and the reaction is apparently rapid. On the TGA curves recorded with the highest heating rates, it is seen as the faster dehydration on the top part of the curves (Fig. 6). Using larger crystal fragments (broken line, Fig. 6) will slow down step 1 because of the growing importance of the diffusion rate.

Step 2: loss of another three waters per f.u. During this step, single crystals turned opaque and polycrystalline. A continuation and completion of the step 1 reaction would lead to an unstable square-planar $K(OH_2)_4$ coordination. A tetrahedral water arrangement, using half the original water positions would give either too long K–O distances, or very weakened hydrogen bonds to the silicate layers. To reach a stable K coordination with four waters per f.u., silicate O atoms must be involved. The following mechanism is suggested: as more than one water per f.u. is lost, the K^+ ion tends to move out of the position in the mirror plane towards an O(2) square in the silicate layer above or below. This will trigger the release of two more water molecules per f.u. and finally allow the K^+ ion to take a position between four water O atoms and the O(2) square. The rearranged K coordination will require a change in puckering and spacing of the silicate layers and result in K–O distances of approximately 3·0 Å. An increase in the a and a decrease in the c axis has been reported (Chao, 1971; Bartl & Pfeifer, 1976). These structural changes explain the breakdown of the single crystals.

Step 3: loss of the remaining water. This step leaves an amorphous residue.

A high heating rate experiment performed on hydroxyapophyllite (Larsen, 1981) was interpreted as having an initial step with a 25% water loss and a

final step where the rest of the water left. This result may depend on experimental conditions but a difference in the dehydration process between fluorapophyllite and hydroxyapophyllite may not be ruled out until further investigations have been performed.

References

BARTL, H. & PFEIFER, G. (1976). *Neues Jahrb. Mineral. Monatsh.* (2), 58–65.
BECKER, P. J. & COPPENS, P. (1974). *Acta Cryst.* A30, 129–147.
BECKER, P. J. & COPPENS, P. (1975). *Acta Cryst.* A31, 417–425
CAVINATO, A. (1927). *Atti Lincei (Roma)*, 5, 907–910.
CHAO, G. Y. (1971). *Am. Mineral.* 56, 1234–1242.
COLVILLE, A. A., ANDERSON, C. P. & BLACK, P. M. (1971). *Am. Mineral.* 56, 1220–1233.
DUNN, P. J., ROUSE, R. C. & NORBERG, J. A. (1978). *Am. Mineral.* 63, 196–199.
EINSPAHR, H. & BUGG, C. E. (1980). *Acta Cryst.* B36, 264–271.
GOSSNER, B. & KRAUS, O. (1928). *Z. Kristallogr.* 68, 595–615.
KOESTER, L., RAUCH, H., HERKENS, M. & SCHROEDER, K. (1981). Kernforchungsanlage Report JUL-1755.
KVICK, Å., STÅHL, K. & SMITH, J. V. (1985). *Z. Kristallogr.* 171, 141–154.
LARSEN, A. O. (1981). *Nor. Mineral. Tidsskr.* 61, 297–300.
LUNDGREN, J.-O. (1983). Report No. UUIC-B13-4-05. Univ. of Uppsala, Sweden.
PRINCE, E. (1971). *Am. Mineral.* 56, 1243–1251.
ROUSE, R. C., PEACOR, D. R. & DUNN, P. J. (1978). *Am. Mineral.* 63, 199–202.
SHULL, C. G. (1972). Private communication.
TAYLOR, W.-H. & NÁRAY-SZABO, ST (1931). *Z. Kristallogr.* 77, 146–158.

Magnesium Bis(hydrogen maleate) Hexahydrate, [Mg(C₄H₃O₄)₂].6H₂O, Studied by Elastic Neutron Diffraction and *Ab Initio* Calculations

BY F. VANHOUTEGHEM AND A. T. H. LENSTRA*

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium

AND P. SCHWEISS†

Laboratoire Leon Brillouin, CEN, Saclay, France

Abstract

Magnesium bis(hydrogen maleate) hexahydrate was investigated at room temperature by neutron diffraction, establishing the H positions and H-bonding scheme with great accuracy. The Mg cation at a centre of inversion is surrounded by six water molecules, which are rotated by 9, 28 and 44°, respectively, out of their ideal O_h planes. A slightly asymmetric intramolecular O(3)–H···O(1) bridge is found in the hydrogen maleate ion, together with an asymmetric crystalline environment of the O atoms: O(1) is also

