Brief Communications

X-ray diffraction investigations of Ag_2ReCl_6 and Ag_2OsCl_6

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Complex salts Ag_2ReCl_6 and Ag_2OsCl_6 were synthesized and characterized by X-ray powder diffraction analysis, elemental analysis, and IR spectroscopy. The resulting compounds were demonstrated to be isostructural. It was found that the principal structural motif of the compounds under study is similar to that of K_2ReCl_6.

Key words: rhenium, osmium, silver, chloride complexes, X-ray powder diffraction analysis, structural motif.

Reductive thermolysis of complex salts containing two or more atoms of different metals is widely used for the preparation of composite metal powders. This method is particularly attractive in the preparation of homogeneous powders of solid solutions of high-melting metals because temperatures at which thermolysis is performed (200—400 °C) are substantially lower than the melting points of pure metals. When studying the reduction mechanism and interpreting the experimental data, it is desirable to have data on the crystal structures of salts, their characteristic features, and metal—metal distances. Therefore, X-ray powder diffraction studies of precursor complex salts is an important step toward the elucidation of relationships between the characteristics of the starting compounds, the course of reductive thermolysis, and the phase state of the resulting metal powders. This work was carried out as part of these investigations.[1,2]

Experimental

Syntheses were performed with the use of commercial reagents of at least chemical-purity grade. Complex salts K_2ReCl_6 and K_2OsCl_6 were synthesized according to standard procedures.[3,4]

Preparation of Ag_2ReCl_6 and Ag_2OsCl_6 (general procedure). A saturated solution of K_2ReCl_6 (K_2OsCl_6), which was acidified with $HClO_4$, was added to a solution containing a small excess of $AgNO_3$ with respect to the stoichiometric amount. Then the reaction mixture was stirred for 5—6 min. The orange polycrystalline precipitate that formed (polycrystals of Ag_2OsCl_6 are gray-green in color) were filtered through a finely porous filter. The precipitate was washed with alcohol and dried in air. The yield was 99.5%. The resulting compounds were characterized by elemental analysis and IR spectroscopy. The total metal contents in the resulting salts are given in Table 1.

The IR spectra of the complexes were recorded on a Specord 75 IR instrument in KBr pellets and on a Specord M80 instrument in Nujol mulls. The M—Cl vibration bands for

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Table 1. Data of elemental analysis

Compound	$\frac{\text{Found}}{\text{Calculated}}$ (%)
Ag_2ReCl_6	$\frac{65.3\pm03}{65.37}$
Ag_2OsCl_6	$\frac{65.7\pm0.1}{65.60}$

Table 2. Crystallographic data for Ag_2ReCl_6 and Ag_2OsCl_6

Parameter	Ag_2ReCl_6	Ag_2OsCl_6
a/Å	13.159(5)	13.122(4)
c/Å	16.742(6)	16.589(5)
V/Å^3	2510.6	2473.7
Z	12	12
Molecular weight	614.661	618.654
d/g cm^{-3}	4.878	4.983

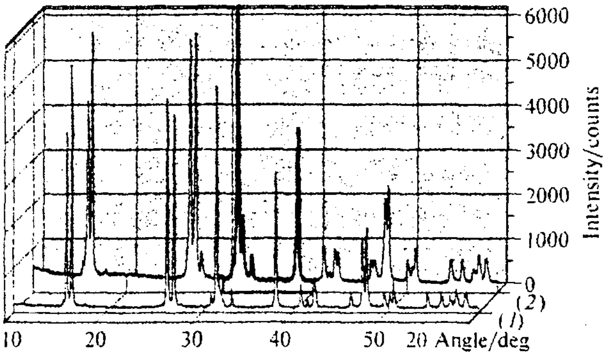

Fig. 1. X-ray powder diffraction patterns for Ag_2ReCl_6 (*1*) and Ag_2OsCl_6 (*2*).

Ag_2ReCl_6 and Ag_2OsCl_6 are observed at 312 and 305 cm^{-1}, respectively, and virtually coincide with those for the corresponding potassium salts.

The density of Ag_2ReCl_6 was estimated. The powder was pressed into a pellet. The pressing pressure was 10^9 Pa. The density of the Ag_2ReCl_6 pellet was 4.8±0.1 g cm^{-3}.

