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Abstract

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ACIDIC PROPERTIES OF THE cis- AND trans-ISOMERS OF $(Pt(glh)_2(NH_3)_2)Cl_2$*

One of us, as early as 1931 ([1]), measured the acidic properties of the trans-isomer $(Pt(glh)_2(NH_3)_2)Cl_2$ and in this way was able to provide confirmation of H. Bjerrum' s theory of amino acids.

We set ourselves the task of quantitatively characterizing the acidic properties of both stereoisomers of $(Pt(glh)_2(NH_3)_2)Cl_2$. The cis- and trans-isomers of $(Pt(glh)_2(NH_3)_2)Cl_2$ were obtained by the methods recommended by A. A. Grinberg and B. V. Ptitsyn ([2]). The cis-isomer was subjected to additional recrystallization. The preparations used were analyzed for Pt and Cl:

trans-$(Pt(glh)_2(NH_3)_2)Cl_2$.	Found %:	Pt 43.17; Cl 15.72
cis-$(Pt(glh)_2(NH_3)_2)Cl_2$.	Found %:	Pt 43.54; Cl 16.14
	Calculated %:	Pt 43.35, Cl 15.74

The determination of the acid dissociation constants of the isomers was carried out by potentiometric titration of their solutions with alkali, using a glass electrode according to the previously described procedure ([3]). Figure 1 gives the titration curves of 75 ml of 0.005 M solutions of the trans- and cis-isomers with 0.195 N NaOH solution in 0.5 M $NaNO_3$ solution to create constant ionic strength. As can be seen from Fig. 1, 2 equivalents of alkali are used in the titration of the complex, i.e., the ion $(Pt(ghl)_2(NH_3)_2)^{2+}$ is a dibasic acid, and since the titration curve has no jumps, the successive dissociation constants are close to one another.

The dissociation constants were calculated from the titration curves by the formula

$$\frac{a_H^2 B}{2a - B} = a_H \cdot \frac{(a - B)}{(2a - B)} \cdot k_1 + k_1 k_2,$$

used by Speakman ([4]) and others for determining the dissociation constants of dibasic acids. In this formula: a is the concentration of the acid in mol/l, a_H is the activity of hydrogen ions, $B = b + a_H$, where b is the concentration of added alkali in mol/l, and k_1 and k_2 are the successive dissociation constants. We calculated the constants in the range of 25-75% neutralization of the acid,

where this formula is most accurate. The dissociation constants determined in this way are not thermodynamic, since we could not take into account the activity coefficients of the complex ions and molecules, and they refer to the given ionic strength. Table 1 presents the data from one of the experiments.

Table 1 gives the volume of added NaOH solution in ml; X and Y are equal to:

$$X = \frac{a_{\mathrm{H}}^2 B}{2a - B}, \quad Y = \frac{a_{\mathrm{H}}(a - B)}{2a - B}.$$

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* glh –a glycol molecule.

Table 1

Results of titration of a 0.005 M solution of trans-$(Pt(glh)_2(NH_3)_2)Cl_2$ in 0.5 N $NaNO_3$ with 0.195 N NaOH solution

V_{NaOH}, ml	pH	$a_H \cdot 10^3$	$a_H^2 \cdot 10^6$	$b \cdot 10^3$	$B = (b + a_H) \cdot 10^3$	$(a - B) \cdot 10^3$	$(2a - B) \cdot 10^3$	$X \cdot 10^6$	$Y \cdot 10^4$
1.20	2.80	1.58	2.50	3.12	4.70	0.30	5.30	2.20	0.89
1.60	2.94	1.12	1.25	4.16	5.28	−0.28	4.72	1.40	−0.66
2.00	3.04	0.91	0.83	5.22	6.13	−1.13	3.87	1.31	−2.67
2.20	3.14	0.72	0.52	5.73	6.45	−1.45	3.55	0.94	−2.94
2.40	3.22	0.60	0.36	6.27	6.87	−1.87	3.13	0.79	−3.58
2.60	3.30	0.50	0.25	6.76	7.26	−2.26	2.74	0.66	−4.12
2.80	3.40	0.40	0.16	7.28	7.68	−2.68	2.32	0.53	−4.62

