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Abstract

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ON THE QUESTION OF THE STABILITY OF COMPLEX COMPOUNDS OF DIVALENT PLATINUM

Compounds of the Tetrammine Type

Compounds of the tetrammine type, containing in their composition the complex ion $[PtA_4]^{2+}$, where A denotes molecules of ammonia or an amine, have been studied fairly well. At the same time, there are no data in the literature on the thermodynamic stability of these complex ions. From preparative data it is known that ammonia molecules, as well as molecules of aliphatic amines, in their tendency toward complex formation with the divalent platinum ion surpass Cl^-, Br^-, and J^-.

As for the relative strength of complexes with ammonia and amines, some conclusions may be drawn from the literature. Chatt and Gamlen ([1]), studying equilibria of the type

$$\text{trans-}[C_2H_4H_2OPtCl_2] + A \rightleftharpoons \text{trans-}[C_2H_4APtCl_2] + H_2O,$$

found that, for the case $A = NH_3$, $\log K = 7.8$, while for the case $A = CH_3NH_2$, $\log K = 8.6$. It follows from this that methylamine molecules are held in the inner sphere more strongly than ammonia molecules.

A study of the acidic properties of complexes of tetravalent platinum with ammonia and aliphatic amines ([2]) showed that the acid dissociation constant of the newly synthesized ion $[Pt(CH_3NH_2)_4NH_3Cl]^{3+}$ is $K_1 = 1.7 \cdot 10^{-7}$, whereas the corresponding value for the ion $[Pt(NH_3)_5Cl]^{3+}$ under the same conditions is $6.4 \cdot 10^{-9}$. Therefore it may be concluded that a methylamine molecule, being coordinated in the inner sphere of Pt^{IV}, is deformed to a greater degree than an ammonia molecule.

The present work is devoted to determining the overall instability constants of the ions $[PtA_4]^{2+}$, containing in the inner sphere molecules of ammonia, methylamine, ethylamine, and ethylenediamine.

Experimental Part

The determination of the overall instability constants of complex tetrammines of divalent platinum was carried out by the potentiometric method previously used by us for the study of platinites ([3]). Measurements were made of the e.m.f. of the chains

$$\overset{+}{\mathrm{Pt}} \mid [\mathrm{PtA_4}]\mathrm{Cl_2},\ \mathrm{A},\ \mathrm{KNO_3} \parallel \mathrm{KCl},\ \mathrm{Hg_2Cl_2} \mid \mathrm{Hg}$$

$$c_1 \qquad\qquad c_2 \qquad\qquad \text{saturated}$$

at various concentrations of the complexes and addends.

The measurements were carried out according to the usual compensation scheme with a PRTV-49 potentiometer and a pointer galvanometer. The vessels with the electrodes under investigation and the saturated calomel electrode were kept in a thermostat at a temperature of $18 \pm 0.5^{\circ}$. The electrodes were made of platinum foil 20×10 mm^2 in size and were coated electrolytically with platinum black.

In practice the measurements were made as follows. Into special vessels were introduced 10 ml of a solution of ammonia or of the corresponding amine of a definite concentration. A weighed portion of the complex was added to the solution.

and, finally, KNO_3 in the amount necessary to maintain in the solution a constant ionic strength equal to unity. Then an electrode and a salt bridge filled with a 1 N KNO_3 solution were immersed in the solution. The vessel was placed in a thermostat, and the solution was saturated with nitrogen. Measurements were made over the time from the moment the salt dissolved until an essentially constant value of the potential was established.

The substances studied were synthesized as follows.

Tetrammineplatinum chloride $[\mathrm{Pt(NH_3)_4}]Cl_2$. Peyrone' s salt ([4]) was obtained from potassium chloroplatinite; on dissolving it in an excess of ammonia and subsequent crystallization, the required tetrammine was isolated. For comparison, experiments were also carried out with a tetrammine obtained by Gildengershel' s method ([5]) directly from platinite.

Tetramethylammineplatinum chloride $[\mathrm{Pt(CH_3NH_2)_4}]Cl_2$. From potassium chloroplatinite, cis-diiododimethylammineplatinum was synthesized, then cis-dichlorodimethylammineplatinum ([6]), on dissolving which in an excess of methylamine the tetrammine was obtained in solution. The solution was concentrated to a syrupy state, and on cooling crystals of tetramethylammineplatinum chloride separated.

