X-RAY DIFFRACTION STUDY OF [M(I)(NH3)5Cl][M(II)Br6]  
(M(I) = Rh, Ir; M(II) = Re, Ir) POLYCRYSTALS

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Based on the X-ray diffraction data for polycrystals, the crystal structures of double complex salts [Rh(NH3)5Cl][ReBr6] and [Ir(NH3)5Cl][ReBr6] are refined. The structure of [Rh(NH3)5Cl][IrBr6] is determined. Initial models are constructed using the Monte Carlo method in the straight space. Further refinement is made by the Rietveld method. It is shown that such an approach is suitable for the refinement of crystal structures composed of isolated rigid polyhedra and can be used to determine the structure of salts without structural analogues.

Keywords: powder X-ray analysis, full-profile analysis, Rietveld method, crystal chemistry, double complex salts of Rh, Ir and Re, Ir.

INTRODUCTION

It is not always possible to obtain the compounds and phases relevant to research and practical needs in the form of single crystal suitable for X-ray diffraction analysis. Therefore, the experts in crystal chemistry demonstrate an unflagging interest to the methods determining crystal structures based on the polycrystalline X-ray diffraction data. With the development of the method (both its equipment and software components), the interpretation of the crystal structure of polycrystalline phases turned from a problem complicated in solution (and often just unsolvable) into a routine experiment. By now, the literature offers comprehensive guidance on the crystal structure determination based only on the analysis of the polycrystalline X-ray diffraction data recorded on commercial laboratory diffractometers. We would like to mention here the main recent publications: multi-author books [1, 2] and reviews [3-5]. However, despite the significant progress in this area, the application of this method has its limitations. First, there are requirements for the source data quality and integrity [6]. Second, it is infeasible to solve the structures with large number of atoms in the independent part of the cell without additional information on the molecular geometry and relative molecular positions in the crystal structure [7]. The most difficult part in the determination of new structure is to find the structural motif and construct a complete model that would be further refined by the full-profile Rietveld analysis.

Information on the construction and size of polyhedra or molecules forming the crystal, interatomic and intermolecular distances, molecular packing in the crystal significantly simplifies the crystal structure determination by powder X-ray diffraction technique. One promising approach is the algorithm used in the FOX software [8]. This approach is based on the Monte Carlo method implemented in the straight space. If the geometry of structural blocks is known, on the first stage of the crystal structure determination, the locations of their center of mass in the cell and their mutual orientation.
should be found. Then, certain block characteristics are refined by the Rietveld method. This approach, initially developed to determine the crystal structures of complex metal hydrides, proved to be quick, efficient, and relatively simple for determining the crystal structures of both organic and complex inorganic phases [9].

We are interested in double complex salts (DCSs) containing both coordination cations and anions. These compounds are interesting not only as precursors to prepare nanosized polymetal phases, but also as models to investigate packing of isometric coordination particles and particles of more complex geometry. The crystal structure of most DCSs was determined using single crystal X-ray diffraction (see, for example, [10]). One of the most fully studied DCS groups are the salts with the composition \([M^I(NH_3)_5Cl][M^{II}Cl_6]\) and \([M^I(NH_3)_5Cl][M^{II}Br_6]\) \((M^I = Co, Rh, Ir, Ru, Os; M^{II} = Os, Pt, Re, Ir)\). All chloride salts of this series are isostructural among themselves, and in some cases, this made it possible to refine the structures based on the data for polycrystals using the previously known analogues as initial models [11]. The structure of bromide DCSs is often different from that of chloride ones, and they are not isostructural among themselves. Due to a relatively low solubility, bromide salts \([M^I(NH_3)_5Cl][M^{II}Br_6]\) cannot be obtained in the form of perfect single crystals, so the crystal structures were determined only for two salts with the composition \([Rh(NH_3)_5Cl][PtBr_6]\) [12] and \([Rh(NH_3)_5Cl][ReBr_6]\) [13]. Therefore the only way to determine the crystal structures of bromides is to use the X-ray diffraction data for polycrystals.

The purpose of this work is to determine the crystal structures of \([Rh(NH_3)_5Cl][ReBr_6]\), \([Ir(NH_3)_5Cl][ReBr_6]\), and \([Rh(NH_3)_5Cl][IrBr_6]\).

**EXPERIMENTAL**

The synthesis of \([Rh(NH_3)_5Cl][ReBr_6]\) and \([Ir(NH_3)_5Cl][ReBr_6]\) was described in our works [13, 14].

In order to synthesize \([Rh(NH_3)_5Cl][IrBr_6]\) DCS, a warm water solution of \([Rh(NH_3)_5Cl]Cl_2\) (0.024 M) was mixed with the solution of \(K_2[IrBr_6]\) (0.025 M). Iridium salt was taken in 5% mole excess relative to the 1:1 stoichiometry. In 30 minutes, quickly formed violet crystals were filtered, rinsed with water, acetone, and dried in the air. Yield was 84-93%. Found, %: Rh+Ir 33.3\pm0.2. Calculated, %: Rh+Ir 33.01. IR spectrum, cm\(^{-1}\): 3279(s), 3191(m), (v(NH_3)); 1628 (d(NH_3)); 1317(s) (s(NH_3)); 820 (r(NH_3)).

Polycrystals of synthesized DCS were studied on a STADI-P STOE diffractometer (Cu\(K_\alpha\) radiation, position-sensitive detector, angle range of \(2\theta = 2-120^\circ\) (for \([Rh(NH_3)_5Cl][IrBr_6]\) the angle range was 2-70\(^\circ\), step of 0.02\(^\circ\), accumulation time of 2040 s per point). In all cases, samples appeared to be single-phased; diffraction patterns were fully indexed by the unit cell parameters shown in Table 1.

**DETERMINATION OF CRYSTAL STRUCTURES**

\([Rh(NH_3)_5Cl][ReBr_6]\). The crystal structure of this phase has been previously determined by single crystal X-ray diffraction [13], though of rather low quality \((R = 14.9\%)\). However, some geometric characteristics could be used as a benchmark in the development of the technique for the structure determination and refinement. The compound crystallizes in triclinic symmetry. The cell volume is enough to place 8 octahedra (4 cations and 4 anions); therefore, there would be 2 independent cations and 2 independent anions. An initial model was constructed using the FOX software [8, 15]. As a starting model, two regular \([ReBr_6]\) octahedra with Re–Br distances of 2.50 Å and two \([RhN_5Cl]\) octahedra with Rh–N and Rh–Cl distances of 2.08 Å and 2.30 Å and angles of 90\(^\circ\), arbitrarily located in the unit cell, were used. At the zero cycle of the refinement, the diffraction pattern profile was decomposed into individual reflections using the Le Bail method [16], where the intensities were treated as the refining parameters. The obtained line profile parameters were not additionally refined. Then, with the fixed octahedral geometry (interatomic distances varied in a \(\pm0.02\) Å range and bond angles in a \(\pm0.1^\circ\) range) 5 independent cycles of the model determination by the Monte Carlo method were carried out (each cycle included 10\(^6\) steps). Consequently, the total \(R\) factor was \(\sim15\%\) evidencing the validity of the model determination. The Rietveld refinement