bottlenecks are encountered (Vumax ≈ 1.7-2) by the sodium for several migration directions. The structure of $K_2CoP_2O_7$ [9] (tetragonal, S.G.: $P4_2/mnm$, a=7.926 Å, c=11.350 Å) consists of $[CoP_2O_7]_\infty$ layers with alkali metal cations lying between the layers. The cation motion seems to be bidimensional in the (001) planes with Vumax 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

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 Mo^{5+} but only the Rij value for Mo^{6+} was tabulated. So in a first time we compute the **Rij constant for Mo^{5+} of 1.879 with 86 $Mo(V)O_6$ octahedra**. This values works very well and latter Zocchi [3] found a Rij=1.8788 which associated to B=0.3046 works for all oxidation states from +3 to +6.

During the studies of compounds containing **$Mo^{5+}_{12}M^{2+}P_8O_{62}H_x$ 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 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 PO_4 tetrahedra for phosphorus and from 42 $Mo^{5+}O_6$ octahedra sharing only

edges in Mo_6 rings. So **R_{ij} values of 1.890 and 1.615 were obtained for 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 Mo^{5+} and from 4.73 to 5.40 for P in the compounds exhibiting $Mo_{12}MP_8O_{62}H_x$. The most amazing result deduced from the bond valence sum calculations was that **three oxygen atoms of the Mo_6O_{24} rings are hydroxyl groups** (lack of 0.9 v.u.) so the ring consist of six edge sharing MoO_5OH octahedral leading to the formulation $Mo_6O_{21}(OH)_3$. on the other hand the valence sums received by the phosphorus tetrahedral show that they belong to the PO_4, or PO_3OH, or $PO_2(Oh)_2$ species according to the other cations in the structure. So the cluster will be $[Mo_{12}M^{2+}O^{24}(OH)_6(PO_4)_x(PO_3OH)_y(PO_2(OH)_2)_{8-x-y}]$. 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[a], Rolf W. Berg[a], K. Michael Eriksen[a], Rasmus Fehrmann[a]. [a]*Chemistry Department, Technical University of Denmark, Lyngby, Denmark.* E-mail: kenny@kemi.dtu.dk

Keywords: caesium disulfate, coordination geometry, phase transition

The crystal structures of $Cs_2S_2O_7$ have been determined at 120 and 273 K from MoKα data: T=120 K, P-1, Z=20, a=14.941(2), b=16.036(2), c=19.300(2) Å, α=85.025(2), β=67.630(2), γ=74.968(2)°; T=273 K, P-1, Z=10, a=7.5229(5), 15.959(1), c=17.973(1) Å, α=90.207(1), β=90.418(1), γ=102.206(2)°. 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.
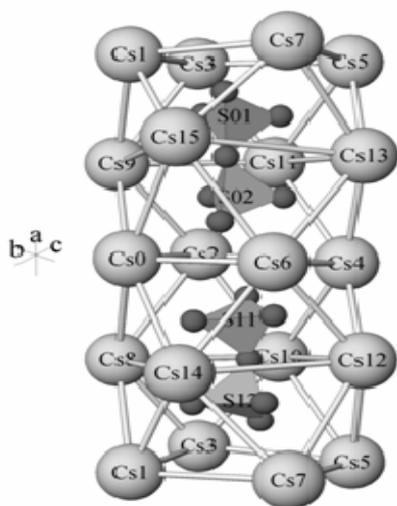
Figure 1. The "tube" part of the $Cs_2S_2O_7$ structure at 120 K. The indicated Cs – Cs distances are between 4.3 and 5.9 Å.

It is interesting to note that this type of tube structure, filled or empty, is also found in high pressure structures of group I, II and V metals, although with shorter metal – metal distances [2]. At 273 K two disulfate groups are partially disordered. As a result one caesium ion has an apparent C.N. of only seven, and a valence sum of 0.75. At 120 K the structure is fully ordered in a doubled unit cell, resulting in more regular caesium coordination and disulfate groups. The structure will be presented and discussed in terms of coordination geometry, and bond strength, and compared to other alkali disulfate structures.

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