Inorg. Chem. **1981**, *20*, 609–614

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Crystal and Molecular Structure of μ-Carbonato-di-μ-chloro-tetrakis(bis(3-aminopropyl)amine)tetracopper(II) Chloride Hydrate

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Received June 13, 1980

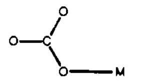
$[Cu_4(dpt)_4(CO_3)Cl_2]Cl_4 \cdot 7.5H_2O$ (dpt = bis(3-aminopropyl)amine) crystallizes in the triclinic space group $P\bar{1}$, with a = 9.246 (3) Å, b = 13.957 (3) Å, c = 25.898 (6) Å, α = 121.87 (1)°, β = 106.82 (1)°, and γ = 96.02 (1)°. The crystal structure was solved by using the intensities of 6753 reflections measured on a four-circle automated diffractometer using monochromatic Mo $K\alpha_1$ radiation. A total of 4905 reflections with $I > 2.3\sigma_I$ were used in refinement which converged to a final R_1 = 0.053. Each cation consists of four Cu atoms arranged in a rectangle with Cl atoms bridging the shorter sides (Cu–Cl = 2.519, 2.520, 2.549, 2.508 (2) Å) and a disordered carbonate group at the center bonded to all four Cu atoms. Alternately, one carbonate oxygen atom bridges each pair of adjacent Cu atoms (average Cu–O = 2.075 (7) Å). The other two carbonate O atoms are each bonded to one of the remaining two Cu atoms (average Cu–O = 2.041 (13) Å). These atoms all lie in a rough plane. dpt ligands coordinate to the Cu atoms at right angles to this plane (average Cu–N(terminal) = 2.004 (6) Å, average Cu–N(central) = 2.029 (5) Å).

Introduction

Our interest in the coordination of carbonate groups to Cu(II) began with the structure of $[(CuL)_2CO_3](ClO_4)_2$ (L = 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene),[1] a Cu(II) complex which was diamagnetic as a result of strong antiferromagnetic coupling. The X-ray structure analysis revealed a new mode of carbonate coordination with the carbonate being bidentate to each of two Cu atoms (see 3L,2M below), giving a Cu–O–Cu angle of 176.6 (2)°.

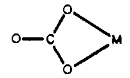
The seemingly simple carbonate ion has proven to be a surprisingly versatile ligand. The wide range of bonding modes which have been reported to date are shown below. The bonding is classified according to the number of donor atoms that bond to metal atoms (L = ligate) and the number of metal atoms bonded to the carbonate ion (M = metallic):[2]

1L,1M



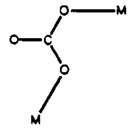
e.g., $[Co(NH_3)_5(CO_3)]Br \cdot H_2O$[3] and *trans*-$K_2[Co(CO_3)_2(H_2O)_4]$[4]

2L,1M



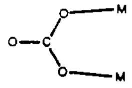
e.g., $[Co(NH_3)_4(CO_3)]Br$[5] and $Na_2Cu(CO_3)_2(H_2O)_3$[6,7]

2L,2M syn,anti



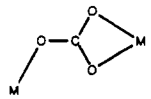
e.g., $Na_2Cu(CO_3)_2$[8] and $Na_2Cu(CO_3)_2(H_2O)_3$[6,7]

2L,2M syn,syn



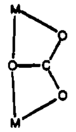
e.g., $KAgCO_3$[9] and $Cs_4[Rh_2(CO_3)_4(H_2O)_2] \cdot 6H_2O$[10]

3L,2M



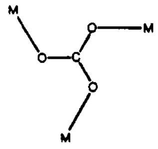
e.g., $((C_6H_5)_4Sb)_2CO_3$[11] and $Rh_2(CO_3)(PPh_3)_5 \cdot C_6H_6$[12]

3L,2M



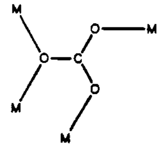
e.g., $[(CuL)_2CO_3](ClO_4)_2$[1] and $[(CuCl(tetramethyl\text{-}1,3\text{-}propanediamine))_2CO_3]$[13]