* Author to whom correspondence should be addressed.
† On leave of absence from Kernforschungszentrum Karlsruhe, INFP, D-7500 Karlsruhe and Universität Marburg, Institut für Mineralogie, D-3550 Marburg, Federal Republic of Germany.

an acceptor to an intermolecular H bridge to the $Mg(OH_2)_6$ cluster, whereas O(3) is not. Experimental bond lengths and angles are compared with those obtained from geometry-relaxed 4-21G *ab initio* calculations of the free hydrogen maleate ion. Observed differences are of the same magnitude as those expected for crystal-field effects. The experimental hydrogen maleate ion is not planar, the carboxyl groups being rotated out of the carbon plane in a disrotatory fashion. Experimental observations in a similar molecule (lithium hydrogen phthalate) as well as calculations on the free hydrogen maleate ion suggest this to be energetically favoured over a conrotatory movement. Crystal data: $M_r = 362.5$, monoclinic, $P2_1/c$, $a = 10.207$ (5), $b = 11.829$ (5), $c = 6.745$ (3) Å, $\beta = 104.2$ (1)°, $V = 789.5$ Å^3, $Z = 2$, $D_x = 1.53$ Mg m^{-3}, $\lambda = 0.8320$ Å, $T = 300$ K, $wR = 0.048$ for 1409 reflections.

Introduction

An X-ray single-crystal analysis by Gupta, Van Alsenoy & Lenstra (1984) of the title compound (Fig. 1) revealed a number of interesting phenomena. First, the Mg cation is coordinated by six water molecules and the hydrogen maleate ion (henceforth abbreviated as HM) does not take part in the Mg coordination. Hence, the compound is well suited for the study of the geometry of a *nearly isolated* HM ion in a

crystalline environment. Second, the carboxyl groups (COOH and COO⁻) are rotated out of the carbon plane in a disrotatory fashion, whereas a conrotatory movement seems the more efficient mechanism to reduce steric crowding. Third, a very short and very asymmetric intramolecular H bond in the HM ion was found [O(3)···O(1) = 2.410 (1), O(3)–H = 0.88 (1), O(3)H···O(1) = 1.57 (1) Å, ∠O(3)–H···O(1) = 167 (1)°; asymmetry parameter $\Delta = 0.69$ Å, defined as the distance O(1)···H minus the distance O(3)–H]. No disorder was observed in this H bond. The results are in semiquantitative agreement with geometry-relaxed *ab initio* calculations at the 4-31G level by George, Bock & Trachtmann (1983). These authors calculated an asymmetry parameter $\Delta = 0.48$ Å for the free HM ion. On the other hand an extensive review by Olovsson, Olovsson & Lehmann (1984) showed much smaller Δ values in neutron analyses of other acid salts of maleic acid. The largest Δ value observed was 0.29 Å. Possible rationalizations are the following. First, the discrepancy is real and stems from the fact that H positions from X-ray diffraction are not sufficiently reliable. Second, there is no true controversy because the double-well potential governing the H positioning between O(3) and O(1) is strongly dependent upon crystal-field effects. When Fig. 2(a) represents the energy curve in the free ion, then crystal fields could lead to the curves in Figs. 2(b–e), changing the barrier
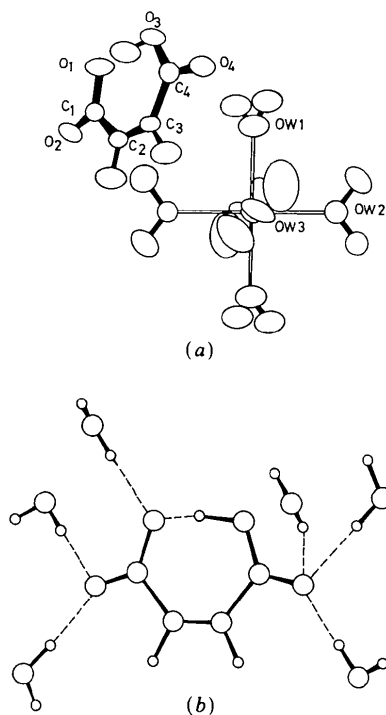

