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An Independent Investigation of the Crystal Structure of $Na_2Cu(CO_3)_2(H_2O)_3$ with Diffractometer Data

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Crystals of $Na_2Cu(CO_3)_2(H_2O)_3$ were found to be monoclinic, $P2_1/c$, $Z=4$, with unit-cell dimensions $a=9·691$ (2), $b=6·091$ (1), $c=17·111$ (3) Å, $\beta=126·40$ (1)°. The crystal structure has been determined from 2373 intensities measured on a diffractometer with monochromated Mo $K\alpha$ radiation. A conventional R value of 0·042 was obtained from the full-matrix least-squares refinement using anisotropic thermal parameters as well as an isotropic extinction parameter. The fundamental features of the structure agree with those reported by Brotherton & White [*J. Chem. Soc. Dalton* (1973), pp. 2338–2340] who, in an independent study based on 995 visually estimated intensities, found that one water, one bidentate carbonate, and a pair of crystallographically equivalent carbonates coordinate with the copper atom in a distorted square-pyramidal configuration. The diffractometer study presented here has allowed additional information to be obtained from the structure: (1) the positions of the hydrogen atoms were located in a difference Fourier synthesis and (2) the distortion of the carbonate ions from the D_{3h} symmetry of the free ion to approximately C_{2v} symmetry was clearly demonstrated. This distortion is such that the non-coordinated oxygen–carbon bond length is considerably shorter, 0·037 Å on the average, than the coordinated oxygen–carbon bond length.

Introduction

A study of the infrared spectrum of several aquo-carbonato transition-metal complexes suggested that both mono- and bidentate carbonate ligands were present in the copper salt $Na_2Cu(CO_3)_2(H_2O)_3$ (Scott, 1967). While the crystal structure was under investigation in our laboratory, Brotherton & White (1973), hereinafter BW, published the results of their own study based on 995 visually estimated intensities. We have confirmed that their structure is fundamentally correct and that the one reported by Kupčík (1962) is in error. With 2373 diffractometer intensities, we have been able to locate the hydrogen atoms and, more important, to show that the bidentate and bridging carbonate ligands undergo a distortion from D_{3h} symmetry found for the free carbonate ion. These features were not elucidated in BW's study.

Table 1. *Crystal data*

$Na_2Cu(CO_3)_2(H_2O)_3$, F.W. 283·58
Monoclinic, $P2_1/c$, $Z=4$
a $=9·691$ (2), $b=6·091$ (1)
c $=17·111$ (3) Å, $\beta=126·40$ (1)°
V $=813·0$ Å^3, μ(Mo $K\alpha$)$=29·18$ cm^{-1}
$D_m=2·314$, $D_x=2·317$ g cm^{-3}

Table 2. *Final atomic coordinates and thermal parameters for* $Na_2Cu(CO_3)_2(H_2O)_3$

