Chemistry

Corresponding Member of the Academy of Sciences of the USSR G. B. Bokii and G. A. Kukina

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Abstract

Full Text

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ON THE STRUCTURE OF CRYSTALS OF cis-ETHYLENEAMMINEDIBROMIDE OF PLATINUM

Before the war, in our laboratory a study was begun of the chloro analogue of the compound named in the title ([1]). The symmetry of the crystals and the dimensions of the unit cell were determined. The crystals proved to belong to the tetragonal system. Their body-centered unit cell, containing 16 molecules, had dimensions $a \sim 10$ Å and $c \sim 24$ Å.

Fig. 1. Projection of the interatomic function along the direction [001]

After this, the first proposal concerning the structural motif was made, proceeding from chemical data on the addition of ethylene to a platinum atom through carbon and on the possible dimeric form in analogous compounds ([2]). Neither the one nor the other was subsequently confirmed (see below).

The war prevented the continuation of this work; therefore it was decided to publish the preliminary tentative data in the raw form in which they had been left at that time.

Since 1950, work on trans influence in the crystalline state was begun in our laboratory ([3]). In 1957 we published a review article on this question ([4]), in which data were reported on the crystal structures of a number of compounds and, in particular, on the structure of Zeise's bromide salt—$K(PtC_2H_4Br_2)\cdot H_2O$ ([4]). In the latter structure it was proved that the proper plane of the ethylene molecule is situated perpendicular to the plane of the $PtBr_3$ group and that the bromine atom located opposite the ethylene group is indeed at a considerably greater—

···at greater distances from the platinum atom than the two other bromine atoms (2.50 and 2.42, respectively). In that article it was pointed out that the interatomic distances may be affected by the outer sphere. Therefore we again

Fig. 2. Two variants of the arrangement of atoms: a—horizontal, b—vertical

Figure 2: Fig. 2. Two variants of the arrangement of atoms: a—horizontal, b—vertical

turned to the substance indicated in the title, as one free from this drawback. It was decided to determine its structure completely anew; moreover, as in Peyrone' s salt, for greater accuracy in determining the metal-halogen interatomic distances it was decided to carry out the investigation on the bromide salt.

Fig. 2. Two variants of the arrangement of atoms:
a —horizontal, b —vertical

M. N. Lyashenko undertook the task of synthesizing this compound for us and determining its optical constants. The crystals proved to be uniaxial positive, $N_g = 1.88$ and $N_m = 1.770$. According to goniometric data, the crystals belong to the tetragonal system and are a combination of a tetragonal prism with a pinacoid.

In the unit cell with dimensions: $a = 10.51$ Å± 0.02 and $c = 24.80$ Å± 0.05, there are 16 molecules of $PtC_2H_4NH_3Br_2$. The space group of symmetry $C_{4h}^6 = I4_1/a$ is determined unambiguously from the extinction rules

$$(hkl - h + k + l = 2n;\ hk0 - h = 2n \text{ and } k = 2n;\ 00l - l = 4n).$$

The crystals belong to the diffraction class $4/m$.

Table 1

Atoms	X	Y	Z
Pt	0.250	0.000	0.125
Br_1	0.434	0.040	0.188
Br_2	0.425	0.040	0.063

Interatomic distances

$$Pt—Br_1 = 2.52 \text{ Å};$$

$$Pt—Br_2 = 2.43 \text{ Å}.$$

A complete X-ray structural investigation was carried out from projections of the interatomic function along the directions [001] (Fig. 1), [100], and from projections of the electron density onto the YZ plane. The investigation was

Fig. 3. Projection of electron density onto the YZ plane

Figure 3: Fig. 3. Projection of electron density onto the YZ plane

performed with $K\alpha$Cu radiation, since recording radiographs with $K\alpha$Mo radiation considerably increased the exposure time because of the small size of the crystal and at the same time did not increase the number of reflections.

Analysis of the projections of the interatomic function shows that all the atoms are situated in a general sixteenfold position, with the platinum atoms located on the 4_1 axis, halfway between the symmetry planes. From the projections it was established that the complexes are arranged parallel to the Z axis and that the plane of the complex makes an angle of about 17° with the latter. This arrangement of the plane of the complex is confirmed by the optical data. Thus, having determined the arrangement of the complex as a whole with the platinum atom at the center, we proceeded to determine the arrangement of the bromine atoms. Two variants of their arrangement in the cell are possible: horizontal and vertical (Fig. 2). In order to decide which variant is realized in the structure, projections of the electron density onto the YZ plane were constructed for both variants. The signs of the structural amplitudes were determined initially from the coordinates of the Pt atom and two Br atoms, the bromine atoms being taken at equal distances from the Pt atom (the coordinates were obtained from projections of the interatomic function). From the positions and relative heights of the maxima obtained in the corresponding projections, it follows that the vertical variant of the arrangement of the bromine atoms is the correct one. In the projection the Pt and Br atoms are clearly revealed, and it was established that the Br atoms are at different distances from the Pt atom. The data obtained agree well with the results obtained in the study of Peyrone' s bromide salt ([4]). The coordinates of the atoms are given in Table 1.

Next, two assumptions were made: 1) opposite the Br atom located at the shorter distance from platinum (Pt–Br = 2.43 Å) there is an NH_3 group, while C_2H_4 is opposite the Br atom located at a distance of 2.52 Å from Pt, and 2) opposite the Br atom located at a distance of 2.43 Å from the Pt atom there is a C_2H_4 group, while NH_3 is opposite the Br atom located at a distance of 2.52 Å from Pt. On the basis of these assumptions, the signs of the structure amplitudes for the Pt, Br_1, Br_2, and NH_3 atoms were again calculated; the coordinates of the latter were taken from stereochemical considerations. The constructed projection of the electron density for the first variant is given in Fig. 3.

Fig. 3. Projection of electron density onto the plane YZ

It is evident from the projection that the maximum at point A is higher than the maxima at points B, C, D, which is explained by the superposition at this point of the Br atom and the NH_3 group, whereas at points B, C, D there are no such superpositions. The solid line shows the complex with the central Pt atom

at height along $x = 1/4$ (the plane of this complex is almost perpendicular to the plane of the drawing), while the dashed line shows the complex with the Pt atom at height along $x = 3/4$ (its plane almost coincides with the plane of the drawing). The projection of the electron density for the second variant showed that all maxima are identical in height.

This permits the conclusion that the ethylene molecule is located opposite the greater distance (analogously to Zeise' s salt). In the opposite case the maximum D would have had to be higher. Thus it may be considered proven that interatomic distances are affected by the group in the trans position—an idea expressed by us conjecturally about ten years ago. With an increase in the trans effect, the interatomic distances between the central atom and the labilized addend increase. We have now obtained X-ray patterns of all layer lines, calculated the signs of the structure amplitudes, and transmitted the data to the Computing Center for calculation of electron-density sections, which will probably make it possible to determine the coordinates of the light atoms and refine the coordinates of the others.

In conclusion, the authors consider it their pleasant duty to thank M. A. Porai-Koshits for valuable advice and assistance in the work.

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