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Langbeinite-Type Cubic Dithallium Dicadmium Sulfate

Abderrahim Guelylah,[a] Gotzon Madariaga[a] and Tomasz Breczewski[b]

[a]*Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, Bilbao 48080, Spain, and* [b]*Departamento de Física Aplicada II, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, Bilbao 48080, Spain. E-mail: wmbgugua@lg.ehu.es*

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Abstract

The structure of the cubic phase of langbeinite-type $Tl_2Cd_2(SO_4)_3$ at 295 K has been refined from X-ray diffraction data. The bond-valence sums for the monovalent cations show anomalously low values, indicating that some Tl atoms are very loosely bonded. The possible relevance of this result in the phase-transition scheme of compounds similar to $Tl_2Cd_2(SO_4)_3$ is discussed.

Comment

Langbeinite-type crystals have the general formula $A_2B_2(SO_4)_3$, where A = K, Tl, Cs, Rb or NH_4, and B = Mg, Zn, Fe, Ni, Cd, Co, Ca or Mn, and take their names from the natural mineral langbeinite, $K_2Mg_2(SO_4)_3$. The structure of $K_2Mg_2(SO_4)_3$ was solved at room temperature by Zeemann & Zeemann (1957), and the chemical stability of other isostructural double sulfates has been investigated by Gatow & Zeemann (1958).

Langbeinites have a common high-temperature cubic phase (space group $P2_13$), and many of them exhibit phase transitions to ferroelectric or ferroelastic phases as the temperature is lowered. Up to now, two different sequences of phase transitions have been observed among langbeinites. Compounds classified as type I [*e.g.* $(NH_4)_2Cd_2(SO_4)_3$, $Tl_2Cd_2(SO_4)_3$ and $Rb_2Cd_2(SO_4)_3$] undergo a series of phase transformations from cubic to orthorhombic ($P2_12_12_1$) through two phases; one monoclinic ($P2_1$) and one triclinic ($P1$) (Brezina & Glogarova, 1972; Glogarova & Fousek, 1973; Yamada & Kawano, 1977). The so-called type II compounds [*e.g.* $K_2Mn_2(SO_4)_3$ and $K_2Cd_2(SO_4)_3$] show only a single phase transition to an orthorhombic structure ($P2_12_12_1$) as temperature is lowered (Abrahams, Lissalde & Bernstein, 1978; Hikita, Chubachi & Ikeda, 1978; Yamada, Maeda & Adachi, 1981). Based on group theoretical analysis, Dvorák (1972) has shown that a spatially homogeneous phase transition could result only from a phonon instability at the points M and Γ of the cubic Brillouin zone. An instability at the M point would lead to an improper ferroelectric phase ($P2_1$) with a doubled unit-cell volume (type I compounds), while an instability at the Γ point leads to a potentially ferroelastic phase ($P2_12_12_1$) with no change in the unit-cell volume (type II compounds).

There are several reports of type I compounds, which are of interest because of the ferroelectric character of the low-temperature phases. In particular, crystals of $Tl_2Cd_2(SO_4)_3$ (hereinafter TCdS) were first studied by Brezina & Glogarova (1972), who discovered three phase transitions at about 98, 127 and 130 K by dielectric and optical measurements. Based on the work of Dvorák (1972), they suggested that the space groups of the low-temperature phases of TCdS are those cited above for type I compounds. A few years later, Ikeda & Yasuda (1975) confirmed the assignment of the space groups by X-ray diffraction and spontaneous polarization measurements; $Tl_2Cd_2(SO_4)_3$ was considered to be a typical langbeinite of type I. Recently, Cao, Dalley & Boerio-Goates (1993) determined the structure of TCdS at room temperature by X-ray diffraction. However, an incomplete correction for absorption prevented an accurate structure solution (R = 8.6%) and hindered observation of such details as the anisotropy of the atomic displacements. Here, we report a more reliable structure determination for TCdS. The calculated bond-valence sums (Brown & Altermatt, 1985) show anomalies when compared with those of typical langbeinites of type II, which could indicate a possible mechanism responsible for the two different sequences of phase transitions shown by langbeinites.

The structure of TCdS is similar to that of the sulfates belonging to the langbeinite family (Speer & Salje, 1986; Abrahams *et al.*, 1978, Yamada *et al.*, 1981; Zeemann & Zeemann, 1957), and comprises SO_4 tetrahedra and distorted coordination polyhedra around the metal cations. The metal cations occupy special positions along the threefold axes. Each Tl atom is surrounded by nine O atoms that form a complicated polyhedron. Cd1 and Cd2 are each coordinated by six O atoms, forming distorted octahedra, which are generated by the application of the threefold axes on the symmetry independent atoms O3, O4, O1 and O2. Cd1 and Cd2 are not at the midpoints of the octahedra, but are shifted by 0.03 (3) Å toward the O4 triplet for Cd1 and 0.13 (3) Å toward the O2 triplet for Cd2.

