589	21.0	33.1
0.0622	1.0	3.8	298	546	22.5	32.7
0.0452	0.1	5.4	445	693	17.5	32.4
0.055	0.1	3.9	322	570	21.7	32.1
0.0294	0.1	2.6	194	442	26.2	32.5
Average . . .						32.8

If analogous calculations are made for the methylamine complex $[Pt(CH_3NH_2)_4]^{2+}$, then from the constant of Chatt and Gamlen and the formula of J. Bjerrum we come to the conclusion that $K^{-1}_{\text{overall}} = 1.56 \cdot 10^{-37}$, whereas on the basis of our measurements $K^{-1}_{\text{overall}} = 0.8 \cdot 10^{-40}$. Apparently, in the case of methylamine, which is more strongly bound to Pt^{2+} than ammonia, there is also a greater difference in the bond strength of the molecules split off successively. In the present case the statistical effect plays a smaller role.

Returning to the ammines, with the aid of the above values of the stepwise constants, and also the available data on the constants of stepwise dissociation of chloride ions, we can approximately estimate the values of the overall constants for tri-, di-, and monoamine Pt^{2+}. It may be assumed that the constant corresponding to the splitting off of the chloride ion from the ion $[Pt(NH_3)_3Cl]^+$ should be close to the constant for the splitting off of chlorine from the ion

cis-$[Pt(NH_3)_2H_2OCl]^+$. For this constant Reischus and Martin[5] give the value $4 \cdot 10^{-5}$.

Then, taking for NH_3 molecules $k_1^{-1} \cdot k_2^{-1} \cdot k_3^{-1} = 5.4 \cdot 10^{-20} \cdot 6 \cdot 10^{-9} = 32 \cdot 10^{-29} = 3.2 \cdot 10^{-28}$, we find $K^{-1} = 3.2 \cdot 10^{-28} \cdot 4 \cdot 10^{-5} = 12.8 \cdot 10^{-33} = 1.28 \cdot 10^{-32}$. The value we found for K^{-1} for the ion $[Pt(NH_3)_3Cl]^+$ is on average $1.6 \cdot 10^{-33}$.

For the diamine we correspondingly find:

$$K^{-1} = 5.4 \cdot 10^{-20} \cdot 3 \cdot 10^{-3} \cdot 4 \cdot 10^{-5} = 64.8 \cdot 10^{-28} = 6.48 \cdot 10^{-27}.$$

As for the monoamine, in order to carry out the calculation it is necessary to estimate the constants for the elimination of chloride ions and for the elimination of one ammonia molecule. We determined the constant corresponding to the process:

$$[\mathrm{PtNH_3Cl_3}]^- + \mathrm{H_2O} \rightleftharpoons [\mathrm{PtNH_3H_2OCl_2}] + \mathrm{Cl}^-$$

($0.8 \cdot 10^{-2}$ at 18°). For the elimination of a chloride ion from the molecule $[\mathrm{PtNH_3H_2OCl_2}]$ the constant should be somewhat smaller than for the elimination of a chloride ion from cis-$[\mathrm{Pt(NH_3)_2Cl_2}]$ ($3 \cdot 10^{-3}$), and larger than for the elimination of chlorine from $[\mathrm{Pt(H_2O)_2Cl_2}]$ (10^{-5}). It may be taken as close to 10^{-4}. Finally, the constant corresponding to the process $[\mathrm{PtNH_3(H_2O)_2Cl}]^+ + \mathrm{H_2O} \rightleftharpoons [\mathrm{PtNH_3(H_2O)_3}]^{2+} + \mathrm{Cl}^-$, should be close to the constant for

$$[\mathrm{Pt(H_2O)_3Cl}]^+ + \mathrm{H_2O} \rightleftharpoons [\mathrm{Pt[H_2O)_4}]^{2+} + \mathrm{Cl}^-,$$

i.e., to k_1^{-1} for $[\mathrm{PtCl_4}]^{2-}$. Meanwhile, according to data of one of us and G. A. Shagisultanova, for $[\mathrm{PtCl_4}]^{2-}$ $k_4^{-1} = 1.6 \cdot 10^{-2}$ (18°), and k_3^{-1} is close to 10^{-4}. Since the overall constant for $[\mathrm{PtCl_4}]^{2-}$ is $4 \cdot 10^{-17}$ (18°), then

$$k_2^{-1} \cdot k_1^{-1} = \frac{4 \cdot 10^{-17}}{1.8 \cdot 10^{-6}} \approx 2 \cdot 10^{-11}.$$

In the present case, owing to the electrostatic effect, k_2^{-1} should be larger than k_1^{-1}, and at the same time smaller than k_3^{-1}; therefore it may be assumed that k_2^{-1} should be of the order of 10^{-5}, and k_1^{-1} of the order of 10^{-6}.

Thus assuming that k_1^{-1} for the ion $[\mathrm{Pt(NH_3)_4}]^{2+}$ should be of the order of 10^{-10}, we find that K^{-1} for the ion $[\mathrm{PtNH_3Cl_3}]^- = 10^{-2} \cdot 10^{-4} \cdot 10^{-6} \cdot 10^{-10} = 10^{-22}$. The mean value we found for the overall instability constant of $[\mathrm{PtNH_3Cl_3}]^-$ is $8 \cdot 10^{-25}$. Of course, all these calculations are of a wholly approximate character, but nevertheless they agree more or less with the values of the constants found by us experimentally.

In conclusion, we note that our attempt to estimate the stepwise constants for $[\mathrm{PtCl_4}]^{2-}$ by the method of A. K. Babko was unsuccessful.

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Note: Figure translations are in progress. See original paper for figures.