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The Crystal and Molecular Structure of a Polynuclear Cu(II)-Complex; *catena*-μ-(Carbonato-*O*,*O*′:*O*″)-2,2′-Dipyridylamine-Copper(II) Trihydrate

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The structure of *catena*-μ-(carbonato-*O*,*O*′:*O*″)-2,2′-dipyridylamine-copper(II) trihydrate has been determined by X-ray crystallographic methods. The crystals are monoclinic, space group $P2_1/c$, a=11.243(1) Å, b=7.155(1) Å, c=17.343(2) Å, β=101.15(1)°. The structure was solved by conventional heavy atom method and was refined to an R of 0.023 including 2162 reflections up to $\sin\theta/\lambda$=0.59.

The structure consists of polymeric chains in which the carbonate ions serve as bridges between metal ions. The carbonate is bidentately coordinated to one Cu–ion, and monodentately to another. The Cu-coordination is slightly distorted square-pyramidal with bidentate carbonate and 2,2'-dipyridylamine in the basal plane, the apical position being occupied by monodentate carbonate. Cu–N distances are 1.975(2) and 1.970(2) Å; Cu–O in basal plane are 1.986(1) and 1.980(1) Å; and Cu–O apical is 2.295(1) Å.

Up till now the structures of four copper compounds in which a carbonate ion acts as bridging ligand for extended polynuclear arrays, have been reported.[1–6] In all of these compounds evidence of magnetic exchange between Cu-ions has been found.[7–12] In three of the compounds the ferromagnetic interactions predominate.[7–10] In these compounds the carbonate is monodentately bonded to two Cu-ions, and the third oxygen is uncoordinated. In the fourth compound, $Cu(NH_3)_2CO_3$, where the carbonate is bidentately coordinated to one copper ion and monodentately to another, the interaction is antiferromagnetic in character.[11–12] In the present structure carbonate ions are bridging copper ions in a manner similar to that found in $Cu(NH_3)_2CO_3$. Hence this compound may be of significance for determining relations between structural characteristics and magnetic properties in these carbonate bridged extended systems.

The present structure investigation came about accidentially during work on binuclear copper complexes. One of the syntheses, aimed at producing an oxamato-bridged binuclear copper complex, gave a mixed reaction products; one of the species being the compound described in this paper (see Experimental).

EXPERIMENTAL

The procedure described for the synthesis of a binuclear copper complex with an oxamate group as bridging ligand, 2,2′-dipyridylamine as outer ligand, and nitrate as counter ion, was used.[13] The product obtained clearly consisted of two types of crystals; green micro crystals and turquoise needle-shaped crystals. The former type had the colour described for the binuclear complex.[13] However, despite numerous attempts, crystals suitable for X-ray analysis were not obtained. The turquoise compound gave, on the other hand, nice crystals on recrystallization from water; and the subsequent structure analysis showed this to be a carbonato-bridged polymer. Apparently an oxidation of part of the oxamic acid has taken place in the reaction mixture.

A needle-shaped crystal of 0.09×0.14×0.49 mm was selected for X-ray data collection. Data were recorded at room temperature on an Enraf-Nonius CAD-4 diffractometer using mono-

0302-4377/84 $2.50

Table 1. Final atomic parameters from the least squares refinement. For the anisotropically refined non-hydrogen atoms the isotropic equivalent thermal parameter is given: $B_{eq}=\frac{4}{3}\sum_i\sum_j B_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$. Hydrogen atoms were isotropically refined. Isotropic temperature factor: $\exp[-B\sin^2\theta/\lambda^2]$.

