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$[Cd_2(Te_6O_{13})][Cd_2Cl_6]$ and $Cd_7Cl_8(Te_7O_{17})$: Novel Tellurium(IV) Oxide Slabs and Unusual Cadmium Chloride Architectures

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Initial attempts to prepare new Ln–Cd–Te–O–Cl compounds led to the isolation of two novel cadmium tellurium(IV) oxychlorides with two different types of structures, namely, $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$ and $Cd_7Cl_8(Te_7O_{17})$. Both compounds feature novel polymeric tellurium(IV) oxide anions and unusual cadmium chloride substructures. The structure of $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$ is composed of 1D $[Cd_2Cl_6]^{2-}$ double chains and (002) $[Cd_2(Te_6O_{13})]^{2+}$ layers. The 1D $Te_6O_{13}{}^{2-}$ slab of the $[Cd_2(Te_6O_{13})]^{2+}$ layer is formed by TeO_3, TeO_4, and TeO_5 groups via corner- and edge-sharing, and it contains six- and seven-membered tellurium(IV) polyhedral rings. The structure of $Cd_7Cl_8(Te_7O_{17})$ features a 3D network with long-narrow tunnels along the *b* axis. The two types of structural building blocks are 1D $[Te_7O_{17}]^{6-}$ anions and unusual corrugated $[Cd_7Cl_8]^{6+}$ layers based on “cyclohexane-like” Cd_3Cl_3 rings.

Introduction

Metal tellurites adopt many unusual structures because of the presence of the stereochemically active lone pair of Te(IV) and the existence of a variety of isolated or polymeric Te(IV)O_x ($x = 3, 4, 5$) polyhedra.[1] The asymmetric coordination polyhedron adopted by the Te(IV) atom may also result in noncentrosymmetric structures with consequently interesting physical properties, such as nonlinear optical second harmonic generation (SHG).[2−4] Transition metal Te(IV) oxyhalides can be regarded as “chemical scissors”, and they are promising new low-dimensional magnets.[5−9] A number of transition metal Te(IV) oxychlorides have been reported.[5−17] Very recently, a series of lanthanide transition metal (Cu or Mn) Te(IV) oxychlorides have been prepared by our group.[15] Our exploration of new lanthanide cadmium(II) Te(IV) oxychlorides produced two novel cadmium tellurium(IV) oxychlorides instead, namely, $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$ and $Cd_7Cl_8(Te_7O_{17})$, which display several unusual structural building blocks: two new types of 1D tellurium(IV) oxide anions ($Te_6O_{13}{}^{2-}$ and $Te_7O_{17}{}^{6-}$), 1D $[Cd_2Cl_6]^{2-}$ double chains, and 2D $[Cd_7Cl_8]^{6+}$ sheets. So far, no cadmium

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tellurium(IV) oxychlorides has been reported and only a few cadmium tellurium(IV) or Te(IV)/Te(VI) mixed metal oxides have been structurally described.[18] Herein, we report the syntheses and crystal structures of $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$ and $Cd_7Cl_8(Te_7O_{17})$.

Experimental Section

Materials and Instrumentation. All of the chemicals except $CdCl_2$ were analytically pure from commercial sources and used without further purification. Transition metal or lanthanide oxides were purchased from the Shanghai Reagent Factory; TeO_2 (99+%) was purchased from ACROS ORGANICS. $CdCl_2$ was synthesized by dehydration of $CdCl_2 \cdot 2H_2O$ at 200 °C for 12 h. X-ray powder diffraction (XRD) patterns were collected on an XPERT-MPD $\theta-2\theta$ diffractometer. IR spectra were recorded on a Magna 750 FT-IR spectrometer as KBr pellets in the range of 4000−400 cm^{-1}. Microprobe elemental analyses on Cd, Te, and Cl for both compounds were performed on a field-emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy-dispersive X-ray spectroscope (EDS, Oxford INCA).

