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Refinement of β-Alum $CsTi(SO_4)_2 . 12H_2O$

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Crystals of $CsTi(SO_4)_2 . 12H_2O$ were grown under nitrogen atmosphere from a refrigerated solution. The space group was found to be *Pa*3 both at 23 °C and at − 171·5 °C with cell dimensions a = 12·45 and a = 12·393 (5) Å respectively. The crystal structure of $CsTi(SO_4)_2 . 12H_2O$ was refined from 665 independent reflexions, collected from three-dimensional X-ray diffraction film data at − 171·5 °C to R = 6·6 %. The structure was found to be isomorphous with β-alum $CsAl(SO_4)_2 . 12H_2O$. Shifts for all atomic coordinates with respect to those of the CsAl alum were less than 0·012 of the unit-cell edge. The Cs–O_W(1), Cs–O_S(2) and Ti–O_W(2) bond distances were 3·314 (5), 3·493 (5) and 2·028 (5) Å respectively. The S–O_S(1) and S–O_S(2) bond distances were found to be 1·475 (9) and 1·484 (4) Å respectively. The structure exhibits a high degree of perfection in its three structural features.

Introduction

Intermittently over the past 15 years, investigations have been conducted on the electron-paramagnetic-resonance spectrum of the Ti^{3+} ion. Studies at low and very low temperatures ($\sim$ 100 °K and $\sim$ 1–3 °K respectively) on powders and single crystals of $CsTi(SO_4)_2 . 12H_2O$ revealed an anomalous spectrum when compared with spectra obtained at higher temperatures (Bleany, Bogle, Cooke, Duffus, O'Brien & Stevens, 1955; Bose, Chakravarty & Chatterjee, 1960). These and later electron-spin-resonance studies at very low temperatures (Dionne, 1966; Mackinnon, 1966; Woonton & Mackinnon, 1968) on Ti^{3+}-substituted α and β aluminum alums suggested that the anomalous behaviour may be due to the distortions caused in the octahedral crystal field about the trivalent cation when the larger Ti^{3+} ion (r = 0·76 Å) is substituted for the smaller Al^{3+} ion (r = 0·51 Å). To date, the effect of both a large monovalent cation and a large trivalent cation on the crystal structure of an alum has not been examined. Thus in order to understand this effect better, a low-temperature crystal-structure investigation was made of $CsTi(SO_4)_2 . 12H_2O$.

Experimental

Crystals of caesium–titanium alum suitable for X-ray studies were obtained from a Zn-reduced solution collected under nitrogen atmosphere and refrigerated for several days. The crystals were purple in colour and had the shape of well formed octahedra with edges of 0·1 to 2 mm. They could be kept indefinitely if stored in a refrigerator in their mother liquor under nitrogen atmosphere. Upon exposure to air for more than one hour the crystals begin to decompose. Smaller crystals decomposed more rapidly than larger ones. Under subsequent X-ray examination many well formed octahedra were found to be composed of more than one individual. Two octahedral crystals were selected, each composed of more than one individual, but which were sufficiently well aligned to be suitable.

Crystal I was a distorted octahedron with edges 0·24 (1) and 0·22 (1) mm in the plane of the data collection. Crystal II was a well formed octahedron 0·31 (1) mm on edge.

The crystals were mounted and sealed in thin-walled sodium glass capillaries. Under these conditions, the crystals could be kept for a sufficient length of time to obtain at least one level of data.

The compound has the space group *Pa*3 with unit-cell edge of 12·45 Å at 23 °C. The measured density is 2·013 (15) g cm^{-3}; the calculated density for $Z = 4$ is 2·019 g cm^{-3}.

