Crystal Structures of Copper(II) Sodium Carbonate Trihydrate (Chalconatronite)

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The crystal structure of the title compound has been determined from single-crystal photographic *X*-ray diffraction data by heavy-atom methods, and refined to *R* 0·13 for 995 visually estimated reflections. Crystals are monoclinic, space group $P2_1/n$, a = 13·81(2), b = 6·10(1), c = 9·70(1) Å, β = 91·7(2)°, Z = 4.

The copper atom is co-ordinated in a distorted square pyramidal configuration by a water molecule at the apex [Cu–O 2·38(1) Å], a bidentate carbonate group [Cu–O,O′, 1·92, 1·97(1) Å], and a pair of crystallographically equivalent bridging carbonate groups [Cu–O,O′, 1·99, 1·98(1) Å] generating infinite anionic chains parallel to *b* about the crystallographic screw axes. The other two water molecules occupy lattice sites.

COPPER(II) sodium carbonate exists in two well-established forms: the anhydrous form, $Na_2Cu(CO_3)_2$, whose structure and properties have recently been described,[1,2] and the trihydrate $Na_2Cu(CO_3)_2,3H_2O$. A brief report of the structure of the latter has appeared,[3] together with investigations of its magnetic properties[4] and i.r. spectrum.[5] We now report the structure determination of the trihydrate.

EXPERIMENTAL

Blue crystals of the complex were prepared by a standard method[6] and checked analytically. Photographic *X*-ray data were collected by the multiple-film equi-inclination Weissenberg method about *b* and *c* (layers $h0$—$4l$ and $hk0$—4) on a block 0·09 × 0·16 × 0·12 mm, the edges being coincident with the axes. Cell calibration was effected by superimposing aluminium powder lines (a_{298} = 4·0494 Å)[7] on zero-layer photographs.

Crystal Data.—$C_2H_6CuNa_2O_9$, M = 283·6, Monoclinic, a = 13·81(2), b = 6·10(1), c = 9·70(1) Å, β = 91·7(2)°, U = 817 Å^3, D_m (by flotation) = 2·28(2) g cm^{-3}, Z = 4, D_c = 2·31 g cm^{-3}, $F(000)$ = 524. Space group $P2_1/n$ (C_{2h}^5, No. 14),[8] Cu-K_α radiation (Ni filtered) λ = 1·5418 Å,[9] μ = 53 cm^{-1}; transmission coefficient range 0·40—0·68. 995 Visually estimated independent reflections.

The data set was generated and the structure solved and refined by our usual methods.[1] At convergence, *R* was 0·13, weighting-scheme constants a = 16·2, b = 0·017 [$w = (a + |F_o| + b|F_o|^2)^{-1}$], and parameter shifts for all atoms $<0·2\ \sigma$; a difference Fourier map showed no significant features. Scattering factors were for neutral atoms (except singly charged sodium were taken from ref. 10), those for copper and sodium being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[11] Final observed and calculated structures are listed in Supplementary Publication No. SUP 20789 (3 pp., 1 microfiche)†. Standard deviations given in the Tables are derived from a (3 × 3, 6 × 6) block-diagonal refinement procedure; 17 reflections which appeared to be heavily affected by extinction were deleted from the data set. Positional and thermal parameters are listed in Table 1; anisotropic thermal parameters are of the form: $\exp\text{-}[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl]$.

DISCUSSION

The present $P2_1/n$ cell is in agreement within the limits of error with $P2_1/c$ cell reported earlier,[3] when appropriately transformed. The disposition of the cell contents is shown in the Figure. The asymmetric unit, $Na_2Cu(CO_3)_2,3H_2O$ is an inadequate description of the

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† For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full size copies.)

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[2] P. C. Healy and A. H. White, *Spectrochim. Acta*, 1973, **29A**, 1191.

[3] V. Kupcik, *Proc. 7th I.C.C.C.*, p. 80, 1J8.

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[6] M. P. Appleby and K. W. Lane, *J. Chem. Soc.*, 1918, **113**, 609.

[7] B. W. Delf, *J. Appl. Phys.*, 1963, **14**, 345.

[8] 'International Tables for *X*-Ray Crystallography,' vol. I, 2nd edn., Kynoch Press, Birmingham, 1965, p. 99.

[9] Ref. 8, vol. III, 1962, p. 59.

[10] Ref. 9, pp. 210ff.

[11] Ref. 9, pp. 213ff.

