Thermal Motion of the Sulfate Group in Sodium Alum NaAl(SO₄)₂.12H₂O*

By M. I. Kay

Puerto Rico Nuclear Center, Mayaguez, Puerto Rico

and Don T. Cromer

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, U.S.A.

In the structure refinement of Na alum by Cromer, Kay & Larson ([*Acta Cryst.* (1967). **22**, 182]) the unusual anisotropic thermal parameters of the SO₄ group were explained by a coupled rotation about and translation along the threefold axis. S and O(1) are on the threefold axis and O(2) is in a general position. O(2) thus follows a spiral path on the surface of a cylinder. In the present work the scattering over the spiral path was calculated by integrating numerically and taking numerical derivatives. It was then evident that a torsional oscillation also exists. Based on the formation developed by Kay & Behrendt, a model that adds a torsional oscillation to the screw motion was calculated. In addition, thermal parameters parallel and perpendicular to the threefold axis were applied to the whole group. The thermal motion is then described by only five parameters instead of the ten used in the earlier anisotropic refinement. A result of this treatment is that the bond lengths can be expressed in terms of equilibrium positions and are as accurate as the data and potentials allow. The resulting bond lengths are S–O(1)= 1·476 (6) and S–O(2)= 1·491 (4) Å. The uncorrected lengths from the anisotropic refinement are 1·461 and 1·459 Å. The Cruickshank rigid body correction increases these bond lengths to 1·475 and 1·483 Å and the Schomaker–Trueblood analysis increases them to 1·476 and 1·500 Å.

Introduction

All of the alums crystallize in the cubic space group *Pa*3 with sulfate groups lying on threefold axes. One of the oxygen atoms, which we call O(1), and the sulfur atom lie in special positions on the threefold axes. The other oxygen atom, O(2), is in a general position, and the threefold operation on this atom completes the sulfate group. One would expect *a priori* that a major contribution to the total motion of these sulfate groups would be an oscillation of the group about the symmetry axis. Under that condition the major axis of the O(2) thermal ellipsoid would be approximately perpendicular to the threefold axis.

In the X-ray and neutron diffraction study of sodium alum NaAl(SO₄)₂.12H₂O, by Cromer, Kay & Larson (1967) (hereafter CKL), the O(2) atom was found to have a large and very anisotropic thermal motion. The major axis, with a root-mean-square amplitude of 0·361 Å ($B=10·3$ Å²), makes an angle of 65·5° with the threefold axis rather than the expected 90°. In order to explain this orientation, CKL postulated that the sulfate group undergoes a coupled rotational–translational motion about, and parallel to, the threefold axis. There is a moderately short (2·62 Å) hydrogen bond between O(2) and one of the water molecules, and the O(2)–H distance in this hydrogen bond is 1·64 Å. The major axis of the O(2) ellipsoid makes an angle of 80° with this O(2)–H vector. An r.m.s. motion of 0·361 Å by O(2) changes the distance from O(2) to

the equilibrium position of H to 1·61 Å. However, if this 0·361 Å motion were directed along a line normal to the S–O(2) vector and to the threefold axis, this distance would be reduced by 0·13 Å. Since there are three of these O(2)–H contacts it seems reasonable that as the SO₄ group rotates it is forced to translate in order to maintain a longer O(2)–H distance if O(2) and H undergo independent motion, *i.e.* such a translational–rotational motion would follow a lower potential path than would the *a priori* expected motion normal to the threefold axis. In this postulated motion the O(2) atom traces out a spiral path on the surface of a cylinder.

Pertinent results from an anisotropic refinement are given in Table 1. These results are slightly different from those reported by CKL because somewhat different weights were used in the original work. In all of the present calculations unmodified weights obtained from the counting statistics (Evans, 1961) were used.

The above screw motion was explicitly included in the structure factor calculation and a least-squares refinement was carried out. At the conclusion of this refinement it became evident that the remaining amplitudes included a torsional motion about the S atom. The scattering from the torsional oscillator was also calculated and another refinement made. The final result is that the S–O distances can be directly obtained from the equilibrium atomic positions without any *a posteriori* corrections for thermal motion.