Preparation of $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$. Single crystals of the title compound (needle-shaped and colorless) were initially prepared by the solid-state reaction of a mixture of Nd_2O_3 (0.101 g, 0.3 mmol), MoO_3 (0.043 g, 0.3 mmol), $CdCl_2$ (0.055 g, 0.3 mmol), and TeO_2 (0.192 g, 1.2 mmol) in our attempt to obtain a Nd−Mo−Cd−Te−O−Cl phase. The reaction mixture was thoroughly ground and pressed into a pellet, which was then sealed into an evacuated quartz tube. The quartz tube was heated at 750 °C for 6 days and then cooled to 300 °C at 4.5 °C/h before we switched off the furnace. The results of the single-crystal X-ray diffraction analysis indicate the absence of both Nd and Mo. Microprobe elemental analysis on several single crystals gave a Cd/Te/Cl molar ratio of 3.8/5.8/6.3, which is in good agreement with that from structural analysis. After crystal structure determination, a colorless crystalline sample of $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$ was obtained quantitatively by the reaction of a mixture of $CdO/CdCl_2/TeO_2$ in a molar ratio of 1/3/6 at 670 °C for 6 days. The purity of $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$ was confirmed by XRD powder diffraction studies. IR (KBr, cm^{-1}): 790 (m), 771(m), 748 (s), 733 (s), 691 (s), 659 (s), 615(s), 556 (s), 500 (m), 468 (m), 415 (w).

Preparation of $Cd_7Cl_8(Te_7O_{17})$. Colorless needle-shaped crystals of $Cd_7Cl_8(Te_7O_{17})$ were initially prepared by the solid-state reaction of a mixture containing Er_2O_3 (0.096 g, 0.25 mmol), CdO (0.032 g, 0.25 mmol), $CdCl_2$ (0.046 g, 0.25 mmol), and TeO_2 (0.240 g, 1.5 mmol) in an attempt to obtain an erbium(III)−cadmium(II)−tellurium(IV) oxychloride. The reaction mixture was thoroughly ground and pressed into a pellet, which was then sealed into an evacuated quartz tube. The quartz tube was heated at 720 °C for 6 days and then cooled to 300 °C at 4 °C/h before we switched off the furnace. Single-crystal X-ray diffraction studies indicate that the compound contains no erbium(III) ion. Microprobe elemental analysis on several single crystals indicate the Cd/Te/Cl molar ratio is 7.1/6.7/8.4, which is in good agreement with that from structural analysis. After structural analysis, a colorless crystalline sample of $Cd_7Cl_8(Te_7O_{17})$ was then obtained quantitatively by the reaction of a mixture of $CdO/CdCl_2/TeO_2$ in a molar ratio of 3/4/7 at 720 °C for 6 days. The purity of $Cd_7Cl_8(Te_7O_{17})$ was confirmed by XRD powder diffraction studies: the mismatch of intensities for several reflections is probably the result of the orientation effect. IR (KBr, cm^{-1}): 747 (s), 686 (s), 640 (s), 563 (s), 491 (w), 443 (w), 410 (w).

Table 1. Crystal Data and Structural Refinements for $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$ and $Cd_7Cl_8(Te_7O_{17})$

	$[Cd_2(Te_6O_{13})][Cd_2Cl_6]$	$Cd_7Cl_8(Te_7O_{17})$
empirical formula	$Cd_4Te_6O_{13}Cl_6$	$Cd_7Te_7O_{17}Cl_8$
fw	1635.94	2235.67
space group	$P\bar{1}$ (No.2)	$Pca2_1$ (No. 29)
a (Å)	7.9203(4)	14.4725(8)
b (Å)	9.9079(5)	6.7259(4)
c (Å)	13.9864(3)	28.043(1)
α (deg)	75.41(1)	90
β (deg)	74.17(1)	90
γ (deg)	89.98(1)	90
V (Å^3)	1019.12(8)	2729.7(3)
Z	2	4
D_c (g cm^{-3})	5.331	5.440
μ(Mo Kα) (mm^{-1})	13.378	13.534
GOF on F^2	1.137	1.079
R1, wR2^a [$I > 2\sigma(I)$]	0.0461, 0.0964	0.0250, 0.0511
R1, wR2^a (all data)	0.0576, 0.1037	0.0262, 0.0517

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$.

