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Energy Analyses for the Alkaline-Earth Formates

BY MASANORI MATSUI

Chemical Laboratory, Kanazawa Medical University, Uchinada, Ishikawa-ken 920-02, Japan

AND TOKUNOSUKÉ WATANABÉ

Osaka University, Yamada, Suita 565, Japan

Abstract

The structures of the alkaline-earth formates have been investigated in terms of lattice energy calculations. The lattice energy E was approximated to be the sum of electrostatic and repulsive terms, where the repulsive potential used was in the form: $(1/12)f(R_\alpha + R_\beta)^{13} r^{-12}$ (r, interatomic distance; f, arbitrarily chosen standard force; R_α, repulsive radius of an atom α). The potential parameters concerned were obtained with the structures of α-Ca(HCOO)$_2$, α-Sr(HCOO)$_2$ and Ba(HCOO)$_2$. These potential parameters were successfully used for the determination of the structure of β-Sr(HCOO)$_2$, for the differentiation of the structures of α-Sr(HCOO)$_2$ and Ba(HCOO)$_2$, and for the interpretation of the large anisotropy of thermal vibrations in β-Ca(HCOO)$_2$.

Introduction

The crystal structures of the alkaline-earth formates are manifold. They can be shown by the following scheme, where each box stands for a type of crystal structure.
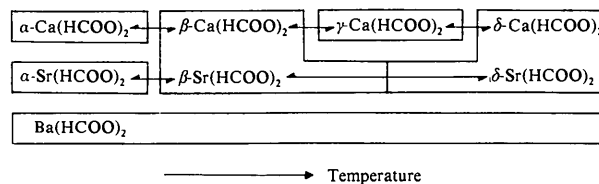
Thus, the isomorphism does not hold for α-Ca(HCOO)$_2$, α-Sr(HCOO)$_2$ and Ba(HCOO)$_2$, which are the stable modifications at room temperature under atmospheric pressure (Watanabé & Matsui, 1978). β-Ca(HCOO)$_2$ and β-Sr(HCOO)$_2$ and δ-Ca(HCOO)$_2$

and δ-Sr(HCOO)$_2$ are respectively isostructures (Matsui, Watanabé, Kamijo, Lapp & Jacobson, 1980). Sr(HCOO)$_2$ has no counter-part of γ-Ca(HCOO)$_2$, instead the transition β-Sr(HCOO)$_2$ $\rightarrow$ δ-Sr(HCOO)$_2$ is progressive (Mentzen & Comel, 1974). It is the aim of the present investigation to find out what kinds of interaction determine these various structures. A consistent potential-energy model for these formate structures is proposed, where a repulsive potential of the form $(1/12)\,f(R_\alpha + R_\beta)^{13}\,r^{-12}$ (r, interatomic distance; f, arbitrarily chosen standard force; R_α, repulsive radius of an atom α), is presented. The repulsive radii of the atoms concerned and the fractional charge on each atom of the formate ion are derived with the three crystal structures, α-Ca(HCOO)$_2$, α-Sr(HCOO)$_2$ and Ba(HCOO)$_2$. The reliability of the potential parameters is demonstrated, and applications of the method to the determination of the crystal structure of β-Sr(HCOO)$_2$ and to the interpretation of the observed conspicuous anisotropy of the thermal parameters of β-Ca(HCOO)$_2$ are presented.

An expression for the lattice energy of ionic crystals

In the following the lattice energy E is approximated to be

$$E = \tfrac{1}{2} \sum_i \sum_j (q_\alpha\, q_\beta\, r_{ij}^{-1} + A_{\alpha\beta}\, r_{ij}^{-12}), \qquad (1)$$

where r_{ij} is the interatomic distance between atoms i and j, $A_{\alpha\beta}$ is the coefficient of the repulsive interaction between atomic species α and β, and q_α is the net charge on an atomic species α. The dispersion attraction terms are neglected, for which a discussion will be given later. The summation over i includes one asymmetric unit, and j is summed over all atoms in the crystal except those which are bonded both directly and indirectly to the atom i. To facilitate the computation of the Coulomb sum, the convergence-acceleration method (Williams, 1971) was used. The convergence constant K was set equal to 0·12. The direct-lattice sum was truncated at 13·4 Å, and the reciprocal-lattice sum was ignored; the estimated accuracy of the equation was found to be at least 99%.