The mean values of k_1 and k_2, calculated by the method of least squares, are:

$$k_1 = 2.84 \cdot 10^{-3}; \quad k_2 = 6.80 \cdot 10^{-4}; \quad k_1/k_2 = 4.2^*.$$

In the same way, under the same conditions ($a = 5 \cdot 10^{-3}$ mole/l and in 0.5 N $NaNO_3$ solution), the dissociation constants of cis-$(Pt(glh)_2(NH_3)_2) \cdot Cl_2$ were determined:

$$k_1 = 3.4 \cdot 10^{-3}; \quad k_2 = 6.10 \cdot 10^{-4}; \quad k_1/k_2 = 5.6.$$

In these experiments the accuracy of determination of k_1 was approximately ±20%, and of k_2, ±10%.

We also titrated 0.01 M solutions of the isomers $(Pt(glh)_2(NH_3)_2)Cl_2$ in 0.1 N $NaNO_3$ with alkali, since the use of a smaller salt background should lead to

an enhancement of the difference in the successive dissociation constants. The following values were obtained:

$$\text{for the trans-isomer } k_1 = 6.1 \cdot 10^{-3}; \quad k_2 = 9.5 \cdot 10^{-4}; \quad k_1/k_2 = 6.4;$$

$$\text{for the cis-isomer } k_1 = 14.3 \cdot 10^{-3}; \quad k_2 = 10 \cdot 10^{-4}; \quad k_1/k_2 = 14.$$

When a 0.01 M solution of trans-$(Pt(glh)_2(NH_3)_2)Cl_2$ was titrated with alkali, at the end of the experiment a white precipitate of sparingly soluble $(Pt(gl)_2 \cdot (NH_3)_2)$ ** was formed, which was analyzed for Pt.

Found, %: Pt 51.62
$(Pt(gl)_2(NH_3)_2)$. Calculated, %: Pt 51.73

A certain dependence of k_1 and k_2 on the experimental conditions may be explained, on the one hand, by the effect of the change in ionic strength, and, on the other hand—which applies especially to k_1—by its rather large magnitude, owing to which in dilute solutions dissociation in the first stage may fail to obey the law of mass action. This fact was noted by Speakman (4) for oxalic acid ($k_1 = 5 \cdot 10^{-2}$), where constancy of the thermodynamic dissociation constant k_1 was observed only in solutions whose concentration exceeded 0.005 M.

For oxalic acid, a strong discrepancy in the value of k_1, according to data from various authors (5), is also characteristic.

The data obtained characterize the ions $(Pt(glh)_2(NH_3)_2)^{2+}$ as rather strong acids with close successive dissociation constants; moreover, both isomers have either practically coincident dissociation constants (in 0.005 M solution), or the acidic properties of the cis-isomer

* The dissociation constants calculated by the method of least squares agree, within the indicated accuracy, w

$$k_1 = \frac{X_1 - X_2}{Y_1 - Y_2}, \quad k_2 = \frac{X_2Y_1 - X_1Y_2}{X_1 - X_2}$$

for a series of points of the titration curve.

** gl is the ion $NH_2CH_2COO^-$.

in a more concentrated solution, are somewhat greater than the acidic properties of the trans isomer.

Considering amino acids, according to Bjerrum, to be strong acids with $pK = 2.33$, which corresponds to the dissociation of the ion $NH_3CH_2COOH^+$, one may

Fig. 1. Curves of potentiometric titration of 0.005 M solutions of trans- (a) and cis- (b) isomers of (Pt(glh)2(NH3)2)Cl2 in 0.5 M NaNO3 solution with 0.195 N NaOH solution

