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Abstract

Full Text

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THE STRUCTURE OF THE COMPOUND $NH_4Na[MoO_3C_2O_4] \cdot 2H_2O$ AND ITS PLACE IN THE CLASSIFICATION OF MOLYBDENUM COMPOUNDS

The generally known ability of $C_2O_4^{2-}$ ions to form complex compounds with ions of various metals. Earlier (^{1}) we noted an analogy between the compounds $M_2[OsO_3C_2O_4] \cdot 2H_2O$ and $M_2[MoO_3C_2O_4] \cdot 2H_2O$ and suggested a structure for compounds of this type. It was assumed that both the Os compounds and the Mo compound should contain linear groupings of the type O—Mo—O. In order to test this assumption, a series of structural investigations was undertaken, including an X-ray structural investigation of $NH_4Na[MoO_3C_2O_4] \cdot 2H_2O$.

The compound was synthesized by the method of (^{2}). Crystals of $NH_4Na[MoO_3C_2O_4] \cdot 2H_2O$ belong to the prismatic symmetry class of the monoclinic system. The lattice parameters were determined in an RKOP camera using CuK_α radiation and refined in a KFOR camera with a NaCl standard using MoK_α radiation: $a = 9.30 \pm 0.3$ Å, $b = 13.43 \pm 0.01$ Å, $c = 7.85 \pm 0.03$ Å, $\beta = 98^\circ$, $Z = 4$, space group $P2_1/C$.

The X-ray structural investigation was begun by constructing Patterson projections $P(UV)$, $P(UW)$, and $P(VW)$, from which the coordinates of the Mo atom were determined. The subsequent construction of electron-density projections by F with signs calculated from the coordinates of the Mo atom made it possible to elucidate the rough structure of the compound. The details of the structure were refined by constructing weighted projections $\sigma^A(hk1)$ and $\sigma^A(hk2)$. A more thorough refinement of the coordinates of all atoms is currently being carried out by constructing sections of the three-dimensional electron-density distribution.

The structure of $NH_4Na[MoO_3C_2O_4] \cdot 2H_2O$ is built of $[MoO_3C_2O_4]^{2-}$ octahedra linked into a bent chain through oxygen atoms (Fig. 1). The group $[\ldots MoO_3C_2O_4 \ldots]^{2-}$ has a form close to a pseudotetragonal pyramid (semioctahedron), at the vertices of which oxygen atoms are located, two oxygen atoms at the base of the pyramid belonging to the oxalic-acid residue. The Mo atom is located at the center of the base of the pyramid. The $[MoO_3C_2O_4]^{2-}$ pyramids approach one another (apex to base, Fig. 1) and are connected along the

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Fig. 1. Structural motif of NH4Na[MoO3C2O4] • 2H2O

Figure 1: Fig. 1. Structural motif of NH4Na[MoO3C2O4] • 2H2O

Fig. 2. Structural motif of Na2[Mo2O7]

Figure 2: Fig. 2. Structural motif of Na2[Mo2O7]

z axis of the crystal into bent infinite chains by donor-acceptor bonds formed by the electron pair of the oxygen situated at the apex of the pyramid and the vacant level of Mo in the next pyramid. Such a genesis of chain structures is confirmed by the different distances and by the nonlinearity of the chains …O—Mo—O—Mo…. In contrast to Mo in $NH_4Na[MoO_3C_2O_4] \cdot 2H_2O$, osmium in $K_2[OsO_3C_2O_4] \cdot 2H_2O$ has no vacant level for accepting electrons. It follows from this that, if the assumption we previously made (^{1}) is not satisfied for the compound $NH_4Na[MoO_3C_2O_4] \cdot 2H_2O$, then for osmium complexes of this kind it apparently should hold. Consequently, unlike the chain compounds of Mo in the cis form, osmium compounds of the type $R_2[OsO_3C_2O_4] \cdot nH_2O$ must contain a linear O—Os—O bond (trans form) and be monomers.

Numerous works have been devoted to the investigation of the interaction of MoO_4^{2-} and $C_2O_4^{2-}$ ions in solutions.

Chikiryan and Vardapetyan (^{3}), and later G. S. Savchenko (^{4}), on the basis of the study of optical-density curves, indicate the existence of

in solution the complex ion $[MoO_3C_2O_4]^{2-}$. According to K. B. Yatsimirsky and I. I. Alekseev $^{(5)}$, upon interaction of Na_2MoO_4 with an excess of $H_2C_2O_4$, the complex anion $[MoO_3C_2O_4]^{2-}$ is also formed.

