An IR Study of a Chromium Oxide Hydroxide of $K_2Cr_3X_9$ Stoichiometry

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Recently the crystal structure of a series of compounds assigned the formula $M_2{}^I Cr_3 O_9$ ($M^I =$ Na, K, Rb) was reported by Wilhelmi, Jonsson and Lagervall.[1] The new structure type reported is formed of CrO_6 octahedra arranged in strings by sharing edges. To this string four-co-ordinated chromium atoms are attached to form a chain. The chains are held together by potassium atoms. The large difference between the chromium-oxygen distances found in the CrO_4 tetrahedra and the CrO_6 octahedra cannot be explained solely as due to the difference in coordination number but indicates a particular segregation of the valencies of the chromium atoms.

In Ref. 1 it was assumed that chromium has a valency of six in the tetrahedral and four in the octahedral positions.

This paper gives the IR-spectrum of the compound and a short interpretation of the result.

The infrared spectrum was registered at 298°K using a Perkin Elmer 337 IR spectrophotometer in the region $4000-400$ cm⁻¹. Finely powdered crystals of the compound (*vide infra*) was mulled with KBr and pressed to a disk. The spectrum is presented in Fig. 1a together with a spectrum of $K_2Cr_2O_7$ for comparison (Fig. 1b). The absorption band at 3400 cm⁻¹ in Fig. 1a is interpreted as belonging to the stretching vibration of an OH group, indicating a hydrogen bond of medium strength. The same frequency shows up as the absorption from the symmetric stretching vibration of solid water at $-78°C$.[2] This points to a potential distribution along the $O-H\cdots O$ distance with a barrier well above the ground state. There is a rough correlation between the $O-O$ distances and the observed $O-H$ stretching frequencies.[3] OH stretching frequencies of comparatively weak hydrogen bonds occur in the region 3400 cm⁻¹ when the $O-O$ distances are in the range $2.7-3.0$ Å.

This is contrary to the conditions for $HCrO_2$[4,5] where neutron diffraction and IR studies have demonstrated the presence of an essentially symmetric hydrogen bond and an observed $O-O$ distance of 2.49 Å. The IR-spectrum of $HCrO_2$ shows a very broad and intense band centered near 1650 cm⁻¹, arising from an $O-H$ stretching vibration of a hydrogen in a strong hydrogen bond and a strong, narrow band
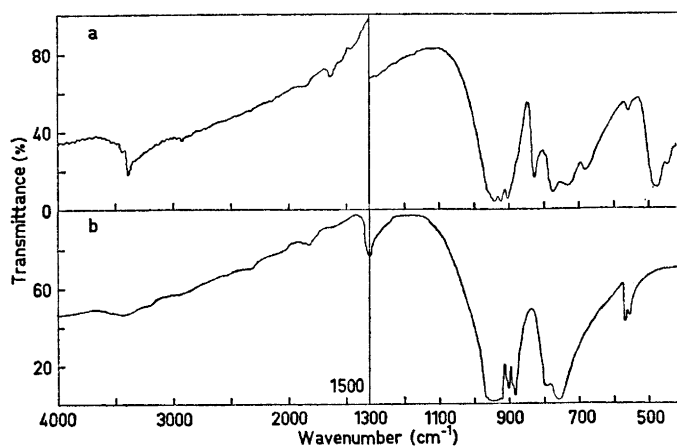

Fig. 1. Infrared spectrum of (a) $K_2Cr_3O_8OH$ (b) $K_2Cr_2O_7$ at 298°K in KBr disks.

attributed to the $\angle$OHO bending mode which appears at 1229 cm^{-1} which is normal for the bending mode of a strongly hydrogen-bonded hydrogen atom.

The infrared spectrum of the compound shows also a whole series of absorption bands which can be assigned to chromium-oxygen vibrations by comparison with the IR-spectrum of $K_2Cr_2O_7$ (Fig. 1a—b and Ref. 6).

