REGULAR STRUCTURAL PAPERS

Refinement of the structure of Tl$_2$AlF$_5$.H$_2$O

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Abstract

New refinement of the Tl$_2$AlF$_5$.H$_2$O structure, formerly described as 'Tl$_2$AlF$_5$', yielded an octahedral (AlF$_5$)$_n$ *trans* chain with a bridging angle Al—F—Al of 177° and the distances Al—F(bridge) 1.871 Å, Al—F(terminal) 1.774 Å. Short O$\cdots$F contacts of 2.73 Å suggest hydrogen bonds attached to neighbouring octahedra similar to those in isostructural Tl$_2$MnF$_5$.H$_2$O and the corresponding Rb compounds. Tl is 12-coordinated by 10 F and 2 O atoms.

Comment

Since the pioneering work of Brosset (1937) the 'Tl$_2$AlF$_5$' structure is referred to frequently as an archetype, characterizing chain structures built by octahedra sharing *trans* vertices. Fourquet, Plet & De Pape (1981) gave evidence that Brosset really had a crystal of the hydrate Tl$_2$AlF$_5$.-H$_2$O. When we were working on the related Jahn-Teller distorted Mn^{III} compound Tl$_2$MnF$_5$.H$_2$O (Nuñez *et al.*, 1992) we became interested in the detailed geometry of the Al analogue as an electronically inert reference structure. Crystals of Tl$_2$AlF$_5$.H$_2$O grew from a solution of 5 mmol Al and 5 mmol TlF in 10 ml aqueous HF (40%) when ethanol was allowed to diffuse slowly into the container at 278 K.

Single-crystal investigations confirmed the orthorhombic unit cell reported by Brosset with a slight enlargement of all axes (max. 0.3%). Instead of the $C222_1$ space group given by Brosset we found *Cmcm* as reported for Tl$_2$MnF$_5$.H$_2$O and the Rb compounds Rb$_2$MF$_5$.H$_2$O [M = Al (Fourquet, Plet & De Pape, 1981), Fe (β-form) (Fourquet, De Pape, Teillet, Varret & Papaefthymiou, 1982) and Mn (Günter, Mathieu & Oswald, 1978; Bukovec & Kaučič, 1978)]. Indeed, inspection of Brosset's powder diagram 'Tl$_2$AlF$_5$' gave no measured intensities for reflections $h0l$, l = odd contradicting the extinctions of *Cmcm*. On the other hand, calculated powder intensities based on our single-crystal data in *Cmcm* are in good agreement with Brosset's calculated values from his powder data.

The results of our structure refinement (Tables 1 and 2) yielded the expected octahedral *trans* chain structure with a remarkable lengthening of the bridging Al—F3 bonds (1.871 Å) with respect to the terminal bonds of 1.774 Å (mean Al—F 1.806 Å) and a bridge angle Al—F3—Al' of 177(1)°. The geometry closely resembles that of the isotypic Rb$_2$AlF$_5$.H$_2$O (Fourquet, Plet & De Pape, 1981). Tl is 12-coordinated by 10 F and 2 O atoms, there is no significant indication of a steric effect by the lone pair of Tl^I. O$\cdots$F contacts of 2.73 Å suggest hydrogen bonds attached to terminal fluorine ligands of neighbouring octa-
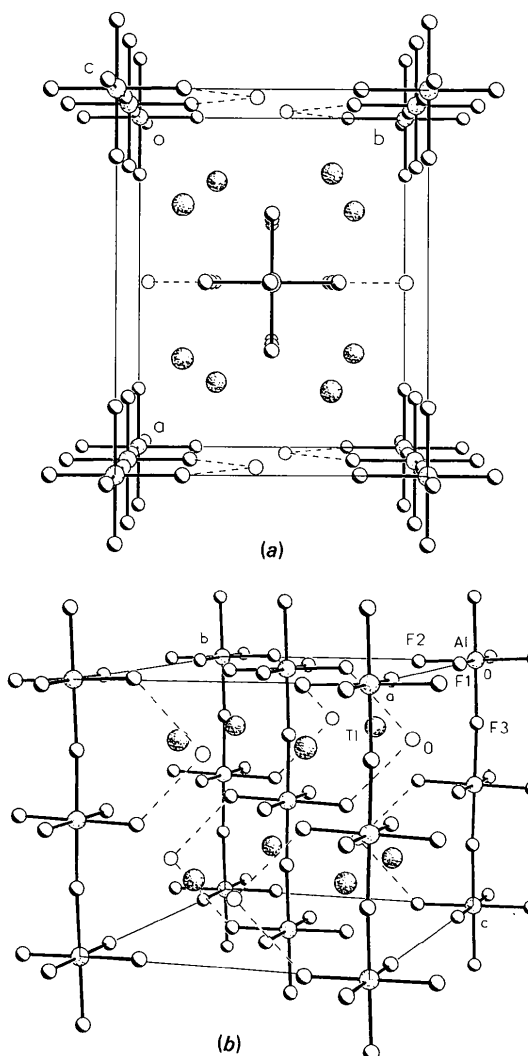