When there exist n different atomic species, $\tfrac{1}{2}n(n + 1)$ repulsive parameters are required to specify all the pair interactions if use is made of (1). In order to decrease the number of these parameters, the method which Gilbert (1968) applied to the Born–Mayer potential $B_{\alpha\beta}\exp(-r_{ij}/\rho_{\alpha\beta})$ was used in the $A_{\alpha\beta}\,r_{ij}^{-12}$ repulsive potential. The repulsive parameter $A_{\alpha\beta}$ can now be expressed by (2), where $R_{\alpha\beta}$ is the distance between atoms α and β, being pushed together against repulsive force alone, by an arbitrarily chosen standard force f:

$$A_{\alpha\beta} = (1/12)\,fR_{\alpha\beta}^{13}. \qquad (2)$$

The repulsive radius R_α is defined as $R_\alpha = \tfrac{1}{2}R_{\alpha\alpha}$, and assuming that an additive rule, $R_{\alpha\beta} = R_\alpha + R_\beta$, holds for the radii, the parameter $A_{\alpha\beta}$ can be expressed by

$$A_{\alpha\beta} = (1/12)\,f(R_\alpha + R_\beta)^{13}. \qquad (3)$$

In the following the lattice energy E is expressed by

$$E = \tfrac{1}{2} \sum_i \sum_j [q_\alpha\, q_\beta\, r_{ij}^{-1} + (1/12)\,f(R_\alpha + R_\beta)^{13}\, r_{ij}^{-12}]. \qquad (4)$$

The standard force f was kept unchanged at 1 kJ Å^{-1} mol^{-1} throughout.

Derivation of the potential parameters

To deal with calcium, strontium, and barium formates, the energy parameters require the net charges q_α and the repulsive radii R_α for the six atomic species Ca, Sr, Ba, O, C, and H. Of these the net charges on Ca, Sr, and Ba ions were all taken as fixed at $+2|e|$, and the sum $q_C + q_H + 2q_O$ was constrained to equal $-1|e|$. There remain eight energy parameters. These eight parameters were derived from the three known structures, α-Ca(HCOO)$_2$, α-Sr(HCOO)$_2$ and Ba(HCOO)$_2$, with the minimization of F:

$$F = \sum_i w_i (\partial E/\partial p_i)_0^2, \qquad (5)$$

where p_i are the structural parameters including the cell parameters and atomic coordinates, and the subscript zero means that all p other than p_i are kept fixed. The weights, w_i, are arbitrarily taken as $|a|^2\,(|b|^2, |c|^2)$ for the cell parameters and 1 otherwise. The space group of each structure was unchanged, and the formate ions were treated as rigid bodies.

The structural parameters for α-Ca(HCOO)$_2$ were taken from the neutron diffraction analysis (Burger, Fuess & Mason, 1977), and those for α-Sr(HCOO)$_2$ and Ba(HCOO)$_2$ were from the X-ray crystal analysis (Watanabé & Matsui, 1978). The coordinates of H atoms in α-Sr(HCOO)$_2$ and Ba(HCOO)$_2$ were calculated assuming planar formate ions with C—H = 1·08 Å. α-Ca(HCOO)$_2$ crystallizes in space group $Pbca$ with $Z = 8$. Two structures, α-Sr(HCOO)$_2$ and Ba(HCOO)$_2$, are different, in spite of crystallizing in the same space group $P2_12_12_1$ with $Z = 4$. In all the three formate structures, there exist one metallic ion and two independent formate ions in the asymmetric uint, all the atoms lying on the general positions. The structural parameters employed as observed quantities were, for each of the three structures, the three cell parameters, a, b and c, and the three coordinates, x, y and z, for the metallic ion and each of the carbon atoms as the reference atoms of the two rigid formate ions. The units are all taken in Å. The equation of the

orientation of each formate ion was neglected. Thus, from the three structures, 36 observations were available. The minimization of F was performed with the *SIMPLEX* method (Nelder & Mead, 1965).