The structure determination was carried out at − 171·5 °C using a low-temperature apparatus constructed by the author (Sygusch, 1969). The temperature was continuously monitored throughout the data collection. The stability of the temperature at the crystal was maintained to within ± 1 °C. The space group was found to be *Pa*3 and is the same as at room temperature, with a unit-cell edge of 12·393 (5) Å [λ(Cu $K\alpha$) = 1·54178 Å]. The intensity data were recorded on a Nonius Weissenberg camera with a 3-film (Ilford G) pack using Ni-filtered Cu radiation. A collimating system was chosen such that the crystals would be totally bathed in the constant-intensity cross-section of the incident beam (Jeffrey & Whitaker, 1965). In order to acquire rapidly a sufficient number of data, intensities were integrated in the translation direction. This arrangement permitted more accurate measurements with the densitometer since it could scan along the white radiation streaks. For crystal I, only *hk*0 data could be acquired before decomposition was noticed. Five levels of data about [110] and one level about [112] were collected from crystal II. In all, 665 independent reflexions were collected, each measured an average of four times. Intensities were scanned with a Joyce Double Beam Recording Microdensitometer Mk III

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Cs in the direction of zero-level white radiation streak. The diffracted profiles were then planimetered. Peaks extending into the non-linear response region of the film were corrected for non-linearity (Sygusch, 1969). Weak intensities were eye-estimated and placed on a common scale with the densitometered intensities. The lower film intensities were scaled to the top film and combined. The intensities were then corrected in the usual way for Lorentz and polarization effects. Because of the high linear-absorption coefficient $\mu = 215{\cdot}08\ \text{cm}^{-1}$ [calculated from values by Frazer (1969)], a $12 \times 12 \times 12$ Gaussian grid was used to calculate the transmission factors. A program written by the author (Sygusch, 1969) was used for this purpose. The various levels were then placed on a common scale based on the procedure of Hamilton, Rollett & Sparks (Fox & Holmes, 1966).

Refinement of the structure

The atomic positions found by Cromer, Kay & Larson (1966) (hereafter referred to as CKL) for $CsAl(SO_4)_2.12H_2O$ were used as starting values for a full-matrix refinement of non-hydrogen parameters. Anomalous dispersion corrections were included. Anisotropic thermal parameters were used in the form

$$\exp\,[-\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2 + 2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]\,.$$

Series expansions of the scattering factors were used for all atoms (Onken & Fischer, 1969). The scattering-factor coefficients of Cromer & Waber (1965) were used for caesium and titanium and those given by Onken & Fischer (1969) for sulphur and oxygen and, later, hydrogen. The anomalous-dispersion factors used were from *International Tables for X-ray Crystallography* (1962). The quantity minimized was

$$\sum w(F_o-F_c^*)^2:$$

$$F_c^*=KF_c\left\{1+g\left[\frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2}\right]A^{-1}\ \frac{dA}{d\mu}^*\ \text{Lp}\,F_c^2\right]^{-1/2}$$

where K is the scale factor, g is the secondary extinction parameter (Zachariasen, 1963), Lp the Lorentz-polarization factor, A the absorption factor, $dA^*/d\mu$ the absorption component of the secondary extinction factor (Larson, 1967).

The weighting scheme employed was based on the reciprocal of the variance of the structure factor. Besides the explicit error of intensity measurement, implicit errors – neglect of peak width, alignment, mass absorption values, crystal shape measurement – were allowed to contribute to the variance of the structure factor (Sygusch, 1969).

At the end of the refinement all parameter shifts $\Delta\xi_i/\sigma(\xi_i)$ were less than 10^{-3} for all non-hydrogen atoms. The positional shifts from the starting values were less than 0·13 Å. The weighted residual R_w at this point was 0·081. A three-dimensional difference synthesis was then made using low-order structure factors ($\lambda^{-1}\sin\theta < 0{\cdot}4$ Å^{-1}). The hydrogens of the water molecules about the Ti^{3+} were easily found but those of the water molecules about the Cs^+ could not be as clearly resolved *a priori.* Since there is only one consistent hydrogen-bonding scheme (CKL), the Cs^+ water hydrogen atom positions were chosen accordingly. Several unsuccessful attempts were made including blocking certain parameters to prevent, on refinement, the hydrogen thermal parameters from becoming negative. The residuals R_w and R were independent of the values of the hydrogen B's and as a result the hydrogen B values obtained by CKL were scaled linearly to −171·5°C and set to an average value of 1·4 and held constant during refinement. The final residuals were $R_w = 0{\cdot}077$ and $R = 0{\cdot}066$ for all reflexions. To test whether the inclusion of the hydrogen atoms is significant at the $\frac{1}{2}$% level, Hamilton's R-factor ratio test was used (Hamilton, 1965).