Fig. 1. (a) Structure of the title compound with numbering of atoms and (b) H-bonding scheme between the HM ion and water molecules.
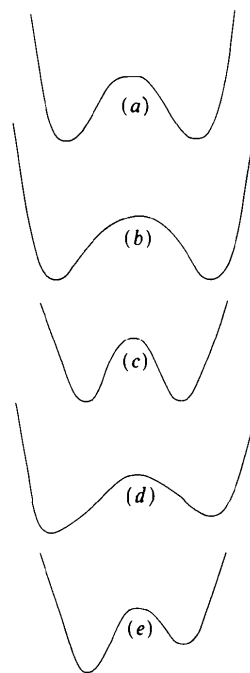

Fig. 2. Variation of potential energy as the H atom moves from O(3) to O(1). The free HM ion case corresponds to curve (a); HM in a symmetrical environment might correspond to curve (b) or (c); HM in an asymmetrical environment might correspond to curve (d) or (e).

Table 1. Positional parameters and their e.s.d.'s

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

	x	y	z	B (Å²)
O(1)	0·6366 (3)	0·3598 (3)	0·2246 (7)	3·71 (9)
O(2)	0·7632 (3)	0·2088 (3)	0·2806 (7)	3·57 (9)
O(3)	0·4008 (3)	0·4086 (3)	0·1380 (7)	3·17 (9)
O(4)	0·2081 (3)	0·3221 (3)	0·0857 (7)	3·44 (9)
C(1)	0·6524 (3)	0·2527 (3)	0·2313 (5)	2·43 (6)
C(2)	0·5303 (3)	0·1786 (3)	0·1817 (5)	2·44 (6)
C(3)	0·3988 (3)	0·2053 (3)	0·1367 (5)	2·35 (6)
C(4)	0·3319 (3)	0·3181 (3)	0·1179 (5)	2·26 (6)
H(C2)	0·5567 (6)	0·0886 (6)	0·189 (1)	4·7 (2)
H(C3)	0·3261 (6)	0·1362 (6)	0·106 (1)	4·6 (2)
H(O3)	0·5176 (6)	0·3877 (6)	0·179 (1)	4·2 (2)
Mg	0·000	0·000	0·000	1·78 (9)
O(W1)	−0·1391 (4)	0·0065 (3)	0·1775 (6)	4·00 (9)
O(W2)	−0·0077 (4)	0·1735 (3)	−0·0231 (6)	3·08 (9)
O(W3)	0·1602 (4)	0·0102 (3)	0·2556 (6)	3·30 (9)
H(11)	−0·1581 (6)	−0·0538 (6)	0·260 (1)	4·6 (2)
H(21)	−0·1791 (6)	0·0717 (6)	0·216 (1)	4·3 (2)
H(12)	−0·0821 (6)	0·2156 (6)	−0·090 (1)	4·4 (2)
H(22)	−0·0681 (6)	0·2226 (6)	0·019 (1)	4·2 (2)
H(13)	0·1631 (6)	0·0558 (6)	0·373 (1)	5·1 (2)
H(23)	0·2259 (6)	−0·0371 (6)	0·280 (1)	7·7 (2)

height as well as the positions and relative depths of the energy minima. It is conceivable that the distance between the minima is increased (Figs. 2b,d) under the influence of an internal rotation in the HM moiety induced by packing, while the distance is decreased (Figs. 2c,e) under the influence of H-bridge formation and/or Coulomb interactions with neighbouring ions.

In order to investigate these matters we performed (i) a single-crystal neutron diffraction analysis and (ii) a series of ab initio calculations. Elastic neutron diffraction allows information about the H positions and the H-bonding scheme to be obtained with an accuracy five to ten times greater than an X-ray analysis. The ab initio calculations reported here are intended to provide preliminary information about the influence of crystal fields.

Experimental

Crystals were grown from a hot solution of the title compound in water, prepared by addition of maleic acid to magnesium carbonate. A crystal of about $5\times5\times5$ mm was used. Intensity data were collected at 300 K on the four-circle diffractometer at the ORPHEE reactor (Laboratoire Leon Brillouin, Saclay, France) using the ω step-scan technique. The primary neutron beam was monochromatized by reflection on the (220) plane of a copper crystal. We selected $\lambda = 0·8320$ (4) Å. The flux at the sample was $5·75\times10^6$ neutrons cm^{-2} s^{-1}.

Lattice parameters of the monoclinic cell, $P2_1/c$, $a = 10·207$ (5), $b = 11·829$ (5), $c = 6·745$ (3) Å, $\beta = 104·2$ (1)°, were determined from 25 reflections with $0 < \theta < 40°$.

