

Cesium Hydrogen Tartrate and Anomalous Dispersion of Cesium

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Cesium hydrogen (+)-tartrate is orthorhombic, $P2_12_12_1$, $a = 8.076$ (3), $b = 11.621$ (5), $c = 7.692$ (3) Å, $Z = 4$, $D_x = 2.594$ g cm⁻³, at 22°C. Its structure, nearly the same as that of ammonium hydrogen tartrate, was refined to $R = 0.016$ for 2442 reflections ($F^2 > 3\sigma$) out to $d = 0.66$ Å. Our least-squares program was modified to treat anomalous-dispersion terms as independent adjustable parameters, and f'' for cesium was determined as 2.22 (6) e for Mo $K\alpha$ radiation. In the determination of absolute configuration or polarity, refinement of f'' for a heavy atom has the advantage that one can detect inversion twinning, as well as save on computational time.

Introduction

Anomalous scattering of X-rays and its use in diffraction analysis is receiving wide attention (Ramaseshan & Abrahams, 1975), but there remains a need for more detailed and accurate knowledge of these dispersion effects, especially for the heavier atoms and near the L edges. The availability of synchrotron radiation (Phillips, Wlodawer, Goodfellow, Watenpugh, Sieker, Jensen & Hodgson, 1977, and references therein) as a sharply tunable and intense source permits diffraction experiments at arbitrary wavelengths and gives a new opportunity for experimental measurement of the dispersion corrections.

There is strong correlation between scattering factors, thermal parameters, and scale factors, and relatively few reflections can be observed at long wavelengths. These facts require one to have independent information of some of the parameters if accurate scattering factors are to be obtained from the diffraction intensities. In anticipation of experiments with cesium in the neighborhood of the L edges, we have determined the crystal structure of cesium hydrogen (+)-tartrate using Mo $K\alpha$ radiation, for which the dispersion corrections are relatively small, and incidentally derived a value for f'' for Cs at this wavelength.

Cell dimensions, slightly smaller than our values, were reported by Hémon (1931), but there appears to have been no further X-ray study of this cesium salt. The full structure was determined for the isomorphous ammonium hydrogen tartrate by van Bommel & Bijvoet (1958).

Anomalous dispersion in least squares

The method of least squares requires the derivatives:

$$\frac{\partial |F|}{\partial u} = \frac{A}{|F|} \frac{\partial A}{\partial u} + \frac{B}{|F|} \frac{\partial B}{\partial u} \quad (1)$$

where u is a parameter and $F = A + iB$. If $f = f_0 + f' + if''$ for a particular element, the derivatives with respect to f' and f'' have the simple forms:

$$\frac{\partial A}{\partial f'} = \sum T \cos Q \quad (2a)$$

$$\frac{\partial B}{\partial f'} = \sum T \sin Q \quad (2b)$$

$$\frac{\partial A}{\partial f''} = \sum -T \sin Q \quad (2c)$$

$$\frac{\partial B}{\partial f''} = \sum T \cos Q \quad (2d)$$

where $Q = 2\pi(hx + ky + lz)$ and T is the temperature factor. The sums include all the atoms of the particular element in the unit cell, whether they are related by symmetry or not.

In the calculation of f' or f'' by a series expansion (Hönl, 1933) the largest angle-dependent terms go as $\cos 2\theta = 1 - 2 \sin^2 \theta$. As a first step in looking for such effects in our experiments, we have expressed the dispersion corrections as:

$$f' = f'_1 + f'_2 \lambda^{-2} \sin^2 \theta \quad (3a)$$

$$f'' = f''_1 + f''_2 \lambda^{-2} \sin^2 \theta \quad (3b)$$

because of the custom of listing form factors as a function of $\lambda^{-1} \sin \theta$. Then the derivatives with respect to the angle-independent parts f'_1 and f''_1 are the same as given above for f' and f'' , and the derivatives with respect to f'_2 and f''_2 differ only by the factor $\lambda^{-2} \sin^2 \theta$:

$$\frac{\partial A}{\partial f'_2} = \lambda^{-2} \sin^2 \theta \frac{\partial A}{\partial f'_1}, \text{ etc.} \quad (4)$$

Similar relations occur if $\lambda^{-2} \sin^2 \theta$ is replaced by some other function of θ .