Estimated standard deviations are in parentheses.
B for hydrogen atoms is 6·0 Å^2. Anisotropic thermal parameters are $\times 10^4$ and have the form $\exp[-(h^2\beta_{11}+\ldots+2kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0·05735 (5)	−0·00986 (8)	0·18029 (3)	19 (1)	49 (1)	11 (0)	−5 (1)	9 (0)	−10 (1)
Na(1)	0·4918 (2)	−0·0227 (3)	0·5979 (1)	88 (2)	141 (5)	25 (1)	7 (3)	29 (1)	1 (2)
Na(2)	0·3659 (2)	0·2636 (3)	0·2014 (1)	88 (3)	121 (4)	30 (1)	1 (3)	34 (1)	7 (2)
O(1)	0·0781 (3)	0·2204 (5)	0·2650 (2)	66 (4)	173 (9)	35 (2)	−31 (5)	29 (2)	−35 (3)
O(2)	0·1871 (3)	0·4741 (4)	0·3783 (2)	62 (4)	116 (7)	24 (1)	3 (4)	23 (2)	−8 (3)
O(3)	0·3448 (3)	0·3467 (4)	0·3321 (2)	68 (4)	135 (8)	38 (2)	−15 (5)	36 (2)	−16 (3)
O(4)	0·0805 (3)	−0·2609 (5)	0·1135 (2)	55 (4)	168 (8)	29 (2)	−8 (5)	20 (2)	−22 (3)
O(5)	0·2980 (3)	−0·0823 (4)	0·2335 (2)	70 (4)	113 (7)	27 (1)	−3 (4)	25 (2)	−14 (3)
O(6)	0·3490 (3)	−0·3602 (4)	0·1678 (2)	89 (5)	121 (7)	40 (2)	18 (5)	42 (2)	0 (3)
O(7)	0·0520 (4)	0·2672 (5)	0·0819 (2)	120 (5)	167 (9)	27 (2)	4 (6)	32 (3)	7 (3)
O(8)	0·3026 (3)	−0·1004 (5)	0·4326 (2)	106 (5)	141 (8)	35 (2)	−26 (5)	31 (3)	−9 (3)
O(9)	0·3988 (3)	0·1557 (5)	0·0791 (2)	103 (5)	147 (8)	27 (2)	20 (5)	24 (2)	−7 (3)
C(1)	0·2065 (4)	0·3471 (6)	0·3242 (3)	63 (5)	84 (9)	20 (2)	13 (6)	22 (3)	4 (3)
C(2)	0·2466 (4)	−0·2400 (6)	0·1710 (3)	61 (5)	102 (9)	21 (2)	−1 (6)	22 (3)	3 (4)

	x	y	z		x	y	z
H(1)	0·010	0·260	0·015	H(4)	0·210	−0·025	0·400
H(2)	0·030	0·400	0·095	H(5)	0·330	0·120	0·020
H(3)	0·270	−0·240	0·410	H(6)	0·480	0·050	0·115

Experimental

The crystal selected for this investigation was supplied by D. R. Scott (1973) and had dimensions of 0·15 × 0·23 × 0·35 × 0·31 mm perpendicular to (10$\bar{2}$), (002), ($\bar{1}$11), and (11$\bar{1}$) respectively. Preliminary investigation of the crystal on a G. E. XRD-5 diffractometer yielded crystal system and space group information; lattice parameters were refined from 20 high-angle reflections ($106° < 2\theta < 156°$, Cu $K\alpha_1$, $\lambda = 1{\cdot}54050$ Å) by the least-squares method. Table 1 summarizes the crystal data, with the unit cell chosen in the conventional way with an axial glide; these are in good agreement with BW's values when appropriately transformed to their $P2_1/n$ unit cell.

The crystal was mounted on a Syntex $P2_1$ diffractometer with Mo $K\alpha$ radiation monochromatized by a graphite crystal. The θ–2θ scan technique was employed to collect intensity data for 2958 independent reflections in the range $4° < 2\theta < 65°$. The reflections were scanned from 0·8° in 2θ below the $K\alpha_1$ peak to 1·2° above the $K\alpha_2$ peak. The scan rate varied from 2·0 to 5·0° min^{-1} dependent on the number of counts accumulated in a preliminary scan of each reflection. Background measurements were taken at both ends of the scan range, each for a time equal to one-half the scan time. The intensities of four standard reflections were measured after every 46 reflections; the average intensity of these reflections dropped by 1·0% during

Table 3. *Interatomic angles* (°) *for* $Na_2Cu(CO_3)_2(H_2O)_3$

(I) Angles related to Figs. 1(*a*), 1(*b*), 1(*c*), and 1(*d*); the copper coordination sphere, the carbonate groups, and the water molecule containing O(7), H(1), and H(2)