Intensity data up to $\theta = 65°$ were measured giving 1880 reflections in the ranges $-12 \le h \le 12$, $-14 \le k \le$

Table 2. Geometry of the Mg(OH₂)₆ cluster and hydrogen-bonding scheme between the H₂O molecules of the cluster and the HM ions

Mg is at an inversion centre. Distances in Å, angles in decimal degrees, e.s.d.'s in parentheses. D: donor, A: acceptor.

Mg–O(W1)	2·082 (4)	O(W1)–Mg–O(W2)		89·3 (2)
Mg–O(W2)	2·070 (3)	O(W1)–Mg–O(W3)		91·7 (2)
Mg–O(W3)	2·080 (4)	O(W2)–Mg–O(W3)		90·7 (2)
		H(11)–O(W1)–H(21)		106·8 (7)
H(11)–O(W1)	0·959 (8)	H(11)–O(W1)–Mg		125·2 (5)
H(21)–O(W1)	0·944 (8)	H(21)–O(W1)–Mg		126·6 (5)
		H(12)–O(W2)–H(22)		109·0 (7)
H(12)–O(W2)	0·934 (7)	H(12)–O(W2)–Mg		125·7 (5)
H(22)–O(W2)	0·960 (7)	H(22)–O(W2)–Mg		124·9 (5)
		H(13)–O(W3)–H(23)		110·4 (7)
H(13)–O(W3)	0·957 (8)	H(13)–O(W3)–Mg		125·7 (5)
H(23)–O(W3)	0·863 (8)	H(23)–O(W3)–Mg		122·8 (5)

H(11)–O(W1)–Mg–O(W2)	164 (1)	H(22)–O(W2)–Mg–O(W1)	30 (1)
H(11)–O(W1)–Mg–O(W3)	−74 (1)	H(22)–O(W2)–Mg–O(W3)	122 (1)
H(21)–O(W1)–Mg–O(W2)	0 (1)	H(13)–O(W3)–Mg–O(W1)	−39 (1)
H(21)–O(W1)–Mg–O(W3)	91 (1)	H(13)–O(W3)–Mg–O(W2)	50 (1)
H(12)–O(W2)–Mg–O(W1)	−158 (1)	H(23)–O(W3)–Mg–O(W1)	128 (1)
H(12)–O(W2)–Mg–O(W3)	−66 (1)	H(23)–O(W3)–Mg–O(W2)	−143 (1)

D–H···A	H···A	D···A	D–H···A
O(W1)–H(11)···O(4$^{\text{iii}}$)	1·939 (8)	2·891 (5)	176·1 (6)
O(W1)–H(21)···O(2$^{\text{iv}}$)	1·815 (8)	2·747 (5)	171·8 (7)
O(W2)–H(12)···O(2$^{\text{i}}$)	1·837 (7)	2·765 (5)	176·0 (7)
O(W2)–H(22)···O(4$^{\text{ii}}$)	1·821 (7)	2·773 (5)	176·3 (6)
O(W3)–H(13)···O(4$^{\text{v}}$)	2·008 (7)	2·933 (5)	163·1 (7)
O(W3)–H(23)···O(1$^{\text{vi}}$)	1·865 (7)	2·711 (5)	168·6 (7)

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

0 and $-8 \le l \le 8$. Out of these 1409 were considered above the background. Backgrounds were calculated by a least-squares fit, $B = ax + b$, through the first six and last six detector steps. If $a > 0·05$ was found in the interval $5 < 2\theta < 50°$ or $a > 0·15$ in the interval $50 < 2\theta < 65°$ then B was made horizontal after inspection and possibly correction of the peak profile.

Starting from the parameters of Gupta et al. (1984), the structure was refined by full-matrix least squares on F (Busing, Martin & Levy, 1962), with weights $w = \sigma^{-2}$, where σ is the e.s.d. of a structure factor obtained from counting statistics. Scattering lengths for Mg, O, C and H of 5·20, 5·75, 6·63 and −3·72 fm (International Tables for X-ray Crystallography, 1974) were used. The refinement converged to $wR = 0·048$, with largest correction for isotropic extinction (yF_c), $y = 0·59$. $\Delta/\sigma_{\text{max}} < 0·01$.