Tetraethylammineplatinum chloride $[Pt(C_2H_5NH_2)_4]Cl_2$. To a solution of chloroplatinite a calculated amount of ethylamine solution was added. On the following day the same amount of ethylamine was again poured into the solution containing the precipitate; the precipitate dissolved with constant stirring on a boiling water bath, the solution was concentrated, and after cooling, tetraethylammineplatinum chloride was precipitated with alcohol ([5]).

Diethylenediammineplatinum chloride $[Pt(NH_2C_2H_4NH_2)_2]Cl_2$ was synthesized analogously to tetraethylammineplatinum chloride. The composition of all four substances was established by chemical analysis.

Ammonia and the amines were purified by distillation. All solutions were prepared with twice-distilled water.

The experimental data obtained for the indicated tetrammines are given in Tables 1–4.

From the electrode potentials, the concentration of Pt^{2+} ions was calculated (taking the normal potential of Pt/Pt^{2+} as equal to 1.2 V), and then the values of the overall instability constants according to the formula:

$$K^c = \frac{[Pt^{2+}] \cdot [A]^4}{[PtA_4^{2+}]} \qquad \text{for } A = NH_3,\ CH_3NH_2,\ C_2H_5NH_2;$$

$$K^c = \frac{[Pt^{2+}][C_2H_4(NH_2)_2]^2}{[Pt(NH_2CH_2CH_2NH_2)_2{}^{2+}]} \qquad \text{for } A = C_2H_4(NH_2)_2.$$

Table 1

Determination of the instability constant of $[Pt(NH_3)_4]^{2+}$

No.	Conc. $[Pt(NH_3)_4]Cl_2$, mol/L	Conc. NH_3, mol/L	$E = E_{Pt} - E_{cal}$, mV	E_{Pt}, mV	$-\lg[Pt^{2+}]$	pK^c
1	0,0029	$0{,}92 \cdot 10^{-1}$	2	250	32,8	34,5
2	0,0429	$0{,}92 \cdot 10^{-1}$	23	271	32,1	34,9
3	0,0024	$4{,}2 \cdot 10^{-2}$	28	276	31,9	34,7
4	0,0352	$4{,}2 \cdot 10^{-2}$	46	294	31,3	35,4
5	0,0077	$4{,}2 \cdot 10^{-3}$	124	372	28,6	36,0
6	0,0418	$4{,}2 \cdot 10^{-3}$	170	418	27,0	35,1

No.	Conc. $[Pt(NH_3)_4]Cl_2$, mol/L	Conc. NH_3, mol/L	$E = E_{Pt} - E_{cal}$, mV	E_{Pt}, mV	$-\lg[Pt^{2+}]$	pK^c
7	0,0023	$4{,}2 \cdot 10^{-4}$	246	494	24,4	35,3
8	0,0085	$6{,}9 \cdot 10^{-4}$	240	488	24,6	35,2
9	0,0356	$6{,}9 \cdot 10^{-4}$	227	475	25,0	36,2
10	0,0051	$1{,}2 \cdot 10^{-5}$	403	651	18,9	35,5
11	0,0012	$1{,}2 \cdot 10^{-5}$	408	656	18,8	36,2

Average value of $pK^c = 35,3$

Along with solutions of the free bases, 1 N solutions of ammonium nitrate (in the case of $[Pt(NH_3)_4]Cl_2$) and a 1 N solution of methylamine hydrochloride (in the case of $[Pt(CH_3NH_2)_4]Cl_2$) were used. The concentrations of NH_3 and CH_3NH_2 were calculated from the hydrolysis constants of the salts and from the pH measurement data in the solutions studied. The experimental data and the calculation of the instability constants for these solutions are given in Nos. 10, 11 (Table 1) and Nos. 8-10 (Table 2).