O(1)—Cu—O(1)^{a}	92·2 (1)	O(1)—C(1)—O(2)	115·6 (4)
O(1)—Cu—O(2)^{a}	88·6 (1)	O(1)^{a}—C(1)^{a}–O(2)^{a}	
O(1)—Cu—O(4)	169·4 (1)	O(1)—C(1)—O(3)	123·3 (4)
O(1)—Cu—O(5)	104·2 (1)	O(1)^{a}—C(1)^{a}–O(3)^{a}	
O(1)—Cu—O(7)	88·0 (1)	O(2)—C(1)—O(3)	121·1 (4)
O(4)—Cu—O(1)^{a}	88·6 (1)	O(2)^{a}—C(1)^{a}–O(3)^{a}	
O(4)—Cu—O(2)^{a}	100·5 (1)	C(1)—O(1)—H(4)	84
O(4)—Cu—O(5)	66·0 (1)	C(1)—O(2)—H(3)^{e}	123
O(4)—Cu—O(7)	95·8 (1)	C(1)—O(2)—H(5)^{k}	113
O(5)—Cu—O(1)^{a}	113·6 (1)	C(1)—O(3)—Na(1)^{c}	113·9 (2)
O(5)—Cu—O(2)^{a}	164·1 (1)	C(1)—O(3)—Na(2)	124·6 (3)
O(5)—Cu—O(7)	90·5 (1)	C(1)—O(3)—H(6)^{f}	131
O(7)—Cu—O(1)^{a}	154·9 (1)	Na(1)^{c}–O(3)—Na(2)	84·0 (1)
O(7)—Cu—O(2)^{a}	99·4 (1)	Na(1)^{c}–O(3)—H(6)^{f}	100
O(1)^{a}—Cu—O(2)^{a}	55·6 (1)	Na(2)–O(3)—H(6)^{f}	92
O(1)—Cu^{b}—O(2)		H(3)^{e}—O(3)—H(5)^{k}	93
Cu—O(2)^{a}–C(1)^{a}	107·9 (3)	O(4)—C(2)—O(5)	113·1 (3)
Cu^{b}—O(2)—C(1)		O(4)—C(2)—O(6)	124·3 (4)
Cu—O(1)^{a}–C(1)^{a}	78·3 (2)	O(5)—C(2)—O(6)	122·6 (4)
Cu^{b}—O(1)—C(1)		C(2)—O(4)—H(1)^{h}	114
Cu—O(1)^{a}–Cu^{a}	151·1 (2)	C(2)—O(4)—H(2)^{g}	106
Cu^{b}—O(1)—Cu		H(1)^{h}—O(4)—H(2)^{g}	85
Cu—O(4)—C(2)	90·1 (2)	C(2)—O(5)—Na(1)^{c}	144·6 (3)
Cu—O(5)—C(2)	90·8 (3)	C(2)—O(5)—Na(2)	119·4 (3)
Cu—O(1)—C(1)	129·9 (3)	Na(1)^{c}–O(5)—Na(2)	83·6 (1)
Cu—O(1)—H(4)	92	C(2)—O(6)—Na(1)^{l}	153·0 (3)
Cu^{b}—O(1)—H(4)	98	C(2)—O(6)—Na(2)^{g}	120·0 (3)
Cu^{b}—O(2)—H(3)^{e}	107	C(2)—O(6)—Na(2)^{j}	106·0 (3)
Cu^{b}—O(2)—H(5)^{k}	113	Na(1)^{l}–O(6)—Na(2)^{g}	81·7 (1)
Cu—O(4)—H(3)^{h}	123	Na(1)^{l}–O(6)—Na(2)^{j}	82·8 (1)
Cu—O(4)—H(2)^{g}	138	Na(2)^{g}–O(6)—Na(2)^{j}	101·7 (1)
Cu—O(5)—Na(1)^{c}	114·5 (1)		
Cu—O(5)—Na(2)	96·2 (1)	Na(2)–O(7)—O(4)^{e}	85·4 (1)
Cu—O(7)—Na(2)	84·7 (1)	Na(2)–O(7)—O(4)^{h}	117·4 (2)
Cu—O(7)—O(4)^{e}	127·9 (1)	Na(2)–O(7)—H(1)	115
Cu—O(7)—O(4)^{h}	130·2 (1)	Na(2)–O(7)—H(2)	99
Cu—O(7)—H(1)	129	O(4)^{e}—O(7)—O(4)^{h}	99·3 (1)
Cu—O(7)—H(2)	112	H(1)—O(7)—H(2)	110
		O(7)—H(1)—O(4)^{h}	176
		O(7)—H(2)—O(4)^{e}	149