Fig. 1. Projection of a unit cell of Tl$_2$AlF$_5$.H$_2$O (*a*) down the *c* axis and (*b*) approximately down the *a* axis. Open circles are water O atoms, the assumed hydrogen bonds are given with dashed lines. Large shaded spheres are the Tl atoms.

hedra within one chain (Fig. 1), as observed in the isotypic Mn^{III} compound and the Rb analogues. By empirical bond strength calculations (Massa & Babel, 1988) a weakening of the bridging Al—F bond of 17% with respect to a regular octahedron, with an average Al—F bond length 1.806 Å, may be derived. In $Tl_2MnF_5.H_2O$ an additional weakening of the bridging Mn—F bond, of 37% in total, is found due to the Jahn–Teller effect. Comparing the relative bond strengths in the isotypic Al and Mn^{III} compounds, we are now able to estimate separately the electronic influence of the Jahn–Teller effect on the weakening of the bridging Mn—F bond to be about 20%.

It must be pointed out that Brosset's structure model for 'Tl_2AlF_5' in $C222_1$ does not correspond to our $Cmcm$ structure (neglecting the water molecule). $C222_1$ is a maximal subgroup of $Cmcm$ but due to an origin shift of 0,0,-1/4 at Brosset's parameters with respect to the $Cmcm$ model, the structures show no symmetry relation. The tilting of the octahedral (AlF_5) chains in the Brosset model is within the ac plane (site symmetry for Al .2.), in our model in the bc plane (Al at $2/m..$). The arrangement of the Tl positions is somewhat different as well. We assume that Brosset really has investigated the same hydrate as us, but was misled to a wrong space group and a wrong origin choice. Besides the crystallographic evidence, a strong chemical argument for this assumption was given by Fourquet et al. (1981): all their attempts to prepare water-free Tl_2AlF_5 failed. Nevertheless, the main feature of the structure, the pseudotetragonal packing of octahedral trans chains was, by the methods of the 1930's, correctly described.

To characterize trans-connected octahedral chain compounds, we propose to use Cs_2MnF_5 ($P4/mmm$; Hahn & Massa, 1990) instead of 'Tl_2AlF_5' as representative with the highest symmetry ('aristotype') for structures with tetragonal chain packing, and $(NH_4)_2MnF_5$ ($Pnma$; Sears & Hoard, 1969) for structures deriving from a pseudo-hexagonal chain packing.

Experimental

Crystal data

$Tl_2AlF_5.H_2O$
$M_r = 548.729$
Orthorhombic
$Cmcm$
$a = 10.0750$ (10) Å
$b = 8.2570$ (10) Å
$c = 7.4820$ (10) Å
$V = 622.42$ (13) $Å^3$
$Z = 4$
$D_x = 5.855$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 7-20°$
$\mu = 52.406$ mm^{-1}
$T = 293$ K
Column
$0.20 \times 0.06 \times 0.06$ mm
Colourless

Data collection

Nonius CAD-4 diffractometer
ω scans

393 observed reflections
$[F_o > 4\sigma(F_o)]$
$R_{int} = 0.036$

Absorption correction:
  SHELX76 Gaussian
  $T_{min} = 0.091$, $T_{max} = 0.133$
952 measured reflections
447 independent reflections

$\theta_{max} = 30°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 9$
2 standard reflections
  frequency: 120 min
  intensity variation: none

Refinement

Refinement on F
Final $R = 0.0382$
$wR = 0.0301$
$S = 2.470$
393 reflections
32 parameters
H atoms not included
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} = 0.01$

$\Delta\rho_{max} = 2.6$ e Å^{-3}
$\Delta\rho_{min} = -3.0$ e Å^{-3}
Extinction correction: empirical isotropic correction (SHELX76)
Extinction coefficient: 5.9 (4)$\times 10^{-8}$
Atomic scattering factors from Cromer & Mann (1968)

Data collection: CAD-4 measuring software. Cell refinement: CAD-4 measuring software. Data reduction: XCAD4 (Sheldrick, 1992). Program(s) used to refine structure: SHELX76 (Sheldrick, 1976). Software used to prepare material for publication: PLATON92 (Spek, 1992).

