Chemistry

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Abstract

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ON THE QUESTION OF THE INSTABILITY CONSTANTS OF GEOMETRICALLY ISOMERIC PLATODIAMINES

In 1960 one of us, together with G. A. Shagisultanova (⌒1), for the first time found the values of the instability constants of isomeric diammines of composition $[Pt(NH_3)_2Cl_2]$, corresponding to the process

$$[\mathrm{Pt(NH_3)_2Cl_2}] + \mathrm{H_2O} \rightleftarrows [\mathrm{Pt(NH_3)_2ClH_2O}]\,\mathrm{Cl}.$$

It was thereby found that the instability constant of the trans-isomer is much smaller than that for the cis-isomer, i.e., the trans-isomer is thermodynamically more stable than the cis-isomer.

In the present work we decided to verify the corresponding relations using as an example derivatives of divalent platinum in which ammonia molecules are replaced by molecules of methylamine and ethylamine. The procedure was the same as in the article (⌒1). Preparations of cis- and trans-$[Ptm_2Cl_2]$ and $[Pte_2Cl_2]$, where m is methylamine and e is ethylamine, were synthesized according to the prescriptions set forth in works (^{2},3,⌒4). The preparations were made repeatedly, and their composition was checked by analyses for platinum and chlorine.

For the cis-isomers the constants were determined at $\mu = 0.1$ and 17-18°C. The ratio KCl/complex compound varied within the range 5 : 1—15 : 1. In addition, for the cis-isomers the values of the constants were also found without an "ionic background." For the trans-isomers experiments were carried out only at $\mu = 0.1$ (see Table 1).

Table 1

	Number of experiments, n	μ	K, max.	K, min.	K, mean.*
Cis-$[Pte_2Cl_2]$	23	0.1	$0.6 \cdot 10^{-2} (n = 4)$	$0.3 \cdot 10^{-2} (n = 5)$	$0.43 \cdot 10^{-2}$

	Number of experiments, n	μ	K, max.	K, min.	K, mean.*
Cis-$[Pte_2Cl_2]$ without ionic background	8		$0.2 \cdot 10^{-2}$	$0.1 \cdot 10^{-2}$	$0.18 \cdot 10^{-2}$
Cis-$[Ptm_2Cl_2]$	18	0.1	$0.5 \cdot 10^{-2}$	$0.3 \cdot 10^{-2}$	$0.39 \cdot 10^{-2}$
Cis-$[Ptm_2Cl_2]$ without ionic background	8		$0.2 \cdot 10^{-2}$	$0.1 \cdot 10^{-2}$	$0.16 \cdot 10^{-2}$
Trans-$[Ptm_2Cl_2]$	16	0.1	$0.5 \cdot 10^{-3}$	$0.1 \cdot 10^{-3}$	$0.21 \cdot 10^{-3}$
Trans-$[Pte_2Cl_2]$	7	0.1	$0.4 \cdot 10^{-3}$	$0.2 \cdot 10^{-3}$	$0.32 \cdot 10^{-3}$

* Value of K within the range 0.4—$0.5 \cdot 10^{-2}$ in 14 experiments.

Comparison and discussion of the results

The newly obtained data on the values of the partial instability constant K_4^{-1}, corresponding to dissociation of one chlorine atom, for the cis-isomers studied hardly differ from one another and are very close to the previously published data for cis-$[Pt(NH_3)_2Cl_2]$.

Indeed, according to A. A. Grinberg and G. A. Shagisultanova (ˆ1), K_4^{-1} for cis-$[Pt(NH_3)_2Cl_2]$ at 17-18° $= 3.7 \cdot 10^{-3}$. As is seen from the data presented, for cis-$[Pte_2Cl_2]$ we have $K_4^{-1} = 4.3 \cdot 10^{-3}$, and for cis-$[Ptm_2Cl_2]$ $K_4^{-1} = 3.9 \cdot 10^{-3}$.

For trans-$[Pt(NH_3)_2Cl_2]$, according to the data of Grinberg and Shagisultanova, $K_4^{-1} = 0.8 \cdot 10^{-3}$. True, this is the maximum of the values obtained and was ⋯

is given because even at this value the effect of the contrast between the thermodynamic strength and the kinetic lability of the isomers $[Pt(NH_3)_2Cl_2]$ is manifested quite clearly.

