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Abstract

Full Text

CHEMISTRY

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ON A NEW MODIFICATION OF *cis*-PLATODIGLYCINE

In 1932 one of us, together with B. V. Ptitsyn, obtained *cis*-$[PtGl_2]$* and thereby showed that platodiglycine can exist in the form of two modifications related to one another by *cis*–*trans* isomerism (^{1}). The geometrical configuration of both isomers was rigorously substantiated by a whole series of methods. Later, similar geometrical isomerism of spiro compounds, as required by coordination theory, was discovered by L. M. Volshtein and his coworkers also in complexes of Pt^{2+} with α-alanine (^{2}), α-aminobutyric (^{3}), and α-aminoisovaleric (^{4}) acids. Quite recently, two of us, together with A. I. Dobroborskaya, succeeded in establishing a characteristic difference between the geometrical isomeric platinosalts with respect to solubility in electrolyte solutions (^{5}).

In the course of carrying out the work (^{5}), we encountered an interesting fact: the properties of *cis*-$[PtGl_2]$ preparations differed depending on the conditions of their synthesis. It turned out that *cis*-$[PtGl_2]$ can be isolated in the form of two modifications, which differ in their solubility in water and in the character of their IR absorption spectra in the solid state. The reason for the existence of *cis*-$[PtGl_2]$ in the form of two modifications cannot yet be regarded as clarified; however, the very fact that two forms of this compound exist is beyond doubt.

Fig. 1. Change in the solubility of the β-modification of *cis*-$[PtGl_2]$ with time. a, b, c, d, e—results of different experiments.

It is worth noting that dimorphism of *cis*-isomeric platinosalts occurs not only in the case of *cis*-$[PtGl_2]$, but also in the cases of the dipyridyl complex $[Pt(C_{10}H_8N_2)Cl_2]$ (yellow and red modifications) and *cis*-$[Pt(NH_3)_2Br_2]$ (yellow and orange-red modifications).

Experimental Part

Preparations of *cis*-$[PtGl_2]$ were prepared by the method of A. A. Grinberg and L. M. Volshtein (^{6}) by heating H_2PtGl_4 in aqueous solution. The more soluble modification (β) was obtained under the following conditions. 2 g of freshly prepared $H_2PtGl_4 \cdot nH_2O$ (where n = 2-3) was poured over with 45 ml of distilled water and heated on a boiling water bath for 30–40 min. The resulting solution was passed through a filter and rapidly cooled in a stream of tap water. The precipitated crystals were suction-filtered and washed with alcohol and ether. Yield $\sim$ 1 g. The less soluble form (α) was obtained by recrystallization of the β-form. 2.2 g of β-*cis*-$[PtGl_2]$ were introduced into 200 ml of water and heated, with immersion in a boiling water bath, until complete dissolution. The heating was then stopped, and the water bath

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* $Gl^- = NH_2CH_2COO^-$.

with the solution immersed in it was cooled for several hours (usually overnight). The next day the crystals that had precipitated were filtered off and washed with alcohol and ether. Yield ~1.85 g. The preparations of the α- and β-modifications obtained in this way were practically moisture-free. Analyses for platinum content gave results deviating from the theoretical value by no more than 0.1%.

Solubility was determined by the procedure described in (5). The IR spectra of crystalline samples were measured on a double-beam IKS-14 instrument with NaCl and LiF prisms (see Fig. 2). The samples were prepared by grinding with Vaseline oil, hexachlorobutadiene, and perfluoro-oil. The absorption spectra of solutions in the visible and ultraviolet regions were measured on an SF-4 instrument.

Fig. 2. IR absorption spectra of the α- and β-modifications of cis-$[PtGl_2]$

The solubility of α-cis-$[PtGl_2]$ in water at 25° is 156 mg per 100 ml of solution (below, the concentration of solutions is expressed as the weight amount of substance per 100 ml of solution; the volume of the solvent is not indicated). The initial solubility of the β-modification ranges from 320 to 360 mg. In the course of determining the solubility of the β-form, the concentration of the solution gradually decreases, finally reaching 150–160 mg, the value characteristic of the α-modification. The rate of this change, beginning at a concentration of ~180 mg, becomes very small. This last circumstance explains the solubility value for cis-$[PtGl_2]$ (178 mg) obtained in (1). Some results of determining the solubility of the α-modification of cis-platodiglycine are given in Fig. 1.

Comparison of the IR absorption spectra (Fig. 2) of crystalline samples of the α- and β-forms reveals a number of substantial differences between them: a) differences in the region of the NH stretching vibrations (the frequency values corresponding to the absorption maxima, and the shapes of the bands); b) splitting of the scissoring-vibration band of the CH_2 group (1435 cm^{-1} and 1427 cm^{-1}) in the spectrum of the α-form. In the spectrum of β-cis-$[PtGl_2]$, the corresponding vibrations are represented by a single band with a maximum at 1432 cm^{-1}; c) absence in the spectrum of the β-form of the 1259 cm^{-1} band;

Fig. 3. Absorption spectrum of cis-[$PtGl_2$] in the ultraviolet region.
$\lambda_{max} = 231$ mμ, $\varepsilon_{max} = 593$

Figure 2: Fig. 3. Absorption spectrum of cis-[$PtGl_2$] in the ultraviolet region. $\lambda_{max} = 231$ mμ, $\varepsilon_{max} = 593$

d) splitting in the spectrum of the β-form of the band of symmetric stretching vibrations of CCN into two well-resolved components, 924 and 909 cm^{-1} (in the spectrum of the α-modification the CCN band has a maximum at 912 cm^{-1} and a bend at ~918 cm^{-1}); e) differences in the frequencies of the rocking vibrations of the NH_2 and CH_2 groups, in particular the shift of the 805 cm^{-1} band (α-form) to 835 cm^{-1} (β-form).