Figure 1: Fig. 1. Curves of potentiometric titration of 0.005 M solutions of trans- (a) and cis- (b) isomers of (Pt(glh)2(NH3)2)Cl2 in 0.5 M NaNO3 solution with 0.195 N NaOH solution

say that their coordination both by the ion H^+ and by the ion Pt^{2+} leads to an enhancement of their acidic properties, since for $(Pt(glh)_2(NH_3)_2)^{2+}$ on average $pK_1 = 2.2$—2.5. A slight increase in dissociation under the influence of the charge of the central ion is also observed for the somewhat more weakly dissociating ions $HC_2O_4^-$, for which $k_2 = 4.9 \cdot 10^{-5}$, and for trans-$(Pt(HC_2O_4)_2(NH_3)_2)$ $k_1 = 6.3 \cdot 10^{-4}$ (6). If, however, one takes a very weakly dissociating addend, for example H_2O, having a dissociation constant of $1.8 \cdot 10^{-16}$, then in the state coordinated to Pt^{2+} its dissociation constant increases to $4.8 \cdot 10^{-5}$.

Fig. 1. Curves of potentiometric titration of 0.005 M solutions of the trans- (a) and cis- (b) isomers of $(Pt(glh)_2(NH_3)_2)Cl_2$ in 0.5 M $NaNO_3$ solution with 0.195 N NaOH solution.

Usually the geometrical structure of isomers affects their acidic properties; thus, cases are known where, owing to the interaction of protons in coordinated groups, the acidic properties of the cis isomer exceed the acidic properties of the trans isomer, as, for example, in unsaturated dibasic organic acids and the complex ions $(Pt(NH_2OH)_2(NH_3)_2)^{2+}$, $(PtPn_2 \cdot Cl_2)^{2+}$ (where Pn is propylenediamine) (7). The acid dissociation constant of the coordinated addend in these cases is appreciably smaller than for glycol, for example: for cis-$(Pt(NH_2OH)_2(NH_3)_2)^{2+}$ $k_1 = 3.3 \cdot 10^{-8}$, $k_2 = 6.6 \cdot 10^{-11}$.

In other cases, with a strong manifestation of the trans effect by addends, it leads to an enhancement of the acidic properties of the trans isomer. This is observed for the ions $(Pt(NH_3)_2(H_2O)_2)^{2+}$ (8), $(Co(En)_2(H_2O)_2)^{3+}$ (9), $(Cr(En)_2(H_2O)_2)^{3+}$ (10), where En is ethylenediamine. The closeness of the acidic properties of the cis and trans isomers of $(Pt(glh)_2(NH_3)_2)Cl_2$ investigated by us may be explained by the fact that, with strong dissociation of the addends, the steric effect of the interaction of protons associated with the cis and trans configurations, and the effect of trans influence, cease to be determining.

In summary, it may be said that, when strong acidic properties are present in addends, both as a phenomenon of coordination and as the effect of internal interaction of addends in the complex, they have little influence on the magnitude of their acid dissociation.

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CITED LITERATURE

1. A. A. Grinberg, *Izv. Inst. po izuch. plat.*, vol. 8, 93 (1931).

2. A. A. Grinberg, B. V. Ptitsyn, *Izv. Inst. po izuch. plat.*, vol. 9, 61, 66 (1932).

3. A. A. Grinberg, A. I. Stetsenko, *ZhNKh*, 1, 2349 (1956).

4. J. C. Speakman, *J. Chem. Soc.*, 1940, 855.

5. H. N. Parton, R. C. Gibbon, *Trans. Farad. Soc.*, 35, 542 (1939).

6. A. Grinberg, *ZhRKh*, 4, 204 (1933).

7. A. A. Grinberg, L. V. Vrublevskaya, Kh. N. Gildenhershel, A. I. Stetsenko, *ZhNKh*, 4, 1018 (1959); A. A. Grinberg, A. I. Stetsenko, *ZhNKh*, 6, issue 1 (1961).

8. A. A. Grinberg, D. I. Ryabchikov, *Acta phisicochim. URSS*, 3, 555 (1935); K. A. Jensen, *Zs. Anorg. Chem.*, 242, 87 (1939).

9. J. Bjerrum, S. Rasmussen, *Acta chim. Scand.*, 6, 1265 (1958).

10. F. Woldbye, *Acta Chim. Scand.*, 12, 1072 (1958).

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