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The solid solution $Co_{3.6}Mg_{1.4}Cl_2(TeO_3)_4$

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Key indicators: single-crystal X-ray study; T = 292 K; mean σ(Se–O) = 0.004 Å; disorder in main residue; R factor = 0.044; wR factor = 0.064; data-to-parameter ratio = 30.1.

Single crystals of the cobalt magnesium dichloride tetrakis[trioxotellurate(IV)] solid solution $Co_{5-y}Mg_y(TeO_3)_4Cl_2$ [y = 1.4] were obtained from solid–gas phase reactions in sealed evacuated silica tubes. The crystal symmetry is monoclinic and the compound is isostructural with $Co_5(TeO_3)_4X_2$ and $Ni_5(TeO_3)_4X_2$ (X = Cl, Br). The layered structure comprises distorted MO_6 and MO_5Cl octahedra (M = statistically occupied Co and Mg sites) and TeO_3E tetrahedra (E = stereochemically active electron lone pair of Te^{IV}). Five face-sharing MO_6 octahedra make up claw-like $[M_5O_{16}Cl_2]$ units which form layers by corner-sharing with four other such units and by corner- and edge-sharing with TeO_3E tetrahedra. The layers are held together only by weak van der Waals forces with a closest Te⋯Cl distance of 3.184 (2) Å between two layers.

Related literature

For isostructural compounds, see: Johnsson *et al.* (2003); Becker, Prester, Berger, Johnsson *et al.* (2007); for compounds with the same formula type but different structures, see: Becker, Prester, Berger, Hui Lin *et al.* (2007); Jiang & Mao (2006); Shen *et al.* (2005); for related Te^{IV} containing compounds with transition and alkaline earth metals, see: Feger & Kolis (1998); Takagi & Johnsson (2005, 2006); Takagi *et al.* (2006); for structural peculiarities of Te^{IV} compounds, see: Galy *et al.* (1975); Bondi (1964).

Experimental

Crystal data

$Co_{3.617}Mg_{1.383}Cl_2(TeO_3)_4$
M_r = 1020.08
Monoclinic, $C2/c$
a = 19.8551 (11) Å
b = 5.2584 (2) Å
c = 16.4637 (10) Å
β = 125.3607 (7)°
V = 1401.81 (13) $Å^3$
Z = 4
Mo $K\alpha$ radiation
μ = 12.87 mm^{-1}
T = 292 K
0.11 × 0.10 × 0.08 mm

Data collection

Oxford Diffraction Xcalibur3 diffractometer
Absorption correction: numerical [*X-RED* (Stoe & Cie, 1999) and *X-SHAPE* (Stoe & Cie, 2001)]
T_{min} = 0.145, T_{max} = 0.220
8065 measured reflections
3246 independent reflections
2376 reflections with $I > 3\sigma(I)$
R_{int} = 0.056

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.064
S = 1.48
3246 reflections
108 parameters
$\Delta\rho_{max}$ = 3.82 e $Å^{-3}$
$\Delta\rho_{min}$ = −3.94 e $Å^{-3}$

Table 1
Selected bond lengths (Å).

$Te1—O3^{i}$	1.876 (4)	$M2—Cl1^{vii}$	2.4616 (16)
$Te1—O5^{ii}$	1.881 (5)	$M2—O1^{iv}$	2.069 (4)
$Te1—O6^{iii}$	1.870 (4)	$M2—O3^{viii}$	2.020 (5)
Te2—O1	1.907 (5)	M2—O4	2.218 (5)
Te2—O2	1.834 (5)	M2—O5	2.270 (3)
Te2—O4	1.876 (4)	M2—O6	2.037 (4)
$M1—O1^{iv}$	2.104 (4)	M3—O1	2.191 (5)
$M1—O1^{v}$	2.104 (4)	$M3—O2^{vi}$	2.056 (3)
M1—O4	2.019 (3)	M3—O3	2.035 (5)
$M1—O4^{vi}$	2.019 (3)	M3—O4	2.296 (5)
M1—O5	2.397 (6)	M3—O5	2.072 (4)
$M1—O5^{vi}$	2.397 (6)	M3—O6	2.098 (3)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *JANA2000* (Petříček *et al.*, 2000); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *JANA2000*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2109).