At the outset, all energy parameters were subjected to refinement. It was soon found that out of the eight energy parameters, R_C and R_H were found not to have converged, which implies that contributions from these repulsive terms are only a minor part of the lattice energy in all of the three structures. Accordingly, in further calculations, R_H was fixed at 1.337 Å, which is the converted value of A_{HH} derived by Hagler, Huler & Lifson (1974) ($A_{HH} = 29.936 \times 10^3$ kJ Å^{12} mol^{-1}), and R_C was assumed to be equal to R_O. The iteration history of the minimization of F is given in Table 1, and the optimized potential parameters are given in Table 2. The repulsive radii of the metallic ions are found to be in the expected order: $R_{Ca} < R_{Sr} < R_{Ba}$.

Reliability and transferability of the potential parameters

Now that the potential parameters necessary for the alkaline-earth formates were obtained, the reliability and transferability of these parameters were tested in two ways. Firstly, it was investigated how well they would reproduce the three structures from which they were derived. Secondly, the transferability of these parameters was tested on a crystal which was not used in the derivation.

Each of the three structures α-Ca(HCOO)$_2$, α-Sr(HCOO)$_2$ and Ba(HCOO)$_2$ was calculated by the minimization of the lattice energy E, with (4) and the parameters listed in Table 2, by varying the coordinates of the metallic ion and both the coordinates and orientations of the two independent formate ions, keeping the space groups and the cell parameters of the observed structures unchanged, and the formate ions being taken as rigid bodies having the symmetry $mm2$ with C—O $= 1.25$, C—H $= 1.08$ Å and $\angle$O—C—O $= 125°$, based on the mean values of reliable figures reported for the formate ion. Throughout the rest of this paper, all the lattice-energy-minimization calculations were made in the same way. The minimization was carried out with the *SIMPLEX* method, starting with parameters in the neighbourhood of the observed structure. The agreement between the observed and calculated atomic coordinates are quite satisfactory, as can be seen in Tables 3–5. The mean coordinate discrepancies between the observed and calculated structures are 0.06 Å for α-Ca(HCOO)$_2$, and 0.04 Å for both α-Sr(HCOO)$_2$ and Ba(HCOO)$_2$. Better agreements are found in the nearest-neighbour M^{2+}—O distances, as are shown in Table 6; the mean discrepancies between the observed and calculated structures are only 0.03 Å for both α-Ca(HCOO)$_2$ and α-Sr(HCOO)$_2$, and 0.02 Å for Ba(HCOO)$_2$.

Table 1. *Iteration history of* $F[=\sum_i w_i(\partial E/\partial p_i)_0^2]$

The minimum and maximum F values in each cycle are listed.

Iteration	F (min)	F (max)
0	11245	511922
10	9128	55107
20	3322	11245
30	1956	2716
40	1677	1777
50	1642	1658
100	1469	1485
150	1450	1452
200	1435	1435
250	1380	1399
300	1141	1146
350	1138.8	1138.9
370	1138.8	1138.8

Table 2. *Optimized values of the potential parameters*

$R_{Ca} = 1.591$ Å	$q_{Ca} = q_{Sr} = q_{Ba} = +2^*$ |e|
$R_{Sr} = 1.802$	$q_O = -0.86$
$R_{Ba} = 2.025$	$q_C = +0.87$
$R_O = 1.870$	$q_H = -1 - (q_C + 2q_O) = -0.15$
$R_C = R_O$†	
$R_H = 1.337^*$	

* These values are not refined.
† See text.