For small oscillations one usually assumes that the thermal vibration is fairly well approximated (as indeed it almost always is) by an anisotropic Debye–Waller factor for each atom in the crystal. The motion of the

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atom is assumed to be harmonic and is represented by an ellipsoid describing the r.m.s. amplitude of motion in each direction. If large torsional oscillations are present, one may make an *a posteriori* analysis of the ellipsoids such as Cruickshank (1956) and Schoemaker & Trueblood (1968) have done. If the anharmonicity is large enough, the Debye–Waller expression is inadequate. Various authors have described the scattering of one-dimensional torsional oscillations, or hindered rotations, by infinite series of Bessel functions (King & Lipscomb, 1950; Brown & Chidambaram, 1967) or by simplified expressions using more severe approximations (Kay & Behrendt, 1963; Maslen, 1968) which can take two-dimensional rather than one-dimensional motion into account. The difficulty in deriving such expressions arises from averaging the scattering over the appropriate probability density function, or, in other terms, deriving the Fourier transform of the probability density.

For the present case of coupled translational–rotational motion, which we shall call a spiral motion, our approach has been to evaluate the scattering by numerical integration and, in the least-squares refinement, to calculate numerical derivatives. Thus, no approximations were necessary. For the torsional oscillation the formulation developed by Kay & Behrendt (1963), hereafter KB, was used. It should be noted that Maslen's (1968) results are very similar to those derived by KB several years earlier.

Derivation of the spiral scattering

(a) Statement of the problem

One may classically describe the probability of an atom being in a given region in a potential well by means of Boltzmann statistics. If the potentional is $V(\mathbf{r}_n)$, $\mathbf{r}_n$ being a vector that describes the instantaneous position of atom n, $\mathbf{H}$ the reciprocal lattice vector, f_n the atomic scattering factor and kT the Boltzmann constant multiplied by the absolute temperature, the

average scattering amplitude from atom n is

$$g_n(\mathbf{H}) = \frac{\int_{-\infty}^{\infty} f_n(\mathbf{H}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_n) \exp[-V(\mathbf{r}_n)/kT] d\mathbf{r}_n}{\int_{-\infty}^{\infty} \exp[-V(\mathbf{r}_n)/kT] d\mathbf{r}_n}.$$
(1)

For the present case let us assume that the O(2) atoms also undergo an isotropic motion superimposed on the spiral motion. That is perhaps not the best possible assumption but it does permit making a fairly simple calculation with a small number of parameters having little correlation between different types of thermal motion and is a good first test of the method.

In the following we shall drop the subscript n. Let the isotropic thermal parameter be B, and let $\mathbf{r} = \mathbf{P} + \mathbf{t}$, where $\mathbf{P}$ is the vector to the equilibrium position of the atom at X^0, Y^0, Z^0, and $\mathbf{t}$ is the displacement vector from $\mathbf{P}$ to the instantaneous position of the atom (see Fig. 1). If N is the normalization factor in the denominator of equation (1), then

$$g(\mathbf{H}) = f(\mathbf{H}) \exp(-B \sin^2 \theta/\lambda^2) \exp(2\pi i \mathbf{H}.\mathbf{P}) \, \bar{G}$$
(2)

where

$$\bar{G} = \frac{1}{N} \int_{\infty-}^{\infty} \exp(2\pi i \mathbf{H}.\mathbf{t}) \exp[-V(\mathbf{r})/kT] d\mathbf{r}.$$
(3)

$\bar{G}$ is analogous to a temperature factor and will depend on the probability density function. Because the translation is made proportional to the rotation (for spiral motion), the potentional must be a function of the angular displacement only. If the angular displacement coordinate is θ, we choose

$$V(\theta) = \exp(-V_0 \theta^2/kT)$$
(4)

as the potentional function. The normalized prob-

Table 1. *Sulfate group parameters from anisotropic refinement ($R = 3.66\%$), with ten thermal parameters*

	x	y	z	$\beta_{11} \times 10^5$	$\beta_{22} \times 10^5$	$\beta_{33} \times 10^5$	$\beta_{12} \times 10^5$	$\beta_{13} \times 10^5$	$\beta_{23} \times 10^5$
S	0·2653 (1)	x	x	392 (7)	β_{11}	β_{11}	44 (14)	β_{12}	β_{12}
O(1)	0·3343 (2)	x	x	686 (22)	β_{11}	β_{11}	−322 (44)	β_{12}	β_{12}
O(2)	0·2958 (3)	0·2783 (3)	0·1505 (2)	1358 (41)	725 (31)	514 (24)	−969 (56)	761 (51)	−109 (46)