Single-Crystal Structure Determination. Data collections for the two compounds were performed on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Both data sets were corrected for Lorentz and polarization factors as well as for absorption by the multiscan method.[19a] Both structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 using SHELX-97.[19b] All of the atoms were refined with anisotropic thermal parameters. Crystallographic data and structural refinements for the two compounds are summarized in Table 1. Important bond distances are listed in Table 2. More details on the crystallographic studies as well as atomic displacement parameters are given as Supporting Information.

Results and Discussion

Our initial attempts to prepare new Ln−Cd−Te−O−Cl phases resulted in the formation of two novel cadmium tellurium(IV) oxychlorides instead, namely, $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$ and $Cd_7Cl_8(Te_7O_{17})$, pure samples of which can be prepared by solid-state reactions of cadmium(II) oxide, cadmium(II) chloride, and TeO_2 in different molar ratios at different temperatures. Both compounds feature novel polymeric tellurium(IV) oxide anions and unusual cadmium chloride substructures.

The structure of $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$ features (002) cationic cadmium(II) tellurium(IV) oxide layers and "isolated" anionic cadmium(II) chloride double chains along the a axis (Figure 1). The $[Cd_2Cl_6]^{2-}$ double chain passing through the cell edge is formed by Cd(3), Cd(4), and six chloride anions. Both ions are octahedrally coordinated by six chloride anions with Cd−Cl distances ranging from 2.500(3) to 2.821(3) Å. Cl(1) and Cl(3) are bidentate bridging, and Cl(4) and Cl(5) are tridentate bridging, whereas Cl(2) and Cl(6) are terminal ligands. Each pair of $CdCl_6$ octahedra are interconnected via edge-sharing into a 1D chain parallel to a axis and two such chains are further condensed into a double chain via edge-sharing (Figure 2). Such isolated

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Table 2. Important Bond Lengths (Å) for $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$ and $Cd_7Cl_8(Te_7O_{17})$[a]