Table 3. *Comparison of fractional coordinates between observed and energy-minimized structures for* α-Ca(HCOO)

		x	y	z
Ca	obs*	0.1073	0.1345	0.0277
	calc	0.1094	0.1321	0.0345
C(1)	obs	−0.0489	0.1130	0.3444
	calc	−0.0474	0.1141	0.3386
H(1)	obs	−0.1071	0.1013	0.4631
	calc	−0.1120	0.1106	0.4413
O(1)	obs	−0.0473	0.0357	0.1906
	calc	−0.0437	0.0340	0.1879
O(2)	obs	0.0144	0.2014	0.3665
	calc	0.0179	0.1981	0.3796
C(2)	obs	0.2659	0.1260	−0.3683
	calc	0.2671	0.1322	−0.3570
H(2)	obs	0.2941	0.1555	−0.5224
	calc	0.3065	0.1747	−0.4904
O(3)	obs	0.2014	0.2001	−0.2848
	calc	0.1963	0.1965	−0.2802
O(4)	obs	0.2981	0.0236	−0.2894
	calc	0.2959	0.0226	−0.2913

* Observed values are the transforms of those of Burger, Fuess & Mason (1977): $x' = -y$, $y' = -x$, $z' = -z$ for the non-H atoms; $x' = y$, $y' = -\frac{1}{2} - x$, $z' = \frac{1}{2} + z$ for H(1), and $x' = 1 + y$, $y' = -\frac{1}{2} - x$, $z' = -\frac{1}{2} + z$ for H(2).

The two crystals α-Sr(HCOO)$_2$ and Ba(HCOO)$_2$ are often cited as isomorphous (Groth, 1910; Schutte & Buijs, 1964; Wyckoff, 1966; Comel & Mentzen, 1974). In fact, as Fig. 1 shows, these two structures are closely related, but the orientations of one of the two inde-

Table 4. *Comparison of fractional coordinates between observed and energy minimized structures for* α-Sr(HCOO)$_2$

Calc 1: Starting from the neighbourhood of the observed structure.
Calc 2: Starting from the neighbourhood of the mean structure of α-Sr(HCOO)$_2$ and Ba(HCOO)$_2$.

		x	y	z
Sr	obs	0·2457	0·0857	0·5090
	calc 1	0·2422	0·0831	0·5064
	calc 2	0·2427	0·0831	0·5068
C(1)	obs	−0·1394	0·0506	0·3062
	calc 1	−0·1312	0·0547	0·3113
	calc 2	−0·1309	0·0545	0·3106
H(1)	assumed*	−0·2809	0·0305	0·2458
	calc 1	−0·2753	0·0286	0·2605
	calc 2	−0·2738	0·0296	0·2561
O(1)	obs	0·0030	−0·0239	0·2475
	calc 1	0·0084	−0·0185	0·2446
	calc 2	0·0098	−0·0190	0·2467
O(2)	obs	−0·1248	0·1469	0·4313
	calc 1	−0·1168	0·1557	0·4321
	calc 2	−0·1189	0·1548	0·4326
C(2)	obs	0·4771	0·2591	0·1023
	calc 1	0·4790	0·2584	0·1066
	calc 2	0·4758	0·2603	0·1072
H(2)	assumed*	0·4496	0·2657	−0·0439
	calc 1	0·4619	0·2612	−0·0412
	calc 2	0·4558	0·2654	−0·0402
O(3)	obs	0·5960	0·3555	0·1700
	calc 1	0·5969	0·3504	0·1769
	calc 2	0·5953	0·3510	0·1774
O(4)	obs	0·3894	0·1575	0·1902
	calc 1	0·3793	0·1636	0·1943
	calc 2	0·3778	0·1642	0·1945

* See text.

Table 5. *Comparison of fractional coordinates between observed and energy-minimized structures for* Ba(HCOO)$_2$

Calc 1 and calc 2: same as in Table 4.

		x	y	z
Ba	obs	0·3274	0·0862	0·5380
	calc 1	0·3281	0·0836	0·5414
	calc 2	0·3285	0·0817	0·5443
C(1)	obs	−0·1778	0·0454	0·3714
	calc 1	−0·1767	0·0453	0·3729
	calc 2	−0·1805	0·0425	0·3806
H(1)	assumed*	−0·2511	−0·0454	0·3038
	calc 1	−0·2469	−0·0496	0·3106
	calc 2	−0·2554	−0·0527	0·3234
O(1)	obs	−0·0038	0·0761	0·3256
	calc 1	−0·0006	0·0705	0·3357
	calc 2	−0·0034	0·0610	0·3422
O(2)	obs	−0·2717	0·1115	0·4884
	calc 1	−0·2778	0·1215	0·4767
	calc 2	−0·2777	0·1257	0·4801
C(2)	obs	0·5026	0·2396	0·1041
	calc 1	0·5101	0·2352	0·1021
	calc 2	0·5076	0·2363	0·1048
H(2)	assumed*	0·4884	0·2411	−0·0364
	calc 1	0·5067	0·2251	−0·0385
	calc 2	0·5058	0·2239	−0·0355
O(3)	obs	0·6176	0·3316	0·1705
	calc 1	0·6216	0·3324	0·1663
	calc 2	0·6201	0·3335	0·1679
O(4)	obs	0·4014	0·1450	0·1859
	calc 1	0·4023	0·1486	0·1881
	calc 2	0·3971	0·1525	0·1918