Thermal ellipsoids

	r.m.s. amplitude	B_i	Direction angles relative to crystal axes		
			α	β	γ
S	0·182 (3) Å	2·60 (9) Å²	54·7°	54·7°	54·7°
	0·167 (2)	2·21 (5)			
	0·167 (2)	2·21 (5)			
O(1)	0·166 (10)	2·17 (26)	54·7	54·7	54·7
	0·253 (5)	5·05 (21)			
	0·253 (5)	5·05 (21)			
O(2)	0·361 (5)	10·31 (27)	31 (1)	115 (1)	73 (1)
	0·207 (5)	3·37 (17)	79 (2)	39 (3)	53 (4)
	0·151 (6)	1·81 (14)	119 (1)	117 (4)	42 (4)

ability density function is

$$\mathbf{P}(\theta) = \sqrt{\left(\frac{V_0}{\pi kT}\right)} \exp\left(-V_0\,\theta^2/kT\right)$$

$$= \sqrt{\left(\frac{q}{\pi}\right)} \exp\left(-q\,\theta^2\right) \qquad (5)$$

where $q = V_0/kT$ is a potentional parameter and will be one of the least-squares variables. Letting $G = \exp(2\pi i\,\mathbf{H}\cdot\mathbf{t})$, then

$$G = \sqrt{\frac{q}{\pi}} \int_{-\infty}^{\infty} G\,P(\theta)\,\mathrm{d}\theta \,. \qquad (6)$$

Other potentials might be chosen but any quasi-harmonic model should at least approximate $q\theta^2$ for small θ. The simplest model has been arbitrarily chosen.

(b) Transformation of coordinates and sum over symmetry related atoms

The problem now becomes one of transforming G to a coordinate system in which θ is the only explicit, independent integration variable. The 24 O(2) atoms lie in groups of three 120° apart on circles of radius ϱ_c surrounding the threefold axes. The postulated motion is one in which a rotation of θ is proportional to a displacement parallel to the threefold axis. The transformation chosen is to the cylindrical system in Fig. 1. $X'Y'Z'$ is a right-handed orthogonal system with Z' the axis of rotation and X' passing through the point $X^0 Y^0 Z^0$, the equilibrium position of O(2). We now
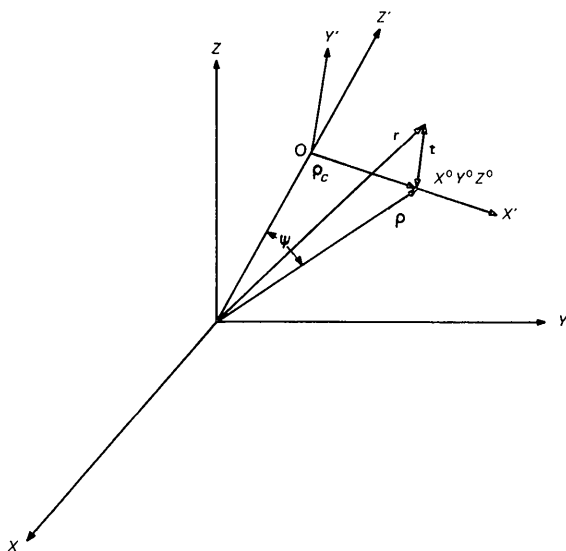

Fig. 1. Coordinate systems used for sodium alum. XYZ is the crystal system. $X'Y'Z'$ is the system used for integration where Z' is parallel to the rotation axis [111], X' is normal to Z' and passes through the equilibrium position of O(2) at $X^0 Y^0 Z^0$ defined by $\mathbf{P}$, and Y' is normal to X' and Z' in a right-handed system. The instantaneouoposition of O(2) is given by $\mathbf{r} = \mathbf{P} + t$. ϱ_c is the radius of the cylindrical system described in Fig. 2.

define a cylindrical system, $\varrho\theta Z'$ with the zero of θ at X'.