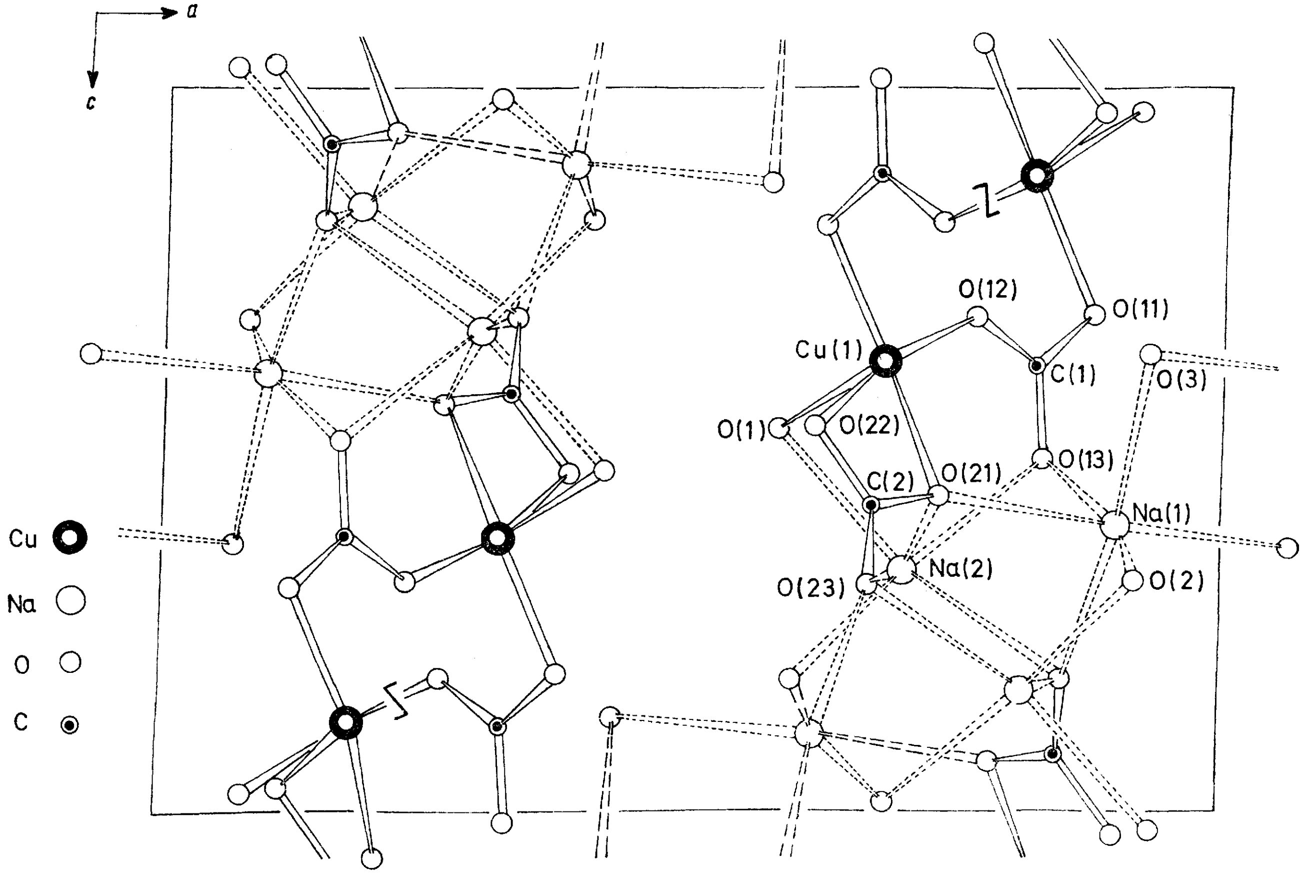
TABLE 1

Final atomic fractional cell parameters and thermal parameters with estimated standard deviations in parentheses

Atom	x	y	z	B/Å^2
Cu	0·6803(2)	0·5113(4)	0·3772(2)	*
Na(1)	0·9025(5)	0·4707(12)	0·6065(7)	*
Na(2)	0·7016(5)	0·2359(11)	0·6640(6)	*
O(1)	0·5822(9)	0·231(2)	0·4716(12)	2·0(2)
O(2)	0·9209(9)	0·847(2)	0·6808(12)	1·8(2)
O(3)	0·9316(9)	0·599(2)	0·3686(13)	2·1(2)
C(1)	0·8258(9)	0·154(2)	0·3823(14)	0·6(2)
O(11)	0·8778(8)	0·029(2)	0·3101(11)	1·3(2)
O(12)	0·7667(8)	0·289(2)	0·3151(11)	1·4(2)
O(13)	0·8328(8)	0·155(2)	0·5141(11)	1·4(2)
C(2)	0·6717(11)	0·740(3)	0·5777(15)	1·0(2)
O(21)	0·7342(7)	0·585(2)	0·5645(10)	0·8(2)
O(22)	0·6156(8)	0·759(2)	0·4681(11)	1·2(2)
O(23)	0·6674(8)	0·863(2)	0·6826(11)	1·6(2)