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supplementary materials

Acta Cryst. (2007). E**63**, i146-i147 [**doi:10.1107/S1600536807024014**]

The solid solution $Co_{3.6}Mg_{1.4}Cl_2(TeO_3)_4$

R. Takagi, D. T. Hjelmqvist and **M. Johnsson**

Comment

The aim of this study was to introduce Mg^{II} into the Co^{II}—Te^{IV}—O—Cl system. Some few transition metal oxohalides comprising both Te^{IV} and an alkaline earth element have been described before, *e.g.* $Ba_2Cu_4Te_4O_{11}Cl_4$ (Feger & Kolis, 1998), $Ca_2CuTe_4O_{10}Cl_2$ (Takagi & Johnsson, 2005), $Sr_2Cu_2TeO_6Br_2$ (Takagi & Johnsson, 2006) and $SrCu_2(TeO_3)_2Cl_2$ (Takagi *et al.*, 2006). In this communication we report the synthesis and crystal structure of the new compound $Co_{3.6}Mg_{1.4}(TeO_3)_4Cl_2$ (I). The refinement proved (I) to be isostructural to $Co_5(TeO_3)_4X_2$ (X = Cl, Br) (Becker, Prester, Berger, Johnsson *et al.*, 2007) and $Ni_5(TeO_3)_4X_2$ (Johnsson *et al.*, 2003). The corresponding Se-compounds are, however, not isostructural and the four compounds $Co_5(SeO_3)_4X_2$ and $Ni_5(SeO_3)_4X_2$ (X=Cl, Br) are all triclinic and crystallize in two different structure types (Becker, Prester, Berger, Hui Lin *et al.*, 2007; Jiang & Mao, 2006; Shen *et al.*, 2005).

There are two crystallographic distinct Te positions that both have a TeO_3E tetrahedral coordination (E = lone pair electrons of Te^{IV}). The Te(1)O_3E tetrahedron is quite regular while the Te(2)O_3E tetrahedron is more distorted. Te(1) has a fourth neighbouring oxygen atom located at 2.706 (5) Å, however, a distance that is too long to be considered as belonging to the primary coordination sphere. Geometrically placing the lone pairs under assumption of a Te - E distance (radius) of 1.25 Å (Galy *et al.*, 1975) gives the fractional coordinates for E(1) with $x = 0.3149$, $y = 0.1870$, $z = 0.2989$, and for E(2) with $x = 0.2073$, $y = 0.2878$, $z = 0.4325$, respectively. The metal positions, *M*, are statistically occupied by Co and Mg. The *M*(1) and *M*(3) sites have a distorted MO_6 octahedral coordination with M—O distances ranging from 2.019 (3) Å to 2.397 (6) Å). The *M*(2) site has a MO_5Cl distorted octahedral coordination with M—O distances ranging from 2.020 (5) to 2.270 (3) Å, while the M—Cl distance is 2.4616 (16) Å (Table 1).

The structural arrangement of (I) is layered, see Figure 1. The layers extend parallel to (100) and consist of TeO_3E, MO_6 and MO_5Cl polyhedra. The *M*-polyhedra make up building blocks constituting five MO_6 octahedra which, by face sharing, make up a claw-like $[M_5O_{16}Cl_2]$ unit. These units form layers by corner-sharing to four other such units and by corner- and edge-sharing to the TeO_3E tetrahedra. The halides and the electron lone-pairs (E) of Te^{IV} protrude from the layers to the empty space. The closest Te—Cl distance between two layers is 3.184 (2) Å. This distance is substantially shorter than the expected van der Waals distance of 3.81 Å (Bondi, 1964) indicating that there is a stronger interaction between two layers.

The highest fraction of Mg is present at the *M*(1) and *M*(3) sites that both coordinate solely to oxygen atoms. The shortest M—*M* distance between two layers is 5.832 (2) Å, which is slightly longer than in the structure of $Co_5(TeO_3)_4Cl_2$ (5.690 (7) Å).