The vector $\mathbf{t}$ then has components $X_t' = \varrho_c \cos\theta - \varrho_c$, $Y_t' = \varrho_c \sin\theta$, $Z_t' = M\theta$ (see Fig. 2) where $M = \Delta Z/\theta a_0$ = screw pitch/a_0 is the slope of the spiral. The same displacement system may be used for the O(2) atoms related by the threefold axis. In this case we introduce the rotation angle φ, where $\varphi = 0$, $\pm 2\pi/3$, which relates the three atoms:

$$\begin{aligned} X_t' &= \varrho_c\,[\cos(\theta+\varphi) - \cos\varphi] \\ Y_t' &= \varrho_c\,[\sin(\theta+\varphi) - \sin\varphi] \\ Z_t' &= M\theta \end{aligned} \qquad (7)$$

Since $\mathbf{t}$ is expressed in the primed system, $\mathbf{H}$ must be transformed in such a way that $\mathbf{H}\cdot\mathbf{t}$ is invariant. For

$$\begin{pmatrix} X' \\ Y' \\ Z' \end{pmatrix} = \mathbf{Q}^{-1} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}, \qquad (8)$$

if $\mathbf{t}$ is in the primed system, $\mathbf{H}\cdot\mathbf{t}$ becomes $\mathbf{H}\cdot\mathbf{Qt}$. Because $\mathbf{Q}^{-1}$ is orthorgonal, $\mathbf{Q} = \tilde{\mathbf{Q}}^{-1}$.

It can be shown that

$$\mathbf{Q} = \begin{bmatrix} a_x & b_x & \alpha \\ a_y & b_y & \beta \\ a_z & b_z & \gamma \end{bmatrix} \qquad (9)$$

where $\alpha\beta\gamma$ are direction cosins of Z',

$$\begin{aligned} b_x &= -(Y^0\gamma - Z^0\beta)/(P\sin\psi) \\ b_y &= -(Z^0\alpha - X^0\gamma)/(P\sin\psi) \\ b_z &= -(X^0\beta - Y^0\alpha)/(P\sin\psi), \end{aligned} \qquad (10)$$

$$\begin{aligned} a_x &= (b_y\gamma - b_z\beta) \\ a_y &= (b_z\alpha - b_x\gamma) \\ a_z &= (b_x\beta - b_y\alpha) \end{aligned} \qquad (11)$$

and ψ is the angle between $\mathbf{P}$ and Z'. For our present purpose this transformation is independent of the shift in origin.

We can write the expression for the scattering amplitude of six O(2) atoms generated by the threefold axis and the center of symmetry as

$$g_{j\bar{j}} = \frac{2f}{N} \exp\left(-B\sin^2\theta/\lambda^2\right)$$

$$\sum_{j=1}^{3} \left\{ \cos 2\pi\mathbf{H}\cdot\mathbf{P}_j \int_{-\infty}^{\infty} \cos 2\pi\mathbf{H}\cdot\mathbf{Qt}_j \exp\left(-q\theta^2\right)\mathrm{d}\theta \right.$$

$$\left. + \sin 2\pi\mathbf{H}\cdot\mathbf{P}_j \int_{-\infty}^{\infty} + \sin 2\pi\mathbf{H}\cdot\mathbf{Qt}_j \exp\left(-q\theta^2\right)\mathrm{d}\theta \right\} . \qquad (12)$$

The θ in the isotropic temperature factor should not be confused with θ the integration variable. In equation (12) $\mathbf{H}$ and $\mathbf{P}$ are the reciprocal lattice and equilibrium atom position vectors in the cell coordinate system, $\mathbf{Q}$ is given by equations (9), (10) and (11), and $\mathbf{t}_j$ by equation (7) where $\varphi = 0$, $+2\pi/3$, $-2\pi/3$, as the index j has a remainder 1, 2, 0 modulo 3. Expressions similar to equation (12) for the other three sets of six atoms are obtained by appropriate modification of $\mathbf{Q}$, i.e. by applying the glide operations of the space group to the

equilibrium coordinates and direction cosines appearing in $\mathbf{Q}$.

The least-squares variables are then B, X^0, Y^0, Z^0, q and M. In this problem the direction cosines of $\mathbf{Z}'$ are fixed by symmetry. In other cases it would be possible, at least in principle, to define a least-squares rotation axis. The variable M appears in $\mathbf{t}$, and X^0, Y^0, Z^0 appear in $\mathbf{Q}$ as well as in $\mathbf{P}$.