Discussion of the neutron geometry

Final atomic positions and thermal parameters* are given in Table 1, the geometry of the Mg(OH₂)₆ cluster in Table 2 and that of the HM ion in Table 3 and Fig. 3. The geometry of the Mg(OH₂)₆ cluster and that of the HM ion were corrected for thermal

Table 3. *Geometry of the HM ion in the title compound*

Bond lengths in Å, angles in decimal degrees, e.s.d.'s in parentheses. Column A: neutron geometry corrected for libration motions. Column B: ab initio 4-21G geometry of the free ion converted to r_a^0 basis.

	A	B*
O(1)–C(1)	1·288 (4)	1·273
O(2)–C(1)	1·219 (4)	1·227
C(1)–C(2)	1·505 (4)	1·520
C(2)–C(3)	1·344 (4)	1·332
C(3)–C(4)	1·502 (4)	1·496
O(3)–C(4)	1·282 (4)	1·307
O(4)–C(4)	1·235 (4)	1·215
C(2)–H(C2)	1·106 (6)	1·091
C(3)–H(C3)	1·099 (6)	1·090
O(3)–H(O3)	1·186 (7)	1·080
O(1)···H(O3)	1·228 (7)	1·365
O(1)···O(3)	2·414 (5)	2·434
O(1)–C(1)–O(2)	122·3 (3)	127·4
O(1)–C(1)–C(2)	118·9 (3)	118·0
O(2)–C(1)–C(2)	118·8 (3)	114·7
C(1)–C(2)=C(3)	130·4 (2)	131·3
C(2)=C(3)–C(4)	130·0 (3)	131·3
O(3)–C(4)–O(4)	120·4 (3)	123·3
O(3)–C(4)–C(3)	121·0 (3)	119·1
O(4)–C(4)–C(3)	118·6 (3)	117·6
C(1)–C(2)–H(C2)	112·1 (4)	110·6
C(3)–C(2)–H(C2)	117·4 (4)	118·1
C(2)–C(3)–H(C3)	117·7 (4)	118·8
C(4)–C(3)–H(C3)	112·2 (4)	109·9
C(4)–O(3)–H(O3)	110·5 (4)	115·0
O(3)–H(O3)···O(1)	176 (1)	169·4
O(1)–C(1)–C(2)=C(3)	−3·3 (4)	0·0
O(2)–C(1)–C(2)=C(3)	175·3 (3)	180·0
C(1)–C(2)=C(3)–C(4)	1·2 (4)	0·0
C(2)=C(3)–C(4)–O(3)	2·8 (4)	0·0
C(2)=C(3)–C(4)–O(4)	−176·0 (3)	180·0

* $r_a^0 = r(4\text{-}21G) + \delta - K_0$. The following correction terms were used δ: C–O, −0·006; C=O, 0·013; C–C, −0·088; C–H, 0·034; O–H, 0·034; K_0: bond lengths including H atoms 0·017 Å, all others 0·002 Å.
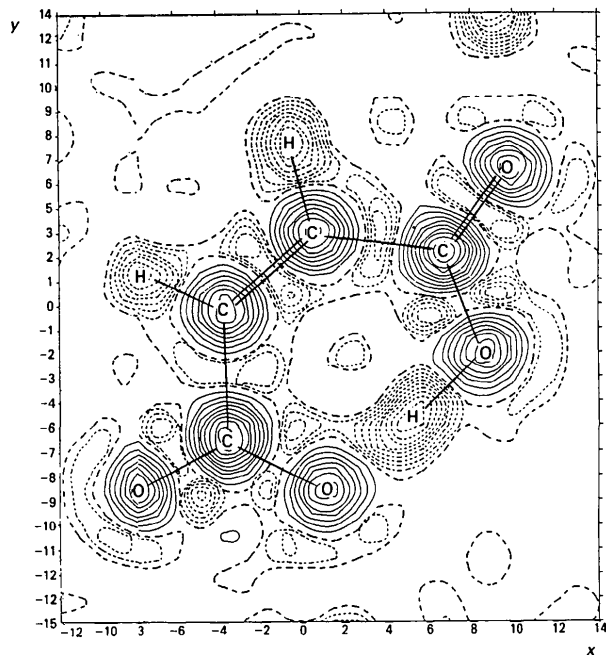

Fig. 3. Fourier section through the plane of the HM ion. Note that, disregarding the sign, H atoms show almost as clearly as C and O atoms.

motion using the program of Trueblood & Schomaker (1968).