* See text.

pendent formate ions, denoted by C(1), O(1) and O(2) in Fig. 1, are completely different (Watanabé & Matsui, 1978). If the potential parameters are sound enough, the results of the energy-minimized structure, starting from common coordinate values in the neighbourhood of the mean structure of the two, should conform to the result of the observed structures for the two. This was successfully proved as can be seen in Tables 4 and 5.

To test the transferability of the potential parameters further, the energy-minimized structure was applied to the structure of β-Ca(HCOO)$_2$ (Matsui, Watanabé, Kamijo, Lapp & Jacobson, 1980), which was not used in the derivation of the potential parameters. β-Ca(HCOO)$_2$ crystallizes in space group $P4_12_12$ with $Z = 4$. The four Ca^{2+} ions lie on the twofold rotational symmetry axes and the eight formate ions lie on the general equivalent positions. The structural parameters include the x coordinate of the Ca^{2+} ion and the three coordinates and three orientations of the formate ion. These seven parameters were adjusted to minimize the lattice energy E, starting from coordinates in the neighbourhood of the observed

values. A good agreement between the observed and calculated structural parameters was obtained, as can be seen in Table 7. The mean discrepancies are 0·02 Å both for the atomic coordinates and nearest-neighbour Ca^{2+}—O distances.

Crystal structure of β-Sr(HCOO)$_2$

β-Sr(HCOO)$_2$ is obtained as a crystalline powder on heating α-Sr(HCOO)$_2$ and exists in the temperature range 298–503 K (Mentzen & Comel, 1974). It can be quenched to room temperature. From an analysis of the powder X-ray diffraction data, it has been reported that β-Sr(HCOO)$_2$ is tetragonal, $P4_12_12$ (or $P4_32_12$) with $a = 7·12$ (1), $c = 9·57$ (2) Å, $Z = 4$ at room temperature. From the lattice parameters, space group, and the general features of the observed intensity data, it was concluded that β-Sr(HCOO)$_2$ is isostructural with β-Ca(HCOO)$_2$ (Matsui, Watanabé, Kamijo, Lapp & Jacobson, 1980; Mentzen & Comel, 1974). Therefore a determination of the atomic coordinates was performed by means of energy minimization, starting from a hypothetical structure based on that of β-Ca(HCOO)$_2$. Here the structural parameters are

seven, the same number as for β-Ca(HCOO)$_2$. The optimized atomic coordinates are given in Table 8. The calculated powder intensities were found to agree well with the observed intensities, as is shown in Fig. 2. Thus the isomorphism between β-Ca(HCOO)$_2$ and β-Sr(HCOO)$_2$ is now established. The isotropic thermal