In our first model the usual anisotropic thermal parameters were applied to S and O(1), and a least-squares calculation using equation (12) and its symmetry related equations for O(2) was carried out. At first a Simpson's rule integration was used for equation (12) and its derivatives, but later a 20-point Gaussian integration was used which was about four times faster and of equal accuracy. The results are given in

Table 2. Although parameters for all other atoms, including hydrogen, were also refined (as in CKL), they were hardly affected and we only list parameters related to the sulfate group.

Spiral and torsional oscillation

Inspection of Tables 1 and 2 shows that O(1) has a much greater motion than has S perpendicular to the threefold axis. This difference suggests that the sulfate group has a torsional oscillation about the S atom as well as the rotational–translational motion. Symmetry requires that O(1) move equally in directions perpendicular to the threefold axis, and, since we are assuming a rigid group, the O(2) atoms can be assumed to have this same isotropic motion about the S–O(2) vectors.

Table 2. *Sulfate group parameters from spiral refinement* $(R=3\cdot83\%)$, *with seven thermal parameters*

	x	y	z	$\beta_{11} \times 10^5$	$\beta_{12} \times 10^5$
S	0·2653 (1)	x	x	390 (7)	49 (15)
O(1)	0·3342 (2)	x	x	671 (22)	−320 (46)
O(2)	0·2969 (3)	0·2789 (3)	0·1488 (3)		

O(2) thermal parameters

$q=11\cdot80(56)$ radians^{-2}; $Ma_0=-0\cdot627$ (38) Å.radian^{-1}; $\overline{\mu^2}^{1/2}=0\cdot179$ (3) Å; r.m.s. amplitude $=1/\sqrt{2q}=0\cdot206$ radians

Thermal ellipsoids

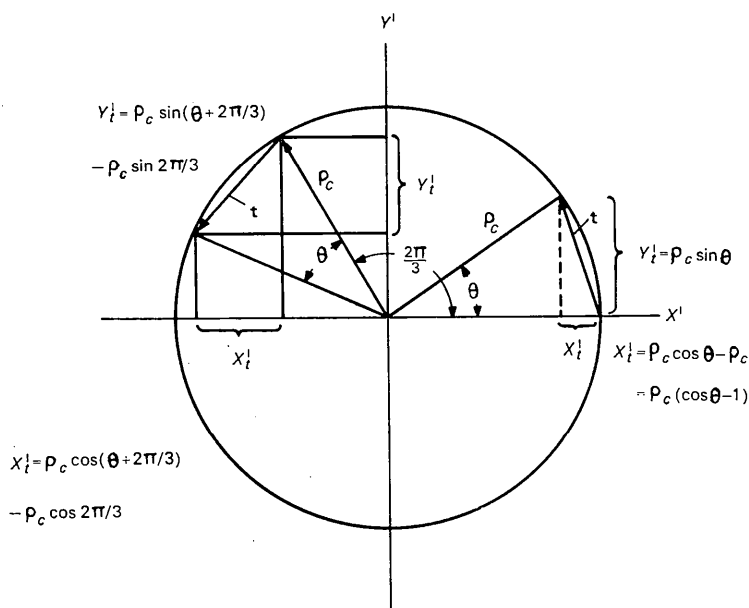|	r.m.s. amplitude	B_i	Direction angles relative to crystal axes		
			α	β	γ
S	0·182 (3) Å	2·62 (10) Å^2	54·7°	54·7°	54·7°
	0·166 (2)	2·18 (6)			
	0·166 (2)	2·18 (6)			
O(1)	0·163 (11)	2·10 (27)	54·7°	54·7°	54·7°
	0·251 (5)	4·95 (22)			
	0·251 (5)	4·95 (22)			

Fig. 2 Cylindrical system looking down Z'. Relationships describe displacement of one O(2) atom and another one 120° from the first in terms of X' and Y'.