The SO_4 group is a distorted tetrahedron with S—O distances ranging from 1.41 (2) to 1.49 (2) Å and O—S—O bond angles ranging from 104.3(13) to 111.6(12)°. This deformation has not been observed in the SO_4 groups of the potassium langbeinites $K_2B_2(SO_4)_3$ (B = Mg, Zn, Ni, Cd, Co, Ca or Mn) (Speer & Salje, 1986; Abrahams *et al.*, 1978; Yamada *et al.*, 1981) or the TCdS structure determined by Cao *et al.* (1993). Zeemann & Zeemann (1957) found the SO_4 group in $K_2Mg_2(SO_4)_3$ to be an almost ideal tetrahedron.

The atomic displacement parameters of the Tl, Cd and S atoms are virtually isotropic. Strong anisotropy appears for the O atoms, which show small displacements in the S—O direction and very large displacements perpendicular to the S—O direction. The displacement ellipsoids are, therefore, very large and disk-shaped. This anisotropy is a common characteristic of the sulfate groups in langbeinite structures, and has also been observed in different potassium langbeinites (Abrahams *et al.*, 1978; Yamada *et al.*, 1981; Speer & Salje, 1986).

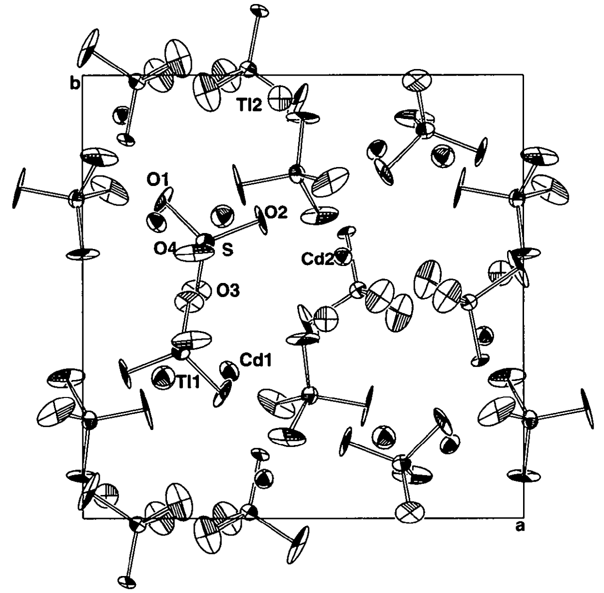

Fig. 1. Projection of the cubic structure of $Tl_2Cd_2(SO_4)_3$ along the (001) direction, showing 50% probability displacement ellipsoids. Only the asymmetric unit is labelled.

In order to compare the cation binding, the bond-valence sums (Brown & Altermatt, 1985) for the atoms forming the unit cell of TCdS were calculated. In Table 3, we can see that the S atoms are systematically tightly bonded. The high values of the bond-valence sums are due to the short S—O bond distances. On the other hand, the values for the Tl atoms are very small, especially for Tl1, indicating that this atom is loosely bonded. This anomaly was not observed for the monovalent cations (K) in $K_2Cd_2(SO_4)_3$ (Percival, Schmahl & Salje, 1989), where the bond-valence sum is practically the same for the two cations K1 and K2. Crystals of $K_2Cd_2(SO_4)_3$, a type II compound, show only a single transformation from the cubic ($P2_13$) to the orthorhombic ($P2_12_12_1$) phase. Although this can not be considered as a general result for langbeinites of type I, the asymmetry present in the bond strength for the Tl1 atoms may suggest that the weakness in the binding of the monovalent cation could be responsible for the transition from the cubic $P2_13$ to the monoclinic $P2_1$ phase.

Experimental

Single crystals of $Tl_2Cd_2(SO_4)_3$ were grown from saturated aqueous stoichiometric solutions by a steady-state method at 360 K. The stock reagents used for synthesis were chemically pure Tl_2CO_3, $CdCO_3$ and H_2SO_4. The product of the synthesis was purified by recrystallization from distilled water; the pH of the solution was adjusted to be approximately 1.5. The crystals obtained were 2 × 2 × 2 mm, colourless and of good optical quality. Their morphology was similar to that of the $Tl_2Cd_2(SO_4)_3$ crystals obtained by Brezina & Havránková (1974). A sphere of radius 0.24 mm, ground using an Enraf–Nonius grinder, was mounted on a glass fibre for data collection.