Experimental

Single crystals of compound (I) were synthesized from MgO (Merck, 99.99%), $CoCl_2$ (Aldrich, +97%), CoO (Alfa Aesar, +99%), and TeO_2 (ABCR, +99%) in the molar ratio 1:1:1:2. The components were mixed in a mortar and placed in a silica tube (length ~5 cm) which was then evacuated. The sample tube was heated at 920 K for 70 h in a muffle furnace to allow for solid-gas phase reactions. The final non-hygroscopic product consisted of a mixture of a purple powder, a brown powder, and blue transparent prismatic single crystals of (I). Analysis by energy dispersive spectrometry (EDS, LINK AN10000) of the crystal used for the diffraction experiment gave (at-%): 36.3% Te, 33.0% Co, 12.5% Mg, and 18.1% Cl. The Co:Mg ratio was thus found to be 73:27 = 2.7 which is in very good agreement with the composition determined from structure refinement (ratio 2.6).

Refinement

The initial refinement presumed a structure without incorporation of magnesium and converged with good residuals, but the occupancy and the displacement parameters for the Co positions proved unsatisfactory. Refinement by assuming fully occupied metal sites and allowing for a statistical occupation of Co and Mg showed that the *M*(1) site is occupied by Mg with approximately 50%, the *M*(2) site with 13%, and the *M*(3) site with 32%. The highest peak and the deepest hole in the residual electron density map are 0.89 Å and 0.71 Å, respectively, from Te(1) and Te(2).

Figures

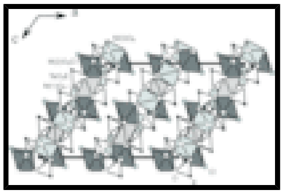

Fig. 1. The crystal structure of (I) in projection along [010].

cobalt magnesium dichloride tetrakis[trioxotellurate(IV)]

Crystal data

$Co_{3.617}Mg_{1.383}Cl_2(TeO_3)_4$

$M_r = 1020.08$

Monoclinic, $C2/c$

Hall symbol: -C 2yc

$a = 19.8551$ (11) Å

$b = 5.2584$ (2) Å

$c = 16.4637$ (10) Å

$\beta = 125.3607$ (7)°

$V = 1401.81$ (13) Å^3

$Z = 4$

$F_{000} = 1809$

$D_x = 4.832$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å

Cell parameters from 5897 reflections

$\theta = 3.9$–36.8°

$\mu = 12.87$ mm^{-1}

$T = 292$ K

Prism, blue

0.11 × 0.10 × 0.08 mm

Data collection

Oxford Diffraction Xcalibur3 diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 292$ K

φ–scan

Absorption correction: numerical [X-RED (Stoe & Cie, 1999) and X-Shape (Stoe & Cie, 2001)]