For our final calculation the following model was used: (1) the whole group was given two anisotropic temperature factors, $\mu_\parallel^2$ and $\overline{\mu_\perp^2}$, with respect to the threefold axis; (2) the whole group was assumed to have a torsional oscillation about the S atom; (3) a screw motion was applied to O(2) as previously described (this motion gives a component parallel to the threefold axis for S and O(1) equal to $4\pi^2 M^2/q$, which must be added to $\overline{\mu_\parallel^2}$ for these two atoms); (4) stretching modes are small and have been ignored; (5) bending modes have an average behaviour similar to torsional motion; and (6) the screw and torsional motions are uncoupled.

An exact calculation of the scattering from the torsional oscillation was considered but it was found to require a two-dimensional numerical integration. Although this calculation is possible it would have required an excessive amount of computer time. The function finally used was a torsional scattering function described by KB (their equation 10). The principal assumption they make is that the amplitude of oscillation is small enough for the approximations $\sin\theta=\theta$ and $\cos\theta=1-\theta^2/2$ to be made. The r.m.s. magnitude of the oscillation, ω, can be estimated in the present case from the difference between the r.m.s. amplitudes of S and O(1) (see Table 2) and the S–O(1) bond length. Thus $\omega \simeq (0.251^2-0.166^2)^{1/2}/1.458 = 0.129$ radian.

The KB expressions are rather complicated and we will not restate them. Because of the present cubic symmetry, and the isotropic torsional oscillation the expressions reduce considerably.

To recapitulate, in this final model we have five thermal parameters. A $\overline{\mu_\parallel^2}$ and $\mu_\perp^2$ is applied to the whole group. A potentional parameter, q, and a slope or pitch parameter, M, describe the coupled rotational and translational motion. These latter two parameters are applied to O(2) and combine to form an additive term to $\mu_\parallel^2$ as applied to S and O(1). Finally, a parameter a (in KB notation) is applied to O(1) and O(2), where $\omega=1/(a\sqrt{2})$ is the r.m.s. ampli-

tude of torsional oscillation. The results of this refinement are given in Table 3.

Discussion

We shall refer to the anisotropic refinement as model 1, the spiral motion as model 2, and the spiral plus torsional oscillation as model 3. Non-sulfate group parameters changed very little and are not given here. Of these parameters only some of the hydrogen parameters shifted by as much as 2σ. Standard deviations increase slightly as the number of parameters is reduced. The R indices also increase, more so than Hamilton's (1965) statistics would predict. The reason for this increase is probably that the usual anisotropic thermal parameters are better able to compensate for systematic errors in data, for errors in the scattering factors (aspherical atoms and bonding electrons) and internal vibrational modes. It was hoped that by setting the center of libration at the sulfur atom, the contributions from the internal bending modes would be fairly well approximated. The potentional chosen for the libration was quadratic in angles making it isotropic about the threefold axis. If the sulfate potential is quasi-tetrahedral, then the same isotropic angular function could be used (and was used) on each O(2). The latter assumption is probably very weak. The stationary-crystal stationary-counter mode of data collection may have introduced a systematic reduction of measured intensity at higher angles.

As expected, the sulfur x parameter remains unchanged. Also, as expected, the O(1) x parameter and the S and O(1) thermal parameters are essentially the same for models 1 and 2. There are a number of consistencies in the motion of the various models. In model 1, the r.m.s. amplitude of O(2) parallel to the threefold axis is 0.240 Å. For model 2 this amplitude is 0.220 Å and for model 3 is 0.226 Å. The total group translation parallel to the threefold axis in model 3 is given by

$$\left[\overline{\mu_\parallel^2} + \frac{M^2}{2q}\right]^{1/2} = 0.174 \text{ Å},$$

in good agreement with the parallel motion of S and O(1) in models 1 and 2. The r.m.s. amplitude of torsional oscillation in model 3 is 0.110 radians, in reasonable agreement with 0.129 radians estimated earlier from the difference between $\overline{\mu_\perp^2}$ for S and O(1). The group $\overline{\mu_\perp^2}$ of model 3 is in good agreement with $\overline{\mu_\perp^2}$ of S in model 1.