There is an excellent agreement between the neutron and X-ray values of bonding parameters involving non-H atoms: the differences $|\Delta P|/\sigma = |P_N - P_X|/[\sigma_N^2 + \sigma_X^2]^{1/2} < 2$ for all bond lengths and angles. It shows that for the heavy atoms in the title compound the difference between nuclear positions (neutron data) and centres of electron clouds (X-ray data) is insignificant. The result is in keeping with Allen (1986) who found small differences between neutron and X-ray distances for CC and CO lengths.

Focusing attention first on the geometry of the $Mg(OH_2)_6$ cluster, one notes that Mg is surrounded by six O atoms in an almost perfect octahedron. When, however, the H atoms of the coordinating water molecules are taken into account the O_h symmetry is broken. Water molecule W1 is rotated over 9° out of the O(W1), O(W1'), O(W2), O(W2') plane, water molecule W2 over 28° out of the O(W2), O(W2'), O(W3), O(W3') plane and water molecule W3 over 44° out of the O(W3), O(W3'), O(W1), O(W1') plane. The distortion is undoubtedly due to H bonding to HM ions (Table 2). The largest distortion (shortest O–H distance, largest out-of-plane rotation) is observed for H(2, W3), which is bridged to O(1). O(1) in turn forms part of the intramolecular O(1)···H–O(3) bridge of the HM ion. The large deformation from O_h symmetry in the $Mg(OH_2)_6$ cluster (and possibly in similar metal clusters) may call for re-evaluation of ab initio studies of ion exchange in metal complexes (e.g. Maynard, Hiskey, Pedersen & Kochler, 1985).

We now turn to the geometry of the HM ion (Table 3). A comparison of the various C–O bond lengths in HM with the standard values given by Allen (1986) for C–OH [1·305 (2) Å], C=O [1·210 (2) Å], and C⋍O [1·251 (2) Å] in COOH and COO⁻ derivatives yields large discrepancies. This shows that it would be an oversimplification to speak about distinct, non-interfering COOH and COO⁻ groups in the HM ion.

The neutron analysis yielded the following details for the short intramolecular H bridge in the HM ion: O(1)···O(3) = 2·414 (5), O(3)–H = 1·186 (7), O(3)H···O(1) = 1·228 (7) Å; asymmetry Δ(OH···O) = 1·228 − 1·186 = 0·042 Å; ∠O(3)–H···O(1) = 176 (1)°. The correlation between bonded O(3)–H and non-bonded O(3)H···O(1) distances in hydrogen maleates proposed by Olovsson et al. (1984), is fully confirmed in the present analysis. The excellent internal consistency of Δ values, ranging from 0·001 to 0·288 Å over a variety of crystalline environments, allows us to conclude that the energy curve associated with the O(3)–H···O(1) linkage in crystalline HM ions has a smaller separation between the minima than in the free ion. In this context we note that O(1) is an acceptor atom in an intermolecular H bond between the HM ion and the

Mg(H₂O)₆ cluster, whereas O(3) is not. Although at the present stage we cannot discriminate between Figs. 2(c) and 2(e), we venture to state that asymmetry in crystalline environment can lead to greater symmetry in the O(3)–H···O(1) geometry, i.e. smaller Δ parameters.

Ab initio calculations

In this section we compare the experimental HM geometry with that of *ab initio* calculations. The results so far obtained will be useful to assess the transferability of geometries from the free state to the solid. The comparison is not a trivial matter. First of all one needs to bring both sets of geometries to the same geometrical basis. The most logical choice seems to be the neutron geometry corrected for thermal translational and rotational effects. This will closely approach an r_α^0-type geometry, i.e. one based on averaged nuclear coordinates of the molecule in the vibrational ground state.

An *ab initio* calculation, on the other hand, gives ideally an equilibrium geometry based on nuclear positions of *non-vibrating* atoms. In practice the results also depend upon the choice of atomic basis functions. To bring an *ab initio* distance to r_α^0 basis we use $r_\alpha^0 = r(ab\ initio) - K_0 + \delta$. The correction K_0 is the contribution of the vibration perpendicular to the bond. We will use $K_0 = 0.002$ Å for bonds between non-H atoms and $K_0 = 0.017$ Å for those involving H. Correction terms δ depend upon the atomic basis functions as well as on the type of bond concerned. Only for the 4-21G atomic basis set (Pulay, Fogarasi, Pang & Boggs, 1979) is a set of δ corrections available (Klimkowski, Ewbank, Van Alsenoy, Scarsdale & Schafer, 1982; Van Alsenoy, Klimkowski & Schafer, 1984). Therefore new calculations at the 4-21G level are necessary.