Because of the simplicity of these relations, there is no difficulty in modifying a crystallographic least-squares program to include the anomalous-dispersion parameters as independent variables, apart from the bookkeeping details of the various arrays. We have made such changes in our local program, Zalkin's *LESQ*. However, the rate of convergence and the reliability of the result are contingent on avoidance of excessive correlation.

With a chiral crystal which is known to be a pure enantiomer, f'' for a heavy atom is determined by the magnitudes of differences in structure factors for Bijvoet pairs, and is little correlated with other variables, assuming that f'' is known or negligible for other atoms in the structure. Thus, one can expect f'' to be well determined by data for a single X-ray wavelength. On the other hand, f' is strongly correlated with thermal parameters and is very subject to errors which are systematic with respect to scattering angle. We expect that its determination will be much improved by combination of data from more than one wavelength.

In this work enantiomeric purity is crucial, and one of our reasons for choosing a tartrate salt is the ready availability of pure (+)-tartrate. It is commonplace that questions of absolute configuration are discussed as binary choices of right- or left-handed structure, without any consideration of mixtures related by inversion twinning. This procedure is appropriate for a crystal known to contain chiral molecules all of the same handedness; it is not appropriate when the chirality exists only in the crystal structure or when one has racemic starting material. The refinement of f'' for a heavy atom is a direct test for inversion twinning. Such twinning results in a magnitude for f'' less than the correct value. The results described below are an example of good agreement with theory for a pure enantiomer. In a recent study of $U(BH_4)_4 \cdot O(C_2H_5)_2$ by Rietz, Zalkin, Templeton, Edelstein & Templeton

(1978), an example of the second kind, this test revealed a 70:30 ratio of enantiomers. Since the addition of one parameter has an insignificant effect on the cost of refinement, this method is also more economical than the more common procedure of refining twice, once with each handedness. If one tests the wrong enantiomer, f'' simply refines to a negative value. The factor by which f'' exceeds its standard deviation can be used as an index of the decisiveness of the determination of configuration. Similar statements apply to the question of absolute orientation of polar but achiral structures, except that then twinning is always possible.

Experimental

Cesium hydrogen (+)-tartrate was prepared from CsCl (Fisher, 'purified') and (+)-tartaric acid (Matheson Coleman and Bell, 'reagent'). Analysis by X-ray fluorescence showed 0.12% Rb, and atomic absorption spectroscopy showed 0.03% K in the CsCl (0.24 mol % Rb and 0.13 mol % K relative to Cs). The best crystals were obtained by using a slight excess of CsCl; 2.9 g (19.3 mmol) tartaric acid and 3.30 g (19.6 mmol) CsCl were each dissolved in 6 ml water. The solutions were mixed and heated for 10 min, then allowed to stand at room temperature. After several days, numerous small crystals had formed in the sirup; some were needles and others were nearly equal in their dimensions. Weissenberg photographs of a needle showed it to be of the same structure as the more nearly square habit.

A crystal about $0.14 \times 0.14 \times 0.25$ mm in size was used for measurements with a Picker FACS-I diffractometer equipped with a graphite monochromator and Mo radiation ($\lambda = 0.70926$ Å for $K\alpha_1$). Cell dimensions were derived by least squares from the setting angles of 12 reflections ($40^\circ < 2\theta < 50^\circ$). Diffraction intensities were measured by the θ - 2θ scan technique at 2° min^{-1} for 2θ , for all reflections in the full sphere ($\pm h, \pm k, \pm l$) up to $2\theta = 55^\circ$, and for the half sphere ($\pm h, \pm k, +l$) up to $2\theta = 65^\circ$ or $d = 0.66$ Å. The scan width was 1° in 2θ (up to 55°) or 1.2° (55 to 65°) plus the α_1 - α_2 splitting. Background was counted for 4 s (or 10 s above 55°) at each end of the scan. Three strong reflections (600, 060, 006) checked at intervals of 200 measurements indicated no decay within the accuracy of the experiment.

Absorption corrections calculated by an analytical integration (Templeton & Templeton, 1973), with the shape defined by 10 plane faces, ranged from 1.539 to 1.907, with $\mu = 50.67 \text{ cm}^{-1}$.

Measurements of 8963 reflections not excluded by the space group were averaged to give 2632 unique reflections (point group 222) for 2442 of which $F^2 > 3\sigma$.