3L,3M



e.g., $Cu_3(OH)_2(CO_3)_2$(azurite)[14] and $[Cu((((2\text{-}(2\text{-}pyridyl)ethyl)imino)methyl)pyridine)(H_2O)]_3(CO_3)(NO_3)_4$[15] and

3L,4M



e.g., $Cu_2(OH)_2(CO_3)$(malachite).[16]

The interesting results obtained for $[(CuL)_2CO_3](ClO_4)_2$ prompted us to look at other Cu–CO_3 compounds with unusual magnetic properties. The preparation of $Cu_3(dpt)_3(CO_3)(ClO_4)_4 \cdot 2H_2O$ (dpt = dipropylenetriamine = bis(3-amino-

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Table I. Crystal Data

$C_{25}H_{83}Cl_6Cu_4N_{12}O_{10.5}$	$V = 2576.9$ Å^3
space group $P1$	$Z = 2$
$a = 9.246$ (3) Å	fw 1186.9
$b = 13.957$ (3) Å	$\mu = 20.57$ cm^{-1}
$c = 25.898$ (6) Å	$\rho_{\text{obsd}}{}^{a} = 1.53$ g cm^{-3}
$\alpha = 121.87$ (1)°	$\rho_{\text{calcd}} = 1.529$ g cm^{-3}
$\beta = 106.82$ (1)°	final $R_1{}^{b} = 0.053$
$\gamma = 96.02$ (1)°	final $R_2{}^{c} = 0.066$

[a] Flotation in $CH_2I_2/C_6H_5NO_2$. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2)^{1/2}$.

Table II. Data Collection

radiation: monochromatic Mo Kα_1 ($\lambda = 0.709\,26$ Å)
θ–2θ scan: 2° min^{-1}
base scan width[a] and bkgd counts at each limit[b]
  $l = 2n$: $2\theta < 30°$, 1.5°, 10 s; $30° \leqslant 2\theta < 45°$, 1.3°, 10 s
  $l = 2n + 1$: $2\theta < 30°$, 1.5°, 10 s; $30° \leqslant 2\theta < 45°$, 1.2°, 20 s
no. of reflctns
  $l = 2n$: 3378, 3040 with $I > 2.3\sigma_I$
  $l = 2n + 1$: 3375, 1865 with $I > 2.3\sigma_I$

[a] Also corrected for Kα_1–Kα_2 dispersion. [b] Stationary crystal, stationary counter.

propyl)amine) and $Cu_4(dpt)_4(CO_3)Cl_6{\cdot}8H_2O$ had been reported by Curtis et al. in 1968;[17] the perchlorate was magnetically normal but the chloride was anomalous with $\mu_{\text{eff}} = 1.23\ \mu_B$ at 81 K and $1.68\ \mu_B$ at 293 K. Furthermore, infrared studies suggested that the carbonate was unidentate in the perchlorate but polydentate in the chloride. More detailed magnetic studies[18] on the chloride have since shown that it obeys the Curie–Weiss law over the range 100–300 K but has a large negative Weiss constant (−144 K); the magnetic moment over this range is now "normal" at $2.04\ \mu_B$.

This paper reports the structure of $Cu_4(dpt)_4(CO_3)Cl_6{\cdot}7.5H_2O$, subsequently referred to as I. The crystals were generously supplied by Dr. Curtis.

X-ray Data Collection

A single, well-formed prismatic crystal of I (0.38 × 0.40 × 0.50 mm) was mounted approximately down the *c* axis. Photographs taken with Cu Kα radiation showed only Laue $\bar{1}$ symmetry and gave approximate unit cell parameters. They also showed that reflections with $l = 2n + 1$ were systematically much weaker than those with $l = 2n$.