(II) Angles related to Fig. 1(*e*); water molecule containing O(8), H(3), and H(4)

Na(1)–O(8)—Na(1)^{c}	92·5 (1)	Na(1)^{c}–O(8)—H(3)	109
Na(1)–O(8)—O(1)	128·1 (1)	Na(1)^{c}–O(8)—H(4)	112
Na(1)–O(8)—O(2)^{g}	118·0 (1)	O(1)—O(8)—O(2)^{g}	111·3 (1)
Na(1)–O(8)—H(3)	122	H(3)—O(8)—H(4)	105
Na(1)–O(8)—H(4)	117	O(8)—H(3)—O(2)^{g}	169
Na(1)^{c}–O(8)—O(1)	79·7 (1)	O(8)—H(4)—O(1)	136
Na(1)^{c}–O(8)—O(2)^{g}	115·7 (1)		

Table 3 (*cont.*)

(III) Angles related to Fig. 1 (*f*); water molecule containing O(9), H(5), and H(6)

Na(1)^{i}–O(9)—Na(2)	81·9 (1)	Na(2)–O(9)—H(5)	134
Na(1)^{i}–O(9)—O(2)^{i}	111·5 (1)	Na(2)–O(9)—H(6)	97
Na(1)^{i}–O(9)—O(3)^{j}	115·2 (1)	O(2)^{i}—O(9)—O(3)^{j}	104·0 (1)
Na(1)^{i}–O(9)—H(5)	112	H(5)—O(9)—H(6)	112
Na(1)^{i}–O(9)—H(6)	118	O(9)—H(5)—O(2)^{i}	174
Na(2)–O(9)—O(2)^{i}	138·7 (2)	O(9)—H(6)—O(3)^{j}	167
Na(2)–O(9)—O(3)^{j}	104·6 (1)		

(IV) Angles related to Fig. 1(*g*); sodium ion, Na(1), coordination sphere

O(8)—Na(1)–O(3)^{c}	104·7 (1)	O(3)^{c}—Na(1)–O(9)^{k}	161·3 (1)
O(8)—Na(1)–O(5)^{c}	174·7 (1)	O(5)^{c}—Na(1)–O(6)^{d}	79·2 (1)
O(8)—Na(1)–O(6)^{d}	105·8 (1)	O(5)^{c}—Na(1)–O(8)^{c}	87·6 (1)
O(8)—Na(1)–O(8)^{c}	87·5 (1)	O(5)^{c}—Na(1)–O(9)^{k}	84·0 (1)
O(8)—Na(1)–O(9)^{k}	93·7 (1)	O(6)^{d}—Na(1)–O(8)^{c}	166·3 (1)
O(3)^{c}—Na(1)–O(5)^{c}	77·3 (1)	O(6)^{d}—Na(1)–O(9)^{k}	93·6 (1)
O(3)^{c}—Na(1)–O(6)^{d}	84·9 (1)	O(8)^{c}—Na(1)–O(9)^{k}	88·5 (1)
O(3)^{c}—Na(1)–O(8)^{c}	88·8 (1)		

(V) Angles related to Fig. 1(*h*); sodium ion, Na(2), coordination sphere

O(3)—Na(2)–O(5)	77·5 (1)	O(5)—Na(2)–O(6)^{f}	80·2 (1)
O(3)—Na(2)–O(7)	91·4 (1)	O(7)—Na(2)–O(9)	91·0 (1)
O(3)—Na(2)–O(9)	175·4 (1)	O(7)—Na(2)–O(6)^{e}	85·2 (1)
O(3)—Na(2)–O(6)^{e}	89·5 (1)	O(7)—Na(2)–O(6)^{f}	160·1 (1)
O(3)—Na(2)–O(6)^{f}	83·5 (1)	O(9)—Na(2)–O(6)^{e}	94·6 (1)
O(5)—Na(2)–O(7)	79·9 (1)	O(9)—Na(2)–O(6)^{f}	93·0 (1)
O(5)—Na(2)–O(9)	99·1 (1)	O(6)^{e}—Na(2)–O(6)^{f}	114·0 (1)
O(5)—Na(2)–O(6)^{e}	159·8 (1)		