$$\mathcal{R}_{12,616,\ 0{\cdot}005} = 0{\cdot}081/0{\cdot}077 = 1{\cdot}052\,.$$

From tables $\mathcal{R} = 1{\cdot}023$ (Hamilton, 1965). Thus the inclusion of the hydrogen atoms is significant at the 0·005 level. The test does not establish whether the sub-

Table 1. *Atomic and thermal parameters for* $CsTi(SO_4)_2.12H_2O$

All parameters are × 10^5.

$g = 1{\cdot}49\ (25) \times 10^{-5}$.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cs	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	198 (3)	β_{11}	β_{11}	−16 (3)	β_{12}	β_{12}
Ti	0	0	0	168 (8)	β_{11}	β_{11}	0 (7)	β_{12}	β_{12}
S	32762 (12)	x	x	173 (5)	β_{11}	β_{11}	15 (7)	β_{12}	β_{12}
$O_S(1)$	25892 (40)	x	x	267 (29)	β_{11}	β_{11}	−45 (24)	β_{12}	β_{12}
$O_S(2)$	28055 (36)	33455 (37)	43747 (34)	283 (29)	257 (29)	169 (27)	16 (27)	81 (22)	−56 (24)
$O_W(1)$	15855 (39)	5390 (43)	29153 (41)	142 (29)	247 (33)	294 (31)	−42 (26)	6 (24)	29 (24)
$O_W(2)$	16367 (40)	24 (37)	49 (38)	149 (34)	279 (39)	299 (41)	50 (32)	− 2 (23)	86 (25)
H(1)	61091 (954)	21480 (797)	19966 (938)	1·4*					
H(2)	73506 (962)	21055 (937)	98583 (1026)	1·4					
H(3)	71119 (927)	6081 (925)	53324 (823)	1·4					
H(4)	51988 (845)	19874 (885)	56799 (968)	1·4					

* The isotropic temperature factors of the hydrogen atoms were kept constant during the refinement.

sequent information derived is valid. Table 1 gives the final least-squares parameters.[*]

Discussion

The interatomic distances and bond angles are given in Table 2 and the thermal ellipsoid parameters obtained from the thermal parameters, in Table 3. The errors were computed using the complete variance–covariance matrix including the effect of lattice-parameter error and allowing the hydrogen-atom positions to vary.

Table 2. *Interatomic distances and angles in* $CsTi(SO_4)_2.12H_2O$

Standard deviations in parentheses apply to the last digits. Distances corrected for thermal motion are in brackets.

$Ti–6O_W(2)$	2·028 (5) Å
$Cs–6O_W(1)$	3·314 (5)
$Cs–6O_S(2)$	3·493 (5)
The sulphate group	
$S–O_S(1)$	1·475 (9) [1·499]
$S–3O_S(2)$	1·484 (4) [1·508]
$O_S(1)–3O_S(2)$	2·418 (8)
$O_S(2)–2O_S(2)$	2·420 (8)
$O_S(1)–S–O_S(2)$	109·6 (2)°
$O_S(2)–S–O_S(2)$	109·3 (2)
$O_S(2)–O_S(2)–O_S(2)$	60·0
$O_S(2)–O_S(2)–O_S(1)$	60·0 (1)
$O_S(2)–O_S(1)–O_S(2)$	60·1 (3)
Water molecules	
$O_W(1)–H(1)$	0·875 (128) Å [0·876]
$O_W(1)–H(2)$	0·875 (149) [0·873]
$O_W(2)–H(3)$	1·046 (116) [1·045]
$O_W(2)–H(4)$	0·976 (122) [0·972]
$H(1)–O_W(1)–H(2)$	89·5 (9·5)°
$H(3)–O_W(2)–H(4)$	118·1 (10·2)

The atomic coordinates correspond closely to those given by CKL. The only significant difference is in the greater x coordinate of the $O_W(2)$ atom. However, this can be attributed to the larger radius of the Ti^{3+} ion in comparison with the Al^{3+} ionic radius. The Ti^{3+}'s octahedron is virtually aligned along the crystal axis and consequently negligibly distorted.

