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Lazaraskeite, $Cu(C_2H_3O_3)_2$, the first organic mineral containing glycolate, from the Santa Catalina Mountains, Tucson, Arizona, U.S.A.

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Abstract

A new organic mineral species, lazaraskeite, ideally $Cu(C_2H_3O_3)_2$ with two polytypes M_1 and M_2, was discovered in the high elevation of the Santa Catalina Mountains, north of Tucson, Arizona, U.S.A. Both lazaraskeite-M_1 and -M_2 occur as euhedral individual crystals (up to 0.20 × 0.20 × 0.80 mm) or aggregates, with the former being more equant crystals and the latter bladed crystals elongated along the *c* axis. Associated minerals include chrysocolla, malachite, wulfenite, mimetite, hydroxylpyromorphite, hematite, microcline, muscovite, and quartz. Both polytypes are greenish-blue in transmitted light, transparent with white streak, and a vitreous luster. They are brittle and have a Mohs hardness of ~2; cleavage is perfect on {101}. No parting or twinning was observed. The measured and calculated densities are 2.12(2) and 2.138 g/cm^3, respectively, for lazaraskeite-M_1 and 2.10(2) and 2.086 g/cm^3 for lazaraskeite-M_2. Optically, lazaraskeite-M_1 is biaxial (−), with α = 1.595(3), β = 1.629(8), γ = 1.645(5), $2V_{meas}$ = 69(2)°, $2V_{cal}$ = 67°. Lazaraskeite-M_2 is also biaxial (−), with α = 1.520(5), β = 1.578(6), γ = 1.610(5), $2V_{meas}$ = 73(2)°, $2V_{cal}$ = 70°. Lazaraskeite is insoluble in water or acetone. An electron microprobe analysis for Cu and an Elemental Combustion System equipped with mass spectrometry for C yielded an empirical formula, based on 6 O apfu, $Cu_{1.01}(C_{1.99}H_{2.99}O_3)_2$ for lazaraskeite-M_1 and $Cu_{1.01}(C_{1.98}H_{3.00}O_3)_2$ for lazaraskeite-M_2. The measured $\delta^{13}C$ ‰ values are –37.7(1) and –37.8(1) for lazaraskeite-M_1 and -M_2, respectively.

Both lazaraskeite-M_1 and -M_2 are monoclinic with the same space group $P2_1/n$. The unit-cell parameters are *a* = 5.1049(2), *b* = 8.6742(4), *c* = 7.7566(3) Å, β = 106.834(2)°, *V* = 328.75(2) Å^3 for M_1 and *a* = 5.1977(3), *b* = 7.4338(4), *c* = 8.8091(4) Å, β = 101.418(2)°, *V* = 333.64(3) Å^3 for M_2. Lazaraskeite-M_1 is the natural analog of synthetic bis(glycolato)copper(II), $Cu(C_2H_3O_3)_2$. Its crystal structure is characterized by layers made of octahedrally coordinated Cu^{2+} cations and glycolate $(C_2H_3O_3)^-$ anionic groups. These layers, parallel to (101), are linked together by the strong hydrogen bonds (O-H···O = 2.58 Å). The CuO_6 octahedron is highly distorted, with four equatorial Cu-O bonds between 1.92 and 1.94 Å and two axial bonds at 2.54 Å. Lazaraskeite-M_2 has the same topology as lazaraskeite-M_1 and possesses all structural features of the low-temperature phase transformed from lazaraskeite-M_1 at 220 K (Yoneyama et al. 2013). The major di ferences between the two polytypes of lazaraskeite include: (1) M_1 has $b > c$, with β = 106.8°, whereas M_2 has $b < c$, with β = 101.4°; (2) the CuO_6 octahedron in M_1 is more elongated and distorted than in M_2; and (3) there is a relative change in the molecular orientation between the two structures.

Lazaraskeite represents the frst organic mineral that contains glycolate. Not only does its discovery imply that more glycolate minerals may be found, but also suggests that glycolate minerals may serve as a potential storage for biologically fxed carbon.

Keywords: Lazaraskeite, organic mineral, glycolate, crystal structure, X-ray diffraction