

Studies of Zinc-Chromium Hydroxy Salts. I. Thermal Decomposition of $[Zn_2Cr(OH)_6]X \cdot nH_2O$, Where $X^- = F^-, Cl^-, Br^-, I^-, \frac{1}{2}CO_3^{2-}$, and NO_3^- . M. LAL AND A. T. HOWE*, Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT, England. We have characterized the layered anion-exchange compounds $[Zn_2Cr(OH)_6]X \cdot nH_2O$, where $X^- = F^-, Cl^-, Br^-, I^-, \frac{1}{2}CO_3^{2-}$, and NO_3^- , and studied their thermal decomposition. The precipitated particles were less than a few hundred angstroms in size, and they could not be easily aged. Upon heating, a considerable amount of surface water, up to $n = 1$ in the formula, was initially lost, followed by the ill-defined stages represented by loss of waters of hydration ($n \leq 2$), first stage of dehydroxylation, loss of X (over temperature ranges between 200 and 500°C), and final dehydroxylation (up to 700°C). Interest in such possible mixed $O^{2-}/OH^-/X^-$ decomposition intermediates as ionic conductors is discussed.

Studies of Zinc-Chromium Hydroxy Salts. II. Composite Anion Conductors of Pressed Disks of $[Zn_2Cr(OH)_6]X \cdot nH_2O$, where $X^- = F^-, Cl^-, Br^-, I^-, NO_3^-$, and $\frac{1}{2}CO_3^{2-}$. M. LAL AND A. T. HOWE*, Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT, England. We have found that pressed disks of the layered anion-exchange compound $[Zn_2Cr(OH)_6]Cl \cdot 2H_2O$ exhibits reversible interparticle swelling to take up appreciable quantities of water, dependent on the relative humidity. This has a marked effect on the disk conductivity, enabling the chloride ions to easily pass through the channels so created to give a maximum conductivity of $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 17°C. The transport number for Cl^- ions was found to be 1 ± 0.1 , and there was estimated to be the equivalent of approximately eight water layers separating the particles in the disks. Such a large swelling probably has similar origins to the large swelling which can occur within the particles of the expandable clays, and probably arises because of the ease of donation of the Cl^- ions from the surfaces into the interparticle solution. The maximum conductivities of composites of the compounds with $X^- = F^-, Br^-, I^-, NO_3^-$, and $\frac{1}{2}CO_3^{2-}$ were in the range 10^{-3} – $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$, which we also attribute to anion conduction.

NMR Study of Water Reorientation in Molybdic Acids: $MoO_3 \cdot 2H_2O$ and Yellow $MoO_3 \cdot H_2O$. R. H. JARMAN, P. G. DICKENS, AND R. C. T. SLADE*. Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, England. Proton NMR relaxation times (T_2 , T_1 , $T_{1\rho}$) are reported for powder samples of $MoO_3 \cdot 2H_2O$ and yellow $MoO_3 \cdot H_2O$ in the temperature range 150–325 K and at 20 and 60 MHz. No translation of hydrogen atoms is detected but the spinlattice relaxation behavior indicates reorientation of H_2O molecules. The waters coordinated to Mo atoms undergo 180° flips (about their C_2 axes) with similar motional parameters in both compounds. The interlayer waters in $MoO_3 \cdot 2H_2O$ undergo 180° flips with different parameters. An assumed Arrhenius-type temperature dependence of correlation times leads to preexponential factors which are "anomalously" low. The possible involvement of temperature-dependent activation barriers is discussed.

Preparation and Properties of the System $Fe_{1-x}Cr_xNbO_4$. B. KHAZAI, R. KERSHAW, K. DWIGHT, AND A. WOLD*. Department of Chemistry, Brown University, Providence, Rhode Island 02912. Members of the system $Fe_{1-x}Cr_xNbO_4$ were prepared and their magnetic and electronic properties investigated. It was shown that chromium substitution favored the formation of the rutile structure, which resulted in a decrease in the electrical conductivity because of randomization of the transition metal ions in the structure. The replacement of a few percent of Fe^{3+} with Cr^{3+} caused a significant lowering of the lowest optical band gap, whereas the higher-energy transitions remained essentially unchanged. This resulted in increased response to the longer wavelengths of the solar spectrum.