The crystal was mounted on a Picker FACS-1 four-circle automated diffractometer employing graphite-monochromated Mo Kα radiation, and cell dimensions were determined from the setting angles of 11 accurately centered reflections. Crystal data are given in Table I. The intensities of 6753 unique reflections with $2\theta < 45°$ were measured, and of these 4905 with $I > 2.3\sigma_I$ (σ_I is the standard deviation in the intensity derived from counter statistics and a precision factor of 0.03) were regarded as observed and used in structure solution and refinement. Table II summarizes the experimental conditions. Two standards measured after every 75 reflections showed a small decrease in average intensity, and data were scaled accordingly. No absorption correction was applied.

Determination and Refinement of the Structure

The ratio of the average intensities of reflections with *l* even to reflections with *l* odd ranged steadily from 34 for $0.0 < (\sin\theta)/\lambda < 0.316$ through to 13 for $0.502 < (\sin\theta)/\lambda < 0.541$. It was therefore apparent that an approximate solution would be obtained by using only inner *l* even reflections and adding the symmetry operations $x, y, {}^1/_2 + z$ and $\bar{x}, \bar{y}, {}^1/_2 - z$. This "structure" was solved by conventional heavy-atom procedures, revealing an asymmetric unit $Cu_2Cl_4(dpt)_2(H_2O)_2$ and atoms of occupancy 0.5 consistent with a disordered carbonate ion and a disordered water molecule. Refinement on 1005 *l*-even observed reflections with $2\theta \leq 30°$ and anisotropic temperature factors for the Cu and Cl atoms converged to $R_1 = 0.067$. This solution placed the center of the carbonate ion at 0, 0, 0; all atomic coordinates were therefore shifted to $x, y, {}^1/_4 + z$ so that the center of inversion would be removed from the carbonate ion when the full data set was considered.

To introduce the odd data, it was necessary to break the pseudosymmetry. A MULTAN refinement[19] was used to phase 58 *l*-odd reflections (151 *l*-even reflections with high *E* values and phases as determined above were included in the starting set). A Fourier synthesis of these 58 reflections showed the direction of small shifts in some of the Cu and Cl positions which were sufficient to cause a concerted breaking of the pseudosymmetry in most of the unit cell during least-squares refinement with the full data set. "Cl(23)" and "Cl(14)" gave unreasonably high temperature factors so their occupancies were refined, yielding values of 0.56 and 0.51, respectively. They were therefore considered to be water molecules in further refinement. In addition, the occupancies of OW(16) and OW(26) (initially both 0.5) were allowed to vary, giving values of 0.50 and 1.08, respectively; subsequently OW(16) was fixed at 0.5 and OW(26) at 1.0.

The carbonate group, however, remained disordered. Least-squares refinement was attempted for each orientation, but both gave very similar agreement factors with high temperature factors for the carbonate O atoms and with large peaks in the difference-Fourier map corresponding to the O atoms of the other orientation. It therefore appears that the carbonate group is genuinely disordered. The two sites of the central C atom, however, were too close together to be resolved and were therefore regarded as a single C atom (occupancy 1.0) while the six O sites were each given occupancies of 0.5. The possibility still remains that the disorder might be removed by using space group $P1$, but such an attempt would experience major correlation problems as the bulk of the structure would remain centrosymmetric.

The coordinates of the dpt H atoms were determined geometrically (sp^3 coordination at C and N; $r_{\text{C-H}} = 0.95$ Å, $r_{\text{N-H}} = 0.90$ Å), and water H atoms were placed on hydrogen-bonding contacts ($r_{\text{O-H}} = 0.85$ Å). Each H atom was assigned the same temperature factor as the atom to which it was bonded. The H atom scattering contribution was included in all subsequent calculations; the parameters were not refined but were recalculated frequently during refinement of the nonhydrogen parameters.

Anisotropic temperature factors were used for the Cu, Cl, and C atoms and OW(26), all of which had shown indication of anisotropy in difference-Fourier maps. Refinement was terminated at this point: final $R_1 = 0.053$, $R_2 = 0.066$. All shift-to-error ratios in the final cycle were <1.5 (exclusive of the atoms of the propylene rings all ratios were <0.4). The refined coordinates of the Cu and Cl atoms of the cation do not show a center of inversion at (0, 0, $^1/_4$). This confirms that the shift of the center of the cation from 0, 0, 0 to 0, 0, $^1/_4$ was correct even though it was originally performed in an unsuccessful attempt to remove the disorder of the carbonate group.