The segregation of the charge distribution of chromium atoms into two valency states has been observed in some cases, *i.e.* the compounds of $M^ICr_3O_8$ stoichiometry (M^I=Li, Na, K, Rb, Cs, and Tl)[7] and Cr_5O_{12}.[8] The average valency of the chromium atoms is here 5 or close to 5 and the $(Cr-O)_{oct}$ and $(Cr-O)_{tetr}$ distances agree very well with those found in compounds containing tri- and hexavalent chromium atoms, respectively. This was taken as strongly indicating a segregation into $+3$ and $+6$ for the chromium atoms. This view was later on supported by magnetic susceptibility measurements on KCr_3O_8 [9] and by further structural analogies.

The suggested valency distribution of $+4$ and $+6$ for the family of compounds, given the formula $M_2^ICr_3O_9$, was considered unusual. Generally the $+4$ valency state seems to be unstable and rather few compounds containing Cr^{4+} have been observed. The appearance of the infrared spectrum of the potassium compound clearly shows that the compound contains hydrogen atoms. The formula, required by this observation and the crystal structure, may be written $K_2Cr_3(O,OH)_9$. In order to obtain the very plausible segregation of the chromium valencies into $+3$ and $+6$, a hydrogen content of one atom per formula unit would be required. For this reason we propose the formula $K_2Cr_3O_8OH$. From the discussion of the IR-spectrum given above it seems reasonable that the hydrogen atom is attached to the oxygen atom (in a twofold position) which belongs solely to the strings of octahedra and which does not form any bridges between tetrahedra and octahedra. The formula $K_2Cr_3O_8OH$ of the compound might then also be written $K_2Cr^{III}(OH)(Cr^{VI}O_4)_2$.

A chemical analysis by straight-forward techniques of this compound presents considerable difficulties and so far it has not been possible to support the conclusions given above in such ways. Observations in connection with the preparative work, however, help in understanding the forma-

tion of a product containing hydrogen. Originally the crystals of $K_2Cr_3O_8OH$ were grown according to the method described by Bither, Gillson and Young [10] by heat treatment of a dry mixture of CrO_3 and $M_2^ICrO_4$ at 25 kb in a girdle apparatus with pyrophyllite as a pressure medium. In further experiments with CrO_3 replaced by CrO_2 and water, the yields of the new phase increased considerably. Similar results have been obtained when investigating the system MoO_3-MoO_2 at 25 kb in the same high pressure apparatus. It was found that the compound $Mo_4O_{10}(OH)_2$ was obtained [11] and the formation of this material was found to be due to the presence of pyrophyllite in the apparatus. Actually in the temperature interval 600—1000°C pyrophyllite gives off hydrogen in quantities which can explain the partial reduction of the trioxide. Such observations are evidently in accordance with the proposed formula $M_2Cr_3O_8OH$.

Detailed reports of the results from the structural work, the IR measurements and additional studies on the formation and properties of this type of compounds will be given elsewhere.

1. Wilhelmi, K.-A., Jonsson, O. and Lagervall, E. *Acta Chem. Scand.* **23** (1969) 1074.
2. Haas, C. and Hornig, D. F. *J. Chem. Phys.* **32** (1960) 1763.
3. Pimentel, G. C. and Sederholm, C. H. *J. Chem. Phys.* **24** (1956) 639.
4. Hamilton, W. C. and Ibers, J. A. *Acta Cryst.* **16** (1963) 1209.
5. Rush, J. J. and Ferraro, J. R. *J. Chem. Phys.* **44** (1966) 2496.
6. Stammreich, H., Bassi, D., Sala, O. and Siebert, H. *Spectrochim. Acta* **13** (1958) 192.
7. Wilhelmi, K.-A. *Chem. Comm.* **1966** 437.
8. Wilhelmi, K.-A. *Acta Chem. Scand.* **19** (1965) 165.
9. Klemm, W. *Z. anorg. allgem. Chem.* **301** (1959) 323.
10. Bither, T. A., Gillson, J. L. and Young, H. S. *Inorg. Chem.* **5** (1966) 1599.
11. Wilhelmi, K.-A. *Acta Chem. Scand.* **23** (1969) 419.

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