X-ray powder diffraction studies of polycrystals of Ag_2ReCl_6 and Ag_2OsCl_6 were carried out on DRON-3M and DRON-UM1 diffractometers (Cu-Kα radiation, Ni filter). Samples were prepared as thin layers on polished sides of standard quartz cells. Initially, the X-ray diffraction pattern for Ag_2ReCl_6 was indexed and the hexagonal unit cell parameters were refined using the single reflections (440) and (408) (the 2θ angles are 55.85° and 54.35°, respectively). Based on a comparison of the X-ray diffraction patterns of the compounds under study (Fig. 1), it was concluded that these compounds are isostructural, and the X-ray diffraction pattern for Ag_2OsCl_6 was indexed by analogy. The unit cell parameters of the latter compound were refined using 16 single reflections in the 2θ angle range of 38—64°. The crystallographic data are given in Table 2.

Results and Discussion

An analysis of the X-ray diffraction patterns revealed the following systematic absence conditions: for *hkil*, $k - h + l = 3n$; for $h\bar{h}0l$, $2h + l = 3n$; for $000l$, $l = 3n$, which indicated the space groups $R3$, $R\bar{3}$, $R32$, $R3m$, or $R\bar{3}m$.

Based on the experimental density for Ag_2ReCl_6, the formula units (*Z*) per unit cell can be determined: $Z = 12$.

The molecular weight of one of the structural fragments, *viz.*, the complex anion $[MCl_6]^{2-}$ (M = Re or Os), is noticeably larger, which made it possible to study the mutual arrangement of these fragments or the structural motif by the method of cationic sublattices.[5] Recall that three reflections were chosen from the X-ray diffraction pattern so that their indices *hkl* form a matrix whose determinant (D) is equal to the number of heavy fragments per unit cell. For both compounds, the triads of intense reflections (taking into account the repetition, Lorentz, and polarization factors) with the (0 2 1), (2 0 1), and (0 0 3) indices gave the sought-for value D = 12. It should be noted that the first two reflections were chosen out of six other reflections related to (2 0 1) by symmetry operations merely because these reflections lead to the most isometric sublattice. The vectors of the sought-for sublattice are as follows: $\mathbf{a}_k = \mathbf{a}/6 + \mathbf{b}/6 + \mathbf{c}/3$; $\mathbf{b}_k = -\mathbf{b}/2$; $\mathbf{c}_k = \mathbf{a}/2$. The metrics of the cationic sublattices (the Re or Os atoms should approach their vertices) were calculated using the known program[6]; the linear parameters should be taken as the appraising Re—Re or Os—Os distances. For $AgReCl_6$: a_k = 6.75 Å, b_k = 6.58 Å, c_k = 6.58 Å, α_k = 60.0°, β_k = 60.8°, γ_k = 60.8°. For Ag_2OsCl_6: a_k = 6.70 Å, b_k = 6.56 Å, c_k = 6.56 Å, α_k = 60.0°, b_k = 60.7°, γ_k = 60.7°. Therefore, the cationic sublattices in both structures can be described as weakly distorted rhombohedral lattices with the following parameters: $a_k \approx 6.64$ Å and $\alpha_k \approx 60.5°$ for Ag_2ReCl_6 and $a_k \approx 6.61$ Å and $\alpha_k \approx 60.5°$ for Ag_2OsCl_6. The fact that the α_k angles are close to 60° made it possible to go to the face-centered cubic unit cell. Clearly, the volume of the latter unit cell is twice as large as that of the rhombohedral cell and that there are two complex anions per unit cell. For Ag_2ReCl_6 and Ag_2OsCl_6, $a_k \approx 9.39$ Å and $a_k \approx 9.35$ Å, respectively.

A comparison of the metrics of the cationic sublattices with the unit cell parameters[7] of K_2ReCl_6 (a = 9.795 Å, space group $Fm3m$) revealed their similarity. Actually, the unit cell parameters of K_2ReCl_6 in the hexagonal system (a = 13.852 Å, c = 16.965 Å) are close to those of the complexes under study (see Table 2). Therefore, we can say that the replacement of potassium atoms by silver atoms in the structure of K_2ReCl_6 results in a hexagonal distortion of the cubic unit cell, the major motif of the mutual arrangement of the complex anions $[MCl_6]^{2-}$ (M = Re or Os) being retained. It should be noted that the class of compounds of the general formula A_2BX_6 is rather representative, and most of these compounds belong to the K_2PtCl_6 structural type. We found no compounds belonging to that structural type, which was established in the present study, in the available literature.

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