$T_{\min} = 0.145$, $T_{\max} = 0.220$

8065 measured reflections

3246 independent reflections

2376 reflections with $I > 3\sigma(I)$

$R_{\text{int}} = 0.056$

$\theta_{\max} = 36.8°$

$\theta_{\min} = 4.1°$

$h = -33 \rightarrow 33$

$k = -6 \rightarrow 8$

$l = -23 \rightarrow 27$

Refinement

Refinement on F

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.064$

$S = 1.48$

3246 reflections

108 parameters

Weighting scheme based on measured s.u.'s $w = 1/(\sigma^2(F) + 0.0004F^2)$

$(\Delta/\sigma)_{\max} = 0.018$

$\Delta\rho_{\max} = 3.82$ e Å^{-3}

$\Delta\rho_{\min} = -3.94$ e Å^{-3}

Extinction correction: none

Special details

Refinement. Single crystal X-ray data was collected on an Oxford Diffraction Xcalibur3 diffractometer using graphite-monochromated Mo Kα radiation, λ = 0.71073 Å. The intensities of the reflections were integrated using the supplied software CrysAlis (Oxford Diffraction, 2006) by the manufacturer. Numerical absorption correction was performed with the programs *X-RED* (Stoe & Cie, 1999) and *X-SHAPE* (Stoe & Cie, 2001). The structure was solved by direct methods: *SHELXS97* (Sheldrick, 1997) and refined by full matrix least squares on F using the program JANA2000 (Petříček *et al.*, 2000). All atoms including the mixed Co and Mg positions were refined with anisotropic temperature parameters. Molecular graphics were prepared with the program *DIAMOND* (Brandenburg, 1996).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Te1	0.37266 (2)	0.19170 (7)	0.36070 (2)	0.01174 (14)	
Te2	0.14654 (2)	0.28795 (7)	0.37921 (2)	0.01156 (13)	
Co1	0	−0.2441 (3)	0.25	0.0193 (7)	0.500 (10)
Mg1	0	−0.244 (3)	0.25	0.0193 (7)	0.500 (10)
Co2	0.09308 (5)	−0.22203 (15)	0.47692 (6)	0.0126 (3)	0.874 (7)
Mg2	0.09308 (5)	−0.22203 (15)	0.47692 (6)	0.0126 (3)	0.126 (7)
Co3	−0.01002 (6)	0.22050 (18)	0.38052 (6)	0.0129 (4)	0.685 (8)
Mg3	−0.01002 (6)	0.22050 (18)	0.38052 (6)	0.0129 (4)	0.315 (8)
Cl1	0.25953 (10)	−0.1767 (3)	0.40309 (12)	0.0252 (6)	
O1	0.0661 (2)	0.5050 (7)	0.3715 (3)	0.0140 (14)	

O2	0.1135 (3)	0.3485 (8)	0.2513 (3)	0.0199 (17)
O3	−0.0733 (2)	0.3903 (7)	0.4283 (3)	0.0144 (15)
O4	0.0777 (2)	0.0109 (7)	0.3549 (3)	0.0144 (15)
O5	−0.0432 (2)	−0.1600 (7)	0.3564 (3)	0.0142 (15)
O6	0.0971 (2)	0.1415 (8)	0.5224 (3)	0.0169 (16)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Te1	0.01354 (16)	0.01096 (16)	0.01182 (15)	0.00027 (11)	0.00798 (12)	0.00053 (10)
Te2	0.01231 (15)	0.01128 (16)	0.01157 (14)	0.00008 (11)	0.00718 (12)	−0.00018 (10)
Co1	0.0244 (9)	0.0110 (7)	0.0117 (7)	0	0.0041 (6)	0
Mg1	0.0244 (9)	0.0110 (7)	0.0117 (7)	0	0.0041 (6)	0
Co2	0.0178 (4)	0.0093 (4)	0.0134 (4)	0.0010 (3)	0.0107 (3)	0.0004 (3)
Mg2	0.0178 (4)	0.0093 (4)	0.0134 (4)	0.0010 (3)	0.0107 (3)	0.0004 (3)
Co3	0.0161 (5)	0.0106 (5)	0.0149 (4)	0.0008 (3)	0.0107 (4)	0.0006 (3)
Mg3	0.0161 (5)	0.0106 (5)	0.0149 (4)	0.0008 (3)	0.0107 (4)	0.0006 (3)
Cl1	0.0197 (6)	0.0307 (8)	0.0244 (7)	0.0018 (6)	0.0122 (5)	−0.0025 (6)
O1	0.0169 (17)	0.0094 (16)	0.0149 (15)	0.0027 (14)	0.0088 (13)	0.0015 (13)
O2	0.025 (2)	0.0213 (19)	0.0144 (16)	−0.0048 (17)	0.0123 (15)	0.0025 (15)
O3	0.0213 (18)	0.0119 (16)	0.0154 (15)	0.0028 (15)	0.0136 (14)	0.0039 (13)
O4	0.0169 (17)	0.0123 (16)	0.0173 (16)	−0.0040 (14)	0.0118 (14)	−0.0029 (13)
O5	0.0154 (17)	0.0096 (16)	0.0200 (17)	−0.0001 (14)	0.0116 (14)	0.0015 (13)
O6	0.0240 (19)	0.0121 (16)	0.0156 (16)	0.0012 (16)	0.0120 (15)	−0.0002 (14)

Geometric parameters (Å, °)

