CRYSTAL STRUCTURE OF CADMIUM BROMIDE DIPYRIDINATE

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Fig. 1

Figure 1: Fig. 1

Abstract

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CRYSTALLOGRAPHY

T. I. MALINOVSKII, Yu. A. SIMONOV

CRYSTAL STRUCTURE OF CADMIUM BROMIDE DIPYRIDINATE

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Mac Gillavry and Beijvoet showed ([1]) that the addition products of ammonia to cadmium chloride (and, correspondingly, bromide) have a chain structure with coordination number 6 at cadmium.

Fig. 1

One of the authors, together with A. V. Ablov ([2]), succeeded in showing that cadmium iodide dianilinate has a molecular structure, in which the addends are coordinated around the central atom according to the tetrahedral law. According to the conclusions of Williams ([3]), drawn from ligand-field theory, replacement of ammonia by aromatic amines in addition products with cadmium halides should not lower the coordination number at the central atom. However, in the addition product of aniline with cadmium iodide the coordination number was not retained, but was even lowered. It was therefore of interest to determine the structure of cadmium bromide dipyridinate.

An X-ray structural investigation was undertaken of crystals of composition $CdBr_2 \cdot 2Py^*$.

$CdBr_2 \cdot 2(C_5H_5N)$.	Found	% :	Cd 25.90
	Calculated	% :	Cd 26.11

The crystals have the form of needles, which split along the needle axis. The parameters were determined by the oscillation method on an X-ray camera for determining unit-cell parameters of Moscow State University design, using Co $-K_\alpha$ radiation, and were checked from Weissenberg photographs. The crystals belong to the rhombic system with parameters $a = 3.98 \pm 0.02$ Å, $b = 8.81 \pm 0.03$ Å, $c = 18.29 \pm 0.01$ Å, $z = 2$.

The X-ray structural investigation was carried out from X-ray goniometer photographs taken with unfiltered Mo$-K$ radiation. Layer-line photographs $(0kl)$,

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

(1kl), (2kl), ($R0l$) with 323 reflections were obtained. Intensiv-

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* The crystals were obtained and analyzed by V. Ya. Ivanova in the laboratory of inorganic chemistry of the Academy of Sciences of the Moldavian SSR.

intensities were estimated visually with the aid of blackening standards. Analysis of the extinctions leads to the Fedorov space groups $P_{mnn} = D_{2h}^{22}$ and $P_{nn} = C_{2v}^{10}$.

Further work on determining the crystal structure was carried out using the ordinary (Fig. 1) and conditional (Fig. 2) projections of interatomic vectors and electron density along the x axis. The symmetry of the projection of the structure along (100) belongs to the plane group pgg. In this case two cadmium atoms in the projection must be located at centers of inversion. Analysis of the first and second layer lines (1kl) and (2kl), as well as of the conditional projections of interatomic vectors $P_1(yz)$ and $P_2(yz)$, makes it possible to choose, as a working hypothesis—subsequently fully confirmed—the space group $D_{2h}^{12} = P_{mnn}$, since $P_2(yz)$ completely repeats the pattern of $P_0(yz)$ in the geometry and heights of the maxima. In this case two cadmium atoms must occupy a twofold position with coordinates 000, 1/2 1/2 1/2, and four bromine atoms—a fourfold special position on a plane of symmetry. In special positions on planes of symmetry there must also be the planar rings of pyridine.

Fig. 2

Fig. 3

Analysis of the projection of interatomic vectors $P_0(yz)$ (Fig. 1) revealed a number of peaks that could be interpreted. A triplet of peaks lying on one straight line is identified with the vectors Cd—Br and Br—Br, while peaks No. 3 correspond to the vector 2(Br—Br), No. 4 Cd—Cd, No. 5 Cd—Br, No. 6 2(Br—Br) (cf. Figs. 1 and 3).

Fig. 4

From the coordinates of Cd and Br, the signs of the structural amplitudes were

Fig. 4

Figure 4: Fig. 4

calculated and the projection of electron density onto the yz plane was constructed. Pyridine molecules were also revealed in the projection. Then, using the signs and taking into account all light atoms except hydrogen, a projection of electron density onto the yz plane was constructed (Fig. 4). Further refinement of the position

of all atoms was carried out by the method of differential synthesis on the "Strela" electronic computer. The reliability coefficient $R_{0kl} = 18.8$.

To refine the model, the R-factor was calculated for the second layer line; it proved to be equal to 20.3. From the coordinates of the Cd, Br, and N atoms, the distances Cd–Br, equal to 2.76, and Cd–N, equal to 2.12, were determined.

The X-ray structural investigation carried out showed that crystals of cadmium bromide dipyridinate have a chain structure with coordination number 6 at the cadmium atom. The bromine atoms are located at the same distance from two neighboring cadmium atoms, forming a chain.

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CITED LITERATURE

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