The character and degree of these differences indicate that in the solid state the α- and β-modifications of cis-[$PtGl_2$] are indeed two different substances. It should be noted that the data available in the literature on the IR spectra of solid cis-[$PtGl_2$] (7–9) refer to the α-modification.

The different nature of the described modifications of cis-platodiglycine is also confirmed by the results of measuring their specific gravities. The determinations were carried out by the pycnometric method in CCl_4 at a temperature of 25°. For the α-modification the value found was 3.25, and for β, 3.10 g/cm^3. The relative error of the determinations did not exceed 1%. Of fundamental interest is the question of whether the differences between the α- and β-forms are retained or disappear when cis-[$PtGl_2$] passes into solution. Some experiments carried out by us to clarify this question are described below.

1. The absorption spectra of freshly prepared aqueous sol—

of both modifications in the ultraviolet region of the spectrum. The absorption curve, which proved to be identical for both solutions, is shown in Fig. 3.

2. The course with time of the process of opening of the glycol rings by hydrochloric acid was followed spectrophotometrically:

$$\text{cis-}[PtGl_2] + 2HCl \rightarrow \text{cis-}[Pt(HG)_2Cl_2].$$

For the measurements, wavelengths of 256 and 300 mμ were selected, corresponding to the maximum differences in the optical density of the solution in the initial and final states. The reaction proceeded at room temperature in 0.5 *N* HCl. Its rate in solutions prepared from both modifications proved to be identical from the very beginning of the process.

Fig. 3. Absorption spectrum of cis-[$PtGl_2$] in the ultraviolet region.
$\lambda_{max} = 231$ mμ, $\varepsilon_{max} = 593$

3. Freshly prepared aqueous solutions of the α- and β-forms of cis-[$PtGl_2$] were oxidized with an alcoholic solution of iodine. The brown precipi-

tates [$PtGl_2J_2$], formed almost instantaneously, were separated from the solution, washed, and dried. Their infrared spectra proved to be identical.

Determination of the molecular weight of β-cis-[$PtGl_2$] by the cryoscopic method showed that monomeric molecules are present in aqueous solution; cryoscopic measurements in the case of the α-modification proved impossible because of the low solubility of the substance.

Thus, at present there are no data indicating preservation of differences between the two modifications of cis-[$PtGl_2$] in the dissolved state. Of interest are certain features of the transformation of β-cis-[$PtGl_2$] into the α-form during slow isothermal recrystallization under the conditions of solubility determination. In several experiments (3 and 18) the initial concentration of the solution of the β-modification (320–360 mg) remained unchanged for 2–5 hours, after which it began to decrease rapidly and after 9–10 hours reached the value usual for the α-modification, 150–160 mg. The indefinite duration of this initial delay (as a rule, short-lived) is the reason for the considerable scatter in the concentration values of [$PtGl_2$] in samples taken in different experiments at equal short time intervals (20 or 40 min) from the beginning of dissolution of the sample. The measure of this scatter for each moment of time is the height of the shaded region in Fig. 1. The presence of the delay and its variable duration indicate that the formation of nuclei of the α-phase is kinetically hindered and occurs at a moment determined by uncontrolled causes.

Identification of the solid phases corresponding to different concentrations of the cis-[$PtGl_2$] solution was carried out by measuring their IR spectra. It is noteworthy that already at a solution concentration of 250 mg the crystalline phase consists practically entirely of the α-modification. This apparently means that even in the presence of a large number of nuclei the process of crystallization of the α-form proceeds with considerable supersaturation. It is precisely the tendency of the α-form to form supersaturated solutions that explains the ease of obtaining the metastable β-form of cis-[$PtGl_2$]. It should be noted that by rapidly cooling a solution of α-cis-[$PtGl_2$] saturated on heating, it was possible to obtain crystals of the β-form.

The transformation $\beta \to \alpha$, which proceeds spontaneously during slow recrystallization, does not occur to any noticeable extent in the solid state. Preparations of β-cis-[$PtGl_2$] undergo no changes either on storage (several months) or on heating (75° for 12 h). The described modifications of cis-platodiglycine may differ from one another both with respect to the manner of mutual arrangement of identical structural elements [$PtGl_2$] (crystal-chemical differences), and with respect to the structure

of these elements themselves or in the way in which they are linked to one another (molecular differences). Elucidation of the nature of the difference between the α- and β-forms of cis-[$PtGl_2$] requires a detailed investigation of their structure. According to data obtained at our request by P. M. Zorkii and A. M. Porai-Koshits, the α- and β-modifications of cis-platodiglycine are characterized by practically identical Debyegrams (the coincidence of the Debyegrams is noteworthy, given the obvious, although small, difference in the values of the specific gravity). The identity of the Debyegrams apparently argues in favor of the assumption of a different structure of the $[PtGl_2]$ groups or of a different character of the interaction between them in crystals of the α- and β-modifications, with the same (or only slightly different) mutual arrangement of these groups.

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