* Anisotropic thermal parameters ($\times 10^4$)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	19(1)	46(6)	30(2)	26(5)	0(2)	−24(7)
Na(1)	29(3)	110(21)	49(7)	−18(14)	7(7)	−7(21)
Na(2)	26(3)	71(19)	46(6)	−10(12)	13(8)	9(20)



The unit cell contents projected down b, showing the atomic numbering system. Bonds within the anionic chain are shown as solid lines, other contacts as short-dashed lines, and contacts to adjacent upper and lower cells as long-dashed lines

structure: the sodium cations are discrete species as are two of the three water molecules which occupy lattice sites about the sodium ions. Within the anionic residue, $Cu(CO_3)_2,H_2O^{2-}$ (x,y,z), each copper atom is surrounded in a pseudo-square pyramidal environment by a water molecule at the apex [Cu–O(1), 2·38(1) Å], a bidentate carbonate group [Cu–O(21, 22), 1·99, 1·98(1) Å], and two crystallographically equivalent carbonate groups which bridge to other copper atoms with similar environments at ($1\frac{1}{2} - x, y + \frac{1}{2}, \frac{1}{2} - z$) [Cu–O(11, 12) 1·97, 1·92(1) Å]; O(12) also has a distant contact to the adjacent copper atom in the sixth co-ordination position [Cu–O(12), 2·64(1) Å]. The anion is thus linked in infinite chains, being parallel to b and generated by the crystallographic screw axis. The initial report on this structure,[3] although vague as to the actual nature of the species, reported a copper–copper distance of 2·81 Å and drew a parallel with copper acetate monohydrate, 2·64 Å.[12] No evidence for magnetically abnormal behaviour in the present substance has been found, however;[4] this is in keeping with the result of the present structure determination in which the closest copper–copper distance (within the chain) is 4·37 Å. Because of the constraints imposed by the bidentate carbonate group [O(12)–Cu–O(22) 65·3°], the copper geometry is highly distorted, the angles in the equatorial plane differing markedly from 90° (Table 2) as do those about the apical O(1). As expected, the copper atom lies somewhat (0·13 Å) above the plane

[12] J. H. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, 1953, **6**, 227.

TABLE 2

Selected interatomic distances (Å) and angles (deg.), with estimated standard deviations in parentheses

(*a*) The copper environment ($<3{\cdot}0$ Å)

Cu–O(1)	2·38(1)	O(1)–Cu–O(12)	88·8(5)
Cu–O(11$^{\mathrm{II}}$)	1·97(1)	O(1)–Cu–O(21)	90·7(4)
Cu–O(12)	1·92(1)	O(1)–Cu–O(22)	96·1(5)
Cu–O(21)	1·99(1)	O(1)–Cu–O(12$^{\mathrm{II}}$)	154·9(4)
Cu–O(22)	1·98(1)	O(12)–Cu–O(11$^{\mathrm{II}}$)	89·4(5)
Cu–O(12$^{\mathrm{II}}$)	2·64(1)	O(21)–Cu–O(11$^{\mathrm{II}}$)	163·7(5)
O(21)–Cu–O(22)	65·3(4)	O(22)–Cu–O(11$^{\mathrm{II}}$)	101·1(5)
O(21)–Cu–O(12$^{\mathrm{II}}$)	113·3(4)	O(11$^{\mathrm{II}}$)–Cu–O(12$^{\mathrm{II}}$)	55·0(4)
O(22)–Cu–O(12$^{\mathrm{II}}$)	87·9(4)	O(12)–Cu–O(21)	103·1(4)
O(1)–Cu–O(11$^{\mathrm{II}}$)	100·0(5)	O(12)–Cu–O(12$^{\mathrm{II}}$)	92·5(4)

(*b*) The sodium environments: (i) Na(1) ($<3{\cdot}0$ Å)

