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# A new synthetic cobalt tellurate: $Co_3TeO_6$

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Single crystals of tricobalt(II) tellurium(VI) hexaoxide, $Co_3TeO_6$, were synthesized *via* transport reactions using HCl as transporting agent. The compound crystallizes in the monoclinic system (space group $C2/c$). The Te atoms are positioned in $4b$ ($\bar{1}$) and $8f$ positions, while the Co atoms are in $4e$ (2) and $8f$ positions. The structure consists of (100) oxygen layers packed in a hhchhc sequence, with $Te^{VI}$ in octahedral coordination and $Co^{II}$ in both octahedral and tetrahedral coordination. The structure contains face-sharing $CoO_6$ octahedra, as well as edge-sharing $CoO_4$ tetrahedra. $Co_3TeO_6$ is the first oxide that is isostructural with the $\beta$-$Li_3MF_6$ family of compounds ($M$ = Al, Cr, Ga, Ti and V).

## Comment

The crystal chemistry of the metal tellurates, $M_3TeO_6$, has proved to be rich, and a number of compounds with various crystal structures have previously been described, for example, $Ni_3TeO_6$ (Bayer, 1967; Newnham & Meagher, 1967), $Cu_3TeO_6$ (Falck *et al.*, 1978) and $Mg_3TeO_6$ (Schulz & Bayer, 1971). $Ni_3TeO_6$ and $Mg_3TeO_6$ crystallize in the rhombohedral space group $R3$, with a corundum-related structure of octahedrally coordinated Ni, Mg and Te atoms substituting for Al. $Cu_3TeO_6$ crystallizes in the cubic space group $Ia\bar{3}$, with a bixbyite-type structure of cubic close-packed O atoms and octahedrally coordinated Cu and Te atoms. The crystal structure of $Co_3TeO_6$ was thus impossible to predict, since $Co^{II}$ can occur in both tetrahedral and octahedral coordinations, as seen, for instance, in $Co_6(TeO_3)_2(TeO_6)Cl_2$ (Becker & Johnsson, 2004). Indeed, $Co_3TeO_6$ was found to crystallize with a different structure type corresponding to that of the lithium cryolite family, $\beta$-$Li_3MF_6$. Several $\beta$-$Li_3MF_6$ compounds have been described previously for $M$ = Al, Cr, Ga, Ti and V (Massa & Rüdorff, 1971; Tyagi & Köhler, 1992, 1997, 1999, 2000; Tyagi *et al.* 1996). To the best of our knowledge, $Co_3TeO_6$ is the first oxide with this structure type.

$Co_3TeO_6$ crystallizes in the monoclinic space group $C2/c$. The two crystallographically distinct $Te^{VI}$ cations occupy octahedral sites such that $TeO_6$ octahedra are not directly connected to each other. Four of the five crystallographically distinct $Co^{II}$ cations (Co1, Co2, Co3 and Co4) occupy octahedral sites, although Co3 is only five-coordinated in a square-pyramidal fashion because the Co3—O2 bond is elongated (Table 1). Atom Co5 occupies a tetrahedral site. The Te and Co atoms can be regarded as being arranged in layers (Fig. 1). The Co atoms form a pseudo-hexagonal arrangement in the [201] direction and the Te atoms are located in the channels. The O atoms are approximately close packed in a mixed hexagonal–cubic hhchhc six-layer sequence along [100]. The 'c' layer contains atoms O4, O8 and O9, while the two 'h' layers contain atoms O1, O2, O3, O5, O6 and O7 (Fig. 1).