Somewhat later, the instability constants for cis- and trans-$[Pt(NH_3)_2Cl_2]$ were also determined by Martin’ s group in the USA (^{5}). For cis-$[Pt(NH_3)_2Cl_2]$, at 25° and $\mu = 0.318$, it was found that $K_4^{-1} = 3.3 \cdot 10^{-3}$, and $K_3^{-1} \cong 0.4 \cdot 10^{-3}$. For trans-$[Pt(NH_3)_2Cl_2]$, Martin and Adams respectively found ($t = 25°$, $\mu = 0.318$) $K_4^{-1} = 0.32 \cdot 10^{-3}$ and $K_3^{-1} < 0.02 \cdot 10^{-3}$.

For completeness, we add that one of us, in joint work with M. I. Gel' fman (^{6}), by measuring the concentration of the chlorine ion with a silver chloride electrode, found for 18° and $\mu = 1.0$, for cis-$[Pt(NH_3)_2Cl_2]$, $K_4^{-1} = 2 \cdot 10^{-3}$, and for trans-$[Pt(NH_3)_2Cl_2]$, $K_4^{-1} = 0.5 \cdot 10^{-3}$.

In work (^{1}), when comparing the values of the constants found at $\mu = 0.1$ and without an ionic background as applied to $K_2[PtCl_4]$, practically no effect of the ionic background on the magnitude of the constant K_4^{-1} was detected. However, in the present work it is seen that the value of K_4^{-1} at $\mu = 0.1$ is approximately 2.4 times higher than in the absence of a specially created ionic background. This applies both to cis-$[Pte_2Cl_2]$ and to cis-$[Ptm_2Cl_2]$. According to Martin and Adams, as applied to trans-$[Pt(NH_3)_2Cl_2]$, the values of K_4^{-1} at $\mu = 0.318$ are 4 times greater than the values in the absence of an ionic background.

For cis-$[Pt(NH_3)_2Cl_2]$ there are no direct data on the dependence of the magnitude K_4^{-1} on μ. The temperature dependence of this quantity is represented by only two points (for 25 and 35°).

Comparing the data obtained in our laboratory for cis-$[Pt(NH_3)_2Cl_2]$, we can note good agreement of the figures obtained by different methods in works jointly with G. A. Shagisultanova and M. I. Gel' fman. In the case of trans-$[Pt(NH_3)_2Cl_2]$, the value of K_4^{-1}, obtained with the aid of a silver chloride electrode and equal to $0.5 \cdot 10^{-3}$, occupies an intermediate position between the values obtained in works (^{1}) and (^{5}). The figures for the constants obtained for the geometrically isomeric diamines of composition $[Pt(NH_3)_2Cl_2]$ by the American authors, with corrections introduced for temperature and ionic strength, are somewhat lower than our constants. For cis-$[Pt(NH_3)_2Cl_2]$, at 18° and $\mu = 0.318$, $K_4^{-1} \cong 2.8 \cdot 10^{-3}$. With the transition to $\mu = 0.1$, Martin' s figure should decrease somewhat further. As for the American figure for trans-$[Pt(NH_3)_2Cl_2]$, for $t = 18°$ and $\mu = 0.318$ it should be close to $0.25 \cdot 10^{-3}$. With a decrease in ionic strength to $\mu = 0.1$, it may fall to $\sim 0.15 \cdot 10^{-3}$.

Thus, taking into account all the available material, it can be said that K_4^{-1} for cis-$[Pt(NH_3)_2Cl_2]$ at 18° lies within the range $2–4 \cdot 10^{-3}$, and for trans-$[Pt(NH_3)_2Cl_2]$—within the range $0.8–0.2 \cdot 10^{-3}$.

The values of K_4^{-1} found by us for geometrically isomeric derivatives of methylamine and ethylamine also fall within the indicated limits. Thus it may be said that the values of K_4^{-1} for complexes of the type $[Pta_2Cl_2]$, where a is ammonia, methylamine, or ethylamine, coincide practically within the limits of experimental error. The trans isomers in this case too are thermodynamically stronger than the cis isomers.

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