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Abstract

Full Text

Chemistry

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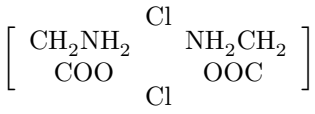
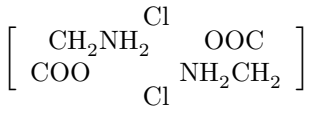
On New Geometrical Isomers $[PtGl_2Cl_2]$

According to Werner' s coordination theory, a compound of composition $PtGl_2Cl_2$ should exist in five geometrically isomeric forms:

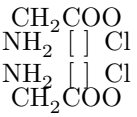
(I)



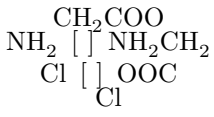
(II)



(III)



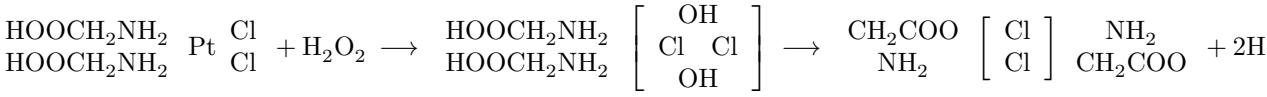
(IV)



(V)

Isomers (I) and (II) were obtained by one of us by two routes ([1,2]). The routes for the synthesis of the last three, with cis-positioned chlorine atoms, were unclear. The peculiar reaction of intrasphere neutralization found by us ([3]) was used in an attempt to synthesize isomers (III) and (IV).

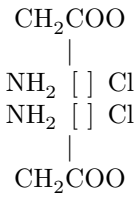
If cis-$[Pt(GlH)_2Cl_2]^*$ ([4]) is taken as the starting product, then the reaction should proceed according to the scheme:



Thus isomer (III) should be formed. However, in this case two substances of one and the same composition, $PtGl_2Cl_2$, were obtained. Owing to their different solubility in water, the substances were separated from each other. One of them crystallizes in needles, while the other gives rectangular plates. The plate-like crystals are colored a more intense yellow than the needle-like ones. In aqueous solution the needle-like form proved unstable and gradually changes into the plate-like form. Both substances, on reaction with potassium oxalate, give cis-$[PtGl_2]$ in a yield of 60%. On reaction with alkalis, the isomers $[PtGl_2Cl_2]$

are reduced to compounds of Pt^{II}. On prolonged heating on a water bath, the needles and plates dissolve in concentrated hydrochloric acid with formation of an intensely yellow solution. Thus it becomes evident that both forms are derivatives of cis-diglycinoplatinum. The needle-like and plate-like compounds $[PtGl_2Cl_2]$ differ noticeably from one another and from the known isomers (I), (II) in their infrared spectra and melting points.

It appears highly probable that the needle-like form corresponds to the coordination formula

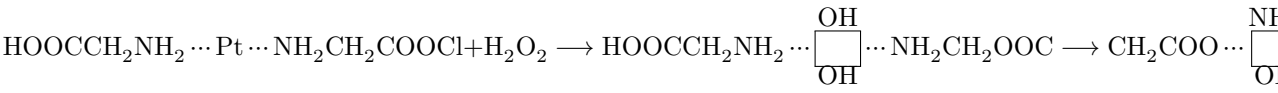


As for the plate-like form, it could represent either another crystalline modification of the same isomer (dimorphism),

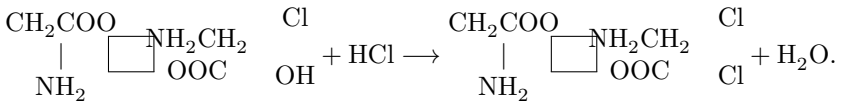
or isomer (IV). The first possibility attracted our attention, since recently two of us, together with E. N. In' kova (5), succeeded in obtaining a second crystalline modification of cis-$PtGl_2$. In the second case, it is necessary to assume the breaking of one carboxyl oxygen–platinum bond, followed by closure of the ring at the position of chlorine, while the chlorine is displaced to the position previously occupied by the oxygen atom.

To resolve this question it is necessary to synthesize a substance that, by its method of preparation, would correspond to isomer (IV), and to compare this substance in its properties with the described plate-like form $[PtGl_2Cl_2]$.

