

Tetrahedral Tellurate

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A tetraethylammonium (TEA) salt of TeO_4^{2-} was synthesized by reacting $\text{Te}(\text{OH})_6$ with tetraethylammonium hydroxide. X-ray structural analysis of $(\text{TEA})_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ confirmed that this new compound consists of discrete TeO_4^{2-} anions of distorted tetrahedral structure together with TEA cations and water molecules of crystallization [$a = 8.0820(9)$ Å, $b = 13.7730(12)$ Å, $c = 20.1590(18)$ Å, $V = 2244.0(4)$ Å³, $Z = 4$, and space group *Pccb*]. The ¹²⁵Te NMR spectrum indicated that water reacts with the TeO_4^{2-} anion to regenerate octahedral tellurate species in solution.

Almost every textbook of inorganic chemistry states that tetrahedral telluric acid or tellurate anions do not exist or are virtually nonexistent.¹ Yet the congeneric selenic and sulfuric acids, oxo acids of the elements that lie just above tellurium in the periodic table, exist only in the tetrahedral form.² Periodic acid, isoelectronic with telluric acid, exists in both tetrahedral and octahedral forms.³ Thus, the nonexistence of tetrahedral telluric acid or tellurate is inconsistent with these findings. There has been a report that, in the confined environment of a mixed oxide $\text{Rb}_6\text{Te}_2\text{O}_9$, half of the Te atoms in the compound are tetrahedrally coordinated by four O atoms.⁴ There is also a report that all of the Te atoms in Cs_2TeO_4 are tetrahedrally coordinated by O atoms, although the crystallographic data given in the paper fail to reproduce tetrahedral TeO_4 units.⁵ These reports suggest that tetrahedral coordination of Te^{VI} by four O atoms is possible. However, the mixed oxide $\text{Rb}_6\text{Te}_2\text{O}_9$ has no solution

chemistry and there are anomalously strong Cs–O interactions (2.87 Å) in Cs_2TeO_4 . So, the existence of truly discrete tetrahedral tellurate ions, especially in solution, remains unconfirmed.

We now report that discrete tetrahedral tellurate ion exists in both the solid and solution states. We have successfully synthesized and structurally characterized a tetrahedral tellurate as its tetraethylammonium (TEA) salt.

The TEA salt of TeO_4^{2-} was synthesized by reacting $\text{Te}(\text{OH})_6$ with aqueous tetraethylammonium hydroxide (TEAOH), evaporating the solution under vacuum, and crystallizing the deliquescent solids thus obtained from acetonitrile.⁶ Crystals suitable for X-ray structural analysis were obtained by recrystallizing these crude crystals from dimethyl sulfoxide.⁷ Single crystal diffraction studies revealed that the crystal consists of TEA cations, water molecules of crystallization, and discrete TeO_4^{2-} anions having the structure shown in Figure 1. As can be seen from the figure, the TeO_4^{2-} anion assumes a tetrahedral structure analogous to that of SO_4^{2-} . There exist significant hydrogen-bonding interactions between the tellurate anions and the lattice–water molecules ($\text{O1} \cdots \text{O12}$, 2.793 Å; see Figure 2). As a result, the four Te–O bonds in the TeO_4^{2-} anion are

- (6) $\text{Te}(\text{OH})_6$ (1.17 g, 5.10 mmol) was dissolved in 15.0 mL of 10% aqueous TEAOH (10.2 mmol). The solution was stirred for 90 min before it was evaporated under vacuum to yield deliquescent colorless compound. The compound was then dissolved in 30 mL of acetonitrile, and the solution was evaporated to dryness under vacuum. After this dissolution–evaporation process was repeated three times, the colorless solids obtained were dissolved in 10 mL of acetonitrile under N_2 by heating the mixture with a heat gun for 10 min. The resulting pale-yellow solution was allowed to cool to ambient temperature and then allowed to stand at -35 °C overnight. The colorless plate-shaped crystals that formed were collected by filtration and washed with 2 mL of cold acetonitrile under N_2 to yield 2.30 g (4.63 mmol, 90.8% on Te) of analytically pure product. Anal. Calcd for $(\text{TEA})_2\text{TeO}_4 \cdot 2.5\text{H}_2\text{O}$ ($\text{C}_{16}\text{H}_{45}\text{N}_5\text{O}_{6.5}\text{Te}$): C, 38.65; H, 9.12; N, 5.63; Te, 25.7. Found: C, 38.56, H, 9.11; N, 5.92; Te, 26.0. IR (Nujol mull, 1000–400 cm^{-1}): 783 (vs), 721 (m), 676 (m), (610) (m), 510 (w), 418 (w). ¹⁷O NMR (40.68 MHz, CD_3CN): 164 ppm (25 °C, $\Delta\nu_{1/2} = 104$ Hz, $J_{\text{O}-\text{Te}} = 700$ Hz).
- (7) Single crystals of $(\text{TEA})_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ are, at 110(2) K, orthorhombic, space group *Pccb*, with $a = 8.0820(9)$ Å, $b = 13.7730(12)$ Å, $c = 20.1590(18)$ Å, $V = 2244.0(4)$ Å³, and $Z = 4$. A colorless crystal of dimensions $0.40 \times 0.20 \times 0.10$ mm³ was used for data collection. Diffraction data were collected on a Rigaku R-Axis Rapid diffractometer using Mo $K\alpha$ radiation. The final agreement factors were $R = 0.050$ for 2206 reflections with $F^2 > 2\sigma(F^2)$ and $wR(F^2) = 0.127$ for 2584 unique reflections.