	$[Cd_2(Te_6O_{13})][Cd_2Cl_6]$		
Cd(1)−O(4)#1	2.339(8)	Cd(1)−O(6)#2	2.355(7)
Cd(1)−O(1)#1	2.363(8)	Cd(1)−O(10)	2.388(7)
Cd(1)−O(1)#3	2.408(8)	Cd(1)−O(9)	2.442(8)
Cd(1)−O(8)	2.550(8)	Cd(2)−O(6)#1	2.307(8)
Cd(2)−O(8)#1	2.314(7)	Cd(2)−O(11)	2.329(8)
Cd(2)−O(4)#1	2.387(8)	Cd(2)−O(8)	2.478(8)
Cd(2)−O(5)#1	2.511(8)	Cd(3)−Cl(2)	2.523(3)
Cd(3)−Cl(3)	2.594(3)	Cd(3)−Cl(1)	2.609(3)
Cd(3)−Cl(5)	2.612(3)	Cd(3)−Cl(4)	2.755(3)
Cd(3)−Cl(5)#4	2.776(3)	Cd(4)−Cl(6)	2.500(3)
Cd(4)−Cl(3)#4	2.584(3)	Cd(4)−Cl(1)#5	2.591(3)
Cd(4)−Cl(4)	2.598(3)	Cd(4)−Cl(4)#5	2.790(3)
Cd(4)−Cl(5)	2.821(3)	Te(1)−O(1)	1.872(8)
Te(1)−O(3)	1.970(7)	Te(1)−O(2)	2.010(8)
Te(1)−O(7)#6	2.164(8)	Te(2)−O(4)	1.857(7)
Te(2)−O(5)	1.959(7)	Te(2)−O(2)	1.978(7)
Te(2)−O(3)	2.205(7)	Te(3)−O(6)	1.852(7)
Te(3)−O(5)	1.969(7)	Te(3)−O(7)	1.988(7)
Te(3)−O(3)#3	2.167(7)	Te(4)−O(8)	1.860(7)
Te(4)−O(9)	1.942(7)	Te(4)−O(7)	2.156(7)
Te(4)−O(11)	2.167(8)	Te(5)−O(10)	1.941(8)
Te(5)−O(13)#3	2.014(8)	Te(5)−O(9)	2.059(7)
Te(5)−O(10)#7	2.131(7)	Te(5)−O(12)#8	2.365(8)
Te(6)−O(12)	1.878(8)	Te(6)−O(11)	1.907(7)
Te(6)−O(13)	1.957(8)		
	$Cd_7Cl_8(Te_7O_{17})$		
Cd(1)−O(5)#1	2.244(5)	Cd(1)−O(9)#2	2.338(5)
Cd(1)−O(16)#3	2.399(6)	Cd(1)−Cl(6)#4	2.620(2)
Cd(1)−Cl(4)	2.635(2)	Cd(1)−Cl(1)#1	2.702(2)
Cd(2)−O(10)	2.230(6)	Cd(2)−O(13)#1	2.289(5)
Cd(2)−O(5)#1	2.528(6)	Cd(2)−Cl(7)#1	2.556(2)
Cd(2)−O(11)#5	2.595(5)	Cd(2)−Cl(8)	2.650(2)
Cd(2)−Cl(4)	2.868(2)	Cd(3)−O(16)	2.206(5)
Cd(3)−O(3)	2.369(6)	Cd(3)−O(14)#6	2.380(6)
Cd(3)−Cl(6)	2.582(2)	Cd(3)−Cl(1)#6	2.654(2)
Cd(3)−Cl(3)	2.723(2)	Cd(4)−O(1)#7	2.248(6)
Cd(4)−O(2)#5	2.328(5)	Cd(4)−O(3)	2.542(5)
Cd(4)−Cl(5)	2.592(2)	Cd(4)−Cl(6)	2.624(2)
Cd(4)−Cl(3)#1	2.736(2)	Cd(5)−O(3)	2.303(6)
Cd(5)−O(7)#8	2.349(5)	Cd(5)−O(1)#9	2.385(5)
Cd(5)−Cl(2)	2.541(2)	Cd(5)−Cl(5)	2.634(2)
Cd(5)−Cl(3)	2.734(2)	Cd(6)−O(14)	2.245(6)
Cd(6)−O(12)#5	2.460(5)	Cd(6)−O(10)	2.488(6)
Cd(6)−Cl(7)	2.498(2)	Cd(6)−O(5)	2.508(5)
Cd(6)−Cl(4)	2.676(2)	Cd(6)−Cl(1)	2.803(2)
Cd(7)−O(15)#9	2.247(6)	Cd(7)−O(11)#7	2.330(5)
Cd(7)−O(1)#7	2.492(6)	Cd(7)−O(13)#8	2.535(6)
Cd(7)−Cl(2)#1	2.551(2)	Cd(7)−Cl(8)#10	2.673(2)
Cd(7)−Cl(5)	2.866(2)	Te(1)−O(3)#11	1.874(5)
Te(1)−O(17)	1.908(6)	Te(1)−O(8)	1.998(5)
Te(1)−O(2)	2.226(5)	Te(2)−O(13)#1	1.865(5)
Te(2)−O(1)#5	1.887(5)	Te(2)−O(4)#1	2.073(6)
Te(2)−O(7)	2.221(6)	Te(3)−O(9)#4	1.856(5)
Te(3)−O(14)#11	1.860(5)	Te(3)−O(17)#4	2.103(6)
Te(3)−O(6)	2.161(5)	Te(4)−O(11)#12	1.857(5)
Te(4)−O(5)#11	1.872(5)	Te(4)−O(12)	2.073(6)
Te(4)−O(6)#12	2.219(5)	Te(5)−O(16)#11	1.866(5)
Te(5)−O(2)#12	1.874(5)	Te(5)−O(8)	1.965(5)
Te(5)−O(9)#12	2.357(5)	Te(6)−O(10)#11	1.876(5)
Te(6)−O(12)	1.939(6)	Te(6)−O(6)	2.022(5)
Te(6)−O(15)	2.443(6)	Te(7)−O(15)#5	1.892(5)
Te(7)−O(7)	1.903(6)	Te(7)−O(4)	1.915(6)