It has been proposed that the oxidation of the monochloride (4) with hydrogen peroxide proceeds as follows:



On treatment of the oxidation product with hydrochloric acid, isomer (IV) should be obtained



However, the reactions proceed somewhat more complicatedly: on oxidation of the monochloride, in addition to $[PtGl_2Cl(OH)]$, $[PtGl_2Cl_2]$ and $[PtGl_2(OH)_2]$ are also formed. The IR spectrum of the $[PtGl_2Cl_2]$ preparation obtained by oxidation of the monochloride is identical with the IR spectrum of the plate-like modification $[PtGl_2Cl_2]$ synthesized by oxidation of cis-$[Pt(GlH)_2Cl_2]$ with hydrogen peroxide. As for the $[PtGl_2Cl_2]$ preparation obtained by the action of hydrochloric acid on $[PtGl_2Cl(OH)]$, according to its IR spectrum and refractive indices it likewise represents mainly the plate-like modification, to which a certain amount of isomer (I) is admixed. The appearance of isomer (I) can be explained by partial rearrangement of isomer (IV). Thus, we have grounds to believe that the needle-like and plate-like modifications are more likely isomers than dimorphic modifications.

In search of direct proof of the cis position of the chlorine atoms in the plate-like and needle-like substances, the interaction of the isomers $[PtGl_2Cl_2]$ with orthophenanthroline was studied. It was assumed that one molecule of orthophenanthroline could replace two cis-positioned chlorine atoms. Contrary to expectation, however, the behavior of orthophenanthroline toward isomers (I, III, IV) proved to be the same: in all three cases, sparingly soluble compounds of composition $[PtGl_2Cl_2] \cdot 2Ph$ are formed, in which phenanthroline does not enter the inner sphere but is located in the outer sphere.

Experimental Part

Oxidation of cis-$[Pt(GlH)_2Cl_2]$ **with hydrogen peroxide:** 3.00 g of cis-$[Pt(GlH)_2Cl_2]$ is dissolved in 30 ml of 5% H_2O_2 (sixfold excess) with stirring in the cold.

After 1–3 hours a yellowish crystalline precipitate of needle-like habit separates from the solution. If this precipitate is filtered off after one hour, needle-like crystals can be obtained in practically pure form. The crystals are washed with ice water until a negative reaction for H_2O_2, then with alcohol and ether. The needle-like substance crystallizes with three molecules of water, which are readily lost at 80°. From the filtrate, after prolonged standing, crystals separate that are rectangular plates with a certain amount of needle-like crystals. Crystallization proceeds very slowly. After two days the plates contaminated with needles are simi-

were heated on a water bath and, after dissolution of the needle-shaped crystals, were filtered off while hot. The plate-like fraction was washed in the same way as the needle-shaped one and dried at 100°. The needles and plates are formed

Fig. 1. Infrared spectra of the isomers: a–(I), –(II), –(III), –(IV)

Figure 1: Fig. 1. Infrared spectra of the isomers: a–(I), –(II), –(III), –(IV)

in a ratio of $\sim 1 : 2$. If the oxidation of cis-$[Pt(GlH)_2Cl_2]$ is carried out with heating on a water bath, then only plate-like crystals gradually separate from the hot solution. After two hours of heating, the plates are filtered off while hot. From the cooled filtrate, needle-shaped crystals separate, often mixed with an admixture of a small amount of plates. The needles and plates obtained in this way are formed in a ratio of $\sim 1 : 3.5$. The total yield is 70–80%. Results of analysis:

Found for needles, %: H_2O 11.4
Calculated for $[PtGl_2Cl_2] \cdot 3H_2O$, % : H_2O 11.5
Found for needles, %: Pt 46.90, 47.27; Cl 17.13; N 6.69
Found for plates, %: Pt 47.02, 46.98; Cl 17.32; N 6.74
$[PtGl_2Cl_2]$. Calculated, %: Pt 47.13; Cl 17.12; N 6.76

Oxidation of cis-[Pt(GlH)Cl] **with hydrogen peroxide:** 2.00 g of cis-[PtGl(GlH)Cl] are poured into 36 ml of a 2.5% hydrogen peroxide solution. On heating on a water bath, as the starting substance dissolves and a yellow solution forms, a small amount of yellow crystals of composition $[PtGl_2Cl_2]$ separates (fraction I). After half an hour of heating and standing of the solution for ten minutes, the crystals are filtered off. From the filtrate a small amount of a yellow precipitate immediately falls out (a mixture of $[PtGl_2Cl_2]$ and $[PtGl_2Cl(OH)]$–fraction II), which is filtered off after two hours. (Fraction II was isolated in order to make it possible to obtain a pure preparation of $[PtGl_2Cl(OH)]$.) After separation of the second fraction, a yellowish precipitate of composition $[PtGl_2Cl(OH)]$ gradually separates from the mother liquor; it is filtered off, washed with small portions of ice water, and, after repeated washing with alcohol and ether, the product is dried at 90°. Fraction IV was isolated from the filtrate separated from fraction III, with alcohol, in the form of an amorphous precipitate of slightly yellowish color. According to the analytical data, the substance obtained is a mixture of $[PtGl_2Cl(OH)]$ and $[PtGl_2(OH)_2]$.

