KOLLERITE, $(NH_4)_2Fe^{3+}(SO_3)_2(OH)\cdot H_2O$, A NEW SULFITE MINERAL

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Sulfite ions are rare constituents of minerals; so far only eight minerals containing $[SO_3]^{2-}$ groups have been approved by the IMA-CNMNC. During field work in the coal open pit near Köves Hill (Pécs-Vasas, Mecsek Mts., South Hungary) the new mineral kollerite was detected: $(NH_4)_2Fe^{3+}(SO_3)_2(OH)\cdot H_2O$, *Cmcm*, a = 17.803(7) Å, b = 7.395(4) Å, c = 7.096(3) Å, V = 934.2(7) Å^3, Z = 4. Data for structure investigation were collected on a Stoe StadiVari four-circle diffractometer (Dectris Pilatus 300 K pixel detector, MoKα radiation, 100 W air-cooled Incoatec IμS micro-focus X-ray tube, 50 kV, 1 mA).

The Fe^{3+} ion ($<Fe^{[6]}—O>$ = 1.963(2) Å) has site symmetry 2/*m*; the atoms S, O1, N, and two of the H atoms belonging to the NH_4 group are located at a mirror plane, the hydroxyl group as well as the O atom belonging to the water molecule (O_w) have site symmetry *m*2*m*. The water molecules exhibit an orientational disorder with (static or dynamic) half-occupied H atom positions. However, there is no hint for a long-range order. Despite the small size of the crystal used for data collection (6H7H65 μm), the atomic coordinates and isotropic displacement parameter of all H atoms could be refined without any restraints.

$<S^{[3]}—O>$ = 1.538(2) Å and O—S—O = 102.71(12) to 104.58(9)° accord with a sulfite group. The $[Fe(O_s)_4(O_h)_2]$ octahedra are corner linked to buckled chains *via* the O_h atoms and represent the backbone of the $[Fe(OH)(SO_3)_2]^{2-}$ chains running parallel to [001]. Similar chain topologies but with $[XO_4]^{2-}$ tetrahedra instead of the $[SO_3]^{2-}$ groups are known from the minerals tancoite, sideronatrit, and sideronatrite-2M.

Intercalated between the $[Fe(OH)(SO_3)_2]^{2-}$ chains are the water molecules and the ammonium cations. Linkage is achieved by hydrogen bonds only. Despite the loose connection, the $(NH_4)^+$ group is ordered and forms clearly defined hydrogen bonds. The N atom of the $(NH_4)^+$ cation has a tetrahedral environment: H—N—H and O···N···O are 101.14(11) to 115.24(8)°. The bond lengths N—H_n (0.81(3) and 0.90(5) Å), O_h—H_h (0.65(7) Å), and O_w—H_w (0.84(7) Å) are in the range expected for X-ray data. The hydrogen bonds are close to linearity (N/O—H···O = 169(4) / 176(4)°). The hydrogen bond lengths in general are relative long emphasising the loose connection of the $[Fe(OH)(SO_3)_2]^{2-}$ chains: N—H_n···O is 2.803(4) to 2.958 Å, O_h—H_h···O_w and O_w—H_w···O2 are 2.747(6) and 3.104(4) Å, respectively. The atomic arrangement accords with the needle-like shape of the crystals: the crystals are elongated parallel to [001], *i.e.,* the direction of the $[Fe(OH)(SO_3)_2]^{2-}$ chains.

Two further phases were found at the same locality: $(NH_4)_9Fe^{3+}(SO_3)_6$ is metastable; $(NH_4)_2Fe^{2+}(SO_3)_2$ crystallizes trigonal, $R\bar{3}m$, a = 5.3879(8) Å, c = 19.980(4) Å, V = 502.3 Å^3.