# Crystal Structure and Physical Properties of Anhydrous Sodium Copper Carbonate

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The crystal structure of the title compound has been established by single-crystal *X*-ray diffraction methods from photographic data. The structure was solved by conventional Patterson and Fourier heavy-atom methods and refined by block-diagonal least-squares techniques to $R$ 0·11 for 286 independent reflections. Crystals are monoclinic, space group $P2_1/a$, with $Z = 2$ in a unit cell with dimensions: $a = 6{\cdot}18(2)$, $b = 8{\cdot}19(2)$, $c = 5{\cdot}64(2)$ Å, $\beta = 116{\cdot}2(2)^\circ$. The asymmetric unit is one half of the formula unit. The structure consists of copper atoms occupying special positions of symmetry $\bar{1}$, co-ordinated by four planar oxygen atoms [Cu–O(1) 1·95(1); Cu–O(2) 1·90(1) Å, O(1)–Cu–O(2) 88·7(5)°), the distortion from the exact square plane not being significant. The copper atoms are bridged by, but not coplanar with, carbonate groups in an infinite two-dimensional polymeric puckered sheet in the *ab* plane, successive sheets being interleaved by sodium ions. The carbonate ions, although planar, are significantly distorted, the non-co-ordinated bond being much shorter [C–O(3), 1·22(2) Å) than the other two (C–O(1), 1·36(2); C–O(2), 1·29(2) Å]. The i.r. spectrum displays splittings providing supporting evidence for distorted stereochemistries of the $CuO_4$ and $CO_3$ groups, the metal–oxygen and carbon–oxygen asymmetric stretching modes being appreciably split, and possibly characteristic of the bridging carbonate group. The magnetic moment of 1·92 ± 0·04 BM over the temperature range 100—400 K is consistent with the requirements of square planar co-ordinated copper(II) and is indicative of little or no copper–copper interaction (Cu ··· Cu, 4·89 Å).

STUDIES of anhydrous complexes of the nitrate ion with transition metals have revealed a wide range of interesting structural configurations.[1] As yet, however, there have been comparatively few structural investigations of transition-metal complexes of the isoelectronic carbonate ion although those structures which have been reported indicate the likelihood of a similar variety and interest. The most thorough case study has been generated among the related simple carboxylate anions such as formate and acetate whose complexes with copper(II) [2-5] display unusual magnetic behaviour [6-13] because of the generation of infinite polymeric lattices (as in the formates) or binuclear species (as in the acetate and derivatives thereof). With copper(II), the parent carbonate anion has been shown to generate infinite polymeric lattices in the minerals malachite [14,15] and azurite [16-18] where it acts as a bridging ligand. Few other carbonate or carboxylate structures of the transition metals are known; in those carbonates whose configurations have been established, uni- [19] and bidentate groups [20,21] have been demonstrated structurally with cobalt(III)-ammine derivatives, while in potassium

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silver carbonate, $KAgCO_3$,[22,23] an unusual linear polymeric structure, consisting of parallel $[Ag(CO_3)^-]_\infty$ chains has been found. In the aforementioned carbonate structures there is appreciable evidence that where the carbonate species acts as a bridging or bidentate ligand, the co-ordinated oxygen–carbon bonds are rather longer than that established for the free ion in calcite of $D_{3h}$ symmetry (1·29 Å),[24] while the non-co-ordinated oxygen–carbon distance is appreciably shorter. This is also true for most of the nitrate complexes.

Because of the higher charge on the carbonate anion, the observation of discrete molecular species of the type $M(CO_3)_n$ comparable to the nitrates is likely to be small; it is more likely that anionic entities will be generated, requiring balancing cations. This and subsequent investigations of the structural chemistry of transition-metal carbonates are centred largely on the formation of double salts. We have undertaken the investigation of a number of these to explore further the structural possibilities and characteristics of the carbonate ligand and to examine, if possible, whether distortions occur within the ligand. We report here the crystal structure of the anhydrous double salt, sodium copper carbonate, $Na_2Cu(CO_3)_2$, with an accompanying study of associated physicochemical properties.