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

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

	x	y	z	U_{eq}
Al	0.00000	0.00000	0.00000	0.0131 (19)
F1	0.1762 (7)	0.00000	0.00000	0.0277 (32)
F2	0.00000	0.2146 (11)	0.0075 (13)	0.0294 (30)
F3	0.00000	−0.0057 (19)	0.25000	0.0246 (44)
O	0.50000	0.0511 (19)	0.25000	0.0310 (59)
Tl	0.20695 (7)	0.29920 (10)	0.25000	0.0286 (3)

Table 2. *Geometric parameters* (Å, °)

Al—F1	1.775 (7)	Tl—F1	3.114 (1)
Al—F2	1.773 (9)	Tl—F1^{iv}	3.114 (1)
Al—F1	1.8711 (5)	Tl—F3	3.27 (1)
Tl—F1^i	2.763 (3)	Tl—F3^v	3.363 (8)
Tl—F1^{ii}	2.763 (3)	Tl—F2^{vi}	3.528 (6)
Tl—F2	2.851 (7)	Tl—F2^{vii}	3.528 (6)
Tl—F2^{iii}	2.851 (7)	Tl—O^{viii}	3.594 (9)
Tl—O	2.95 (1)		
F1—Al—F2	90	F2—Al—F3	89.6 (6)
F1—Al—F3	90	Al—F3—Al^{iv}	177.1 (10)

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

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Mercury(II) Arsenate, a Graphtonite-Type Structure

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Abstract

$Hg_3(AsO_4)_2$ is isostructural with $Hg_3(PO_4)_2$. Both compounds crystallize with a graphtonite-type structure. As a result of the tendency of mercury(II) to form two short linear bonds, there are deviations in the coordination polyhedra between the two structures although the arrangements of the tetrahedral anions are very similar.

Comment

Mercury(II) arsenate, $Hg_3(AsO_4)_2$, has been investigated as part of a project dealing with the coordination of Hg^{II} in inorganic salts. The arsenate is isostructural with the corresponding phosphate (Aurivillius & Nilsson, 1974). Single crystals of Hg_3-

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$(AsO_4)_2$ were grown by heating powder from a commerical source to 455 K in $1M$ HNO_3 for 3 d and slowly decreasing the temperature. Needles with well defined facets were formed.

When coordinated to O atoms, Hg^{II} often forms two short, almost linearly arranged bonds with lengths 2.0–2.2 Å. In addition, three to five O atoms are usually coordinated at distances of 2.4–2.9 Å. This behaviour often causes mercury salts to crystallize in structures different from those of other divalent metal salts. In contrast to this, the arsenate and phosphate salts crystallize in the graphtonite-type structure (Calvo, 1968).

Graphtonite is a mineral with composition $(Fe^{2+},Mn^{2+},Ca^{2+})_3(PO_4)_2$. Other phosphates and arsenates of divalent metal ions, e.g. $CdZn_2(PO_4)_2$, $Cd_2Zn(PO_4)_2$ (Calvo & Stephens, 1968), $Mn_3(PO_4)_2$ (Stephens, 1967), $Fe_3(PO_4)_2$ (Kostiner & Rea, 1974) and $Cd_3(AsO_4)_2$ (Engel & Klee, 1970), crystallize in this type of structure. The anionic arrangement obviously allows the flexibility needed to accommodate different cations. Even the Hg^{2+} ion which normally has a strong influence on the anionic arrangement does not change the basic structure. Small shifts of the oxygen tetrahedra allow mercury to achieve short linear bonds. The anionic arrangements in the structures of $Hg_3(AsO_4)_2$ and graphtonite are compared in Fig. 1.
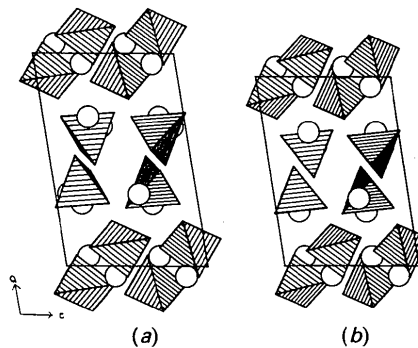

Fig. 1. (*a*) Mercury(II) arsenate and (*b*) graphtonite projected along (010). The differences in the cation polyhedra are due to expansion of the *c* axis in mercury(II) arsenate and small tilts of the tetrahedra. [Cell dimensions in graphtonite: $a = 8.91$ (1), $b = 11.58$ (1), $c = 6.239$ (8) Å, $\beta = 98.9$ (1)°].

The asymmetric unit of mercury(II) arsenate comprises three Hg^{II} atoms and two AsO_4^{3-} tetrahedra (Table 1). Each Hg^{II} has two short Hg—O bonds [Hg—O = 2.06 (1)–2.14 (1) Å, O—Hg—O = 161.8 (6)–170.6 (5)° (see Table 2)]. The O—As—O bond angles are in the range 99.2 (5)–116.3 (5)° with one short and three long As—O bonds. The three long bonds are to the O atoms that participate in the short Hg—O bonds. This arrangement builds up two