Te1—O2^{i}	2.706 (5)	M2—Mg3	2.8920 (7)
Te1—O3^{ii}	1.876 (4)	M2—Cl1^{viii}	2.4616 (16)
Te1—O5^{iii}	1.881 (5)	M2—O1^{v}	2.069 (4)
Te1—O6^{iv}	1.870 (4)	M2—O3^{ix}	2.020 (5)
Te2—O1	1.907 (5)	M2—O4	2.218 (5)
Te2—O2	1.834 (5)	M2—O5	2.270 (3)
Te2—O4	1.876 (4)	M2—O6	2.037 (4)
M1—O1^{v}	2.104 (4)	M3—O1	2.191 (5)
M1—O1^{vi}	2.104 (4)	M3—O2^{vii}	2.056 (3)
M1—O4	2.019 (3)	M3—O3	2.035 (5)
M1—O4^{vii}	2.019 (3)	M3—O4	2.296 (5)
M1—O5	2.397 (6)	M3—O5	2.072 (4)
M1—O5^{vii}	2.397 (6)	M3—O6	2.098 (3)
M2—M3	2.8920 (12)		
O2^{i}—Te1—O3^{ii}	65.95 (16)	Cl1^{viii}—M2—O4	108.86 (13)
O2^{i}—Te1—O5^{iii}	78.97 (17)	Cl1^{viii}—M2—O5	174.24 (13)
O2^{i}—Te1—O6^{iv}	156.31 (14)	Cl1^{viii}—M2—O6	97.62 (11)
O3^{ii}—Te1—O5^{iii}	99.06 (19)	O1^{v}—M2—O3^{ix}	105.78 (17)
O3^{ii}—Te1—O6^{iv}	93.00 (17)	O1^{v}—M2—O4	77.91 (16)

O5^{iii}—Te1—O6^{iv}	94.6 (2)
O1—Te2—O2	95.2 (2)
O1—Te2—O4	88.37 (19)
O2—Te2—O4	99.07 (18)
O1^{v}—M1—O1^{vi}	102.34 (15)
O1^{v}—M1—O4	81.71 (14)
O1^{v}—M1—O4^{vii}	167.7 (2)
O1^{v}—M1—O5	73.18 (17)
O1^{v}—M1—O5^{vii}	121.38 (17)
O1^{vi}—M1—O1^{v}	102.34 (15)
O1^{vi}—M1—O4	167.7 (2)
O1^{vi}—M1—O4^{vii}	81.71 (14)
O1^{vi}—M1—O5	121.38 (17)
O1^{vi}—M1—O5^{vii}	73.18 (17)
O4—M1—O4^{vii}	96.75 (15)
O4—M1—O5	70.82 (18)
O4—M1—O5^{vii}	94.78 (18)
O4^{vii}—M1—O4	96.75 (15)
O4^{vii}—M1—O5	94.78 (18)
O4^{vii}—M1—O5^{vii}	70.82 (18)
O5—M1—O5^{vii}	158.73 (15)
O5^{vii}—M1—O5	158.73 (15)
Cl1^{viii}—M2—O1^{v}	97.67 (12)
Cl1^{viii}—M2—O3^{ix}	87.56 (12)
O1^{v}—M2—O5	76.57 (16)
O1^{v}—M2—O6	153.49 (16)
O3^{ix}—M2—O4	162.76 (17)
O3^{ix}—M2—O5	94.10 (17)
O3^{ix}—M2—O6	96.4 (2)
O4—M2—O5	70.09 (17)
O4—M2—O6	76.70 (17)
O5—M2—O6	87.68 (14)
O1—M3—O2^{vii}	90.70 (17)
O1—M3—O3	109.33 (18)
O1—M3—O4	71.91 (16)
O1—M3—O5	143.3 (2)
O1—M3—O6	85.17 (16)
O2^{vii}—M3—O3	78.53 (19)
O2^{vii}—M3—O4	111.34 (19)
O2^{vii}—M3—O5	95.80 (15)
O2^{vii}—M3—O6	172.04 (17)
O3—M3—O4	170.13 (13)
O3—M3—O5	107.4 (2)
O3—M3—O6	96.41 (18)
O4—M3—O5	72.10 (18)
O4—M3—O6	73.83 (17)
O5—M3—O6	91.56 (14)

Symmetry codes: (i) −*x*+1/2, *y*−1/2, −*z*+1/2; (ii) *x*+1/2, *y*−1/2, *z*; (iii) *x*+1/2, *y*+1/2, *z*; (iv) −*x*+1/2, −*y*+1/2, −*z*+1; (v) *x*, *y*−1, *z*; (vi) −*x*, *y*−1, −*z*+1/2; (vii) −*x*, *y*, −*z*+1/2; (viii) −*x*+1/2, −*y*−1/2, −*z*+1; (ix) −*x*, −*y*, −*z*+1.

Fig. 1