## EXPERIMENTAL

### *Preparation and Physical Properties*

The complex was prepared by a variation of Auger's method. The hydrated double salt $Na_2Cu(CO_3)_2,3H_2O$ was prepared [25] and digested for 24 h in saturated boiling aqueous sodium carbonate–bicarbonate solution.[26,27] Small, elongated, royal blue insoluble single crystals of the anhydrous salt were obtained of maximum size 0·10 × 0·06 mm. They were contaminated with an insoluble white substance but their high density enabled rapid physical separation.

The compound was heated to 500 °C on a Stanton thermobalance; it was found to lose one mole of carbon dioxide (calc.: 19·2. Found: 18·5% by weight) between 250—300 °C.

The i.r. spectrum was recorded, on a Perkin-Elmer 421 spectrophotometer, for Nujol and Fluorolube mulls between caesium iodide plates in the region 2000—300 cm$^{-1}$. The region 4000—2000 cm$^{-1}$ contained a number of indistinct overtone and combination bands, which were not further investigated. The spectrum is presented in Figure 1 and observed frequencies (cm$^{-1}$) and tentative assignments are as follows: 1500, 1362, antisym. CO str; 1058, sym. CO str; 879, overtone (?) (ref. 28) or impurity; 848, $CO_3$ out-of-plane; 743,686, $CO_2$ bend; 415,395, antisym. $Cu–O_4$ str.

The magnetic moment was measured using the Gouy technique [29] (calibrant, $HgCo(CNS)_4$) [30] at a field strength of *ca.* 5000 gauss over the temperature range 100—400 K using a cryostat of conventional design,[31] and was found to be substantially constant throughout the range: $\mu_{eff}$ = 1·92 ± 0·04 BM [where $\mu_{eff} = 2{\cdot}828\ (\chi_M T)^{\frac{1}{2}}$, and $\chi_M$ is the molar susceptibility (*i.e.* per formula unit containing one copper atom) corrected for the diamagnetic Pascal contribution, $\Delta = -80$ e.m.u. mol$^{-1}$ (ref. 32)]. No allowance was made for possible temperature-independent paramagnetism, this being considered negligible.

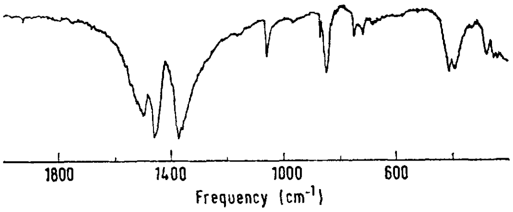

FIGURE 1 I.r. spectrum of sodium copper carbonate, $Na_2Cu(CO_3)_2$, in Nujol mull between caesium iodide plates in the range 2000—300 cm$^{-1}$. Bands at 1460, 1378, and 718 cm$^{-1}$ are ascribable to Nujol. Frequencies and tentative assignments are given in Table 1. Weak bands at *ca.* 1798, 1750 cm$^{-1}$ are ascribed to overtones–combinations

### *Crystal Structure Determination*

Data were obtained by the equi-inclination Weissenberg method with a non-integrating Nonius Weissenberg camera on a single prismatic crystal 0·04 × 0·04 × 0·07 mm elongated in the *c* direction and with *a* and *b* as the section diagonals. There was no evidence from deterioration in reflection quality, later agreement analyses, *etc.*, to suggest that the crystal had decomposed during data collection.

Unit-cell dimensions were obtained from zero-layer Weissenberg photographs, the spindle axis being parallel respectively to *b* and *c*. These were calibrated with aluminium powder lines ($a_{Al}$ 4·0494 Å),[33] using nickel-filtered copper radiation [$\lambda(K_{\alpha1})$ = 1·5406, $\lambda(K_{\alpha2})$ = 1·5444, $\lambda(K_{\beta})$ = 1·3922 Å].[34] In spite of the ready accessibility of high-angle reflections, the accuracy of the unit-cell calibration is limited because of their diffuseness. Intensity data were collected by the multiple-film method with nickel-filtered copper radiation about the *b* and *c* axes for layers *h*0—4*l* and *hk*0—3. The intensities of 286 independent observed reflections were estimated visually using an intensity strip calibrated with a Joyce-Loebl microdensitometer, Mark IIIB, and were used in the subsequent structure determination.