[a] Symmetry transformations used to generate equivalent atoms. For $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$: #1 $-x + 1, -y + 1, -z + 1$; #2 $-x, -y + 1, -z + 1$; #3 $x - 1, y, z$; #4 $-x, -y, -z + 2$; #5 $-x + 1, -y, -z + 2$; #6 $x + 1, y, z$; #7 $-x, -y + 2, -z + 1$; #8 $-x + 1, -y + 2, -z + 1$. For $Cd_7Cl_8(Te_7O_{17})$: #1 $x, y + 1, z$; #2 $x - 1, y, z + 1$; #3 $x, y + 1, z + 1$; #4 $x, y, z + 1$; #5 $x - 1, y, z$; #6 $x, y, z - 1$; #7 $-x + 1, -y + 2, z - 1/2$; #8 $-x, -y + 1, z - 1/2$; #9 $-x + 1, -y + 1, z - 1/2$; #10 $-x + 1/2, y, z - 1/2$; #11 $x + 1, y, z$; #12 $x, y - 1, z$.

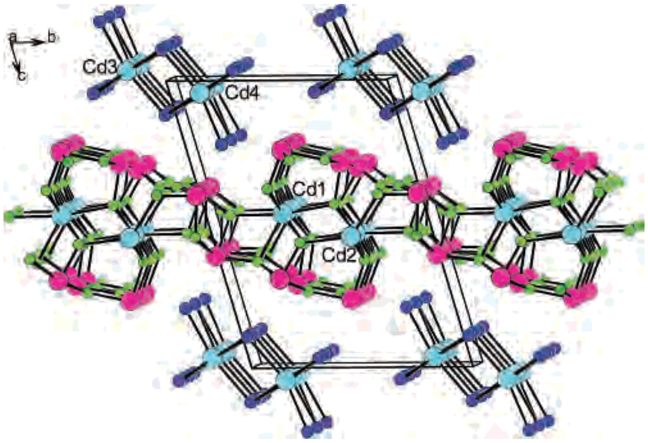

Figure 1. View of the structure of $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$ down the *a* axis. Cd, Te, Cl, and O atoms are drawn as cyan, pink, blue, and green circles, respectively.

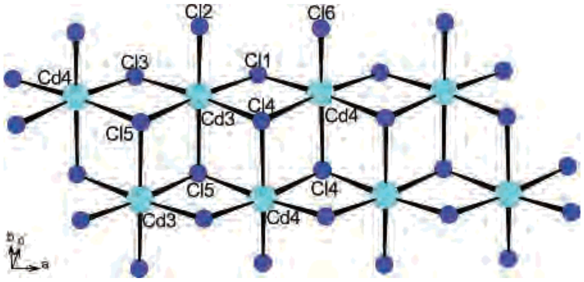

Figure 2. 1D double chain of cadmium chloride in $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$ along the *a* axis.

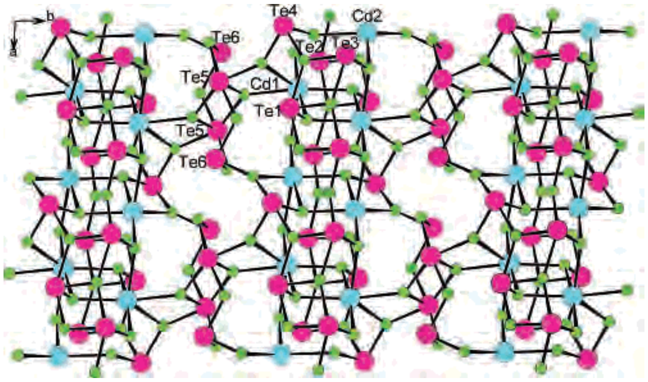

Figure 3. (002) 2D layer of $\{Cd_2(Te_6O_{13})\}$ in $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$. Cd, Te, and O atoms are drawn as cyan, pink, and green circles, respectively.

double chains have only been reported in an organically templated cadmium chloride, $[C_3H_7N_2S][CdCl_3]$.[20]

