

## Crystal structure and spectroscopic behavior of synthetic novgorodovaite $\text{Ca}_2(\text{C}_2\text{O}_4)\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and its twinned triclinic heptahydrate analog

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Synthetic novgorodovaite mineral,  $\text{Ca}_2(\text{C}_2\text{O}_4)\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , is identical to its natural counterpart. Synthetic novgorodovaite analogue  $\text{Ca}_2(\text{C}_2\text{O}_4)\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  is identical to its natural counterpart. It crystallizes in the monoclinic  $I2/m$  space group with  $a = 6.9352(3)$ ,  $b = 7.3800(4)$ ,  $c = 7.4426(3)$  Å,  $\beta = 94.303(4)^\circ$ ,  $V = 379.85(3)$  Å<sup>3</sup> and  $Z = 2$ . The heptahydrate analogue,  $\text{Ca}_2(\text{C}_2\text{O}_4)\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ , crystallizes as triclinic twins in the  $P-1$  space group with  $a = 7.3928(8)$ ,  $b = 8.9925(4)$ ,  $c = 10.484(2)$  Å,  $\alpha = 84.070(7)$ ,  $\beta = 70.95(1)$ ,  $\gamma = 88.545(7)^\circ$ ,  $V = 655.3(1)$  Å<sup>3</sup> and  $Z = 2$ . The crystal packing of both calcium oxalate-chloride double salts favors the directional bonding of oxalate,  $\text{C}_2\text{O}_4$ , ligands to calcium ions as do other related calcium oxalate minerals. The  $\pi$ -bonding between C and O atoms of the  $\text{C}_2\text{O}_4^{2-}$  oxalate group leaves  $sp^2$ -hybridised orbitals of the oxygen atoms available for bonding to Ca. Thus, the Ca-O bonds in both calcium oxalate-chloride double salts are directed so as to lie in the plane of the oxalate group. This behaviour is reinforced by the short O...O distances between the oxygens attached to a given carbon atom, which favours them bonding to a shared Ca atom in bidentate fashion. Strong bonding in the plane of the oxalate anion and wide spacing perpendicular to that plane due to repulsion between oxalate  $\pi$ -electron clouds gives rise to a polymerized structural units which are common to both hydrates, explaining the nearly equal cell constants  $\sim 7.4$  Å which are defined by the periodicity of Ca-oxalate chains in the framework (monoclinic  $b \approx$  triclinic  $a$ ). When compared with novgorodovaite mineral, the higher water content of

$\text{Ca}_2(\text{C}_2\text{O}_4)\text{Cl}_2 \cdot 7\text{H}_2\text{O}$  makes for the major differences observed in their structures and ensuing physical properties. In fact, while keeping the above mentioned  $\text{Ca} \cdots (\text{C}_2\text{O}_4)^{2-}$  directional bonding, the highly polar water molecules displace the chlorine ions from the eight-fold calcium coordination sphere and also surround them through  $\text{OwH} \cdots \text{Cl}$  bonds to prevent the  $\text{Ca}^{2+} \cdots \text{Cl}^-$  close electrostatic contact observed in novgorodovaite. As a results of the above interactions, the  $\text{Ca}_2(\text{C}_2\text{O}_4)\text{Cl}_2 \cdot 7\text{H}_2\text{O}$  solid is arranged in  $\text{Ca}_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_5$  slabs parallel to (001) crystal plane, interspaced by hydrated chlorine slabs, a layered structure that accounts for (001) to be both an easily cleavage and a twinning plane. The infrared and Raman spectra of both salts were also recorded and are briefly discussed.

### **Crystal chemistry of organic minerals - salts of organic acids: the synthetic approach**

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The term 'organic minerals' means naturally occurring crystalline organic compounds including metal salts of formic, acetic, citric, mellitic and oxalic acids. As for the rest of the (inorganic) minerals, the primary tool to disclose their crystal and molecular structure and therefore to understand their mutual relationship with each other and with synthetic analogues and also their physicochemical properties is X-ray diffraction crystallography ever since the dawn of this methodology in 1913. The structure of several synthetic organic minerals was solved well before

the discovery of their natural counterpart. On the other hand, complete crystal structure determination of early discovered organic minerals had to await the advent of combined synthetic and advanced X-ray diffraction methods to fully unveil their crystal structures. We review here the crystal chemistry of organic minerals and show the importance of structural studies on their synthetic analogues. This will be highlighted by case studies on the recently reported synthetic novgorodovaite,  $\text{Ca}_2(\text{C}_2\text{O}_4)\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , and its heptahydrate analogue,  $\text{Ca}_2(\text{C}_2\text{O}_4)\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ , and the isotopic to each other stepanovite,  $\text{NaMg}[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 9\text{H}_2\text{O}$ , and zhemchuzhnikovite,  $\text{NaMg}[\text{Al}_x\text{Fe}_{1-x}(\text{C}_2\text{O}_4)_3] \cdot 9\text{H}_2\text{O}$ .