*Crystal Data.*—$C_2O_6CuNa_2$, $M$ = 230, Monoclinic, $a$ = 6·18 ± 0·02, $b$ = 8·19 ± 0·02, $c$ = 5·64 ± 0·02, $\beta$ = 116·2 ± 0·2°, $U$ = 256 Å$^3$, $D_m$ = 3·1 ± 0·1 (by flotation), $Z$ = 2, $D_c$ = 2·98, $F(000)$ = 174. Space group $P2_1/a$ ($C_{2h}^5$, No. 14, ref. 35) from systematic absences: $\{h0l\}$,

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$h = 2n + 1$; $\{0k0\}$, $k = 2n + 1$. $\mu(\text{Cu-}K_\alpha) = 84$ cm$^{-1}$, transmission coefficient range = 0·59—0·78.

Intensities were corrected for absorption using a local variant of ABSCOR.[36] After correction for Lorentz and polarization factors by use of a local program SCAL 1, the data were internally correlated and scaled by the method of Hamilton, Rollett and Sparks,[37] all reflections being assigned unit weights.

*Structure Determination.*—For $Z = 2$ it is required that the asymmetric unit be one half of the formula unit, which implies occupancy of a special position of symmetry $\bar{1}$ by the copper atom. This was confirmed by an unmodified three-dimensional Patterson synthesis computed on all data, whence the sodium atoms were also located, the carbon and oxygen atoms being located in subsequent three-dimensional electron density distributions. All atoms excepting the copper at (0, 0, 0), ($\tfrac{1}{2}$, $\tfrac{1}{2}$, 0) occupy general positions $[(x, y, z), (\bar{x}, \bar{y}, \bar{z}), (\tfrac{1}{2} - x, \tfrac{1}{2} + y, \bar{z})\ (\tfrac{1}{2} + x, \tfrac{1}{2} - y, z)]$ in the unit cell. Using arbitrary isotropic temperature factors of 2·0 for all atoms $R$ 0·36 was obtained. Refinement by block-diagonal (3 × 3, 6 × 6) least-squares procedures was introduced using independent isotropic thermal parameters, when $R$ converged to 0·14. A weighting scheme[38] of the form $w = (a + |F_o| + b\text{-}|F_o|^2)^{-1}$ was introduced and found appropriate, $a$ and $b$ being adjusted at successive stages in the refinement during which the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized. $R$ converged to 0·128, the weighted discrepancy factor $R'$ being 0·160 ($R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma(w|F_o|^2)]^{\frac{1}{2}}$). Refinement proceeded with anisotropic thermal parameters of the form $\exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)$ for the copper and sodium atoms, and converged to a final $R$ of 0·115 and $R'$ 0·148. Final weighting scheme constants were $a$ 22·1 and $b$ 0·068. (A significance test carried out on the ratios of both $R$ and $R'$ before and after this refinement justified their introduction at the 99% level or better[39]). During the final cycle of least-squares, all positional parameter shifts were $<0·05\sigma$ and all thermal parameter shifts $<0·25\sigma$, the shifts of the heavy atoms being very much less. A difference-Fourier map computed at this stage revealed no significant or spurious peaks, being flat to less than 0·2 of a carbon atom. There was no evidence for disorder in the structure. Scattering factors were drawn from ref. 40 for neutral copper, carbon and oxygen atoms, and for singly charged sodium, those for copper and sodium being corrected for anomalous dispersion.[41] The refinement programs were local modifications of SFLS 1 and SFLS 2 (A. I. M. Rae) and FCURV (B. J. Ong). The final set of observed and calculated structure factors is given in Supplementary Publication No. SUP 20435 (4 pp., 1 microfiche).*

Final atomic positional and thermal parameters are given in Table 1, together with estimated standard deviations derived from a block-diagonal least squares procedure and therefore likely to be underestimates.

