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1964

SovietRxiv

Abstract

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CHEMISTRY

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ON THE ACID-BASE PROPERTIES OF COMPLEX COMPOUNDS OF DIVALENT PLATINUM CONTAINING α-METHYLHYDROXYLAMINE

The study of the acidic properties of isomeric compounds $[P+(NH_3)_2(NH_2OH)_2]Cl_2$ (1,2) showed that NH_2OH is the only amine capable of splitting off H^+ in the field of Pt^{2+}.

The regularities obtained in the ratios of the constants proved to be the reverse of those observed for the dissociation of H_2O in the sphere of Pt^{2+}: K_1 of the cis isomer $> K_1$ of the trans form, and the difference in the stepwise dissociation constants is greatest for the cis form. It remained unclear whence the cleavage of the proton in coordinated NH_2OH arises: from the amido or from the hydroxo group (3). We undertook a study in which α-methylhydroxylamine–NH_2OCH_3– was used for the first time as the addend. Hydrochloric α-methylhydroxylamine was prepared by us by methylation of $KON(SO_3K)_2$ and subsequent hydrolysis of $CH_3ON(SO_3K)_2$ in an acid medium (4,5). Free α-methylhydroxylamine was distilled off from the alkaline solution of the salt at 42–44°.

The synthesis of cis-$[Pt(NH_3)_2(NH_2OCH_3)_2]Cl_2$ was carried out as follows: to 1 g of cis-$[Pt(NH_3)_2Cl_2]$ were added 10 ml of H_2O and then 0.6 ml of α-methylhydroxylamine (2 moles per mole); the solution was heated for 15 min on a boiling water bath until the precipitate dissolved, filtered, and cis-$[Pt(NH_3)_2(NH_2OCH_3)_2]Cl_2$ was precipitated with an excess of alcohol and ether while cooling with ice and rubbing with a glass rod, in the form of white prismatic crystals. The yield was about 1 g, which is 80% of theory.

Found, %: Pt 49.7; 50.0; Cl 18.2; 18.3;
N 14.6; 14.7; C 6.45; 6.70.

Calculated, %: Pt 49.6; Cl 18.0;
N 14.2; C 6.10.

Fig. 1. Course of the change in pH upon addition of 0.09 N NaOH solution to 75 ml of $2.5 \cdot 10^{-3}$ M solution of cis-$[Pt(NH_3)_2(NH_2OCH_3)_2]Cl_2$ in 0.3 N $NaNO_3$ solution (1, points *a*); the same for the trans isomer (1, points *b*); and to 0.3 N $NaNO_3$ solution (1, points *c*). 2—the same for $5 \cdot 10^{-3}$ M solution of cis-$[Pt(NH_3)_2 \cdot (NH_2OCH_3)_2]Cl_2$.

Figure 2: curves of potentiometric titration

Figure 1: Figure 2: curves of potentiometric titration

Trans-$[Pt(NH_3)_2(NH_2OCH_3)_2]Cl_2$ was obtained starting from trans-$[Pt(NH_3)_2Cl_2]$ by dissolving it in CH_3ONH_2, by a method analogous to the above, with the same yield. The substance separated in the form of lustrous white fine needles.

Analysis of trans-$[Pt(NH_3)_2(NH_2OCH_3)_2]Cl_2$ led to the following results:

Found, %: Pt 49.6; 49.7; Cl 18.3; 18.2; N 15.0; C 6.30.

A solution of cis-$[Pt(NH_3)_2(NH_2OCH_3)_2]Cl_2$ forms with $K_2[PtCl_4]$ a green precipitate of cis-$[Pt(NH_3)_2(NH_2OCH_3)_2][PtCl_4]$; the trans form, in this case, depending on the conditions, gives a pink or green precipitate of the same composition.

Potentiometric titration of solutions of the isomers $[Pt(NH_3)_2 \cdot (NH_2OCH_3)_2]Cl_2$ with NaOH solution was carried out using a glass-

···electrode on an LP-58 apparatus in a thermostat at $25.0 \pm 0.1°$, at an ionic strength of 0.3, produced by a $0.3\,M$ solution of $NaNO_3$.

Figure 1 shows the curves of pH change upon addition of alkali to solutions of cis- and trans-$[Pt(NH_3)_2(NH_2OCH_3)_2]Cl_2$. Curve 1 refers to $2.5 \cdot 10^{-3}\,M$ solutions of the cis isomer (a) and the trans isomer (b). For comparison, on the same curve the course of the pH change upon addition of an NaOH solution to the background solution $0.3\,M$ $NaNO_3$ is shown by points (b). The practical coincidence of the points indicates that titration with alkali of solutions of cis- and trans-$[Pt(NH_3)_2(NH_2OCH_3)_2]Cl_2$ does not occur. Curve 2 shows the course of the pH change upon addition of alkali to a $5 \cdot 10^{-3}\,M$ solution of the cis isomer.

Fig. 2. Curves of potentiometric titration with $0.1\,N$ NaOH solution of $2.5 \cdot 10^{-3}\,M$ solutions of cis-$[Pt(NH_3)_2(NH_2OH)_2]Cl_2$ (1) and trans-(2) in $0.3\,N$ $NaNO_3$ solution

Addition of alkali to solutions of the indicated complexes does not cause a change in their color.

Figure 2 gives the previously obtained (1) curves of potentiometric titration with alkali of $2.5 \cdot 10^{-3}\,M$ solutions of cis-$[Pt(NH_3)_2(NH_2OH)_2]Cl_2$—curve 1—and of the trans isomer—curve 2.

From comparison of the curves of Fig. 1 with the curves of Fig. 2 it follows that NH_2OCH_3, unlike NH_2OH, does not possess acidic properties in the field of Pt^{2+}. It could have been assumed that the absence of acidic properties in coordinated NH_2OCH_3 is connected with its more basic character. However, experiment showed the opposite: the dissociation constant determined by us for the hydrate of α-methylhydroxylamine is equal to $3.5 \cdot 10^{-10}$, which is less than K_{diss} of the hydrate of NH_2OH, which is equal to $1 \cdot 10^{-8}$.

From the data obtained by us, indicating the absence of acidic properties in coordinated $Pt^{2+}NH_2OCH_3$, it follows that cleavage of H^+ from NH_2OH in the field of Pt^{2+} occurs not from the amido group, but from the hydroxo group.

The geometrically isomeric bases $[Pt(NH_3)_2(NH_2OCH_3)_2](OH)_2$ are strong bases.

A study of the structures of Pt^{2+} complexes with NH_2OH and NH_2OCH_3 by infrared spectroscopy may lead to proof of the identity of the NH_2 group in these molecules and thereby definitively confirm the decisive role of the OH group in the process of cleavage of H^+ in coordinated $Pt^{2+}NH_2OH$.

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Received
7 VIII 1964

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