Na(1)–O(2)	2·42(1)	O(3)–Na(1)–O(3$^{\mathrm{III}}$)	88·1(5)
Na(1)–O(3$^{\mathrm{III}}$)	2·34(1)	O(3)–Na(1)–O(13)	160·4(5)
Na(1)–O(3)	2·48(1)	O(13)–Na(1)–O(21)	90·7(3)
Na(1)–O(13)	2·32(1)	O(13)–Na(1)–O(23$^{\mathrm{IV}}$)	114·1(4)
Na(1)–O(21)	2·45(1)	O(21)–Na(1)–O(23$^{\mathrm{IV}}$)	79·3(4)
Na(1)–O(23$^{\mathrm{IV}}$)	2·38(1)	O(21)–Na(1)–O(3$^{\mathrm{III}}$)	172·8(5)
O(2)–Na(1)–O(3$^{\mathrm{III}}$)	92·7(5)	O(3$^{\mathrm{III}}$)–Na(1)–O(23$^{\mathrm{IV}}$)	106·4(5)
O(2)–Na(1)–O(3)	87·5(5)	O(3)–Na(1)–O(13*X*	88·8(5)
O(2)–Na(1)–O(13)	160·4(5)	O(3)–Na(1)–O(21)	86·2(4)
O(2)–Na(1)–O(21)	82·5(4)	O(3)–Na(1)–O(23$^{\mathrm{IV}}$)	165·4(5)
O(2)–Na(1)–O(23$^{\mathrm{IV}}$)	92·7(5)		

(ii) Na(2)

Na(2)–O(1)	2·45(1)	O(1)–Na(2)–O(2$^{\mathrm{IV}}$)	90·6(5)
Na(2)–O(2$^{\mathrm{IV}}$)	2·40(1)	O(1)–Na(2)–O(13)	92·3(5)
Na(2)–O(13)	2·41(1)	O(1)–Na(2)–O(21)	80·4(4)
Na(2)–O(21)	2·39(1)	O(1)–Na(2)–O(23$^{\mathrm{IV}}$)	159·9(5)
Na(2)–O(23$^{\mathrm{IV}}$)	2·44(1)	O(1)–Na(2)–O(23$^{\mathrm{V}}$)	85·1(5)
Na(2)–O(23$^{\mathrm{V}}$)	2·33(1)	O(13)–Na(2)–O(2$^{\mathrm{IV}}$)	174·7(5)
Na(2)–O(21)	2·90(1)	O(21)–Na(2)–O(2$^{\mathrm{IV}}$)	98·4(4)
O(21)–Na(2)–O(23$^{\mathrm{IV}}$)	79·5(4)	O(2$^{\mathrm{IV}}$)–Na(2)–O(23$^{\mathrm{IV}}$)	92·9(4)
O(21)–Na(2)–O(23$^{\mathrm{V}}$)	160·6(5)	O(2$^{\mathrm{IV}}$)–Na(2)–O(23$^{\mathrm{V}}$)	160·6(5)
O(23$^{\mathrm{IV}}$)–Na(2)–O(23$^{\mathrm{V}}$)	114·4(5)	O(13)–Na(2)–O(21)	77·6(4)
		O(13)–Na(2)–O(23$^{\mathrm{V}}$)	90·3(4)

(*c*) Water–oxygen contacts (<3 Å) (*i.e.* probable hydrogen bonds)

O(1) ··· O(22$^{\mathrm{V}}$)	2·92(2)	O(2) ··· O(13$^{\mathrm{VII}}$)	2·74(2)
O(1) ··· O(22$^{\mathrm{VI}}$)	2·81(2)	O(3) ··· O(11$^{\mathrm{VII}}$)	2·78(2)
O(2) ··· O(11$^{\mathrm{III}}$)	2·88(2)	O(3) ··· O(12)	2·99(2)

O(22$^{\mathrm{V}}$) ··· O(1) ··· O(22$^{\mathrm{VI}}$)	100·2(5)
O(11$^{\mathrm{III}}$) ··· O(2) ··· O(13$^{\mathrm{VII}}$)	104·4(4)
O(12) ··· O(3) ··· O(11$^{\mathrm{VII}}$)	111·4(5)

(*d*) The carbonate geometries: (i) CO_3(1)

C(1)–O(11)	1·27(2)	O(11)–C(1)–O(12)	116·9(13)
C(1)–O(12)	1·32(2)	O(11)–C(1)–O(13)	121·7(13)
C(1)–O(13)	1·28(2)	O(12)–C(1)–O(13)	121·3(13)
O(11)–O(12)	2·21(2)	C(1)–O(11)–Cu$^{\mathrm{VIII}}$	108·6(9)
O(11)–O(13)	2·23(2)	C(1)–O(12)–Cu	132·0(10)
O(12)–O(13)	2·26(2)		