Fig. 1. Infrared spectra of the isomers: a–(I), –(II), –(III), –(IV).

The yields of the individual fractions were, respectively: fraction I $\sim$ 9%, fraction II $\sim$ 5%, fraction III 30–40%, fraction IV 20–30%. Ob-

overall yield 70–80%. Results of analysis:

Compound	Calculated, % Pt	Calculated, % Cl	Found, % Pt	Found, % Cl
$[PtGl_2Cl_2]$	47.13	17.12	Fr. I 47.11, 47.25;	16.44, 26.78
$[PtGl_2Cl_2]$	47.13	17.12	Fr. II 49.24, 48.16;	10.28, 15.60
$[PtGl_2Cl(OH)]$	49.32	8.96	Fr. III 49.50, 49.22;	9.10, 8.91
$[PtFl_2(OH)_2]$	51.72	0	Fr. IV 50.56, 50.15;	4.68, 4.03

Table 1

Wave numbers (cm^{-1}) **of absorption maxima of the IR spectra of the isomers** $PtGl_2Cl_2$ **in the NaCl-prism region**

I	II	III	IV	Assignment	I	II	III	IV	Assignment
~1710sh	1678s	1658s	1655ssh	stretching asymmetric NH_2 scissoring	1202s	1178s	1193s	1024w	CH_2, NH_2 wagging and twisting CCN stretching asymmetric
1418w	1415m	1427w	1418m	CH_2 scissoring	979m	967m	970sh	912s	CH_2, NH_2 pendular (A)CCN stretching symmetric

I	II	III	IV	Assignment	I	II	III	IV	Assignment
1359s	1341s	1360s	1342s	COO stretching symmetric	835w	812w	827w	818w	NH_2, 740sh NH_2 pendular (B)COO scissoring (or wagging)
1312s	1298s	1284s	1298s	CH_2, NH_2 wagging and twisting	724s	725s	724s	725s	

Note. s –strong, m –medium, w –weak, sh –bend or "shoulder."For assignment of the bands, see work (5).

On heating in a water bath, $[PtGl_2Cl(OH)]$ reacts with 0.2 N HCl with formation of $[PtGl_2Cl_2]$. Yield 80%. Results of analysis:

Found, %: Pt 47.01, 47.26; Cl 17.24, 17.10

$[PtGl_2Cl_2]$. Calculated, %: Pt 47.13; Cl 17.12

The procedure for measuring the IR spectra is described in (5).

The IR absorption spectra of the four isomers $[PtGl_2Cl_2]$ are shown in Fig. 1. They reflect certain characteristic features of their structure. The relative simplicity of the spectrum of the trans isomer (II) is a consequence of the centrosymmetry of its molecule. The absorption spectra of the other three isomers contain a larger number of bands, and the greatest complexity is inherent in the spectrum of isomer (I), which is distinguished by the coplanar arrangement of the glycine rings. A characteristic feature of the spectra of isomers (III) and (IV) (with noncoplanar rings) consists in the splitting of the band of deformation vibrations of the methylene group. The complex contours of the absorption bands corresponding to the stretching vibrations of the amino group are probably associated not only with interaction of vibrations, but also with the presence,

in the crystal structures of the complexes studied, of N—H—-O hydrogen bonds differing in strength and orientation.

Determination of refractive indices by the immersion method under an MP-6 microscope in transmitted light: isomer (I) $N_g = 1.767 \pm 0.006$, $N_p = 1.658 \pm 0.002$; isomer (II) $N_g = 1.767 \pm 0.006$, $N_p = 1.714 \pm 0.003$; isomer (III) $N_g = 1.658 \pm 0.002$, $N_p = 1.638 \pm 0.002$; isomer (IV) $N_g = 1.756 \pm 0.006$, $N_p = 1.737 \pm 0.006$.

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