MEAN STRUCTURE

α-Sr(HCOO)$_2$ Ba(HCOO)$_2$
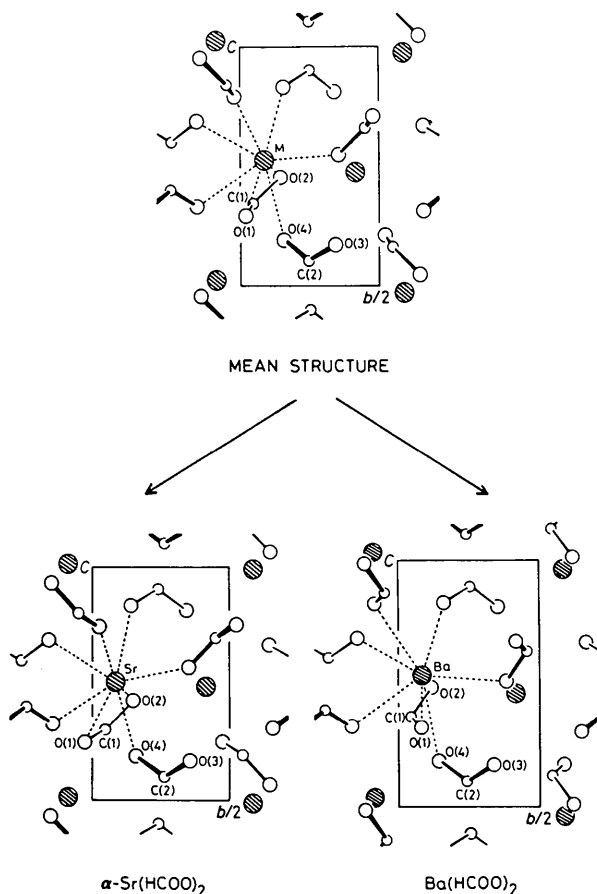
Fig. 1. Crystal structures projected along [100] of α-Sr(HCOO)$_2$ and Ba(HCOO)$_2$, and the mean structure of the two.

Table 7. *Comparison between observed and energy-minimized structures for* β-Ca(HCOO)$_2$

Observed results taken from Matsui *et al.* (1980).

Fractional coordinates

		x	y	z
Ca	obs	0·2169	0·2169	0
	calc	0·2193	0·2193	0
C	obs	0·3039	0·2061	0·3170
	calc	0·3055	0·2057	0·3144
H	obs	0·354	0·173	0·412
	calc	0·3514	0·1735	0·4213
O(1)	obs	0·2766	0·0651	0·2353
	calc	0·2734	0·0627	0·2341
O(2)	obs	0·2813	0·3793	0·2851
	calc	0·2884	0·3831	0·2804

Ca^{2+}—O distances (Å) (two for each)

	Ca^{2+}—O(1)	Ca^{2+}—O(2)	Ca^{2+}—O(1^{ii})	Ca^{2+}—O(2^{iv})
obs	2·484	2·944	2·364	2·311
calc	2·48	2·91	2·33	2·30

Symmetry codes are: (ii) $\frac{1}{2} + y$, $\frac{1}{2} - x$, $-\frac{1}{4} + z$; (iv) $-\frac{1}{2} + y$, $\frac{1}{2} - x$, $-\frac{1}{4} + z$.

Table 8. *Fractional coordinates of the atoms and* Sr^{2+}—O *distances in* β-Sr(HCOO)$_2$ *obtained by energy minimization*

Fractional coordinates

	x	y	z
Sr	0·2255	0·2255	0
C	0·3150	0·2150	0·3137
H	0·3674	0·1958	0·4186
O(1)	0·2858	0·0709	0·2423
O(2)	0·2881	0·3796	0·2729

Sr^{2+}—O distances (Å) (two for each)

Sr^{2+}—O(1)	Sr^{2+}—O(2)	Sr^{2+}—O(1^{ii})	Sr^{2+}—O(2^{iv})
2·60	2·87	2·46	2·47

Symmetry codes are the same as in β-Ca(HCOO)$_2$.

Table 6. *Comparison of the* M^{2+}—O *distances* (Å) *between observed and energy-minimized structures for* α-Ca(HCOO)$_2$, α-Sr(HCOO)$_2$ *and* Ba(HCOO)$_2$

Symmetry codes are the same as those in the paper of Watanabé & Matsui (1978).