The (002) cadmium(II) tellurium(IV) oxide layer in $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$ is formed by novel 1D slabs of $Te_6O_{13}^{2-}$ anions interconnected by Cd(II) ions (Figure 3). Among its two unique Cd atoms, Cd(1) is coordinated by seven oxygen atoms, whereas Cd(2) is octahedrally coordination by six oxygen atoms. The Cd−O distances fall in the range of 2.307(8)−2.550(8) Å, which are comparable to those reported for other cadmium tellurium(IV) oxides.[18] It is interesting to note that the TeO_x ($x = 3, 4, 5$) polyhedra are not isolated but interconnected via edge- and corner-sharing into a novel 1D slab of the $Te_6O_{13}^{2-}$ anion (Figure

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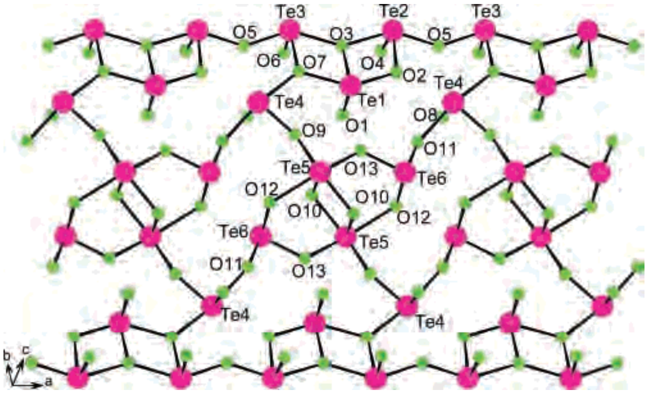

Figure 4. 1D slab of the $[Te_6O_{13}]^{2-}$ anion in $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$.

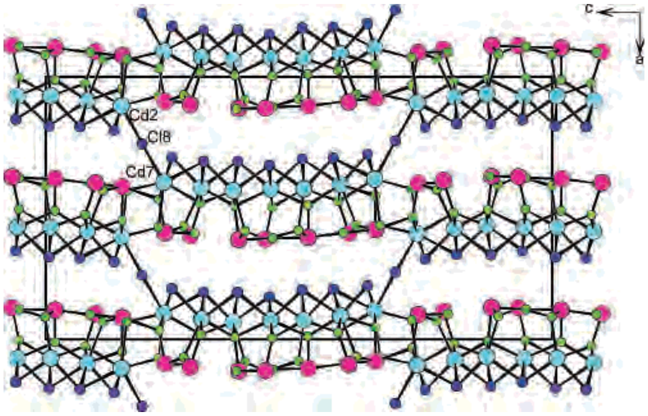

Figure 5. View of the structure of $Cd_7Cl_8(Te_7O_{17})$ down the *b* axis. Cd, Te, Cl, and O atoms are drawn as cyan, pink, deep blue, and green circles, respectively.

4). The Te−O distances are in the range of 1.852(7)−2.365(8) Å, which are comparable to those reported in other tellurium(IV) compounds.[5−18] Bond valence calculations indicate that all six tellurium atoms are 4+, the calculated total bond valences are in the range of 3.57−3.99.[21] Te(1)-O_4, Te(2)O_4, and Te(3)O_4 groups are interconnected via corner- and edge-sharing into a trinuclear unit, and neighboring units are corner-shared (O(5)) into a 1D chain along the *a* axis. Two Te(5)O_5 and two Te(6)O_3 groups form a tetranuclear unit via corner- and edge-sharing. The above 1D chains and tetranuclear units are bridged by Te(4)O_4 groups, through corner-sharing, into a 1D $Te_6O_{13}^{2-}$ slab, forming six- and seven-member polyhedral rings (Figure 4). The width of the slab is about 14.6 Å. Such tellurium(IV) oxide anion slabs have not been reported before. The lone pair electrons of the Te(IV) atoms are oriented in the open space between the cadmium chloride chains and cadmium tellurium(IV) oxide layers (Figure 1).