Symmetry relations for atoms in Fig. 1 and Table 3

(*a*)	$(-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z)$	(*g*)	$(x$	$-1+y$	$z)$
(*b*)	$(-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z)$	(*h*)	$(-x$	$-y$	$-z)$
(*c*)	$(1-x$	$-y$	$1-z)$	(*i*)	$(x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z)$
(*d*)	$(x$	$-\frac{1}{2}-y$	$\frac{1}{2}+z)$	(*j*)	$(1+x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z)$
(*e*)	$(x$	$1+y$	$z)$	(*k*)	$(x$	$\frac{1}{2}-y$	$\frac{1}{2}+z)$
(*f*)	$(1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z)$	(*l*)	$(x$	$-\frac{1}{2}-y$	$-\frac{1}{2}+z)$

the data-collection period and a correction factor as a function of exposure time was applied.

Absorption corrections based on crystal shape were applied to the data (transmission coefficients ranged from 0·48 to 0·69). Conversion to structure amplitudes was completed with the application of Lorentz and polarization factors. Standard deviations in the intensities, $\sigma(I)$, and in the structure amplitudes, $\sigma(F_o)$, were derived directly from counting statistics. Only the 2373 reflections for which $I>3\sigma(I)$ were included in the refinement; weights were assigned as $1/\sigma^2(F_o)$.

Structure determination and refinement

The structure was solved by the Patterson heavy-atom method. Initial full-matrix least-squares refinement of the positional and isotropic thermal parameters converged at a conventional $R=(\sum||F_o|-|F_c||/\sum|F_o|)$ of 0·078 and a weighted $R_w=(|F_o|-|F_c|)^2/\sum w|F_o|^2)^{1/2}$ of 0·084. A difference-Fourier map at this stage revealed the locations of the six hydrogen atoms. Least-squares refinement of the hydrogen atom positions failed however to yield chemically reasonable bond lengths; these atoms were then fixed at the positions found in the difference map and assigned isotropic thermal parameters of 6·0 Å^2. Subsequent refinement of the positional and anisotropic thermal parameters for the non-hydrogen atoms yielded $R=0{\cdot}042$ and $R_w=0{\cdot}042$. Included in the final cycles of refinement was an extinction parameter (Zachariasen, 1968) which converged to a value of $1{\cdot}38\ (3)\times10^{-3}$; prior to its inclusion, a number of intense reflections had large, negative $(|F_o|-|F_c|)$ values. One reflection, $22\bar{6}$, was inexplicably in error and was removed from the data set.

The final conventional R for all 2957 reflections was 0·054. In the final cycle of refinement, the largest shift in any positional parameter was 0·08 σ. The largest peak in the final difference Fourier was located near atom Na(1) and had a height of 0·3 e Å^{-3}. The final positional and thermal parameters are given in Table 2.*

The atomic scattering factors for Cu, Na$^+$, C, and O were those of Cromer & Waber (1965); for H, those of Stewart, Davidson & Simpson (1965) were used.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30853 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The Cu scattering factors were corrected for anomalous dispersion (Cromer, 1965).

Programs used in the solution and refinement of the structure may be found in a report by Harlow, Wells, Watt & Simonsen (1974).

Discussion

Because the basic aspects of the crystal structure of $Na_2Cu(CO_3)_2(H_2O)_3$ have already been discussed by BW, our discussion will be mainly limited to a few comments. The bond distances and hydrogen-bonding interactions are shown in Fig. 1 and Table 3 lists the bond angles. Most distances and angles agree to within 2σ of those reported by BW (the atom-numbering schemes are quite different).

Whether the coordination geometry around the copper atom is described as a square pyramid of the 4,1 type or a distorted octahedron of the 4,1,1 type is a moot point. The argument centers on carbonate oxygen $O(1)^a$ (Fig. 1) which is close enough (2·600 Å) to interact electrostatically with the copper. However, the $C(1)^a$–$O(1)^a$–Cu angle, 78·3°, would seem to preclude any significant overlap of copper and oxygen orbitals. Either way, the Cu–O bond distances fall within the range determined for many 4,1 and 4,1,1 copper–oxygen complexes as reviewed by Dubler, Korber & Oswald (1973).

