Inorganic tricarbonate: high-pressure synthesis of $K_2C_3O_7$

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Abstract

The synthesis of carbonates with novel anionic species is important for chemistry, geoscience, and materials science. Beyond common carbonates containing $[CO_3]^{2-}$ anions known at ambient conditions, high pressures can stabilize various sp^3-carbonates built of tetrahedral CO_4 units. At mild pressures, sp^2-pyrocarbonates with $[C_2O_5]^{2-}$ groups have also been reported. This suggests that the planar CO_3 unit, along with the tetrahedral CO_4 unit, can potentially also be a building block of exotic C-O anions at high pressure. This parallels borate chemistry, where diverse anions comprised of BO_3 and BO_4 building blocks exist. However, aside from the $[C_2O_5]^{2-}$ anion, no other species containing CO_3 units are known.

Here, we present the first inorganic tricarbonate salt, $K_2C_3O_7$, discovered in laser-heated diamond anvil cells at 55(3) and 45(2) GPa.[1] The crystal structure of $K_2C_3O_7$ was determined in situ using synchrotron single-crystal X-ray diffraction from a polycrystalline sample. It features non-planar $[C_3O_7]^{2-}$ anions, which consist of three corner-sharing planar CO_3 groups rotated relative to one another. This anion extends the homologous series of sp^2-carbonates: $[CO_3]^{2-}$ - $[C_2O_5]^{2-}$ - $[C_3O_7]^{2-}$. Raman spectroscopy establishes the characteristic vibrational fingerprint of the $[C_3O_7]^{2-}$ anion. Density functional theory (DFT) calculations corroborate the experimental results and suggest the thermodynamic stability of $K_2C_3O_7$ between 10 and 55 GPa. DFT calculations predict a phase transition between 80 and 90 GPa associated with a polymerization of the $[C_3O_7]^{2-}$ groups, accompanied by a change in the coordination polyhedra of two carbon atoms from triangles to tetrahedra. These findings highlight the rich structural chemistry accessible to carbonates under compression and suggest that additional sp^2- and mixed sp^2/sp^3-carbonates may be stabilized at high pressure.

Reference:

[1] A. Aslandukov, A. Aslandukova, F. I. Akbar, Y. Yin, R. Akilli, G. Garbarino, D. Spahr, B. Winkler, M. Bykov, N. Dubrovinskaia, L. Dubrovinsky, *JACS* **2026**, *148*, 15586–15592.