Atom	x	y	z	B_{eq}(or B)
Cu	0.53130(2)	0.18092(4)	0.37154(1)	1.957(5)
O1A	0.6271(1)	0.0972(2)	0.29336(8)	2.60(3)
O2A	0.4354(1)	0.0452(3)	0.28042(8)	3.01(3)
O3A	0.5286(1)	−0.0322(2)	0.18127(8)	2.54(3)
N1B	0.6657(2)	0.2608(3)	0.45555(9)	1.99(3)
N1C	0.4113(2)	0.1869(2)	0.4410(1)	2.03(3)
N2	0.5456(2)	0.3080(3)	0.55168(9)	2.41(4)
C1A	0.5299(2)	0.0330(3)	0.2489(1)	1.97(4)
C2B	0.6559(2)	0.3085(3)	0.5292(1)	2.05(4)
C3B	0.7569(2)	0.3608(4)	0.5855(1)	2.90(5)
C4B	0.8685(2)	0.3642(4)	0.5658(1)	3.24(5)
C5B	0.8800(2)	0.3163(4)	0.4901(1)	3.13(5)
C6B	0.7782(2)	0.2658(3)	0.4379(1)	2.47(4)
C2C	0.4324(2)	0.2484(3)	0.5160(1)	2.02(4)
C3C	0.3405(2)	0.2545(3)	0.5597(1)	2.61(4)
C4C	0.2263(2)	0.1989(3)	0.5267(1)	2.94(5)
C5C	0.2034(2)	0.1366(3)	0.4491(1)	2.85(5)
C6C	0.2963(2)	0.1322(3)	0.4096(1)	2.49(4)
O1W	0.8083(2)	0.5452(3)	0.2958(1)	4.73(5)
O2W	0.1528(2)	0.4318(3)	0.2195(1)	5.18(5)
O3W	0.9736(2)	0.2630(3)	0.3017(1)	5.60(5)
H2	0.549(2)	0.353(3)	0.589(1)	1.9(4)
H3B	0.745(2)	0.387(3)	0.634(1)	3.0(5)
H4B	0.931(2)	0.397(4)	0.601(1)	4.3(6)
H5B	0.956(2)	0.319(3)	0.472(1)	3.8(6)
H6B	0.782(2)	0.234(3)	0.387(1)	1.9(4)
H3C	0.355(2)	0.290(3)	0.608(1)	3.0(5)
H4C	0.163(2)	0.207(3)	0.553(1)	4.0(6)
H5C	0.131(2)	0.103(3)	0.427(1)	2.6(5)
H6C	0.286(2)	0.089(3)	0.359(1)	2.7(5)
H11W	0.734(3)	0.533(4)	0.277(2)	5.6(7)
H12W	0.827(2)	0.647(4)	0.288(1)	4.3(6)
H21W	0.108(2)	0.511(4)	0.210(1)	5.0(7)
H22W	0.225(3)	0.486(5)	0.218(2)	9(1)
H31W	0.922(3)	0.351(5)	0.289(2)	6.8(8)
H32W	1.020(3)	0.279(4)	0.279(2)	6.9(9)

chromatized Mo$K\alpha$ radiation and the $\theta-2\theta$ scan technique. The scan widths varied according to $\Delta\theta=0.70+35\tan\theta$; and the scan speed from 0.5 to 3.3°/min depending on peak intensity. 2527 reflections were recorded up to $2\theta=50°$; of these 365 had intensities less than 2σ and were not included in the refinement. Three reference reflections all showed a slight but steady decay, averaging 6 % at the end of data collection. Data were scaled accordingly. The error in the intensity of any one reflection was estimated as $\sigma_I=[\sigma_c^2+(0.01N_{net})^2]^{\frac{1}{2}}$. The intensities were corrected for Lorentz and polarization effects, and for absorption; the maximum and minimum transmission factors being 0.867 and 0.809, respectively.

Table 2. Bond distances (Å) with standard deviations in parentheses.

Cu–O1A	1.980(1)	C4B–C5B	1.388(2)
Cu–O2A	1.986(1)	C5B–C6B	1.363(3)
Cu–O3A^{i}	2.295(1)	C6B–N1B	1.358(2)
Cu–N1B	1.970(2)	N2–C2B	1.369(3)
Cu–N1C	1.975(2)	N2–C2C	1.371(3)
C1A–O1A	1.294(2)	N1C–C2C	1.350(2)
C1A–O2A	1.288(2)	C2C–C3C	1.396(2)
C1A–O3A	1.260(2)	C3C–C4C	1.361(3)
N1B–C2B	1.348(2)	C4C–C5C	1.393(3)
C2B–C3B	1.398(2)	C5C–C6C	1.356(3)
C3B–C4B	1.363(2)	C6C–N1C	1.359(3)

CRYSTAL DATA

Catena-μ-(carbonato-O,O′:O″)-2,2′-dipyridylamine-copper(II) trihydrate; $[Cu(dpa)CO_3]\cdot 3H_2O$; $CuO_6N_3C_{11}H_{15}$. Monoclinic, $P2_1/c$ (No. 14), a=11.243(1) Å, b=7.155(1) Å, c=17.343(2) Å, β=101.15(1)°, V=1368.8(4) Å^3, M=348.80, Z=4, D_m=1.70 g cm^{-3}, D_x=1.692 g cm^{-3}, μ(Mo$K\alpha$)=16.92 cm^{-1}.