Bond valence sum (BVS) calculations for the Te atoms give values of 5.90 and 5.79 v.u. (valence units) for Te1 and Te2, respectively, with an $R_0$ value of 1.917 (Brown & Altermatt, 1985). BVS calculations for the Co atoms yield values of 1.93,

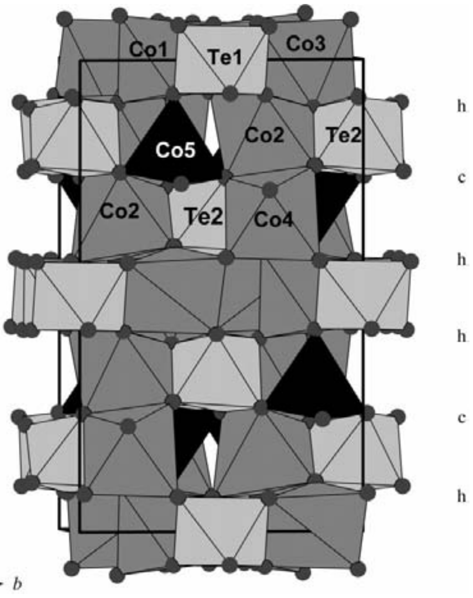

**Figure 1**
Oxygen packing and cation coordination in $Co_3TeO_6$.

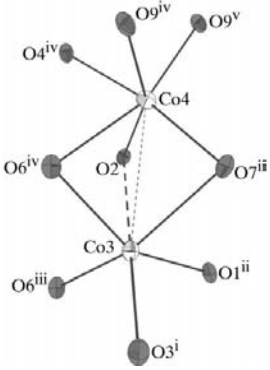

**Figure 2**
Face-sharing between $Co3O_{5+1}$ and $Co4O_6$ octahedra, with an elongated Co3—O2 bond. [Symmetry codes: (i) $-x+1, -y-1, -z$; (ii) $-x+1, -y, -z$; (iii) $-x+1, y, -z+\frac{1}{2}$; (iv) $x, -y-1, z-\frac{1}{2}$; (v) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.]

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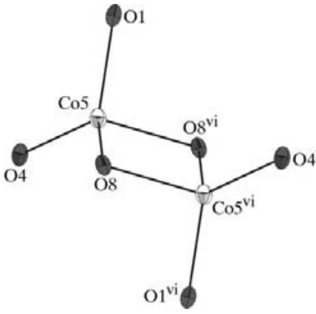

**Figure 3**
Edge-sharing between two $Co5O_4$ tetrahedra. [Symmetry code: (vi) $-x+\frac{3}{2}, -y+\frac{1}{2}, -z+1$.]

1.87 and 1.85 v.u. for Co1, Co2 and Co4, respectively, with an $R_0$ value of 1.685 (Wood & Palenik, 1998). BVS calculations for Co3 (Fig. 2) give a value of 1.86 v.u. when including the five primary Co—O bonds. The sixth O atom (O2) contributes 0.035 v.u. only, which is significantly below the lower limit of 0.08 v.u. (4% of the cation valence) to be regarded as bonded (Brown, 2002). A likely reason for the distortion of the Co3 coordination is discussed below. A similar but smaller distortion is also seen for atom Co2, which retains a formal octahedral coordination. The distortions seen for the $Co2O_6$ and $Co3O_6$ octahedra are also observed in the $LiO_6$ octahedra of the isostructural $\beta$-$Li_3MF_6$ phases. Finally, atom Co5 has a tetrahedral coordination with a bond valence sum of 1.86 v.u.

The Co polyhedra are connected *via* corner-, edge- and face-sharing through the Co—O bonds. Two of the more remarkable situations within the structure are: (i) the edge-sharing between two adjacent $Co5O_4$ tetrahedra, an unusual situation that can only occur in a cubic close packing (Fig. 3), and (ii) the face-sharing between $Co3O_{5+1}$ and $Co4O_6$, which could account for the elongation of the Co3—O2 bond (Fig. 2).

## Experimental

Single crystals of $Co_3TeO_6$ were synthesized *via* chemical vapour transport redox reactions in sealed evacuated silica tubes. The starting materials were $Co_3O_4$ (Alfa Aesar 99.7%), $TeO_2$ (Acros 99%) and $CoCl_2$ (Alfa Aesar 99.9%) mixed in the off-stoichiometric molar ratio 4:3:1. The starting mixture was loaded at one end of a silica tube, which was subsequently evacuated to $10^{-5}$ Torr. HCl gas (electronic grade purity) was introduced as a transporting agent and the tube was sealed off. The ampoule was subsequently placed in a two-zone furnace with charge- and growth-zone temperatures of 973 and 873 K, respectively. After 15 d, dark-violet single crystals of $Co_3TeO_6$ with a size of about 3 × 2 × 1 mm had grown in the centre of the ampoule. The crystal used for the data collection was a fragment of a larger crystal. A number of small crystals of an unknown compound also formed at the cold end of the silica tube.