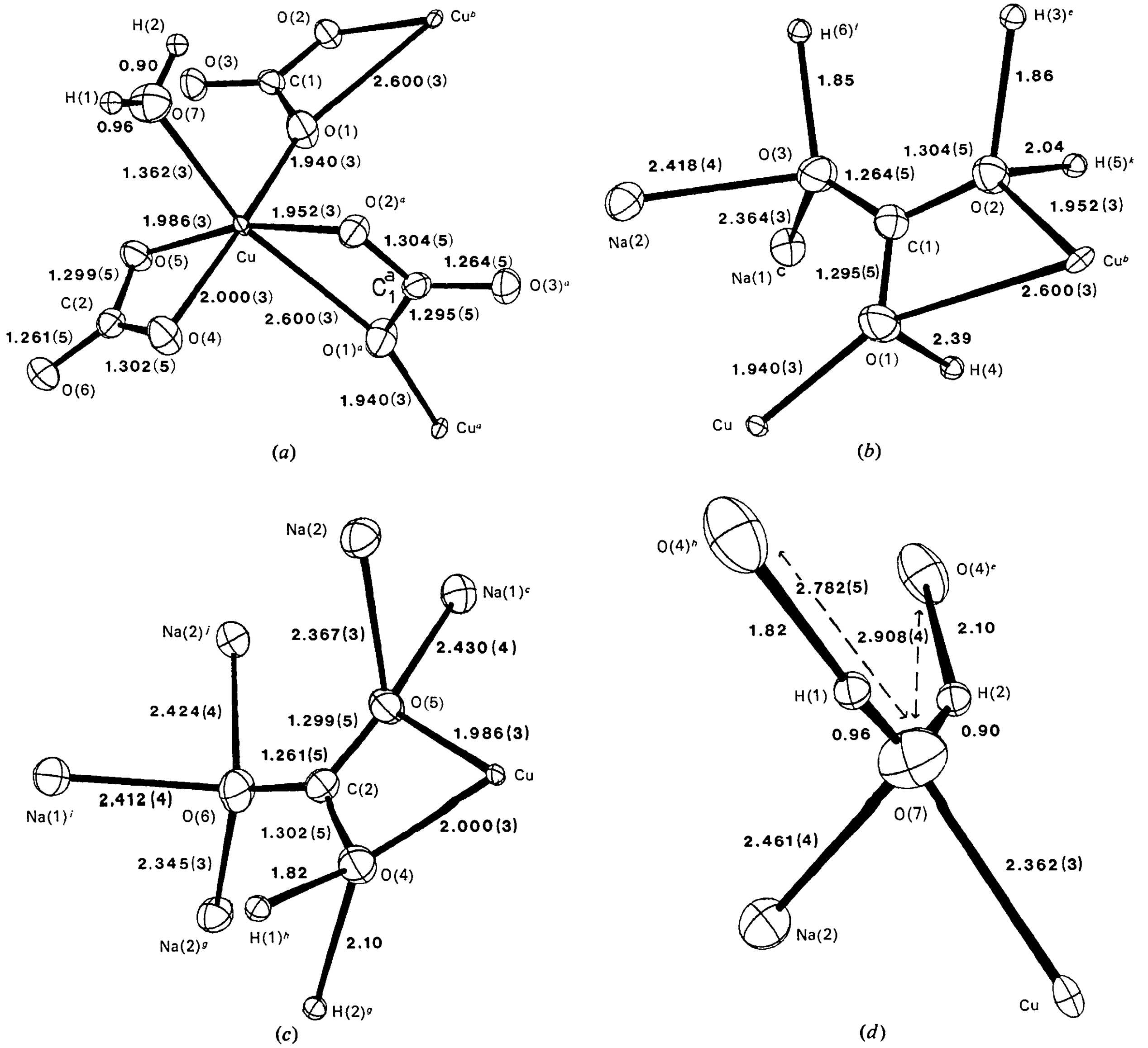

Fig. 1. Interatomic distances: (*a*) copper coordination; (*b*) environment of the bridging carbonate group; (*c*) environment of the bidentate carbonate group; (*d*) environment of one of the three water molecules.