The atomic numbering scheme used is defined in Figure 2. Interatomic distances and angles, together with estimated standard deviations are given in Table 2, and were computed by use of the BONDSCAN program.[42]

TABLE 1

(*a*) Atomic fractional co-ordinates and isotropic thermal parameters

| Atom | $x$ | $y$ | $z$ | $B$/Å$^2$ |
|---|---|---|---|---|
| Cu | 0·0000 | 0·0000 | 0·0000 | |
| Na | 0·672(1) | 0·093(1) | 0·356(2) | |
| C | 0·632(3) | 0·239(3) | 0·815(3) | 1·7(3) |
| O(1) | 0·674(2) | 0·080(2) | 0·790(2) | 2·2(2) |
| O(2) | 0·629(2) | 0·286(2) | 0·032(2) | 2·3(2) |
| O(3) | 0·597(2) | 0·332(2) | 0·628(3) | 2·6(2) |

(*b*) Anisotropic thermal parameters (× 10$^3$) for sodium and copper atoms

| | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Cu | 12(1) | 2(1) | 14(1) | 1(1) | 16(2) | 2(2) |
| Na | 26(3) | 8(1) | 29(3) | −7(3) | 27(5) | 2(4) |

The plane of best fit, together with atomic deviations in Å, was determined for the carbonate species. The equation of the necessarily exact plane (because of the $\bar{1}$ copper

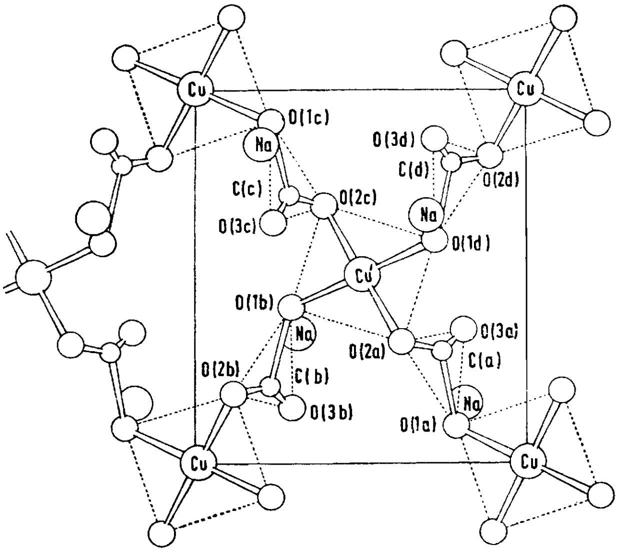

FIGURE 2 The unit cell, viewed perpendicular to the *ab* plane (*a* vertical in the page, *b* horizontal). The structure consists of planar $CuO_4$ and $CO_3$ entities in a crosslinked puckered two-dimensional sheet in the *ab* plane. Successive layers are bound together by interleaving sodium ions

TABLE 2

Molecular geometry

(*a*) Distances (Å)

| | | | |
|---|---|---|---|
| Cu–O(1a) | 1·95(1) | Na(a)–O(1a) | 2·44(1) |
| Cu′-O(2a) | 1·90(1) | Na(a)–O(2a) | 2·35(1) |
| Cu′–O(3a) | 2·77(1) | Na(a)–O(3a) | 2·65(1) |
| C(a)–O(1a) | 1·36(2) | Na(a)–O(3a) | 2·55(1) |
| C(a)–O(2a) | 1·29(2) | Na(a)–O(3b) | 2·46(1) |
| C(a)–O(3a) | 1·22(2) | | |

(*b*) Angles (deg.)

| | | | |
|---|---|---|---|
| Cu′–O(2a)–C(a) | 111·4(5) | O(1a)–C(a)–O(2a) | 117·5(1·6) |
| Cu–O(1a)–C(a) | 117·1(5) | O(1a)–C(a)–O(3a) | 118·7(1·6) |
| O(1d)–Cu′-O(2a) | 88·7(5) | O(2a)–C(a)–O(3a) | 123·8(1·6) |
| O(2a)–Cu′–O(1b) | 91·3(5) | | |

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

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site symmetry) through the copper atom and its four nearest oxygen neighbours was also determined. Both planes are tabulated in Table 3.