Using the gradient method and program *TEXAS* (Pulay, 1969, 1977, 1979) we optimized the geometry of the free HM ion with complete relaxation until the largest residual force on any nuclear coordinate was less than 0.001 mdyn (10^{-11} N). Apart from the expected variation in numerical values, the results are similar to those of George, Bock & Trachtmann (1983), who used the 4-31G basis set. The comparison between the thermally corrected neutron and the theoretical r_α^0 geometry is presented in Table 3. Two phenomena attract attention. First, the differences observed for bond lengths and valence angles are definitely outside the error limits. Second the calculated HM ion is planar, whereas the experimental ion is not. We now have to investigate whether these differences may be due to crystal-field effects.

In an attempt to estimate the order of magnitude of such effects Saebo, Klewe & Samdal (1983) calculated with a double-ζ basis set the relaxed geometry of an isolated cyanoformamide molecule and that of

Table 4. *Ab initio* (4-21G basis) energies (kJ mol⁻¹) of a free HM ion as a function of $T1$ and $T2$ (°)

$T1$: torsion C(3)=C(2)–C(1)–O(1). $T2$: torsion C(2)=C(3)–C(4)–O(3).

$T1$	$T2$	Energy, E	ΔE
0.0	0.0	−1186582·47673	0·
3·0	0·0	·40857	0·06816
0·0	3·0	·39002	0·08671
−3·0	3·0	·36255	0·11418
3·0	3·0	·27668	0·20005

the same molecule taking into account the influence of neighbouring molecules, represented by atomic point charges. The authors found that calculated bond lengths may change by a few hundredths of an Å and valence angles by a few degrees. It is gratifying to see that with the exception of O(3)–H(O3) we observe differences of the same magnitude between the experimental and calculated free-ion geometry. Calculations of HM surrounded by point charges, representing water molecules, are underway and will be reported later.

Finally, *ab initio* calculations of the free HM ion were performed to estimate whether the observed disrotatory movement of the carboxyl groups is energetically more favourable than the intuitively preferred conrotatory movement. Energies were calculated at fixed values of the torsion angles $\omega = O(1)–C(1)–C(2)–C(3)$ and $\varphi = O(3)–C(4)–C(3)–C(2)$ but allowing all other internal parameters to relax freely. The effect of non-planarity on the other geometrical parameters proved negligible; bond lengths remained unchanged within 0.001 Å and valence angles within 0.01°. Five energy points were calculated: the equilibrium geometry $\omega = \varphi = 0°$, the one-sided distortions $\omega = 0°$, $\varphi = 3°$ and $\omega = 3°$, $\varphi = 0°$, the disrotatory movement $\omega = 3°$, $\varphi = -3°$, and the conrotatory movement $\omega = \varphi = 3°$. The calculated energies are given in Table 4 and point to a preference for disrotatory movement, in which the internal H bond remains the shortest, over conrotatory movement. A strong argument for the same conclusion stems from the fact that the disrotatory movement of carboxyl groups is not restricted to maleates, but has also been observed in lithium hydrogen phthalate monohydrate (Kuppers, Takusagawa & Koetzle, 1985).

References

ALLEN, F. H. (1986). *Acta Cryst.* B42, 515–522.
BUSING, W. R., MARTIN, K. O. & LEVY, H. O. (1962). *ORFLS.* Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.

GEORGE, P., BOCK, C. W. & TRACHTMANN, M. (1983). J. Phys. Chem. 87, 1839–1841.
GUPTA, M. P., VAN ALSENOY, C. & LENSTRA, A. T. H. (1984). Acta Cryst. C40, 1526–1529.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
KLIMKOWSKI, V. J., EWBANK, J. D., VAN ALSENOY, C., SCARSDALE, J. N. & SCHAFER, L. (1982). J. Am. Chem. Soc. 104, 1476–1480.
KUPPERS, H., TAKUSAGAWA, F. & KOETZLE, T. F. (1985). J. Chem. Phys. 82, 5636–5647.
MAYNARD, A. T., HISKEY, R. G., PEDERSEN, L. G. & KOCHLER, K. A. (1985). J. Mol. Struct. Theor. Chem. 124, 213–221.