### **Spontaneous enantiomorphism in poly-phased alkaline salts of tris(oxalato) ferrate(III): crystal structure of cubic $\text{NaRb}_5[\text{Fe}(\text{C}_2\text{O}_4)_3]_2$**

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We show here that the phenomenon of spontaneous resolution of enantiomers occurs during the crystallization of the sodium and rubidium double salts of the transition metal complex tris(oxalato)ferrate(III), namely sodium penta-rubidium bis[tris(oxalato) ferrate (III)],  $\text{NaRb}_5[\text{Fe}(\text{C}_2\text{O}_4)_3]_2$ . One enantiomer of the salt crystallizes in the cubic space group  $P4_332$  with  $Z = 4$  and a Flack absolute structure parameter  $x = -0.01(1)$  and its chiral counterpart in the space group  $P4_132$  with  $x = -0.00(1)$ . All metal ions are at crystallographic special positions:

the Fe(III) ion is on a threefold axis, coordinated by three oxalate dianions in a propeller-like conformation. One of the two independent Rb(I) ions is on a twofold axis in an eightfold coordination with neighboring oxalate oxygen atoms, and the other one on a threefold axis in a sixfold  $\text{RbO}_6$  coordination. The sodium ion is at a site of  $D_3$  point group symmetry in a trigonal-antiprismatic  $\text{NaO}_6$  coordination.

### **Vanadio: Un Nuevo elemento estratégico ?**

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Se presentan los aspectos más importantes de la química del vanadio, comenzando con una breve introducción histórica y con un análisis de los depósitos de vanadio en nuestro país así como de su presencia en sistemas biológicos. A continuación se discute la obtención y principales propiedades del metal, presentando luego sus compuestos más importantes, incluyendo sus complejos de coordinación y compuestos organometálicos. Luego se analizan sus aplicaciones y usos más importantes, enfatizando especialmente su utilización en las nuevas baterías redox y discutiendo la eventual importancia que el elemento pueda tener en su desarrollo e implementación a amplia escala en un futuro próximo.

## Structural and spectroscopic behavior of double metal oxalates from the first transition metal series

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A series of double metal oxalates of stoichiometry  $MM'(C_2O_4)_2 \cdot 4H_2O$  (with  $MM' = MnCo, MnNi, MnZn, CoNi, CoCu, CoZn, NiCu, NiZn$  and  $CuZn$ ) have been prepared and characterized. Their structural behavior was investigated by means of X-ray powder diffractometry, showing a strong structural analogy to the orthorhombic, so-called  $\beta$ -modification, of the related simple oxalato complexes of composition  $MC_2O_4 \cdot 2H_2O$ . The vibrational spectroscopic behavior of the double metal oxalates was investigated by infrared and Raman spectroscopy. The results clearly confirmed the close structural analogies between the  $MM'(C_2O_4)_2 \cdot 4H_2O$ ,  $\beta$ - $MC_2O_4 \cdot 2H_2O$  and  $\alpha$ - $MC_2O_4 \cdot 2H_2O$  series of complexes.

## Structural and IR-spectroscopic characterization of pyridinium acesulfamate, a monoclinic twin

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The crystal structure of pyridinium 6-methyl-1,2,3-oxathiazine-4(3*H*)-one-2,2-dioxide [(C<sub>5</sub>NH<sub>6</sub>)(C<sub>4</sub>H<sub>4</sub>NO<sub>4</sub>S)], for short pyH(ace), was determined by X-ray diffraction methods. It crystallizes as a twin in the monoclinic space group *P*2<sub>1</sub>/*c* with *a* = 6.9878(9), *b* = 7.2211(7), *c* = 21.740(2) Å, β = 91.67(1)° and *Z* = 4 molecules per unit cell. The structure was determined employing 1599 reflections with *I* > 2 σ(*I*) from one of the twin domains and refined employing 2092 reflections from both crystal domains to an agreement R1 factor of 0.0466. Besides electrostatic attractions, intermolecular pyH...O=C(ace) hydrogen bonds stabilize the acesulfamate anion and the pyridinium cation into planar discrete units parallel to the (100) crystal plane. The units form stacks of alternating ace<sup>-</sup> and pyH<sup>+</sup> ions along the *a* axis that favors inter-ring π-π interactions. The FT-IR spectrum of the compound was recorded and is briefly discussed. Some comparisons with related pyridinium saccharinate salts are also made.

## **Cobalto: Un elemento crítico y estratégico**

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Se presentan los aspectos más importantes de la química del cobalto, comenzando con una breve introducción histórica y con algunos comentarios de los depósitos de cobalto en nuestro país así como sobre su presencia en sistemas biológicos. A continuación se discute la obtención y las principales propiedades del metal, presentando luego sus compuestos más importantes, incluyendo sus complejos de coordinación y compuestos organometálicos. Luego se analizan sus aplicaciones y usos más importantes, enfatizando especialmente su utilización en las nuevas tecnologías energéticas.