Table 1. Positional parameters for the heavy atoms ($\times 10^4$)

	x	y	z
Cs	3323.4 (2)	324.5 (1)	11598.4 (1)
O(1)	6303 (2)	-1364 (1)	10462 (2)
O(2)	7043 (2)	-3202 (1)	10193 (2)
O(3)	5722 (2)	-3332 (1)	6945 (2)
O(4)	8606 (2)	-1787 (2)	6841 (2)
O(5)	4830 (2)	-1129 (1)	4607 (2)
O(6)	7354 (2)	-1544 (2)	3611 (2)
C(1)	6455 (3)	-2330 (2)	9595 (2)
C(2)	5805 (3)	-2230 (2)	7743 (3)
C(3)	6952 (2)	-1444 (2)	6700 (3)
C(4)	6323 (3)	-1366 (2)	4819 (3)

Crystal data

CsHC₄H₄O₆, space group *P*2₁2₁2₁; at 22 ± 1 °C: *a* = 8.076 (3), *b* = 11.621 (5), *c* = 7.692 (3) Å, *Z* = 4, *V* = 721.90 Å³, *D_x* = 2.594 g cm⁻³.

Structure refinement

Cesium hydrogen tartrate is isomorphous with ammonium hydrogen tartrate, and refinement starting with parameters for that salt (van Bommel & Bijvoet, 1958) converged with little change. Since our axes are chosen according to the convention of Donnay (1943), with *a* and *c* interchanged from the setting of van Bommel & Bijvoet, the coordinates must be transformed as $\frac{1}{4} + z$, $\frac{1}{4} - y$, $\frac{1}{4} + x$ to retain right-handed axes and the standard choice of origin for *P*2₁2₁2₁. Scattering factors for Cs⁺ and neutral C and O were taken from Doyle & Turner (1968) and for H from Stewart, Davidson & Simpson (1965). Dispersion corrections were from Cromer & Liberman (1970).

With isotropic thermal parameters for H, anisotropic parameters for all other atoms, and with *f*'' for Cs as an adjustable parameter, least-squares refinement reduced *R* = Σ|Δ*F*|/Σ|*F*_o| to 0.016 for 2442 reflections with *F*² > 3σ and to 0.019 for all 2632 reflections. The weighted *R*_w = [Σ*w*(Δ*F*)²/Σ*wF*_o²]^{1/2}, the quantity minimized, was 0.016. Zero weight was assigned to reflections weaker than 3σ; for others *w* = [σ(*F*)]⁻²; σ(*F*) was derived from

$$\sigma(F^2) = [S^2 + (0.015 F^2)^2]^{1/2}$$

where *S*² is the variance due to counting statistics. An empirical extinction correction was applied which increased *F* for the strongest reflection by 6% and changed only seven other structure factors by as much as 2%. In the last cycle no parameter changed as much as 0.03 σ. Final coordinates (all atoms) and isotropic thermal parameters (H atoms) are listed in Tables 1 and 2.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33180 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Positional (×10³) and isotropic thermal parameters for the hydrogen atoms

The form of the temperature factor is exp(-*Bλ*⁻² sin² θ).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
H(1)	468 (3)	-186 (2)	774 (3)	1.0 (4)
H(2)	689 (3)	-76 (2)	714 (3)	1.9 (5)
H(3)	474 (5)	-344 (3)	652 (4)	4.8 (8)
H(4)	876 (4)	-237 (3)	638 (4)	3.5 (8)
H(5)	648 (5)	-139 (3)	1158 (5)	5.5 (9)

Results and discussion

The value of *f*'' for Cs refined to 2.22 (6) e, in good agreement with 2.119 calculated by Cromer & Liberman (1970). Another refinement, with *f*'' defined as in (3*b*), yielded *f*'' = 2.1 (1) + [0.3 (5)]λ⁻² sin² θ, with insignificant changes in the other parameters and

Table 3. Bond angles (°) in the bitartrate ion

O(1)-C(1)-O(2)	124.1 (2)	O(5)-C(4)-O(6)	125.2 (2)
O(1)-C(1)-C(2)	112.2 (2)	O(5)-C(4)-C(3)	117.1 (2)
O(2)-C(1)-C(2)	123.7 (2)	O(6)-C(4)-C(3)	117.7 (2)
C(1)-C(2)-C(3)	109.2 (2)	C(2)-C(3)-C(4)	109.2 (2)
C(1)-C(2)-O(3)	110.5 (2)	C(2)-C(3)-O(4)	111.6 (2)
C(3)-C(2)-O(3)	109.9 (2)	C(4)-C(3)-O(4)	113.9 (2)
C(1)-C(2)-H(1)	110 (1)	C(2)-C(3)-H(2)	108 (2)
C(3)-C(2)-H(1)	107 (1)	C(4)-C(3)-H(2)	107 (2)
O(3)-C(2)-H(1)	110 (1)	O(4)-C(3)-H(2)	107 (2)
C(1)-O(1)-H(5)	117 (2)	C(3)-O(4)-H(4)	112 (2)
C(2)-O(3)-H(3)	110 (2)		