α-Ca(HCOO)$_2$				α-Sr(HCOO)$_2$				Ba(HCOO)$_2$		
	obs	calc			obs	calc			obs	calc
Ca—O(1)	2·520	2·48		Sr—O(1)	2·702	2·64		Ba—O(1)	2·777	2·74
—O(1^i)	2·350	2·36		—O(1^i)	2·504	2·50		—O(1^i)	2·892	2·89
—O(2)	2·556	2·58		—O(2)	2·659	2·60		—O(2^{ii})	2·778	2·72
—O(2^{ii})	2·315	2·33		—O(2^{ii})	2·541	2·52		—O(2^v)	2·760	2·74
—O(3)	2·426	2·39		—O(3^{iii})	2·599	2·57		—O(3^{iii})	2·746	2·75
—O(3^{iii})	2·409	2·40		—O(3^{iv})	2·633	2·67		—O(3^{iv})	2·794	2·76
—O(4^{iv})	2·347	2·30		—O(4)	2·594	2·55		—O(4)	2·792	2·81
				—O(4^i)	2·669	2·69		—O(4^i)	2·814	2·82
Ca—O(4)	3·433	3·42						Ba—O(1^{ii})	3·379	3·42

parameters used for the calculation are 2·5 Å² for Sr²⁺, and 3·5 Å² for the others. The scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Each Sr²⁺ ion lies on a twofold rotational axis, and is surrounded by eight O atoms from six formate ions at distances listed in Table 8. The mean Sr²⁺—O distance 2·60 Å can well be compared with that found in α-Sr(HCOO)₂, 2·613 Å, where the coordination number of Sr²⁺ is also eight (Watanabé & Matsui, 1978).

Anisotropic thermal parameters in β-Ca(HCOO)₂

In the structure analysis of β-Ca(HCOO)₂ (Matsui, Watanabé, Kamijo, Lapp & Jacobson, 1980), it was found that U_{11}'s for C, O(1) and O(2) are all much greater than U_{22}'s of the same atoms, as are shown in Table 9. It follows that the formate ion as a whole oscillates with a larger amplitude along the x than along the y direction, which requires a shallower potential well for the formate ion along the x direction than the y direction. The lattice-energy variations as functions of the displacements of the rigid formate ion along each of the x and y directions through the equilibrium position are calculated. The result is shown in Fig. 3, and is as expected.

Since the space group of the crystal is $P4_12_12$ and the twofold rotational symmetry axis runs along [110] passing through the origin, the eight equivalent positions on which all the atoms of the formate ions lie can be placed into two groups:

$$x,y,z; \ \bar{x}, \bar{y}, \tfrac{1}{2}+z; \tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{4}-z; \tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{3}{4}-z;$$
$$(a)$$

$$y,x,\bar{z}; \ \bar{y}, \bar{x}, \tfrac{1}{2}-z; \tfrac{1}{2}-y, \tfrac{1}{2}+x, \tfrac{1}{4}+z; \tfrac{1}{2}+y, \tfrac{1}{2}-x, \tfrac{3}{4}+z.$$
$$(b)$$

The argument given above should be applied to the formate ions occupying positions (a), while the reverse should be applied to those formate ions occupying position (b). Thus, the observed anisotropic thermal parameters can well be accounted for by the potential function and potential parameters presented in this paper.
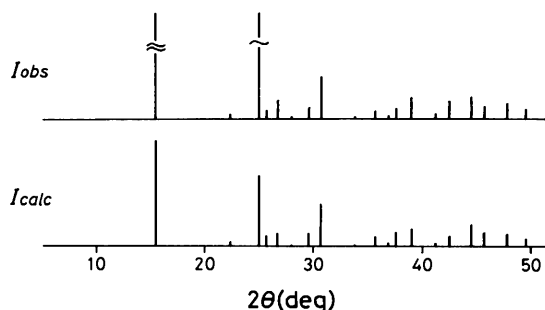

Fig. 2. Observed and calculated powder intensities for β-Sr(HCOO)₂.

Table 9. *Anisotropic thermal parameters* ($\times 10^3$ Å²) *for the non-hydrogen atoms and isotropic thermal parameters* (Å²) *for* H *in* β-Ca(HCOO)₂ *with e.s.d.'s in parentheses*

Anisotropic thermal parameters are of the form
$$\exp\left(-2\pi^2 \sum_i \sum_j U_{ij} h_i h_j a_i^* a_j^*\right).$$