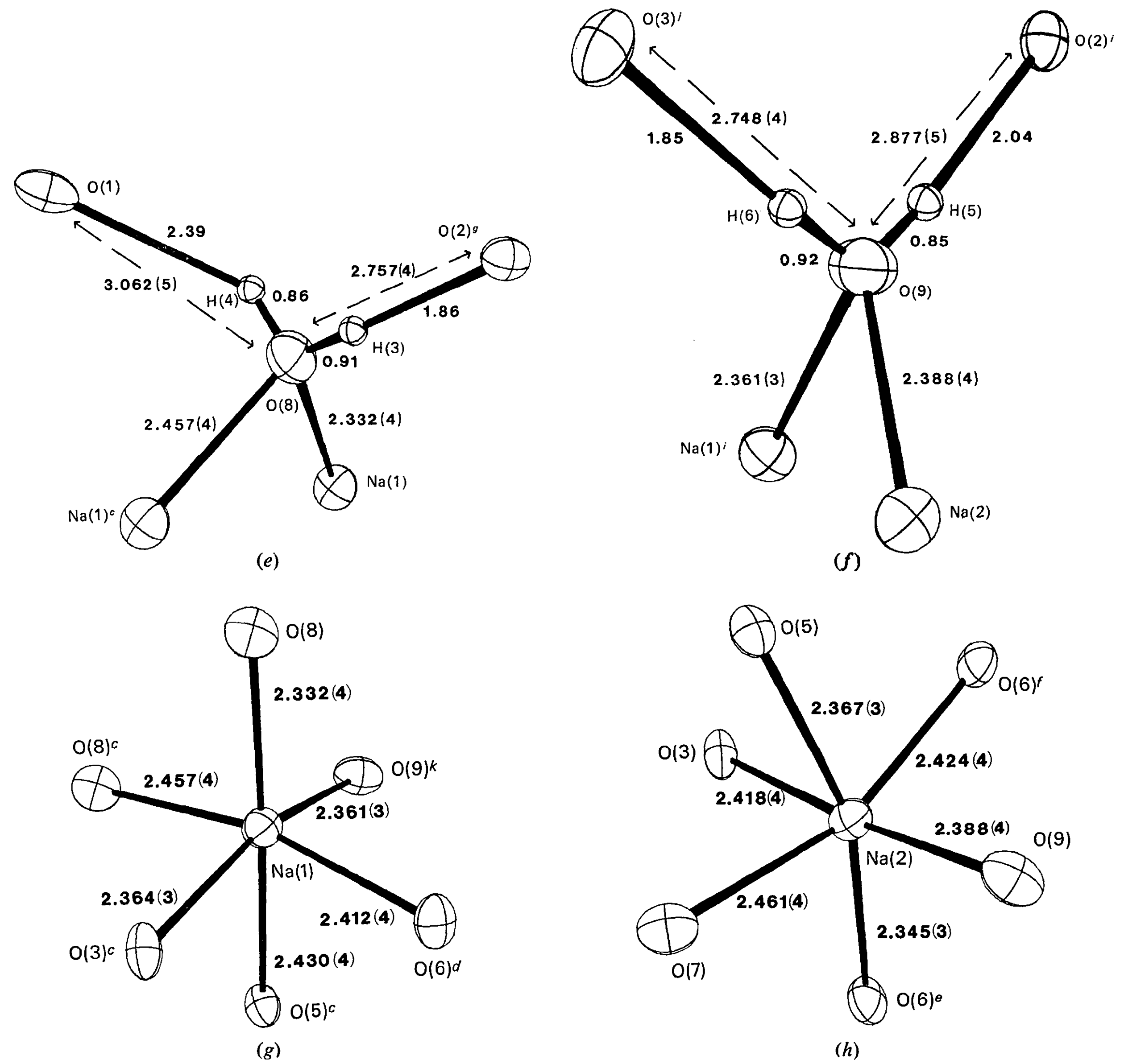

Fig. 1 (*cont.*) (*e*) and (*f*) Environment of the other two water molecules, (*g*) and (*h*) approach of oxygen atoms to each of the sodium ions.