The spiral parameters q and M differ significantly for models 2 and 3. This difference is caused by the different models chosen for the non-spiral component of the motion, in one case an isotropic and in the other case a torsional oscillation plus the group translations. The slope of the spiral, Ma_0/ϱ_c, where a_0 is the lattice constant, gives the cotangent of the angle that the

Table 3. *Sulfate group parameters from spiral and torsional motion refinement* $(R=4.41\%)$, *with five thermal parameters*

	x	y	z
S	0.2653 (1)	x	x
O(1)	0.3350 (3)	x	x
O(2)	0.2971 (3)	0.2788 (3)	0.1482 (3)

$q=17.4$ (14) radians^{-2}, $Ma_0=-0.851$ (78) Å.radian^{-1},
r.m.s. amplitude$=1/\sqrt{2q}=0.169$ radians,
$a=6.45$ (28) radians^{-2} $(\omega=0.110$ radian),
$\mu_\parallel{}^{2\,1/2}=0.098$ (21) Å, $\mu_\perp{}^{2\,1/2}=0.171$ (3) Å.

* This pitch includes both spiral and torsional motion. The pitch for pure spiral motion is

$$-0.851\left[\frac{0.169^2}{(0.169^2+0.110^2)}\right] = -0.598 \text{ Å.radian}^{-1}.$$

motion makes with the threefold axis. For model 2 this angle is 67·1 ± 0·8°, for model 3 it is 67·7 ± 1·5°, and the angle between the major axis of O(2) and the threefold axis is 65·5 ± 3·3° in model 1.

Bond distances and angles are given in Table 4. The results show graphically the fact pointed out by Busing & Levy (1964) that bond lengths are dependent upon the assumed correlation between atomic motions or, to say the same thing, upon the potential or the spatial probability density function to which it gives rise. The approach of putting an assumed probability density into the scattering function and doing a least-squares refinement on the parameters in the averaged scattering function (potentional plus positional) would seem to be more satisfactory than correcting the results of an incorrect function. Our method gives the least-squares equilibrium positional parameters for the chosen potential. It should be pointed out here that the form of the potentials was chosen for its mathematical tractability and with the motions hinted at by the Debye–Waller factors kept well in mind. In other words basic electrostatic interactions are not considered and the potential chosen is somewhat arbitrary so that the results are not necessarily improved over a normal refinement followed by some sort of thermal vibration distance correction based on a likely model.

It is to be noted that functions used to describe the two types of motion gave convergent least-squares refinements; that the technique of numerical integration was successful, and there seems to be no reason why it could not be used for more complex probability density functions; and that the approximation to torsional motion seemed to have terms of a size that makes the approximation used valid (as determined by a debugging run). This is not to say that our physical assumptions were correct, but merely that, given those assumptions, our method of attacking the problem is valid. Table 4 gives bond lengths, angles and certain group thermal parameters. The S-O(2) bond in model 2 and both bonds in model 3 are longer than the uncorrected bond lengths in model 1 by amounts more or less consistent with either the riding model, the rigid-body correction of Cruickshank (1956) or with Schoemaker & Trueblood's (1968) rigid-body analysis. The agreement with the last model is rather good. Since the assumptions used to derive the present scattering expresions and the Schoemaker-Trueblood analysis are rather similar, this agreement is not too surprising.

In models 2 and 3 the O-S-O angles are both closer to the ideal tetrahedral angle. This shift in angle is consistent with a displacement of the equilibrium position of O(2) away from the threefold axis by the introduction of the spiral motion.

Table 4. *Comparison of group thermal parameters, S–O bond lengths and O–S–O angles for various models*

Model	r.m.s. translation $\overline{\mu_1^2}{}^{1/2}$ (Å)	r.m.s. translation $\overline{\mu_1^2}{}^{1/2}$ (Å)	r.m.s. libration ω (radians)	r.m.s. libration ω (radians)	Screw pitch (Å.radian^{-1})	S-O(1) (Å)	S-O(2) (Å)	∠O(1)-S-O(2) (degrees)	∠O(2)-S-O(2) (degrees)
No. 1 Anisotropic uncorrected						1·461 (5)	1·459 (3)	110·1 (1)	108·9 (1)
No. 1 Corrected riding motion Busing & Levy (1964)						1·485	1·496		
No. 1 Corrected by Cruickshank (1956)						1·475	1·483		
No. 1 Corrected by Schomaker–Trueblood (1968) analysis	0·185	0·156	0·220	0·105	−0·52	1·476	1·500	109·8	109·1
No. 2 Screw		0·179	0·206		−0·627	1·458 (5)	1·483 (3)	109·8 (1)	109·1 (1)
No. 2 Corrected for riding motion						1·432			
No. 3 Screw and KB torsional motion	0·174	0·171	0·202	0·110	−0·597	1·476 (6)	1·491 (4)	109·8 (2)	109·1 (2)

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The Crystal Structure of Ammonium 1,1,2,6,7,7-Hexacyanoheptatrienide

BY JAMES EDMONDS, JOHN K. HERDKLOTZ AND RONALD L. SASS

Department of Chemistry, Rice University, Houston, Texas, U.S.A.