Refinement throughout was by full-matrix least squares minimizing the function $\sum w(|F_o| - |F_c|)^2$ where the weights *w* were taken to be $1/\sigma_F^2$. Neutral-atom scattering factors were employed and anomalous dispersion corrections applied for Cu and Cl.[20]

The atomic coordinates and associated thermal parameters are listed in Table III, bond lengths and angles in Table IV, and relevant least-squares planes in Table V. Figure 1 shows the atom labeling scheme of the molecule and Figure 2 the molecular packing within the unit cell.

Computer programs were run on an in-house PDP-8e computer[21] and on the IBM 370/155 computer at this university.[22]

Description and Discussion

The $[Cu_4(dpt)_4(CO_3)Cl_2]^{4+}$ cation consists of four Cu atoms arranged in a rectangle (Cu(11)···Cu(12) = 3.648, Cu(12)···Cu(21) = 4.808, Cu(21)···Cu(22) = 3.680, and Cu(22)···Cu(11) = 4.733 (2) Å), with a disordered carbonate ion at

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Table III. Final Positional and Thermal Parameters for $Cu_4(dpt)_4Cl_6(CO_3)\cdot 7.5H_2O$[a,b] (Nonhydrogen Atoms[c])

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2	d[d]
Cu(11)	0.58513 (9)	0.60292 (7)	0.39181 (3)		Cu(21)	0.42100 (9)	0.39377 (7)	0.10373 (3)		0.13
Cu(12)	0.65572 (9)	0.76372 (6)	0.32252 (4)		Cu(22)	0.34566 (8)	0.23821 (6)	0.17666 (4)		0.04
Cl(10)	0.7006 (2)	0.8165 (2)	0.4364 (1)		Cl(20)	0.3034 (2)	0.1802 (2)	0.0625 (1)		0.06
N(111)	0.7670 (6)	0.5375 (4)	0.3879 (3)	42 (1)	N(211)	0.2425 (6)	0.4634 (4)	0.1063 (2)	39 (1)	0.20
C(112)	0.9200 (8)	0.5991 (6)	0.4475 (3)		C(212)	0.0906 (7)	0.3988 (6)	0.0463 (3)		0.20
C(113)	0.8922 (8)	0.6136 (7)	0.5053 (3)		C(213)	0.1175 (7)	0.3789 (6)	−0.0122 (3)		0.21
C(114)	0.7951 (8)	0.6938 (7)	0.5295 (3)		C(214)	0.2122 (7)	0.2948 (6)	−0.0355 (3)		0.19
N(115)	0.6249 (6)	0.6430 (5)	0.4833 (3)	47 (1)	N(215)	0.3822 (6)	0.3451 (4)	0.0108 (2)	34 (1)	0.19
C(116)	0.5378 (9)	0.7241 (8)	0.5175 (3)		C(216)	0.4697 (8)	0.2646 (6)	−0.0215 (3)		0.17