Table 2

Determination of the instability constant of $[Pt(CH_3NH_2)_4]^{2+}$

No.	Conc. $[Pt(CH_3NH_2)_4]Cl_2$, mol/l	Conc. CH_3NH_2, mol/l	$E = E_{Pt} - E_{cal}$, mV	E_{Pt}, mV	$-\lg[Pt^{2+}]$	pK^c
1	0.002	$1.45 \cdot 10^{-2}$	−45	203	34.4	39.1
2	0.0361	$1.45 \cdot 10^{-2}$	−41	207	34.2	40.1
3	0.0022	$1.58 \cdot 10^{-3}$	15	263	32.3	40.8
4	0.0337	$1.58 \cdot 10^{-3}$	66	314	30.6	40.3
5	0.0026	$1.45 \cdot 10^{-4}$	186	434	26.4	39.4
6	0.0384	$1.45 \cdot 10^{-4}$	215	463	25.4	39.3
7	0.0291	$1.45 \cdot 10^{-5}$	282	530	23.1	40.9

No.	Conc. $[Pt(CH_3NHC_2H_4NH_2)_4]Cl_2$, mol/l	Conc. $C_2H_4(NH_2)_2$, mol/l	$E = E_{Pt} - E_{cal}$, mV	E_{Pt}, mV	$-\lg[Pt^{2+}]$	pK^c
8	0.0021	$2.3 \cdot 10^{-6}$	348	596	20.8	40.5
9	0.001	$1.55 \cdot 10^{-6}$	374	622	19.9	40.1
10	0.0083	$3.46 \cdot 10^{-6}$	338	586	21.2	40.7

Mean value $pK^c = 40.1$

Table 3

Determination of the instability constant of $[Pt(C_2H_5NH_2)_4]^{2+}$

No.	Conc. $[Pt(C_2H_5NH_2)_4]Cl_2$, mol/l	Conc. $C_2H_4(NH_2)_2$, mol/l	$E = E_{Pt} - E_{cal}$, mV	E_{Pt}, mV	$-\lg[Pt^{2+}]$	pK^c
1	0.0019	$3.8 \cdot 10^{-2}$	−45	203	34.4	37.4
2	0.0154	$3.8 \cdot 10^{-2}$	−19	229	33.5	37.3
3	0.059	$3.8 \cdot 10^{-2}$	7	255	32.6	37.1
4	0.0036	$3.9 \cdot 10^{-3}$	85	333	29.9	37.1
5	0.0123	$3.9 \cdot 10^{-3}$	121	369	28.7	36.4
6	0.0608	$3.9 \cdot 10^{-3}$	110	358	29.0	37.4
7	0.0054	$3.9 \cdot 10^{-4}$	222	470	25.2	36.6
8	0.0036	$3.9 \cdot 10^{-5}$	332	580	21.4	36.6
9	0.0216	$3.9 \cdot 10^{-5}$	340	588	21.1	37.1

Mean value $pK^c = 37.0$

Table 4

Determination of the instability constant of $[Pt(NH_2C_2H_4NH_2)_2]^{2+}$

No.	Conc. $[Pt(NH_2C_2H_4NH_2)_2]Cl_2$, mol/l	Conc. $C_2H_4(NH_2)_2$, mol/l	$E = E_{Pt} - E_{cal}$, mV	E_{Pt}, mV	$-\lg[Pt^{2+}]$	pK^c
1	0.003	$1.11 \cdot 10^{-2}$	−54	194	34.7	36.1
2	0.0442	$1.11 \cdot 10^{-2}$	−22	226	33.6	36.2
3	0.0025	$1.11 \cdot 10^{-3}$	−1	247	32.9	36.2

Figure 1

Figure 1: Figure 1

No.	Conc. $[Pt(NH_2C_2H_4NH_2)_2]Cl_2$, mol/l	Conc. $(NH_4)_2C_2O_4$, mol/l	$E = E_{Pt} - E_{cal}$, mV	E_{Pt}, mV	$-\lg[Pt^{2+}]$	pK^c
4	0.0547	$1.11 \cdot 10^{-3}$	+9	257	32.5	37.1
5	0.003	$3.14 \cdot 10^{-3}$	−45	203	34.4	36.9
6	0.0307	$3.14 \cdot 10^{-3}$	−25	223	33.7	36.2
7	0.0035	$1.0 \cdot 10^{-4}$	71	319	30.4	36.0
8	0.0262	$1.0 \cdot 10^{-4}$	58	306	30.8	37.2

Mean value $pK^c = 36.5$

Discussion of the results

The data given in Tables 1–4 show that, when the concentration of the complex is varied, as well as the concentration of the addends over wide limits (by a factor of 1000–10 000), the values of the concentration instability constants remain constant within one to one and a half orders of magnitude.