The structure of $Cd_7Cl_8(Te_7O_{17})$ features a 3D network with long narrow tunnels along the *b* axis with different tellurium(IV) oxide and cadmium chloride substructures (Figure 5). The two structural building blocks are 1D $[Te_7O_{17}]^{6-}$ anions and unusual corrugated $[Cd_7Cl_8]^{6+}$ layers based on cyclohexane-type Cd_3Cl_3 rings. Cd(1), Cd(3), Cd(4), and Cd(5) atoms are octahedrally coordinated by three oxygens and three chloride anions, whereas Cd(2), Cd(6), and Cd(7) atoms are seven coordinated (four oxygens and three chloride anions). The Cd−O and Cd−Cl distances are in the range of 2.206(5)−2.595(5) and 2.498(2)−2.866(2) Å, respectively (Table 2), which are comparable to those in $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$. In constrast to those in $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$, the Cd and Cl atoms in $Cd_7Cl_8(Te_7O_{17})$ form a novel corrugated 2D layer (Figure 6). The layer is based on Cd_3Cl_3 rings. The Cl−Cd−Cl and Cd−Cl−Cd angles within the rings fall in the ranges of 83.70(5)−96.46(6) and 87.88(6)−99.57(7)°. Hence, such Cd_3Cl_3 rings are of the distorted cyclohexane type rather than of the "BN" type in which the B−N−B angles are 120°.[22] These 2D layers can be viewed as the result of removing 1/8 of Cd(II) ions from a perfect "Cd_8Cl_8" 2D layer leaving vacant Cd_6Cl_6 12-member rings with two larger Cd−Cl−Cd (Cd(2)−Cl(8)−Cd(7)) angles of 130.38(7)°. This type of cadmium chloride layer has not yet been reported.

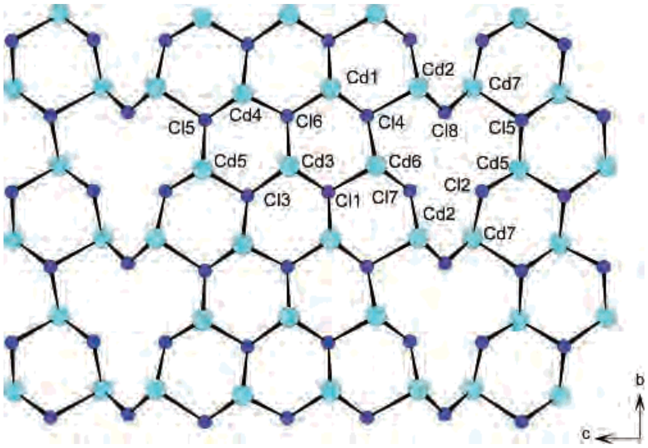

Figure 6. Corrugated 2D cadmium chloride sheet in $Cd_7Cl_8(Te_7O_{17})$.

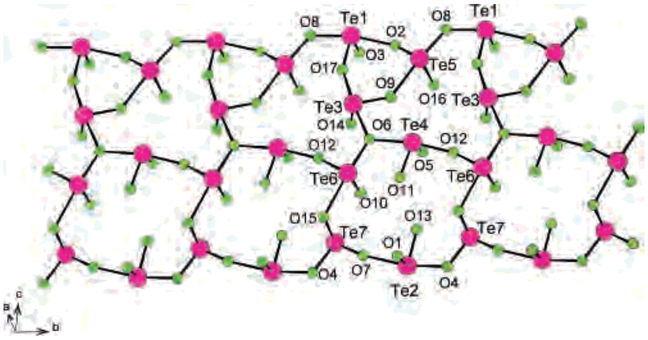

Figure 7. 1D slab of the $[Te_7O_{17}]^{6-}$ anion in $Cd_7Cl_8(Te_7O_{17})$.

