

BONDING OF ANIONIC WATER IN FIBRILLAR CRYSTALS OF SODIUM AND POTASSIUM TRIMOLYBDATES*

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The NMR method has been employed for the investigation of the chain sodium and potassium trimolybdates. The results indicate that the hydrogen-oxygen formations occur in two forms: H_2O and OH . The quantitative analysis of the results obtained lead to the conclusion that the chemical composition of the trimolybdate anion at $-195^\circ C$ corresponds to the following formula: $[MoO_{1-\alpha}(OH)_{2\alpha}(H_2O)_{1-\alpha}O(MoO_4)_2]_n^{2-}$, with $\alpha = 0.19$ for sodium compound and $\alpha = 0.16$ for the potassium one.

1. Introduction

Recently the chain isopolymolybdates of the general stoichiometric formula $X_2O \cdot 3MoO_3 \cdot nH_2O$ (where $X = Li, Na$ and K , and $n = 3$ for the sodium and potassium compound and 5.7 for the lithium one) have been described [1-3]. According to the mechanism of the formation of linear trimolybdates [4], the final products contain one constitution water molecule bound directly to the central molybdenum atom [5]. In our previous paper we reported that the chemical composition of the lithium trimolybdate anion at $-195^\circ C$ corresponds to the following formula: $[McO_{0.85}(OH)_{0.30}(H_2O)_{0.85}O(MoO_4)_2]_n^{2-}$. This means that the part of anionic water exists in the crystal structure in the form of hydroxylic groups.

The purpose of the present research was to examine the character of anionic water in the sodium and potassium compounds.

* Dedicated to Professor Kazimierz Gumiński on the occasion of his 70-th birthday.

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2. Experiment

Proton magnetic resonance spectra were registered for polycrystalline samples at the temperature -195°C on a broad line spectrometer operating with a Robinson-type marginal oscillator at the frequency of 17.455 MHz. Calculations of the second moments of the resonance lines and those leading to the theoretical spectra consistent with the experimental curves, were carried out on an ODRA-1204 digital computer.

3. Results and discussion

In Fig. 1 the first derivatives of the proton resonance absorption lines obtained for sodium and potassium trimolybdates at -195°C are shown. Both lines are similar in shape and consist of two components: a broad and a narrow one. The broad line has the typical shape of the Pake doublet and thus it obviously corresponds to the immobile

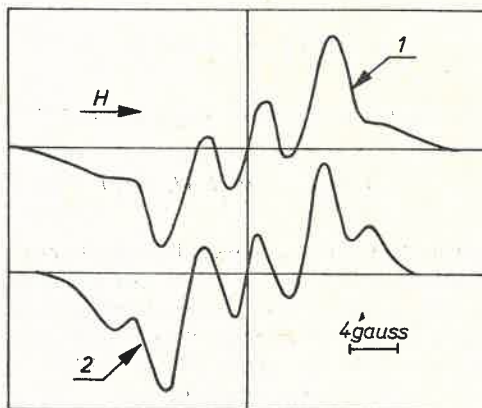


Fig. 1. First derivatives of the NMR spectra at -195°C

water molecules. The narrow component, according to the arguments similar to those of Porte et al. [8], we ascribe to the separate OH groups.

In order to perform a quantitative analysis of these spectra the theoretical line shapes were assumed in the form of the equation

$$F(h) = wf_1(h) + (1-w)f_2(h), \quad (1)$$

and fitted to the experimental lines.

In equation (1), $f_1(h)$ is the Pake function [6, 7] for water molecules, and $f_2(h)$, describing separated OH groups, is taken as a Gaussian function [6]; w — presents that fraction of all protons in a molecule which are situated in water molecules; h — is the distance from the center of the spectrum expressed in gauss.

The best fit parameters: $r_{\text{H-H}}$ — the proton-proton distance in water molecule, β_1^2 — the broadening parameter of the water line, β_2^2 — the broadening parameter of the OH line and “ w ”, for both investigated compounds are listed in the Table. The second moments $M^{(2)}$ of the theoretical and the experimental curves are also included.

TABLE I

The best fit parameters

Parameter	Sodium trimolybdate	Potassium trimolybdate
r_{H-H} [Å]	1.54	1.54
w	0.937 ± 0.002	0.946 ± 0.002
β_1^2 [gauss ²]	3.8 ± 0.2	3.0 ± 0.2
β_2^2 [gauss ²]	1.7 ± 0.2	1.7 ± 0.2
$M_{exp}^{(2)}$ [gauss ²]	29.3 ± 0.6	28.1 ± 0.6
$M_{calc}^{(2)}$ [gauss ²]	28.8 ± 0.3	28.5 ± 0.3

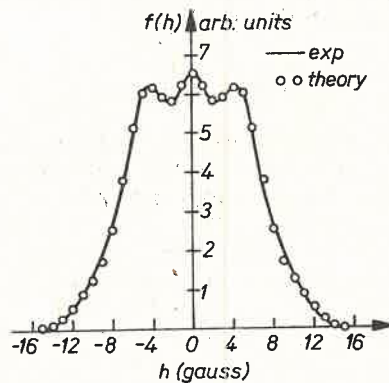


Fig. 2. Theoretical and experimental line shape for the sodium trimolybdate

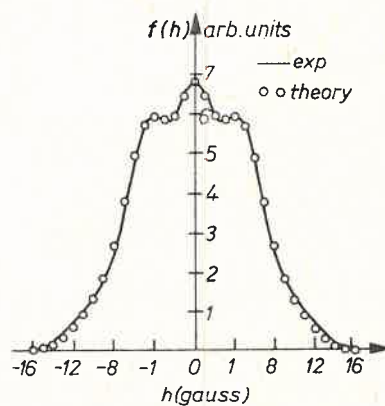


Fig. 3. Theoretical and experimental line shape for the potassium trimolybdate

The open circles in Fig. 2 and 3 represent the theoretical spectra calculated according to equation (1) for the best fit parameters, while the solid lines are the integrated and normalized experimental lines.

The total numbers of protons in the form of H_2O groups, calculated from the "w" values, are 5.62 and 5.68 for sodium and potassium trimolybdates respectively. Thus, the remaining 0.38 and 0.32 protons exist in the form of OH groups.

4. Conclusions

The main conclusion from the presented investigation is that, analogically to the lithium trimolybdate, the hydroxylic groups also exist in the crystal structure of sodium and potassium trimolybdates. This fact shows that the water molecule, mentioned in the introduction, directly bound to the central molybdenum atom occurs in two forms: H_2O and OH. The relative amounts of the two forms at -195°C are 0.81/0.38 for sodium and 0.84/0.32 for potassium trimolybdate. Hence, the relevant formulae of these compounds can be written as $\text{Na}_2[\text{MoO}_{0.81}(\text{OH})_{0.38}(\text{H}_2\text{O})_{0.81}\text{O}(\text{MoO}_4)_2] \cdot 2\text{H}_2\text{O}$ and $\text{K}_2[\text{MoO}_{0.84}(\text{OH})_{0.32}(\text{H}_2\text{O})_{0.84}\text{O}(\text{MoO}_4)_2] \cdot 2\text{H}_2\text{O}$.

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