TABLE 3

Equations of least-squares planes through $CO_3$ and $CuO_4$ groups in the form $AX + BY + CZ = D$. Distances (Å) of relevant atoms from the planes are given in square brackets. Transformations of the co-ordinates ($x$, $y$, $z$) from those given in Table 1 are given in parentheses; atoms included in plane calculation in italics

Plane (a): $CO_3$ $0{\cdot}902X + 0{\cdot}185Y + 0{\cdot}390Z = 3{\cdot}662$

[Cu(1,0,1) 1·64, Cu($\frac{1}{2}$,$\frac{1}{2}$,1) −0·38, *C(a) 0·00, O(1a) −0·00, O(2a)* ($x$,$y$,$1 + z$) *−0·00, O(3a) −0·00*]

Standard deviation of $CO_3$ atoms from plane: 0·002 Å.

Plane (b): $CuO_4$ $-0{\cdot}514X - 0{\cdot}143Y + 0{\cdot}835Z = 3{\cdot}322$

*Cu*($\frac{1}{2}$,$\frac{1}{2}$,*1*) *0·00, O(1d)* ($x - \frac{1}{2}$,$\frac{1}{2} - y$,$z$) *0·00, O(2a)* ($x$,$y$,$1 + z$) *0·00*, C(a) −1·15, C(d) ($x - \frac{1}{2}$,$\frac{1}{2} - y$,$z$) 0·42]

Standard deviations of atoms from plane: 0·000 Å.

* Where $X$, $Y$, and $Z$ are orthogonal co-ordinates in (Å) defined by $X = ax + cz \cos \beta$, $Y = by$, and $Z = cz \sin \beta$.

## DISCUSSION

*Crystal Structure.*—The arrangement of the unit cell contents is shown in Figure 2. Only one half of the $Na_2Cu(CO_3)_2$ formula unit is crystallographically independent. Apart from the sodium ions, there are no other discrete species in the crystal, the carbonate groups linking pairs of square planar co-ordinated copper atoms in a plane contained in the *ab* face. The crystal is thus best formulated as $Na_2[Cu(CO_3)_2]$ or $(Na^+)_{2\infty}$-$[Cu(CO_3)_2{}^{2-}]_\infty$, the sodium ions interleaving the successive layers of $[Cu(CO_3)_2{}^{2-}]_\infty$ which lie parallel to one another and to the *ab* plane. Although the sheets viewed as a whole are contained in the *ab* face of the unit cell, the carbonate groups are not strictly coplanar but project some distance out of it on either side, so that the $[Cu(CO_3)_2{}^{2-}]_\infty$ sheet is puckered by the out-of-plane carbonate groups bridging the strictly planar copper atoms. From the viewpoint of the planar carbonate group, the two copper atoms to which it co-ordinates are non-coplanar with it, their deviations being −0·41 and 1·68 Å (Figure 3).

The copper atom is required by site symmetry to be coplanar with its four nearest neighbour oxygen atoms; it is thus essentially square planar co-ordinated [Cu–O(1) 1·95(1), Cu–O(2) 1·90(1) Å; O(1)–Cu–O(2) 88·7(5)°]. The difference between the observed geometry and that of a perfectly square planar arrangement with all Cu–O fixed at 1·92 Å and O(1)–Cu–O(2) 90° is not significant [with O(1) at 0·6756, 0·0800, 0·7910 and O(2) at 0·6307, 0·2830, 0·0295, $R$ after refinement was 0·115 and $R'$ 0·148 as before].[39] It was concluded that this structure determination could not distinguish significantly between the square planar copper geometry and the distorted solution. The mean copper–oxygen distance, $\langle$Cu–O($i$)$\rangle$ 1·92 Å lies well within the range of values observed for the related complexes previously discussed.[2-5,14,15,16-18] The fifth and sixth co-ordination sites of the copper are unoccupied, the nearest atom being O(3) [Cu–O(3) 2·77 Å; O(2)–Cu–O(3) 52·5°]. There are no close copper–copper contacts, the nearest being (0, 0, 0) — ($\frac{1}{2}$, $\frac{1}{2}$, 0) which is 4·89 Å. Vibration of the copper is such that one of the principal axes of the thermal ellipsoid is at right angles to the $CuO_4$ plane (0·08 Å), the others being almost isotropic in that plane (0·11, 0·14 Å).