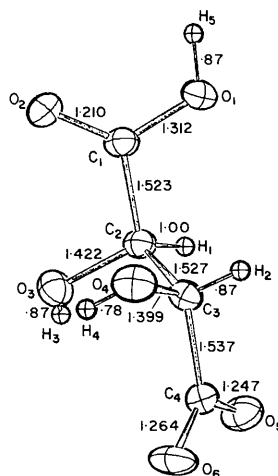


Fig. 1. View of the bitartrate ion with 50% probability ellipsoids, drawn with Johnson's (1965) ORTEP, showing molecular conformation, absolute configuration, and bond distances (in Å). The size of the hydrogen atoms is arbitrary. Standard deviations are about 0.03 Å for bonds to hydrogen and 0.003 Å or less for other bonds.

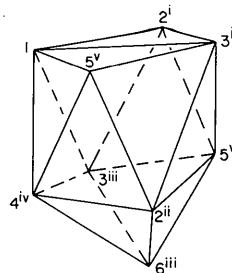


Fig. 2. Coordination polyhedron for oxygen neighbors of the cesium atom. The numbers and symmetry code are the same as in Table 4.

Table 4. *Cesium–oxygen distances* (Å)

Cs–O(1)	3.226 (2)	Cs–O(4 ^{iv})	3.012 (2)
–O(2 ⁱ)	3.008 (2)	–O(5 ^v)	3.113 (2)
–O(2 ⁱⁱ)	3.019 (2)	–O(5 ^{vi})	3.116 (2)
–O(3 ⁱ)	3.321 (2)	–O(6 ⁱⁱⁱ)	3.684 (2)
–O(3 ⁱⁱⁱ)	3.234 (2)		

Symmetry code

(i)	$-\frac{1}{2} + x, -\frac{1}{2} - y, 2 - z$	(iv)	$\frac{3}{2} - x, -y, \frac{1}{2} + z$
(ii)	$1 - x, \frac{1}{2} + y, \frac{3}{2} - z$	(v)	$x, y, 1 + z$
(iii)	$1 - x, \frac{1}{2} + y, \frac{3}{2} - z$	(vi)	$\frac{1}{2} - x, -y, \frac{1}{2} + z$

agreement indices. Thus the precision of this data set is not great enough to reveal any angular dependence of f'' .

The structure is nearly the same as that of ammonium hydrogen tartrate (van Bommel & Bijvoet, 1958). Bond distances (Fig. 1) and angles (Table 3) of the bitartrate ion are identical within about five times the estimated standard deviations. The Cs ion has nine O neighbors (Table 4), eight of them approximately at the corners of a square antiprism, with the ninth, O(6), at a slightly greater distance capping one square face (Fig. 2). A similar arrangement occurs in the ammonium salt, but with shorter distances from N to its O neighbors. Hydrogen bonds from O(1) to O(6), O(3) to O(6), and O(4) to O(5) are the same in the two salts, with corresponding O–O distances 2.58, 2.76 and 2.84 Å in the Cs salt and 2.55, 2.74 and 2.80 Å in the ammonium salt.

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Minimizing the Variance in Densities Evaluated by Fourier Synthesis

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Criteria for minimizing the variance in the Fourier synthesis of scattering densities are established. Their value has been confirmed by applying them to a study of bonding electron density by difference Fourier methods. The procedure has conceptual and practical advantages when compared with other types of weighting for the coefficients in a difference synthesis. It is expected that the minimum-variance criterion will improve the interpretability of some other classes of Fourier synthesis, such as those used in the study of protein structures.

Introduction

The techniques used for the study of the structure of materials by the analysis of diffraction data may be broadly classified as either Fourier-synthesis or least-

squares methods. The latter are more convenient for quantitative work on a wide range of structural problems but there is revived interest in quantitative studies by Fourier methods because of applications in the charge-density and protein-structure fields.