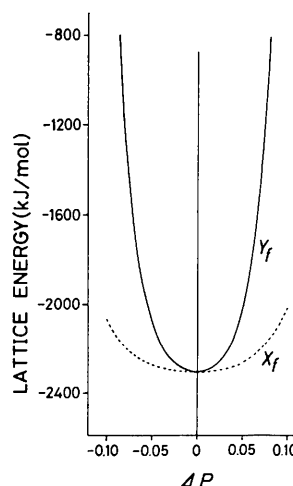|	U_{11} or B	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	17·0 (5)	17·0 (5)	36·7 (5)	0·0 (3)	−3·4 (3)	3·4 (3)
O(1)	40 (2)	24 (2)	37 (1)	−3 (1)	−0 (2)	−1 (1)
O(2)	59 (2)	15 (2)	82 (2)	3 (1)	−1 (2)	5 (2)
C	41 (2)	23 (2)	29 (1)	7 (2)	−1 (2)	−1 (2)
H	5 (1)					

Fig. 3. Lattice energy variation with the displacements of each of the x and y fractional coordinates from the equilibrium position ($\Delta P = 0$) of the formate ion in β-Ca(HCOO)₂.

In conclusion, it must be recalled that the dispersion terms were neglected throughout. Nevertheless, equation (4) with the potential parameters listed in Table 2 has been proved to be very effective in deriving atomic coordinates in crystals. It is suggested that the dispersion interactions would not affect seriously positions of the potential minima in ionic crystals, or the contribution of the dispersion terms would be partly incorporated into the potential parameters derived by the method described in this paper.

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On the Application of Hamilton's Ratio Test to the Assignment of Absolute Configuration and an Alternative Test

BY DONALD ROGERS*

Chemical Crystallography Laboratory, Imperial College, London SW7 2AY, England

Abstract

Examples are given of recent abuses or debatable applications of the R-factor ratio test ($\mathscr{R}$) for the assignment of absolute configuration, and it is shown that some of the enhanced ratios that have been used do not necessarily imply a statistically significant reduction in α, the probability of making a wrong assignment. Reasons are given for believing that α is usually seriously underestimated anyway, and that in marginal situations the weighted ratio, $\mathscr{R}_w$, is a safer guide than $\mathscr{R}$ and can even contradict the assignment based on $\mathscr{R}$. Aids are given to facilitate the estimation of α that are much easier to use than interpolation or extrapolation from Hamilton's tables [Hamilton (1965). *Acta Cryst.* **18**, 502–510]. The misconceptions led to a re-examination of the validity of Hamilton's application of linear-hypothesis testing to this particular problem. A more rigorous justification can be achieved by expressing the atomic scattering factors of all the anomalous scatterers in a crystal in the form $f_{0j} + f'_j + i\eta f''_j$ and refining η, the chirality/polarity parameter. Its standard deviation offers an alternative and more realistic index of the probability of an assignment. A postscript contributed by Professor G. M. Sheldrick reports very encouraging results for η refinement of three structures.

Introduction

The assignment of absolute configuration is best based on direct measurement of the intensities of Bijvoet pairs of reflexions. It is, however, more often obtained as a by-product of normal data collection, in which event it usually involves one or other of two comparison procedures: either a comparison of the R factors of the two enantiomeric models over *all* the measured data, or varied forms of comparison over a limited number of 'sensitive reflexions'. It is usual in the former case to assess the statistical significance of the R-factor ratio, $\mathscr{R}$, by means of Hamilton's (1965) ratio test, but certain abuses and misunderstandings have recently come to my notice, especially while refereeing or being consulted by other referees: they occur often enough to justify the discussion below. In the latter case, a few authors have applied Hamilton's test to the enhanced ratios from 'sensitive reflexions', but apparently without thought as to the legitimacy of doing so. The abuses, together with other considerations which suggested that the ratio test tends to be over-optimistic, prompted me to re-examine the basis of Hamilton's applications of the R-factor test to this problem and led to the conclusion that his argument does not appear to conform to his definition of a linear hypothesis. An attempt is made to validate this application so that the test can continue to be used, but in doing so a proposal is made for an alternative assignment procedure that yields its own independent confidence index which is expected to be more realistic. The first three trials of this alternative procedure look very encouraging.

* Address for correspondence: 11 Salvington Crescent, Bexhill on Sea, East Sussex TN39 3NP, England.