The sodium ion has five near oxygen neighbours at distances of 2·50 ± 0·15 Å (Table 2).

Within the carbonate group, there is evidence for appreciable distortion. The bond C–O(3) is short in comparison with the value of 1·29 Å observed in the unperturbed ion in calcite.[24] Its value of 1·22(2) Å is comparable with values found for the un-co-ordinated carbon–oxygen distance in similar complexes such as the polymeric potassium silver carbonate, $KAgCO_3$,[23] which also has bidentate bridging carbonate groups, and the complex $[Co(NH_3)_4CO_3]I$ with a chelating carbonate group.[20] In both of these, the reported non-co-ordinated oxygen–carbon distance is 1·24 Å, but the reported standard deviations are high (0·06 Å) and the significance of the observation untested. In these studies also, the co-ordinated oxygen–carbon distances are appreciably longer (1·33 Å), as is the case in the present structure [C–O(1) 1·36(2), C–O(2) 1·29(2) Å]. Since all the structures display this type of distortion, albeit with high standard deviations, we constrained the carbon atom to be equidistant from the three oxygen atom [C–O($i$) 1·29; C 0·6400, 0·2325, 0·8210] and refined the remaining parameters to $R$ 0·124 and $R$ 0·154. A significance test indicates that the carbonate is in fact distorted with a confidence level of better than 99%.[39]

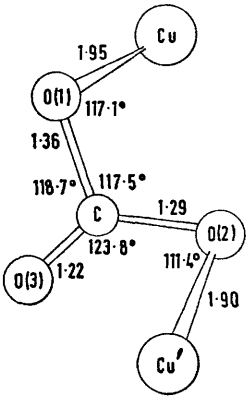

FIGURE 3 The geometry of the carbonate and its co-ordinated copper atoms. The $CO_3$ entity is planar. The copper atoms deviate from the plane by 1·64 Å (Cu) and −0·38 Å (Cu′)

We note further that the copper atom bonded to O(1) is very much out of the plane of the carbonate ion, whereas that bonded to O(2) is much less so (1·64 and −0·38 Å). It may be hypothesized that the difference between the distances C–O(1) and C–O(2) is a necessary consequence of this. If the copper atom is coplanar with the carbonate groups, symmetry forbids the use of the carbonate $p_\pi$ orbitals in copper–oxygen $\sigma$ bond formation, whereas, if the copper atom is greatly out of plane, the oxygen hybrid involved in $\sigma$ co-ordination must draw heavily on the $p_\pi$ orbital thereby decreasing its participation in the carbonate $\pi$-bonding and resulting in the longer C–O(1) bond length observed (1·36 Å).

Whereas, in bidentate ligands which form closed rings by chelation with the metal it is usual for the ring to be planar, in the bridging carbonate systems this planarity of metal and ligand seems by no means usual or necessary. We have calculated least-squares planes for the carbonate ion in those carbonates previously listed in which the ligand bridges two metal atoms using orthogonal co-ordinate systems as defined previously.

Potassium silver carbonate:[23]

$$0{\cdot}737Y + 0{\cdot}675Z = 7{\cdot}333$$
$$[\mathrm{Ag} \pm 0{\cdot}62\ \text{Å}]$$

Malachite:[15]

$$-0{\cdot}303X + 0{\cdot}238Y + 0{\cdot}922Z = -8{\cdot}75$$
$$[\mathrm{Cu(1)} - 0{\cdot}64,\ \mathrm{Cu(2)}\ 0{\cdot}58\ \text{Å}]$$

Azurite:[16]

$$0{\cdot}415X + 0{\cdot}895Y + 0{\cdot}162Z = -2{\cdot}84$$
$$[\mathrm{Cu(1)}\ 0{\cdot}67,\ \mathrm{Cu(2)}\ 0{\cdot}41,\ \mathrm{Cu(3)}\ 1{\cdot}18,\ \mathrm{Cu(4)}\ -1{\cdot}24\ \text{Å}]$$

In all cases, the metal atom is significantly non-planar with the ligand. Although a wide range of deviations are represented here only the first two structures are comparable with ours in the nature of the bridging involved and these are probably not of sufficient accuracy to permit a further test of the hypothesis concerning C–O bond length and the metal deviation from planarity.