STRUCTURE DETERMINATION AND REFINEMENT

The copper ion was located from a Patterson map. The remaining atoms were located in subsequent Fourier maps. The first of these maps revealed that the copper ions were bridged by a four-atomic group rather than by an oxamate ion. Initially it was assumed that NO_3^- ions consti-

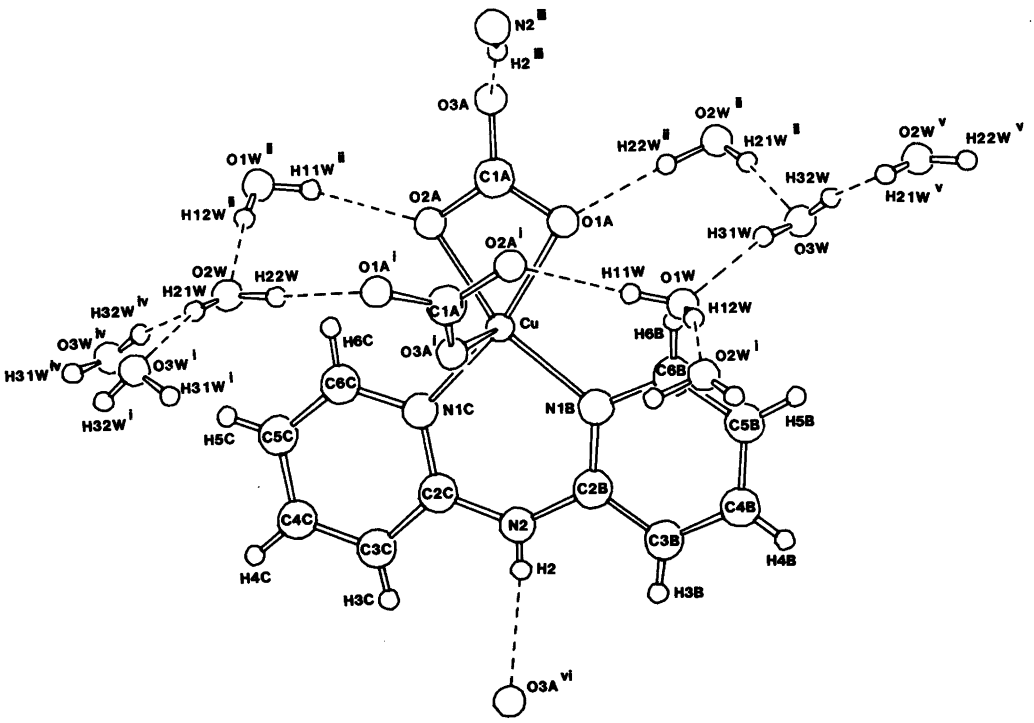

Fig. 1. Molecular unit and its environment. Symmetry operations are: (i) $1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; (ii) $1-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$; (iii) x, $\frac{1}{2}-y$, $-\frac{1}{2}+z$; (iv) $x-1$, y, z; (v) $1+x$, y, z; (vi) x, $\frac{1}{2}-y$, $\frac{1}{2}+z$.

tuted the bridges, as $Cu(NO_3)_2$ was used in the synthesis. However, it soon appeared that this would not give a correct stoichiometry for the compound; and the subsequent refinement indicated an unreasonably high thermal motion for the central atom in the bridging group as compared to the terminal ones. Towards the end of the refinement N was thus substituted by C. This led to a decrease in R-value from 0.033 to 0.029; and a reduction of 0.15 in the standard deviation of an observation of unit weight.

Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in a difference Fourier map and were refined isotropically. The weight assigned to each reflection in the refinement is $w=1/\sigma_F^2$, where $\sigma_F=\sigma_I(I\cdot \mathrm{Lp})^{-\frac{1}{2}}$. The final R-value is 0.023, weighted R-factor is 0.029, and the standard deviation of an observation of unit weight is 2.12.

Atomic scattering factors used were those of Cromer and Waber.[14] All calculations were carried out on a PDP 11/55 computer using the Enraf-Nonius Structure Determination Programs.[15] Final atomic parameters are listed in Table 1. An ORTEP drawing of the molecule (Fig. 1) shows the atomic numbering used, as well as the hydrogen bonding scheme. Bond distances and angles, excluding those involving hydrogen, are listed in Table 2 and 3, respectively. C–H distances are in the range 0.85–0.97 Å with individual standard deviations of 0.02 Å; N–H is 0.71(2) Å. Bond angles involving H are also reasonable; ∠C–C(N)–H range from 111(1) to 124(1)°.

Lists of structure factors and of anisotropic thermal parameters may be obtained from the author.

RESULTS AND DISCUSSION

The structure consists of polymeric chains of $[Cu(dpa)CO_3]$ units; the carbonate ions bridging metal ions related by screw axes translations (Fig. 2). Each carbonate ion coordinates bidentately to a copper ion while the third carbonate oxygen is coordinated to a neighbouring Cu ion, thus propagating the chain. A similar arrangement has

Table 3. Bond angles (°).

Copper coordination			
O1A–Cu–O2A	65.84(4)	O2A–Cu–N1B	162.01(6)
O1A–Cu–O3A^{i}	98.85(4)	O2A–Cu–N1C	99.55(5)
O1A–Cu–N1B	98.82(5)	O3A^{i}–Cu–N1B	99.19(5)
O1A–Cu–N1C	161.81(6)	O3A^{i}–Cu–N1C	92.38(5)
O2A–Cu–O3^{i}	92.72(5)	N1B–Cu–N1C	93.41(6)
Carbonate ion			
Cu–O1A–C1A	90.4(1)	O1A–C1A–O2A	113.2(2)
Cu–O2A–C1A	90.3(1)	O1A–C1A–O3A	122.9(2)
Cu^{ii}–O3A–C1A	130.7(1)	O2A–C1A–O3A	123.9(2)
Dipyridylamine			
Cu–N1B–C2B	125.7(1)	Cu–N1C–C2C	125.5(1)
Cu–N1B–C6B	117.1(1)	Cu–N1C–C6C	117.3(1)
C2B–N1B–C6B	117.2(2)	C2C–N1C–C6C	117.1(2)
N1B–C2B–N2	120.9(2)	N1C–C2C–N2	120.8(2)
N1B–C2B–C3B	121.7(2)	N1C–C2C–C3C	121.6(2)
N2–C2B–C3B	117.4(2)	N2–C2C–C3C	117.7(2)
C2B–C3B–C4B	119.5(2)	C2C–C3C–C4C	119.9(2)
C3B–C4B–C5B	119.4(2)	C3C–C4C–C5C	118.9(2)
C4B–C5B–C6B	118.3(2)	C4C–C5C–C6C	118.6(2)
N1B–C6B–C5B	123.8(2)	N1C–C6C–C5C	123.8(2)
C2B–N2–C2C	133.2(3)		

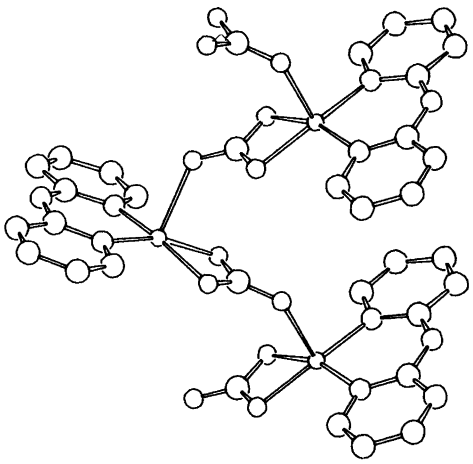

Fig. 2. The polymeric chain.