The $Te_7O_{17}^{6-}$ anion features a 1D structure different from that of the $Te_6O_{13}^{2-}$ anion in $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$ (Figure 7). Only two types of tellurium(IV) oxide polyhedra are found: TeO_3 for Te(7) and TeO_4 for the remaining six tellurium atoms. The Te−O distances are in the range of 1.856(5)−2.443(6) Å, which are comparable to those in $[Cd_2(Te_6O_{13})][Cd_2Cl_6]$ (Table 2). The calculated total bond valences for the tellurium atoms are in the range of 3.59−4.08, indicating that all of the tellurium atoms have oxidation states of 4+.[21] TeO_3 and TeO_4 groups are interconnected

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(21) (a) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244. (b) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

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via corner-sharing into another type of 1D slab, forming two types of six-member polyhedral rings and one type of three-member polyhedral ring (Figure 7). The three-member ring is composed of three TeO_4 groups. One type of the six-member ring is formed by solely TeO_4 groups in a "pear" shape, whereas the other type is made of two TeO_3 and four TeO_4 groups. The width of this 1D slab is 12.1 Å, which is slightly narrower than that of the $Te_6O_{13}^{2-}$ anion in [$Cd_2(Te_6O_{13})$][Cd_2Cl_6].

The above two types of building units are interconnected via Te−O−Cd bridges into a 3D network with long narrow tunnels along the *b* axis (Figure 5). Alternatively, the structure of $Cd_7Cl_8(Te_7O_{17})$ can be viewed as (200) and (100) layers of $Cd_7Cl_7(Te_7O_{17})$ further cross-linked by the eighth chloride anion (Cl(8)) via Cd(2)−Cl(8)-Cd(7) bridges. The stereoactive lone pairs of the Te(IV) atoms are oriented toward the narrow tunnels.

$Cd_7Cl_8(Te_7O_{17})$ crystallizes in the acentric space group $Pca2_1$; hence, it may possess the NLO property. However, the results of our measurements on a homemade instrument using an Nd:YAG laser as the light source indicate that its SHG signal is very weak.

It is interesting to note the polymerization of the Te(IV) polyhedral groups and the formation of novel 1D slabs of tellurium(IV) oxide anions in both [$Cd_2(Te_6O_{13})$][Cd_2Cl_6] and $Cd_7Cl_8(Te_7O_{17})$. The Te(IV) polyhedral groups in the organically templated or organically covalently bonded metal tellurites prepared under normal hydrothermal conditions (120−200 °C) are normally nonpolymerized.[23] Under supercritical hydrothermal methods ($T > 374$ °C, $P > 218$ atm) meta-stable compounds may be formed, and a few examples of polymeric tellurium(IV) oxide anions are observed, such as layered $Te_4O_9^{2-}$ in $K_2Te_4O_9{\cdot}3.2H_2O$ and 3D $Te_2O_6^{4-}$ in $KGaTe_2O_6$.[3d] A few compounds containing extended tellurium(IV) oxide anions were prepared by solid-state reactions at high temperature ($T > 600$ °C), such as layered $Te_2O_5^{2-}$ in Ln(Te_2O_5)X (Ln = Nd, X = Cl, Br; Ln = Gd, X = Cl).[24] Therefore we conclude that the reaction temperature plays an important role in the polymerization of Te(IV)O_x ($x = 3$, 4, 5) groups and the formation of tellurium(IV) oxide anions with extended structural motifs.

Conclusion

In summary, the syntheses and crystal structures of two new cadmium tellurium(IV) oxychloride complexes have been described. It is interesting to note that the Te−O polyhedra in both compounds are condensed into 1D anionic slabs via edge- and corner-sharing. The cadmium chloride substructures in both compounds are also interesting. In $Cd_7Cl_8(Te_7O_{17})$, the interconnection of cadmium(II) ions by bridging chloride anions led to a novel corrugated "defect" 2D layer based on Cd_3Cl_3 rings, whereas the cadmium(II) and chloride anions in [$Cd_2(Te_6O_{13})$][Cd_2Cl_6] form a double chain. It is anticipated that many other new cadmium tellurium(IV) oxyhalides with interesting architectures will be discovered in the future.

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Supporting Information Available: X-ray crystallographic files in CIF format and simulated and experimental XRD powder patterns for $Cd_7Cl_8(Te_7O_{17})$ and [$Cd_2(Te_6O_{13})$][Cd_2Cl_6]. This material is available free of charge via the Internet at http://pubs.acs.org.

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