Spengler and Gencheimer $^{(6)}$, considering possible complex compounds of the indicated type and their properties, note the existence of three compounds: $R_2[MoO_3C_2O_4]$, $R_2[(MoO_3)_2C_2O_4]$, and $R_2[MoO_2(C_2O_4)_2]$. The compound $R_2[(MoO_3)_2C_2O_4]$ was described as early as 1903 by Rosenheim and Bergtheim $^{(7)}$. On the other hand, Kavich $^{(8)}$, on the basis of a study of the interaction of Na_2MoO_4 and $H_2C_2O_4$, comes to the conclusion that formation of the complex $[MoO_3C_2O_4]^{2-}$ is possible only in an alkaline medium, whereas in an acidic medium

Fig. 1. Structural motif of $NH_4Na[MoO_3C_2O_4] \cdot 2H_2O$

Fig. 2. Structural motif of $Na_2[Mo_2O_7]$

the process of isopolymerization proceeds predominantly. Rao and Peni $^{(9)}$ point to the polymerization reaction in solution. However, in a later work Sechava, Rao, and Banerjee $^{(10)}$ come to the conclusion that the process proceeds according to the scheme

$$Na_2MoO_4 + H_2C_2O_4 \rightarrow Na_2MoO_3C_2O_4 + H_2O,$$

as a result of which, in Na_2MoO_4, one of the oxygen atoms is replaced by the group $C_2O_4^{2-}$. The oxalate group most likely occupies two coordination positions, and since the formation of six-coordinate compounds is characteristic of oxygen compounds of Mo, it is assumed that one water molecule enters the inner sphere of the complex, with formation of aquooxalatomolybdate $[MoO_3C_2O_4H_2O]^{2-}$. In a somewhat different form, a similar assumption concerning the solid phase $R_2[MoO_3C_2O_4] \cdot 2H_2O$ was also expressed by us (1). However, as the present study shows, the water molecule does not enter the inner sphere of the complex ion.

I. V. Tananaev and A. A. Vorontsova (11) studied in detail the system Na_2MoO_4—$Na_{xH_{2-x}}C_2O_4$—H_2O in order to determine whether the indicated interaction leads to formation of the complex ion $[MoO_3C_2O_4]^{2-}$, or whether a process of isopolymerization takes place. They showed that, in the system at values of x from 0 to 1, the formation of $[MoO_3C_2O_4]^{2-}$ ions is observed, whereas at values of x from 1 to 2, interaction in the system occurs to a very small extent. The formation of isopolymers, in the authors' opinion, is only of secondary importance. The final product of the interaction considered, in the form of the solid phase $NH_4Na[MoO_3C_2O_4] \cdot 2H_2O$, was studied by us roentgenographically.

Further presentation of the investigation carried out shows that $NH_4Na[MoO_3C_2O_4] \cdot 2H_2O$ should, following Feigl[12], be regarded as the sodium-ammonium salt of the heteropoly acid $H_2[MoO_3C_2O_4] \cdot H_2O$.

It is known that heteropoly acids may be regarded as complex derivatives of polymerized oxygen acids of metals, in which the oxygen atoms may be partially or completely replaced by acid residues. If, in an oxygen acid, the oxygen atoms are replaced by acid residues of the same acid, an isopoly acid is formed. One of the simplest representatives of molybdenum isopoly acids is dimolybdic acid ($H_2Mo_2O_7$). The structure of sodium dimolybdate was investigated by Lindqvist[13]. He showed that the structure consists of oxygen octahedra linked into a bent chain, with Mo atoms located at their centers. An acid residue of molybdic acid is attached through its vertices to two neighboring octahedra of the chain in such a way that two vertices of the MoO_4^{2-} tetrahedron remain free, i.e., the MoO_4^{2-} group is attached to two octahedra and occupies one coordination position in each of them (Fig. 2). It is not difficult to see that there is a deep analogy between $Na_2[MoO_3MoO_4]$ and $NH_4Na[MoO_3C_2O_4] \cdot 2H_2O$. In the latter compound the role of the acid residue is played by oxalic acid.

The O——O distance between the hydroxyl groups in oxalic acid, equal to 2.56 Å, does not allow the oxalic acid residue to attach to two different octahedra (the distance between these vertices of two octahedra in $Na_2Mo_2O_7$ is 3.08 Å, and in $NH_4Na[MoO_3C_2O_4] \cdot 2H_2O$ it is 4.2 Å, whereas in $Na_2[Mo_2O_7]$ the distance between the free oxygen vertices in the octahedron is 2.6 Å). Therefore the $C_2O_4^{2-}$ group, occupying, like MoO_4^{2-}, two coordination positions, is attached to one octahedron (see Fig. 1). Replacement of MoO_4^{2-} in the isopoly acid $H_2[MoO_3MoO_4]_\infty$ by an oxalic acid residue leads to the formation of the heteropoly acid $H_2[MoO_3C_2O_4]_\infty \cdot 2H_2O$.

The X-ray structural investigation carried out on $NH_4Na[MoO_3C_2O_4] \cdot 2H_2O$, the solid product of the reactions considered above, makes it possible to draw the following conclusions:

1. In the course of the reaction between Na_2MoO_4 and $NH_4HC_2O_4$, with formation of the solid phase $NH_4Na[MoO_3C_2O_4] \cdot 2H_2O$, along with the polymerization reaction there also occurs a reaction of substitution of one of the oxygen atoms in the MoO_4^{2-} ion by the $C_2O_4^{2-}$ group.
2. The final product of the reaction is the sodium-ammonium salt of the heteropoly acid $H_2[MoO_3C_2O_4]_\infty \cdot 2H_2O$, and not separate complexes $[MoO_3C_2O_4]^{2-}$ or isopoly acids.

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