been found in $Cu(NH_3)_2CO_3$,[2] whereas in other polymeric Cu-carbonate structures the bridging CO_3^{2-} ion has been found to be monodentately coordinated to two Cu^{2+}-ions while the third oxygen atom is uncoordinated.[1,3-6] The Cu···Cu separation within the chain is 5.470 Å (screw axis translation). The closest interchain Cu···Cu($1-x$, $=y,1-z$) separation is 5.316 Å; thus no through-space interaction seems to be possible in the present structure. The geometry of the carbonate group is in close agreement with the correspondingly coordinated CO_3^{2-} in $Cu(NH_3)_2CO_3$,[2] but it differs from the geometry of the free carbonate ion, where all angles are 120° and all distances 1.294 Å.[16]

The coordination geometry at Cu is that of a somewhat distorted square pyramid (Fig. 1, Tables 2 and 3). In the equatorial plane the ligating atoms are the two ring nitrogens of the dipyridylamine molecule, and the two oxygens of the bidentate carbonate ion. The third oxygen of a screw axis related carbonate ion occupies the apical position, completing the coordination sphere. The equatorially ligating atoms are essentially coplanar, (deviations −0.012, 0.011, 0.009, −0.009 Å for O1A, O2A, N1B, N1C, respectively); the carbonate ion extending approximately in this plane. Cu deviates by 0.20 Å from the equatorial plane towards the apical ligand.

The individual polymeric chains are connected through hydrogen bonds *via* water molecules (Fig. 1). A list of hydrogen bond distances and angles (at H) are given in Table 4. The packing of molecules in the unit cell is illustrated in the stereo drawing in Fig. 3.

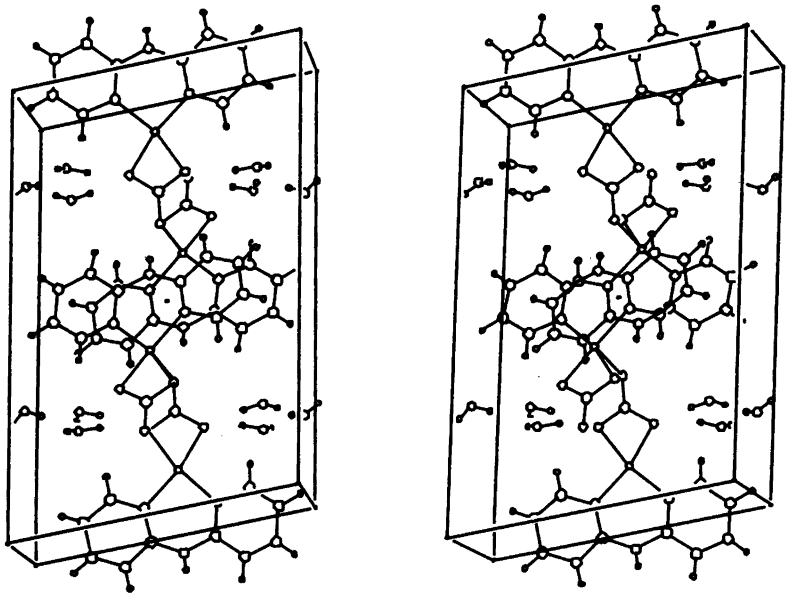

Fig. 3. Unit cell content. Origin is in the upper left hand corner; *a* runs horisontally, *b* towards the viewer.

Table 4. Hydrogen bond lengths and angles. Symmetry operations are listed in the legend to Fig. 1.

A···D	Distance (Å)	∠A···H–D	Angle (°)
O1A···O2W^{ii}	2.790(2)	O1A···H22W^{ii}–O2W^{ii}	175(3)
O2A···O1W^{ii}	2.802(2)	O2A···H11W^{ii}–O1W^{ii}	169(2)
O3A···N2^{iii}	2.798(2)	O3···H2^{iii}–N2^{iii}	166(2)
O1W···O3W	2.733(2)	O1W···H31W–O3W	162(2)
O2W···O1W^{ii}	2.820(2)	O2W···H12W^{ii}–O1W^{ii}	168(2)
O2W···O3W^{iv}	2.944(2)	O2W···H32W^{iv}–O3W^{iv}	160(3)
O3W···O2W^{ii}	2.752(2)	O3W···H21W^{ii}–O2W^{ii}	165(3)

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