The crystal structure of ammonium 1,1,2,6,7,7-hexacyanoheptatrienide, $(NH_4C_{13}H_3N_6)$, has been determined by single-crystal X-ray diffraction techniques. The compound forms monoclinic crystals with $a = 7·11$ (1), $b = 13·405$ (1), $c = 14·199$ (3) Å and $\beta = 101°41'$ (10). There are four formula units in the cell. A total of 865 observed independent reflections were measured with a PAILRED diffractometer. Working in the space group $P2_1/c$, the trial structure was solved by symbolic addition procedures. Least-squares refinement resulted in a conventional R value of 0·069 and a weighted R of 0·031. The anion is only slightly distorted from a planar configuration. Observed molecular dimensions are consistent with those obtained from extended Hückel calculations.

Introduction

Previous crystal structure determinations of ammonium tricyanomethide (Desiderato & Sass, 1965), pyridinium dicyanomethide (Bugg & Sass, 1965), potassium *p*-nitrophenyldicyanomethide (Sass & Bugg, 1967), and dipotassium tetranitroethide (Dyke & Sass, 1968) indicate a certain degree of non-planarity is associated with the trigonally-bonded carbon atom of the carbanion. Ammonium 1,1,2,6,7,7-hexacyanoheptatrienide is a logical extension of these studies because of its conjugated poly-cyano-substituted character.

Experimental

A sample of the ammonium salt of 1,1,2,6,7,7-hexacyanoheptatrienide, $NH_4C_{13}H_3N_6$, was kindly supplied by Dr R. E. Benson of E. I. du Pont de Nemours and Company (Williams, Wiley & McKusick, 1962). The ammonium salt as received consisted of deep green prismatic crystals suitable for study without further recrystallization. Study crystals were usually $0·2 \times 0·1$ mm in cross section, and 2 to 3 mm in length. These were mounted on glass fibers with the crystal needle axis, *a*, parallel to the fiber axis.

Weissenberg and rotation photographs were collected with Cu $K\alpha$ radiation $(\lambda_{K\alpha_1} = 1·54051$ Å). Systematic absences

$$
\begin{array}{ll}
0k0 & k = 2n + 1 \\
h0l & l = 2n + 1 \\
hkl & \text{no conditions}
\end{array}
$$

are consistent with the space group $P2_1/c(C_{2h}^5)$. The *a* axis and β angle cell parameters were determined from sodium chloride $[a_0 (NaCl) = 5·637$ Å] calibrated rotation and Weissenberg photographs, and the *b* and *c* axis parameters determined with the PAILRED diffractometer using Mo $K\alpha$ radiation $(\lambda_{K\alpha_1} = 0·70926$; $\lambda_{K\alpha_2} = 0·71354)$:

$$
\begin{array}{l}
a = 7·11 \ (1) \ \text{Å} \\
b = 13·405 \ (1) \\
c = 14·199 \ (3) \\
\beta = 101°41' \ (10) \ .
\end{array}
$$

The density calculated on the basis of four $NH_4C_{13}H_3N_6$ molecules per unit cell is 1·306 g. cm^{-3}; the density measured by flotation in a mixture of chlorobenzene and bromobenzene is 1·28 g. cm^{-3}.

Two sets of data were collected. The first set was collected on film using two crystals, one $0·2 \times 0·1 \times 0·2$ mm mounted along the *a* axis and one $0·2 \times 0·4 \times 0·2$ mm mounted along the *b* axis. Multiple-film equi-inclination Weissenberg photographs of the $h = 0, 1, 2, 3, 4$ and 5 layers, and $k = 0, 1, 2, 3$ layers were taken