*I.r. Spectrum*.—The split band at *ca.* 400 cm$^{-1}$ is readily identifiable as the metal–oxygen stretching frequency. The two observed components (395 and 415 cm$^{-1}$) suggest the presence of two non-equivalent metal–oxygen bonds. This could be a result of (i) different metal–oxygen bond lengths (and, presumably, force constants), which we have shown the structure determination to be incapable of determining with a satisfactory precision or (ii) a difference in the appendages to the metal–oxygen bonds. In this case, there is a marked difference in the lack of planarity of the metal with respect to the carbonate system depending on whether it is co-ordinated by O(1) or O(2) (Table 3) and this would seem the most probable explanation for the splitting. (iii) It is also possible that a lattice vibration of appropriate symmetry and frequency may be coupled with the metal–oxygen frequency, in view of the polymeric nature of the lattice.

In the region 1600—1000 cm$^{-1}$, instead of the single C–O antisymmetric stretching frequency ($E$ mode) at 1490 cm$^{-1}$ (typical of a carbonate ion of $D_{3h}$ symmetry we observe two very intense bands at 1362 and 1500 cm$^{-1}$, together with a band of moderate intensity at 1058 cm$^{-1}$. Such a splitting of the $E$ mode is typical of a substantial lowering of symmetry[43-49] and we conclude that there are at least two different types of carbon–oxygen bond, probably with differing stretching force constants, if the carbonate remains planar. The splitting of the C–O stretching frequency in this bridging $CO_3$ group (1500 and 1362 cm$^{-1}$) is greater than that found in the case of the unidentate co-ordinated carbonate {[$Co(NH_3)_5(CO_3)$]Cl, (i), 1453 and 1373 cm$^{-1}$} but less than that observed for the bidentate chelated system {[$Co(NH_3)_4(CO_3)$]Cl, (ii), 1593 and 1265 cm$^{-1}$}.[43] The appearance of the $A_1$ symmetric C–O stretching mode at 1058 cm$^{-1}$, inactive in site-symmetry $D_{3h}$, is also typical of substantial lowering of symmetry. In (i) the band appears at 1070 cm$^{-1}$, in (ii) at 1031 cm$^{-1}$. The out-of-plane mode at *ca.* 850 cm$^{-1}$ in (i) and *ca.* 835 cm$^{-1}$ in (ii) appears at 848 cm$^{-1}$ in this compound. The $CO_2$ bending modes at *ca.* 760 and 675 cm$^{-1}$, [(i) and (ii)], appear at 742 and 686 cm$^{-1}$ in this complex. The spectrum is thus qualitatively similar to those of the uni- and bidentate complexes and indicates a maximum symmetry of the carbonate group of $C_{2v}$; the unusual bridging co-ordination, however, has caused noticeable quantitative changes in all frequencies, the most noticeable being the magnitude of the splitting of the doubly degenerate $E$ mode of the free $CO_3^{2-}$ ion, at 1490 cm$^{-1}$. In this and in the other stretching mode at 1058 cm$^{-1}$, we find that the spectrum of the bridging carbonate is intermediate between that of the unidentate and chelated groups and suggest that if this is a general phenomenon, it might be a useful diagnostic tool for the identification of the bridging species.

*Magnetic Data*.—The substantially temperature-independent magnetic moment is consistent with the behaviour usually observed for square planar co-ordinated copper(II) (1·92 ± 0·04 BM).[50] There is no evidence for metal–metal interaction of the copper acetate or formate types and this is consistent with the structure determination in which there are no close copper–copper contacts.

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