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- (2) Examples of octahedral and five-coordinated selenate anions, however, have been discovered recently: Haas, H.; Jansen, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4362–4364.
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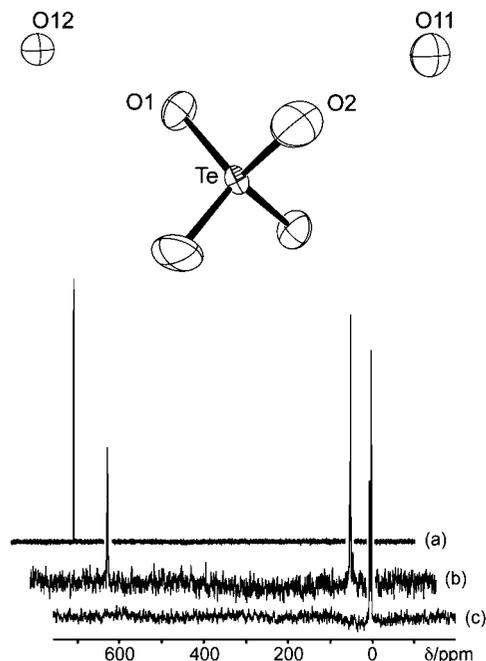


Figure 1. Structure of the TeO_4^{2-} anion (top) and the change of the ^{125}Te NMR spectrum of TeO_4^{2-} with water addition (bottom). O atoms of lattice-water molecules (O11 and O12) are depicted together with the TeO_4^{2-} anion. The ellipsoids are drawn to encompass 50% probability levels: (a) no water added; (b) 10% water; (c) 100% water.

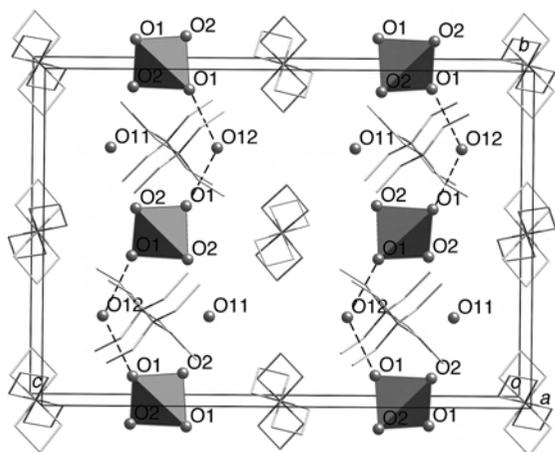


Figure 2. Perspective view of the unit cell along the a axis. The TeO_4^{2-} units are represented by tetrahedra and the TEA cations by wireframes. H atoms are omitted for clarity. One of the two crystallographically independent TEA cations is disordered in two orientations about the inversion center. Significant hydrogen-bonding interactions are indicated by broken lines.

divided into two groups: shorter ones ($\text{Te}-\text{O}_2$, 1.765 Å) and longer ones ($\text{Te}-\text{O}_1$, 1.854 Å). This splitting together with a slight twisting of the tetrahedron reduces the rigorous crystallographic symmetry of the TeO_4^{2-} anion to 2 from its ideal $\bar{4}3m$. However, there are no significant interactions between TEA cations and TeO_4^{2-} anions in the current compound.

The $\text{Te}-\text{O}$ bond lengths in the anion are significantly shorter than those observed for the telluric acid and other tellurate anions where the Te atoms are coordinated by six O atoms that form an octahedron.^{8–11} The lengths of the shorter $\text{Te}-\text{O}_2$ bonds are comparable to those of $\text{I}-\text{O}$ bonds in the tetrahedral IO_4^- ion.^{12,13} These facts are consistent with the tetrahedral structure of the current anion, where the Te atom is coordinated by only four O atoms. Yet the $\text{Te}-\text{O}$ length in the TeO_4^{2-} anion is long for a tetrahedral oxo anion. With the exception of the IO_4^- anion that transforms into the octahedral form under certain conditions, all tetrahedral oxo anions have much shorter bonds. The long $\text{Te}-\text{O}$ distance makes the coordination space around the Te atom relatively uncrowded. All of the $\text{O}\cdots\text{O}$ distances within the TeO_4^{2-} anion are significantly longer than 2.8 Å (twice the ionic radius of O^{2-}), with the longest one as long as 3.024 Å. This openness would make the central Te atom accessible for small molecules such as water. In fact, the ^{125}Te NMR spectra indicated that water reacts with the TeO_4^{2-} anion to form octahedral tellurate species in solution (Figure 1).¹⁴ An acetonitrile solution of $(\text{TEA})_2\text{TeO}_4$ gave a single ^{125}Te NMR signal at 610 ppm at 25 °C. This value is comparable to that reported for Cs_2TeO_4 in the solid state (601 ppm).⁵ When water was added to this solution, another signal assignable to an octahedral TeO_6 species appeared around 0 ppm.^{15,16} Upon further addition of water, the 610 ppm peak totally disappeared, indicating a total conversion of the tetrahedral TeO_4^{2-} anion into octahedral tellurate species.

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Supporting Information Available: Crystallographic data for $(\text{TEA})_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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