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A NMR Study on the Structure of Oxygen–Hydrogen Forms in Potassium Trimolybdate

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Crystalline fractions of fibrillar trimolybdates of lithium $Li_2O\cdot 3MoO_3\cdot 5.7H_2O$ [1], sodium $Na_2O\cdot 3MoO_3\cdot 3H_2O$ [2, 3] and potassium $K_2O\cdot 3MoO_3\cdot 3H_2O$ [4] have been recently isolated. The characteristic shape of the crystals is mainly due to their chain structure [5, 6]. The formation of the chain trimolybdate anion can be described by the following general equation [7]:

$$3nMoO_4^{2-} + 4nH^+ \rightarrow \begin{cases} [Mo(OH)_2O(MoO_4)_2]_n^{2-} \\ \text{or} \\ [MoO(H_2O)O(MoO_4)_2]_n^{2-} \end{cases} + 2nH_2O$$

Hence this anion shoud comprise two OH groups or one water molecule bound directly to the central molybdenum atom. The investigations of the lithium compound showed [8] that both anion forms coexist in the crystal structure and that the chemical formula of the trimolybdate anion is $[MoO_{1-\alpha}(OH)_{2\alpha}(H_2O)_{1-\alpha}O(MoO_4)_2]_n^{2-}$, where $\alpha = 0.15$ at 77 K and increases with temperature [9]. In the present investigation we observed a similar effect for the potassium compound, and moreover we found that the chemical structure of the anion completely changes at 323 K.

Proton magnetic resonance spectra were obtained for a polycrystalline sample in the temperature range 77–370 K on a broad line spectrometer operating with a Robinson type marginal oscillator at the frequency of 17 MHz. Figure 1 shows the temperature dependence of the second moment M_2 of the NMR line. In Figure 2 there are three selected spectra recorded at different temperatures. The spectrum obtained at 77 K (Fig. 2a) consists of two components: a Pake doublet (peak-to-peak width 12 gauss) corresponding to immobile water molecules [10] and a single center line (halfwidth 3.1 gauss) arising from OH groups [11, 12]. Relative integral intensity (reflecting the relative amount of two forms of anion – RATFA) of both components is $I_{OH}/I_{H_2O} = 0.06$.

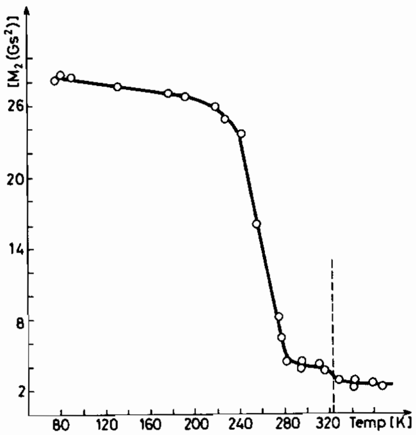

Figure 1. The temperature dependence of the second moment M_2.

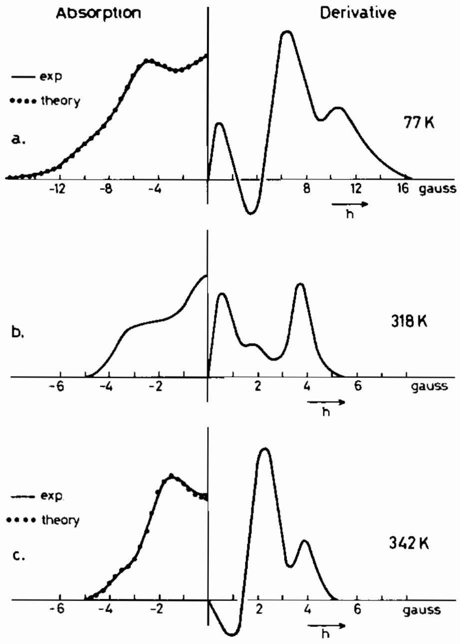

Figure 2. Theoretical and experimental line shape.

The calculations show that the relevant formula of potassium trimolybdate anion at 77 K can be written as $[MoO_{0.84}(OH)_{0.32}(H_2O)_{0.84}O(MoO_4)_2]_n^{2-}$. In the temperature range 77–150 K a slow decrease of the second moment is observed (Fig. 1). At the same time I_{OH}/I_{H_2O} increases. These effects indicate that on raising the temperature an increase of the RATFA occurs. In the temperature region of 150–293 K there is a rapid decrease of M_2. This is caused mainly by molecular movement of water molecules. The line

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shape becomes narrower, but due to the small intermolecular interactions still has a clearly resolvable structure (*cf.* Fig. 2b). Above 293 K the spectrum does not change further and can be resolved into three components: the central single line and two doublets of different intensities and peak-to-peak widths of 3 and 6 gauss. The central line we assign to highly mobile water molecules. The broader and more intense doublet arises from water molecules which undergo 180° jumps around their symmetry axis [13]. The width of this doublet is exactly half of that from Fig. 2a which corresponds to the rigid water molecules. The third component, narrower two-peak line, corresponds to OH groups.

At temperatures close to 323 K an abrupt change of the second moment M_2 and of the line shape occurs. Both H_2O lines (from spectrum 2b), namely the central one and the broader two-peak component, disappear (see Fig. 2c). On cooling the sample back to room temperature the reverse changes in the NMR spectra take place. The spectrum obtained at 342 K has been analyzed. The best fit of the theoretical line shape to the experimental one (Fig. 2c) was obtained assuming three pairs of OH groups in the crystal structure, the protons in one pair being at the distance of about 2.2 Å. Hence, the observed effect is interpret as an abrupt transition which can be described by the following chemical equation:

$$K_2Mo_3O_{10-\alpha}(OH)_{2\alpha}(H_2O)_{1-\alpha}\cdot 2H_2O \xrightleftharpoons{\text{about 323K}} K_2Mo_3O_7(OH)_6$$

The transition of the above type was not observed in the other chain trimolybdates. It is probably the consequence of the fact that different cations have different ability to polarize water molecules in $A^-\cdots aq\cdots Me^+\cdots aq\cdots A^-$ system of bonds in the crystal structure.