

**STRUCTURES AND CRYSTAL CHEMISTRY OF SYNTHETIC  
Co- AND Ni-NATROCHALCITES: THE SHORTEST HYDROGEN BONDS  
AMONG MINERAL-TYPE COMPOUNDS**

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Several compounds with the general formula  $AMe_2(XO_4)_2[(H_2O)(OH)]$  are known as minerals, most of them crystallise in the monoclinic space group  $C2/m$ . They are subsumed in the literature as natrochalcite- or tsumcorite-group. This structure type is of special interest due to the occurrence of formal  $H_3O_2^-$ -units, forming two different hydrogen bonds. Depending on the particular composition, one of them is a very strong to strong H-bond, the other one is intermediate or weak. In the past, some synthetic natrochalcite-type compounds were synthesised and described, mainly focussing on representatives with  $Me = Cu^{2+}$  and  $X = S^{6+}$  or  $Se^{6+}$ , while varying the elements at the A position (e.g. GIESTER & ZEMANN, 1987).

In the present study we focussed on the crystal chemical differences that arise from the substitution of  $Cu^{2+}$  with  $Co^{2+}$  and  $Ni^{2+}$ . Single crystals of the Na-Co-S, Na-Ni-S, Na-Co-Se and K-Co-Se members were synthesised under low-hydrothermal conditions. The structures were determined from single-crystal X-ray CCD data in space group  $C2/m$  (see Table). The new compounds generally comply with the crystal chemical expectations for this structure type. The  $MeO_6$  polyhedra exhibit [2+2+2] co-ordinations (except in K-Co-Se) rather than the typical [4+2] Jahn-Teller distortion of the  $CuO_6$  polyhedron. Special attention was paid to the H-bonding system: with 2.420Å in Na-Ni-S and 2.429Å in the Na-Co-S-phase, the O...O distances of the stronger H-bond belong to the shortest ones known in purely inorganic compounds under ambient conditions.

The nature of the formal  $H_3O_2^-$ -unit was further investigated by polarised single-crystal IR-spectroscopy. The spectra are characterised by an extremely broad and asymmetric band, caused by the O-H stretching vibration of the strong H-bond. In the sulphates, the maximum of this band is located at  $\sim 1000\text{cm}^{-1}$ , while the stretching mode of the longer H-bond occurs at  $\sim 3350\text{cm}^{-1}$ . Summing up, the absorption bands can be assigned to stretching and bending modes of distinct OH- and  $H_2O$ -groups (cf. BERAN et al., 1997, for A-Cu-X). This indicates a non-centrosymmetric configuration of the " $H_3O_2^-$ -unit" and confirms the presence of a split H atom position within the strong hydrogen bond, even at O...O distances as short as 2.42Å.

| A-Me-X   | a (Å) | b (Å) | c (Å) | $\beta$ (°) | Me-O (Å, each 2_)   | O...O <sub>weak</sub> (Å) | O...O <sub>strong</sub> (Å) |
|----------|-------|-------|-------|-------------|---------------------|---------------------------|-----------------------------|
| Na-Ni-S  | 8.605 | 6.185 | 7.336 | 114.78      | 1.979, 2.089, 2.134 | 2.768                     | 2.420                       |
| Na-Co-S  | 8.677 | 6.317 | 7.396 | 115.40      | 2.011, 2.113, 2.190 | 2.750                     | 2.429                       |
| Na-Co-Se | 8.938 | 6.379 | 7.553 | 115.09      | 2.040, 2.098, 2.163 | 2.762                     | 2.459                       |
| K-Co-Se  | 9.078 | 6.471 | 7.687 | 113.99      | 2.061, 2.063, 2.201 | 2.890                     | 2.527                       |
| Na-Cu-S* | 8.809 | 6.187 | 7.509 | 118.74      | 1.954, 2.000, 2.327 | 2.695                     | 2.440                       |

\*GIESTER & ZEMANN (1987)

#### References

- GIESTER, G. & ZEMANN, J. (1987): Z. Kristallogr., 179, 431-442.  
BERAN, A., GIESTER, G. & LIBOWITZKY, E. (1997): Mineral. Petrol., 61, 223-235.