### *Crystal data*

$Co_3TeO_6$
$M_r = 400.39$
Monoclinic, $C2/c$
$a = 14.8167\ (18)$ Å
$b = 8.8509\ (11)$ Å
$c = 10.3631\ (14)$ Å
$\beta = 94.900\ (10)^\circ$
$V = 1354.1\ (3)$ Å$^3$
$Z = 12$
$D_x = 5.892$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 17.18$ mm$^{-1}$
$T = 292\ (3)$ K
Block, purple
0.14 × 0.08 × 0.03 mm

### *Data collection*

Oxford Xcalibur diffractometer
$\omega$ scan at different $\varphi$
Absorption correction: numerical [*X-RED* (Stoe & Cie, 2001) and *X-SHAPE* (Stoe & Cie, 1999)]
$T_{min} = 0.186$, $T_{max} = 0.542$
8340 measured reflections
1333 independent reflections
1256 reflections with $I > 2\sigma(I)$
$R_{int} = 0.076$
$\theta_{max} = 26.4^\circ$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.088$
$S = 1.17$
1333 reflections
139 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2 + 1.2572P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.24$ e Å$^{-3}$
$\Delta\rho_{min} = -1.64$ e Å$^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0051 (2)

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Te1—O5 | 1.908 (3) | Co2—O8 | 2.538 (4) |
| Te1—O7 | 1.938 (3) | Co3—O3 | 1.936 (3) |
| Te1—O1 | 1.951 (3) | Co3—$O6^{iii}$ | 2.032 (4) |
| Te2—O3 | 1.910 (3) | Co3—$O6^{iv}$ | 2.050 (3) |
| Te2—O9 | 1.925 (3) | Co3—$O1^{ix}$ | 2.078 (3) |
| Te2—O6 | 1.927 (4) | Co3—$O7^{x}$ | 2.212 (3) |
| Te2—O2 | 1.927 (3) | Co3—$O2^{i}$ | 2.925 (3) |
| Te2—O8 | 1.933 (3) | Co4—O2 | 1.982 (3) |
| Te2—$O4^{iv}$ | 1.969 (3) | Co4—$O9^{v}$ | 2.030 (3) |
| Co1—O2 | 2.054 (3) | Co4—$O9^{iv}$ | 2.065 (3) |
| Co1—$O5^{vii}$ | 2.107 (3) | Co4—$O7^{v}$ | 2.131 (3) |
| Co1—$O1^{viii}$ | 2.161 (3) | Co4—$O4^{iv}$ | 2.282 (3) |
| Co2—$O3^{v}$ | 1.963 (3) | Co4—$O6^{iv}$ | 2.389 (3) |
| Co2—$O4^{iv}$ | 2.008 (3) | Co5—O4 | 1.929 (3) |
| Co2—O5 | 2.023 (3) | Co5—O1 | 1.966 (4) |
| Co2—$O7^{iv}$ | 2.087 (4) | Co5—O8 | 1.988 (4) |
| Co2—$O9^{v}$ | 2.419 (3) | Co5—$O8^{viii}$ | 1.998 (3) |

Symmetry codes: (i) $-x+1, -y-1, -z$; (iii) $-x+1, y, -z+\frac{1}{2}$; (iv) $x, -y-1, z-\frac{1}{2}$; (v) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (vii) $x-\frac{1}{2}, y+\frac{1}{2}, z$; (viii) $-x+\frac{3}{2}, -y-\frac{1}{2}, -z+1$; (ix) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (x) $x-\frac{1}{2}, -y-\frac{3}{2}, z-\frac{1}{2}$.

The maximum residual electron density is located 0.76 Å from atom Te2, at (0.1119, 0.0058, 0.7768), and the minimum is located 1.03 Å from atom Te1, at (0.4388, −0.0029, 0.0399).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3008). Services for accessing these data are described at the back of the journal.

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