C(117)	0.3586 (9)	0.6720 (9)	0.4793 (4)		C(217)	0.6489 (8)	0.3184 (6)	0.0172 (3)		0.15
C(118)	0.2990 (8)	0.6666 (7)	0.4177 (4)		C(218)	0.7086 (8)	0.3255 (6)	0.0799 (3)		0.13
N(119)	0.3516 (6)	0.5818 (4)	0.3681 (2)	42 (1)	N(219)	0.6534 (6)	0.4083 (4)	0.1283 (3)	43 (1)	0.14
N(121)	0.8521 (6)	0.7246 (5)	0.3105 (3)	48 (1)	N(221)	0.1485 (6)	0.2765 (4)	0.1864 (2)	39 (1)	0.09
C(122)	1.0097 (8)	0.8069 (7)	0.3636 (4)		C(222)	−0.0098 (8)	0.1913 (6)	0.1336 (4)		0.06
C(123)	1.0306 (8)	0.9269 (7)	0.3762 (4)		C(223)	−0.0300 (8)	0.0722 (6)	0.1227 (4)		0.03
C(124)	0.9229 (8)	0.9902 (6)	0.4050 (4)		C(224)	0.0816 (8)	0.0102 (6)	0.0961 (3)		0.04
N(125)	0.7530 (6)	0.9347 (4)	0.3576 (2)	40 (1)	N(225)	0.2521 (6)	0.0691 (4)	0.1454 (2)	35 (1)	0.06
C(126)	0.6650 (8)	1.0165 (6)	0.3877 (4)		C(226)	0.3434 (8)	−0.0123 (6)	0.1174 (3)		0.11
C(127)	0.4933 (9)	0.9789 (6)	0.3415 (4)		C(227)	0.5129 (9)	0.0287 (6)	0.1641 (4)		0.11
C(128)	0.3874 (8)	0.8677 (6)	0.3255 (3)		C(228)	0.6182 (8)	0.1368 (6)	0.1773 (3)		0.07
N(129)	0.4343 (6)	0.7639 (4)	0.2855 (2)	41 (1)	N(229)	0.5700 (6)	0.2418 (4)	0.2149 (2)	38 (1)	0.08
C(1)	0.5026 (8)	0.5008 (6)	0.2486 (3)	29 (1)						0.11
O(10)[e]	0.5715 (9)	0.6090 (7)	0.3124 (4)	21 (2)	O(20)[e]	0.4296 (10)	0.3913 (7)	0.1842 (4)	31 (2)	0.09
O(11)[e]	0.5061 (11)	0.5133 (8)	0.2045 (5)	39 (2)	O(21)[e]	0.5000 (11)	0.4876 (9)	0.2914 (5)	40 (2)	0.14
O(12)[e]	0.4503 (11)	0.4171 (8)	0.2484 (5)	36 (2)	O(22)[e]	0.5542 (11)	0.5842 (9)	0.2486 (5)	42 (2)	0.11
Cl(11)	0.6154 (3)	0.2777 (2)	0.3595 (1)		Cl(21)	0.3467 (2)	0.7395 (2)	0.1426 (1)		0.45
Cl(12)	0.0790 (2)	0.3278 (2)	0.3189 (1)		OW(22)	0.9067 (8)	0.6840 (6)	0.1866 (3)	104 (2)	0.24
OW(13)	−0.1280 (5)	0.4533 (4)	0.2688 (2)	48 (1)	Cl(23)	1.1092 (2)	0.5438 (2)	0.2273 (1)		0.16
OW(14)	0.2532 (7)	0.1206 (5)	0.2767 (3)	82 (2)	OW(24)	0.7270 (9)	0.8863 (6)	0.2275 (4)	119 (2)	0.24
OW(15)	−0.1494 (7)	0.1330 (6)	0.3168 (3)	102 (2)	OW(25)	1.0997 (8)	0.8671 (6)	0.1943 (3)	115 (2)	0.61
OW(16)[e]	0.4280 (15)	0.4168 (12)	0.4256 (7)	106 (4)	OW(26)	0.5867 (7)	0.5990 (5)	0.0986 (3)		0.51

