

bottlenecks are encountered ( $V_{\text{max}} \approx 1.7\text{-}2$ ) by the sodium for several migration directions. The structure of  $\text{K}_2\text{CoP}_2\text{O}_7$  [9] (tetragonal, S.G.:  $P4_2/mnm$ ,  $a=7.926 \text{ \AA}$ ,  $c=11.350 \text{ \AA}$ ) consists of  $[\text{CoP}_2\text{O}_7]_{\infty}$  layers with alkali metal cations lying between the layers. The cation motion seems to be bidimensional in the (001) planes with  $V_{\text{max}}$  less than 1.30 along [110]. The possible motion through adjacent layers ( $c$  axis) seems subsequently difficult. These suggestions are to be confirmed by electrical measurements.

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#### MS43 P03

**Full formula of Molybdenum(V) phosphates out of empiric bond strength evaluation** André Leclaire *CRISMAT-ENSICAEN, CNRS-UMR6508, University of Caen, France.* E-mail: [andre.leclaire@ensicaen.fr](mailto:andre.leclaire@ensicaen.fr)

**Keywords: Bond strength calculations, Molybdenum phosphates, Molybdenum(V).**

Generally the X-ray structures of crystals obtained from hydrothermal synthesis or out of an aqueous solution don't allow distinguishing between an oxygen atom or a hydroxyl group or a water molecule bonded to transition elements, due to the great difficulty to find hydrogen atoms on the Fourier and Difference Synthesis maps. Donnay and Allmann [1] gave a procedure based on the sum of electrostatic valences received by the oxygen atoms. They gave also equations for determining the electrostatic valences given by a central ion to the surrounding oxygen atoms. Latter a more convenient empirical expression was reported:  $v_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$  where  $R_{ij}$  tabulate by Brese and O'Keeffe [2] is characteristic of a cation and  $d_{ij}$  the cation oxygen distances. We synthesized and studied a huge number of **pentavalent molybdenum** phosphates and mixed-valence phosphates containing  $\text{Mo}^{5+}$  but only the  $R_{ij}$  value for  $\text{Mo}^{6+}$  was tabulated. So in a first time we compute the  **$R_{ij}$  constant for  $\text{Mo}^{5+}$  of 1.879 with 86  $\text{Mo(V)O}_6$  octahedra**. This values works very well and latter Zocchi [3] found a  $R_{ij}=1.8788$  which associated to  $B=0.3046$  works for all oxidation states from +3 to +6.

During the studies of compounds containing  **$\text{Mo}^{5+}_{12}\text{M}^{2+}_8\text{P}_8\text{O}_{62}\text{H}_x$  clusters**, the  $R_{ij}$  value of 1.879 lead to valences ranging from 4.63 to 5.05 with a mean value of 4.85 for  $\text{Mo}^{5+}$  whereas valences ranging from 4.60 to 5.27 with a mean value of 4.84 were obtained for phosphorus with the  $R_{ij} = 1.604$  reported by Brese and O'Keeffe [2]. In order to improve the valence calculations, new  $R_{ij}$  values were computed from 328  $\text{PO}_4$  tetrahedra for phosphorus and from 42  $\text{Mo}^{5+}\text{O}_6$  octahedra sharing only

edges in  $\text{Mo}_6$  rings. So  **$R_{ij}$  values of 1.890 and 1.615 were obtained for  $\text{Mo}^{5+}$  and P respectively**. With these values the electrostatic bond valence sums are centered on 4.99 for both polyhedra with valences ranging from 4.77 to 5.20 for  $\text{Mo}^{5+}$  and from 4.73 to 5.40 for P in the compounds exhibiting  $\text{Mo}_{12}\text{MP}_8\text{O}_{62}\text{H}_x$ . The most amazing result deduced from the bond valence sum calculations was that **three oxygen atoms of the  $\text{Mo}_6\text{O}_{24}$  rings are hydroxyl groups** (lack of 0.9 v.u.) so the ring consist of six edge sharing  $\text{MoO}_5\text{OH}$  octahedral leading to the formulation  $\text{Mo}_6\text{O}_{21}(\text{OH})_3$ . on the other hand the valence sums received by the phosphorus tetrahedral show that they belong to the  $\text{PO}_4$ , or  $\text{PO}_3\text{OH}$ , or  $\text{PO}_2(\text{OH})_2$  species according to the other cations in the structure. So the cluster will be  $[\text{Mo}_{12}\text{M}^{2+}\text{O}^{24}(\text{OH})_6(\text{PO}_4)_x(\text{PO}_3\text{OH})_y(\text{PO}_2(\text{OH})_2)_{8-x-y}]$ . One observes also on some oxygen atoms lacks of 0.30 or 0.65 v.u. pointing out that those oxygen atoms receive hydrogen bonds.

In conclusion the use of experimental bond valence sums allowed to establish the real formulation of the clusters containing pentavalent molybdenum obtained by hydrothermal synthesis and also to set up the hydrogen bonds network.

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#### MS43 P04

**The crystal structure of caesium disulfate at 120 and 273 K.** Kenny Stahl<sup>a</sup>, Rolf W. Berg<sup>a</sup>, K. Michael Eriksen<sup>a</sup>, Rasmus Fehrmann<sup>a</sup>. <sup>a</sup>*Chemistry Department, Technical University of Denmark, Lyngby, Denmark.* E-mail: [kenny@kemi.dtu.dk](mailto:kenny@kemi.dtu.dk)

**Keywords: caesium disulfate, coordination geometry, phase transition**

The crystal structures of  $\text{Cs}_2\text{S}_2\text{O}_7$  have been determined at 120 and 273 K from  $\text{MoK}\alpha$  data: T=120 K, P-1, Z=20,  $a=14.941(2)$ ,  $b=16.036(2)$ ,  $c=19.300(2) \text{ \AA}$ ,  $\alpha=85.025(2)$ ,  $\beta=67.630(2)$ ,  $\gamma=74.968(2)^\circ$ ; T=273 K, P-1, Z=10,  $a=7.5229(5)$ ,  $b=15.959(1)$ ,  $c=17.973(1) \text{ \AA}$ ,  $\alpha=90.207(1)$ ,  $\beta=90.418(1)$ ,  $\gamma=102.206(2)^\circ$ . Their crystal structures represent a novel structure type, entirely different from the dichromate type structures of other alkali disulfates [1]: 8/10 of the caesium ions form a "tube" surrounding 2/10 of the disulfates (Fig. 1), while the remaining disulfates enclose the remaining caesium ions in a sandwich structure.