(ii) CO_3(2)

C(2)–O(21)	1·29(2)	O(21)–C(2)–O(22)	111·7(13)
C(2)–O(22)	1·30(2)	O(21)–C(2)–O(23)	124·2(14)
C(2)–O(23)	1·27(2)	O(22)–C(2)–O(23)	124·1(14)
O(21)–O(22)	2·14(2)	C(2)–O(21)–Cu	91·3(9)
O(21)–O(23)	2·26(2)	C(2)–O(22)–Cu	91·7(9)
O(22)–O(23)	2·27(2)		

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at *x*, *y*, *z*:

II $1\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
III $2 - x, 1 - y, 1 - z$
IV $1\frac{1}{2} - x, y - \frac{1}{2}, 1\frac{1}{2} - z$
V $x, y - 1, z$
VI $1 - x, 1 - y, 1 - z$
VII $x, y + 1, z$
VIII $1\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$

of the four equatorial oxygen atoms. The Cu–O(eq) distances are in good agreement with similar distances reported previously.[1]

Each sodium atom has six nearest oxygen neighbours in distorted octahedral arrays, at distances ranging from 2·32 to 2·48 Å and angles from 80 to 106° (Table 2).

Each of the oxygen atoms belonging to the water molecules has two contacts to other oxygen atoms at distances $<3{\cdot}0$ Å. The angles subtended range from 100 to 111° and it is reasonable to assume that these three pairs represent the hydrogen bonds about the water molecules (Table 2).

TABLE 3

Equations of least-squares planes through the CO_3 and CuO_4 groups in the form $pX + qY + rZ = s$, the orthogonal (Å) frame (X,Y,Z) being generated from the lattice co-ordinates (x,y,z) by the transformation $X = ax + cz$ Cos β, $Y = by$, $Z = cz$ Sin β. Atomic deviations (Å) from the plane are given in square brackets

	p	*q*	*r*	*s*	σ(Å)
Plane (i):					
O(12), O(21), O(22) O(11$^{\mathrm{II}}$)	0·6717	−0·6649	−0·3266	7·250	0·03
[O(12) 0·03, O(21) −0·04, O(22) 0·04, O(11$^{\mathrm{II}}$) −0·03, Cu 0·13]					
Plane (ii):					
C(1), O(11)—(13)	0·7172	0·6964	−0·0236	8·679	0·01
[C(1) −0·01, O(11) 0·00, O(12) 0·00, O(13) 0·00, Cu 0·16, Cu$^{\mathrm{II}}$ −0·55]					
Plane (iii):					
C(2), O(21)—(23)	0·6550	0·6406	−0·4009	6·617	0·01
[C(2) 0·01, O(21) −0·00, O(22) −0·00, O(23) −0·00, Cu 0·96]					

The two carbonate groups do not deviate significantly from planarity (Table 3). In the bidentate group, the bidentate O–C–O angle is reduced to 111·7°, comparable to that observed in $[Co(NH_3)_4CO_3]Br$ (110·4°);[13] in the bridging group distortion from trigonal symmetry is not significant. Unlike $Na_2Cu(CO_3)_2$,[1] the non-co-ordinated oxygen–carbon distance C(*i*)–O(*i*3) cannot be shown to be significantly shorter than the ligand oxygen–carbon distances in this structure.

It has been previously suggested[2] that it might be possible to distinguish between bridging and bidentate carbonate groups in a co-ordination complex by determining the i.r. frequency of the out-of-plane ν_2 vibration, the frequencies for unidentate and bridging species being some 10 cm^{-1} higher than that of the bidentate species (*ca.* 840 cm^{-1}). An attempt to observe both frequencies in the present complex was unsuccessful; the ν_2 frequency (Nujol mull, Perkin-Elmer 521) is rather broader than usual and contains peaks at 847 cm^{-1}, *i.e.* the two bands appear to overlap and are unresolved.

The thermal motion of the copper atom is highly anisotropic (root-mean-square principal amplitudes 0·07, 0·12, 0·15 Å) with the shortest vibrational amplitude aligned close to the long Cu–O(1) bond.

We thank B. W. Robinson, who pointed out that this complex is the mineral chalconatronite,[14] and a referee who detected an error and subsequent textual misinterpretation in the original diagram.

[3/443 *Received*, 27*th February*, 1973]

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[13] G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1962, 587.
[14] A.S.T.M. Powder Diffraction File, Card No. 10 442.