OLOVSSON, G., OLOVSSON, J. & LEHMANN, M. S. (1984). Acta Cryst. C40, 1523–1526.
PULAY, P. (1969). Mol. Phys. 17, 197–204.
PULAY, P. (1977). Modern Theoretical Chemistry, Vol. 4, edited by H. F. SCHAFER III, p. 154. New York: Plenum Press.
PULAY, P. (1979). Theor. Chim. Acta, 50, 299–312.
PULAY, P., FOGARASI, G., PANG, F. & BOGGS, J. E. (1979). J. Am. Chem. Soc. 101, 2550–2560.
SAEBO, S., KLEWE, B. & SAMDAL, S. (1983). Chem. Phys. Lett. 97, 499–502.
TRUEBLOOD, K. & SCHOMAKER, V. (1968). Acta Cryst. B24, 63–75.
VAN ALSENOY, C., KLIMKOWSKI, V. J. & SCHAFER, L. (1984). J. Mol. Struct. Theor. Chem. 109, 321–330.

β–α Photoisomerization of Cobaloxime Complexes in the Solid State. I. Different Reaction Rates in Polymorphic Crystals

BY AKIRA UCHIDA, MASAKI DANNO AND YOSHIO SASADA

Department of Life Science, Faculty of Science, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

AND YUJI OHASHI*

Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112, Japan

Abstract

Two crystalline forms of (β-cyanoethyl)bis(dimethylglyoximato)(3-methylpyridine)cobalt(III) (dimethylglyoximato = 2,3-butanedione dioximato), $C_{17}H_{25}CoN_6O_4$, [$Co(C_3H_4N)(C_4H_7N_2O_2)_2(C_6H_7N)$], were obtained from methanol solutions. Form I: $M_r = 436\cdot36$, monoclinic, $P2_1/a$, $a = 23\cdot742 (5)$, $b = 9\cdot496 (2)$, $c = 8\cdot819 (1)$ Å, $\beta = 94\cdot59 (2)°$, $V = 1981\cdot9 (6)$ Å^3, $Z = 4$, $D_x = 1\cdot463$ g cm^{-3}, λ(Mo $K\alpha$) = $0\cdot71069$ Å, $\mu = 8\cdot42$ cm^{-1}, $F(000) = 912$, $T = 298$ K, $R = 0\cdot057$ for 3955 observed reflections; form II: monoclinic, $P2_1/a$, $a = 21\cdot425 (4)$, $b = 9\cdot290 (1)$, $c = 11\cdot517 (2)$ Å, $\beta = 117\cdot58 (2)°$, $V = 2031\cdot6 (7)$ Å^3, $Z = 4$, $D_x = 1\cdot427$ g cm^{-3}, λ(Mo $K\alpha$) = $0\cdot71069$ Å, $\mu = 8\cdot22$ cm^{-1}, $F(000) = 912$, $T = 298$ K, $R = 0\cdot048$ for 4198 observed reflections. The rate of β–α isomerization for form II was much greater than that for form I. The structure analysis has shown that the conformations of the β-cyanoethyl groups in forms I and II are almost the same and that there is greater room around the cyanoethyl group in form II than in form I.

Introduction

The β-cyanoethyl group, $-CH_2CH_2CN$ (1), in the complexes of bis(dimethylglyoximato)cobalt(III), cobaloximes, isomerizes to the α-cyanoethyl group, $-C^*H(CH_3)CN$ (2), on irradiation of powdered samples with visible light (Ohgo & Takeuchi, 1985).
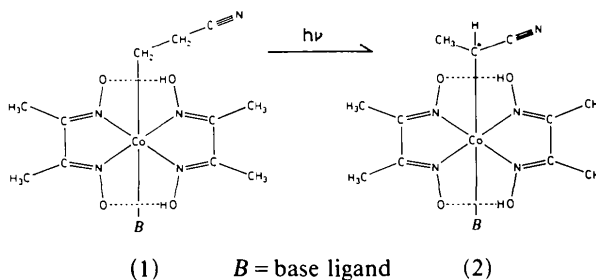
(1)   B = base ligand   (2)

The photoreaction occurs only in the solid state and the reverse reaction is not observed. This finding has stimulated us to make serial studies of (β-cyanoethyl)cobaloxime with different base ligands, because the relation between crystal structure and reactivity in the solid state has been our main interest since the crystalline-state racemization of (α-

---

* To whom correspondence should be addressed.