That carbonate groups generally distort from D_{3h} symmetry when coordinated with metal atoms has been well established. For bidentate and bridging carbonate groups, the two carbon–oxygen bond lengths increase when the oxygen atoms coordinate (decreased C–O π bonding) while the non-coordinating or weakly coordinated oxygen–carbon distance decreases (increased C–O π bonding) (see for examples: Kaas & Sørensen, 1973; Meyer, Singh, Hatfield & Hodgson 1972; Healy & White, 1972; and references therein). Concurrently, the O–C–O angle opposite the shorter bond becomes less than 120°; that this feature is intrinsic to angles opposite bonds with increased π character can be noted from structures of organic compounds containing C=C and C=O double bonds. As a result of these distortions, bidentate bridging carbonate groups approach C_{2v} symmetry.

The structures of $CaCO_3$ (Sass, Vidale & Donohue, 1957), $CaCO_3.6H_2O$ and $CaNa_2(CO_3)_2.5H_2O$ (Dickens & Brown, 1970, 1969) are three examples in which the carbonate group maintains nearly D_{3h} symmetry with little coordination; they provide an average C–O bond distance of 1·289 Å. In the structure reported here, the averages of the C–O bond lengths for the coordinated and non-coordinated oxygen atoms are 1·300 and 1·263 Å, respectively. This clearly shows the distortion of the carbonate groups which BW were unable to demonstrate. The angles opposite the shortened C–O bonds are 113·1 and 115·6° for the bidentate and bridging group respectively; these values show less of a difference than the values obtained by BW; 111·7 and 116·9°, respectively.

With the location of the hydrogen atoms, we have confirmed that hydrogen bonding occurs in accord with the water–oxygen contacts listed by BW as probable hydrogen bonds. The strong hydrogen bonds have nearly linear O–H···O angles, 167 to 176°, as well as short O···O and H···O distances; the H(4)···O(1) distance of 2·39 Å with a O(8)–H(4)···O(1) angle of 136° implies that this is a very weak interaction. These findings are in agreement with a recent review on neutron-diffraction studies of H_2O molecules in various crystals (Ferraris & Franchini-Angela, 1972).

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The Crystal Structure of Calcium *cis*(*N*)-*trans*(O_6)-Bis-(L-aspartato)cobaltate(III)–water(2/15)

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Crystals of $2\{Ca\ cis(N)\text{-}trans(O_6)\text{-}[Co(L\text{-}asp)_2]_2\}.15H_2O$ are hexagonal with space group $P6_3$: $a=15{\cdot}972$ (3), $c=21{\cdot}164$ (6) Å and $Z=3$. The structure was refined by least-squares methods with anisotropic temperature factors to give an R value of 0·054 on the basis of the 2876 observed reflexions collected by diffractometry. The complex anions are held together by N–H···O hydrogen bonds to form left-handed triple helices parallel to the c axis. Calcium ions and water molecules are arranged in and among the helices.

Introduction

There are three isomers of the bis-(L-aspartato)cobaltate(III) ion, in which the ligand is tridentate. The stereochemistry of trifunctional aspartic acid is different from that of other bifunctional amino acids. The three rings join on the face of an octahedron at the asymmetric carbon atom in such a manner that the rings do not define the edges of the octahedron. The presence of such chelate rings leads to complexities in the circular dichroism spectra which made it difficult to correlate the absolute configurations on the basis of circular dichroism. In fact, two opposite assignments have been made to the *cis*(*N*)-*trans*(O_5) and *cis*(*N*)-*trans*(O_6) isomers (Yamada, Hidaka & Douglas, 1971; Legg & Neal, 1973). In order to remove uncertainties about this point, crystals of the title compound have been subjected to crystal-structure analysis, although the structures of the two complex ions were known by the structure determination of a double salt,