The $Ti–O_W(2)$ bond is 2·028 Å, in good agreement with previous determinations (*International Tables for X-ray Crystallography*, 1962). The $Cs–O_S(2)$ distances are a little longer than the $Cs–O_W(1)$ distances (3·493 Å *vs.* 3·314 Å). In addition, the two ends of the $O_W(1)$ trigonal antiprism are separated by only 0·049 Å, which is smaller than the value of 0·062 Å found by CKL.

The oxygens of the sulphate group form a perfect tetrahedron. This can be seen from the equality of $O_S(1)–3O_S(2)–2O_S(2)$ bond distances [2·418 (8) and 2·420 (8) Å respectively] which make up the edges of the tetrahedron. S–O distances were corrected according to the in-phase assumption of Busing & Levy (1964) (see Table 3). The greater $S–O_S(1)$ and $S–O_S(2)$ bond distances, even at a lower temperature than those found by CKL, are due to the greater perfection of the tetrahedron. The thermal vibration analysis of the sulphate group revealed no particular results other than the direction of maximum motion of the $O_S(1)$ is normal to the $S–O_S(1)$ bond, as found by CKL.

Because of their large standard deviations, the hydrogen-bond distances are only included for completion.

Conclusion

The refinement of the crystal structure of $CsTi(SO_4)_2.12H_2O$ shows it to be characteristic of a β-alum and isomorphous with the β-alum $CsAl(SO_4)_2.12H_2O$ refined by CKL. Thus insertion of a larger trivalent cation Ti^{3+} in the position occupied by a smaller trivalent cation Al^{3+} in a β-alum causes no distortions in the surrounding water octahedron. In fact, the substitution for a larger cation increases the regularity of both the trivalent cation's water octahedron and the sulphate group tetrahedron as well as improving the planarity of the water molecules about the monovalent cation.

As shown in the Introduction, it is evident that the reason for the previously discussed anomaly does not lie in the crystal structure but must be sought in the electronic structure of either the octahedral crystal field or the titanium ion itself.

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The least-squares refinement was performed with Prewitt's (1966) *SFLS* program, the difference Fourier synthesis and structure-factor tables with the Ahmed, Hall, Pippy & Huber (1966) *NRC*-2, *NRC*-8, and *NRC*-23 crystallographic programs and the interatomic distances, angles, thermal ellipsoids and the associated standard deviations with Busing, Martin & Levy's (1964) *ORFFE* program.

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[*] The structure-factor table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30270 (5 pp.). Copies can be obtained from the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Thermal ellipsoids in* $CsTi(SO_4)_2.12H_2O$: *principal axes and directions*

	R.m.s. amplitude	Direction angles relative to crystal axes α	β	γ	Relative to [111]
Cs	0·114 (2) Å	54·7°	54·7°	54·7°	0°
	0·129 (1)				90
	0·129 (1)				90
Ti	0·114 (6)	54·7	54·7	54·7	0
	0·114 (4)				90
	0·114 (4)				90
S	0·126 (5)	54·7	54·7	54·7	0
	0·111 (3)				90
	0·111 (3)				90
$O_S(1)$	0·117 (17)	54·7	54·7	54·7	0
	0·156 (11)				90
	0·156 (11)				90
$O_S(2)$	0·160 (8)	33 (18)	102 (26)	60 (8)	49 (23)
	0·147 (9)	111 (25)	156 (15)	78 (16)	128 (24)
	0·090 (12)	115 (6)	69 (8)	33 (6)	63 (6)
$O_w(1)$	0·099 (12)	21 (11)	69 (11)	96 (8)	47 (8)
	0·139 (9)	69 (12)	144 (20)	61 (24)	89 (19)
	0·155 (8)	95 (11)	61 (22)	29 (24)	43 (8)
$O_w(2)$	0·099 (14)	28 (15)	114 (12)	78 (11)	67 (8)
	0·131 (10)	64 (15)	53 (14)	132 (12)	77 (12)
	0·172 (8)	82 (8)	47 (11)	44 (12)	27 (8)

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