Crystal data

$Tl_2Cd_2(SO_4)_3$
$M_r = 921.732$
Cubic
$P2_13$
$a = 10.421\,(1)$ Å
$V = 1131.7\,(3)$ Å^3
$Z = 4$
$D_x = 5.410$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5.5$–$12.2°$
$\mu = 32.71$ mm^{-1}
$T = 295$ K
Spherical
0.24 mm (radius)
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: from azimuthal scans (Flack, 1974)
$T_{\min} = 0.0014$, $T_{\max} = 0.019$
2858 measured reflections
943 independent reflections
685 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.167$
$\theta_{\max} = 35°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 16$
$l = 1 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F
$R = 0.051$
$wR = 0.040$
$S = 1.412$
685 reflections
58 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.056$
$\Delta\rho_{\max} = 7.6$ e Å^{-3}
$\Delta\rho_{\min} = -2.7$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Tl1	0.18250 (8)	$1/2-x$	$1/2+x$	0.0313 (2)
Tl2	0.44820 (8)	$1/2+x$	$1-x$	0.0349 (2)
Cd1	0.33219 (11)	x	x	0.0214 (2)
Cd2	0.58961 (11)	x	x	0.0203 (2)
S	0.2778 (4)	0.6242 (4)	0.5141 (4)	0.0169 (9)
O1	0.1839 (17)	0.718 (2)	0.462 (2)	0.048 (7)
O2	0.4042 (13)	0.6732 (19)	0.4999 (19)	0.040 (5)
O3	0.259 (2)	0.5121 (18)	0.439 (3)	0.051 (7)
O4	0.253 (2)	0.5981 (16)	0.6447 (13)	0.042 (6)

Table 2. *Selected geometric parameters (Å, °)*

Tl1—O1^{i}	3.25 (2)	Cd1—O4^{iii}	2.27 (2)
Tl1—O3^{i}	3.27 (3)	Cd2—O1^{ii}	2.30 (2)
Tl1—O4	3.04 (2)	Cd2—O2	2.32 (2)
Tl2—O1^{ii}	3.01 (2)	S—O1	1.49 (2)
Tl2—O2	2.95 (2)	S—O2	1.42 (2)
Tl2—O3^{ii}	3.26 (2)	S—O3	1.42 (2)
Cd1—O3	2.31 (2)	S—O4	1.41 (2)
O1—S—O2	109.6 (11)	O2—S—O3	111.6 (12)
O1—S—O3	104.3 (13)	O2—S—O4	109.8 (12)
O1—S—O4	110.9 (12)	O3—S—O4	110.5 (12)

Symmetry codes: (i) z, x, y; (ii) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$; (iii) $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$.

Table 3. *Bond-valence sums (v.u.) for the atoms in $Tl_2Cd_2(SO_4)_3$ and $K_2Cd_2(SO_4)_3$*

	$Tl_2Cd_2(SO_4)_3$	$K_2Cd_2(SO_4)_3$†
Tl1	0.61 (3)	0.83 (3) (K1)
Tl2	0.83 (4)	0.88 (3) (K2)
Cd1	2.13 (10)	2.42 (8)
Cd2	2.03 (9)	2.30 (7)
S	6.7 (3)	6.49 (6)
O1	1.96 (9)	2.20 (3)
O2	2.18 (9)	2.17 (3)
O3	2.17 (11)	2.17 (3)
O4	2.25 (9)	2.12 (4)

† 440 K (Percival *et al.*, 1989)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAMEL JOCKEY* (Flack, 1974). Program(s) used to refine structure: *CRYLSQ* in *Xtal*3.2 (Hall, Flack & Stewart, 1992). Molecular graphics: *ORTEP* (Johnson, 1965) in *Xtal*3.2. Software used to prepare material for publication: *BONDLA* in *Xtal*3.2.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: AB1353). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Gadolinium Potassium Hexacyanoferrate(II) Trihydrate

Donald F. Mullica, Jennifer L. Ward and Eric L. Sappenfield

Chemistry Department, PO Box 97348, Baylor University, Waco, Texas 76798-7348, USA. E-mail: vaxsdp@baylor.edu

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Abstract

Gadolinium potassium hexacyanoferrate(II) trihydrate, $GdKFe(CN)_6.3H_2O$, crystallizes in the orthorhombic space group *Pnma* (No. 62). The structure consists of non-linear cyanide bridges linking octahedrally coordinated Fe atoms and eight-coordinate Gd atoms. Cavities within the structure are occupied by potassium and zeolitic water molecules which are within hydrogen-bonding distance of the water molecules bonded to the Gd atoms, $GdN_6(H_2O)_2$.

Comment

The first ferrocyanide containing a lanthanide atom, $CeKFe(CN)_6$, was described by Robinson (1909).