Fig. 1. Dependence of the electrode-potential values on the concentration of the addends at constant complex concentration $C_1 = 0.04$ mole/l.
1 –$[Pt(NH_3)_4]^{2+}$,
2 –$[Pt(C_2H_5NH_2)_4]^{2+}$,
3 –$[Pt(CH_3NH_2)_4]^{2+}$,
4 –$[Pt(NH_2CH_2CH_2NH_2)_2]^{2+}$.

Comparison of the stability of the ethylenediamine complex with other tetrammine complexes directly by the values of the instability constants is not entirely correct, since in the expression for the first constant the molar concentration of the addend enters squared, whereas for the other compounds it enters to the fourth power. It is more correct to compare the concentration of Pt^{2+} ions for different complexes at constant concentrations of the complexes and addends. For this purpose a graph was constructed of the dependence of the emf on $\lg C_A$ (Fig. 1). From Fig. 1 it is seen that, among the amines studied, ethylenediamine forms the most stable complexes.

The data presented in the present work are of interest for comparison with those previously described for platinites. Such a comparison leads to the following series in order of increasing thermodynamic stability:

$$[PtCl_4]^{2-} < [PtBr_4]^{2-} < [PtJ_4]^{2-} < [Pt(NH_3)_4]^{2+} < [Pt(C_2H_5NH_2)_4]^{2+} < [Pt(CH_3NH_2)_4]^{2+} < Pt(CN)_4^{2-} <$$
$$pK \quad 16.6 \qquad 20.4 \qquad 29.6 \qquad 35.3 \qquad 37.0 \qquad 40.1 \qquad 41.0$$
$$< [Pt(NH_2C_2H_4NH_2)_2]^{2+}$$

It should be noted that the complex ions of the tetrammine type studied are simultaneously characterized both by considerable thermodynamic stability and by great inertness in the sense of Taube. At the same time, the ion $[Pt(CN)_4]^{2-}$, which is very stable in the thermodynamic sense, has great lability. The inertness of the tetrammine complexes is apparently associated with the small trans influence of ammonia and amine molecules in the inner sphere of divalent platinum.

It is very interesting that this inertness does not prevent the relatively rapid establishment of the potential on a platinized platinum electrode. It may be supposed that processes of the following type also take place in these systems:

$$Pt^0 + [Pt^{2+}(NH_3)_4]^{2+} \rightarrow Pt^{2+} + [Pt^0(NH_3)_4]^0 \rightarrow Pt^0 + 4NH_3$$

$$Pt^{2+} + 4NH_3 \rightarrow [Pt^{2+}(NH_3)_4]^{2+},$$

i.e., exchange of platinum between the complex ion and the electrode.

The obtained values of the instability constants are, of course, conditional in the sense that they were calculated from the value of the potential

$$Pt^{2+} + 2e \rightarrow Pt,$$

taken as equal to 1.2 V. However, if this value should subsequently be refined, the introduction of the corresponding correction will not affect the sequence of complex ions found by us in terms of stability.

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References

1. J. Chatt, G. A. Gamlen, *J. Chem. Soc.*, **1956**, 2371.

2. A. A. Grinberg, Kh. I. Gildengershel, V. V. Sibirskaya, *ZhNKh*, **6**, No. 1 (1961).

3. A. A. Grinberg, M. I. Gel' fman, *DAN*, **133**, No. 5 (1960).

4. V. V. Lebedinskii, V. A. Golovnya, *Izv. Sekt. platiny Inst. obshch. i neorg. khim. AN SSSR*, **20**, 95 (1946).

5. Kh. I. Gildengershel, *ZhNKh*, **1**, No. 3 (1956).

6. Kh. I. Gildengershel, *ZhNKh*, **1**, No. 8 (1956).

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