atom	U_{11}[f]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(11)	307 (5)	607 (6)	226 (4)	113 (4)	100 (4)	210 (4)
Cu(21)	345 (5)	623 (6)	229 (4)	191 (4)	122 (4)	217 (4)
Cu(12)	282 (5)	282 (5)	524 (5)	25 (4)	101 (4)	197 (4)
Cu(22)	283 (4)	256 (5)	446 (5)	35 (4)	114 (4)	168 (4)
Cl(10)	66 (1)	99 (2)	100 (2)	22 (1)	33 (1)	82 (2)
Cl(20)	69 (1)	98 (2)	88 (2)	25 (1)	37 (1)	78 (1)
C(112)	39 (4)	67 (5)	53 (5)	20 (4)	16 (4)	31 (4)
C(212)	31 (4)	76 (5)	50 (4)	15 (4)	12 (4)	38 (4)
C(113)	43 (4)	74 (6)	44 (4)	5 (4)	−3 (4)	36 (4)
C(213)	34 (4)	74 (5)	48 (4)	14 (4)	4 (3)	40 (4)
C(114)	38 (4)	86 (6)	34 (4)	−2 (4)	2 (3)	33 (4)
C(214)	38 (4)	57 (5)	26 (4)	−5 (4)	−2 (3)	23 (4)
C(116)	56 (5)	127 (7)	34 (4)	19 (5)	24 (4)	32 (5)
C(216)	54 (5)	44 (4)	33 (4)	14 (4)	21 (4)	19 (3)
C(117)	51 (5)	149 (9)	51 (5)	28 (6)	31 (4)	51 (6)
C(217)	51 (5)	56 (5)	41 (4)	22 (4)	29 (4)	23 (4)
C(118)	40 (4)	84 (6)	54 (5)	20 (4)	25 (4)	30 (5)
C(218)	41 (4)	61 (5)	47 (4)	23 (4)	22 (4)	30 (4)
C(122)	35 (4)	66 (5)	59 (5)	14 (4)	16 (4)	32 (4)
C(222)	34 (4)	60 (5)	62 (5)	12 (4)	16 (4)	38 (4)
C(123)	33 (4)	59 (5)	68 (5)	−3 (4)	14 (4)	30 (5)
C(223)	32 (4)	54 (5)	63 (5)	−2 (4)	11 (4)	29 (4)
C(124)	39 (4)	36 (4)	58 (5)	−8 (4)	6 (4)	16 (4)
C(224)	42 (4)	36 (4)	45 (4)	−7 (3)	9 (4)	15 (4)
C(126)	55 (5)	32 (4)	62 (5)	10 (4)	20 (4)	22 (4)
C(226)	59 (5)	32 (4)	47 (4)	10 (4)	24 (4)	18 (4)
C(127)	61 (5)	45 (5)	65 (5)	28 (4)	26 (4)	30 (4)
C(227)	56 (5)	49 (5)	58 (5)	29 (4)	25 (4)	31 (4)
C(128)	42 (4)	59 (5)	58 (5)	23 (4)	23 (4)	32 (4)
C(228)	44 (4)	56 (5)	57 (5)	22 (4)	22 (4)	30 (4)
Cl(11)	90 (2)	98 (2)	70 (2)	2 (1)	31 (1)	55 (1)
Cl(21)	81 (1)	64 (1)	58 (1)	21 (1)	30 (1)	40 (1)
Cl(12)	64 (1)	72 (1)	65 (1)	19 (1)	29 (1)	47 (1)
Cl(23)	37 (1)	51 (1)	50 (1)	12 (1)	20 (1)	31 (1)
OW(26)	80 (4)	58 (4)	134 (6)	15 (3)	44 (4)	47 (4)

[a] Estimated standard deviations of the least significant figures are given in parentheses in this and succeeding tables. [b] The values of the thermal parameters are multiplied by 10^4 for Cu atoms and by 10^3 for others. [c] The calculated coordinates of the hydrogen atoms are listed in Table VI which is deposited as supplementary material. [d] The distance between the atom in column 1 and the image of the atom in column 2 under the pseudosymmetry operation $(\bar{x}, \bar{y}, {}^1/_2 - z)$. [e] Population parameter of 0.5. [f] Anisotropic temperature factors are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + U_{23}klb^*c^*)]$.

Table IV. Interatomic Distances (A) and Angles (Deg)

Cu(11)-Cl(10)	2.519 (2)	Cu(21)-Cl(20)	2.549 (2)	Cu(12)-Cl(10)	2.520 (2)	Cu(22)-Cl(20)	2.508 (2)
	2.538 (2)[a]		2.565 (2)[a]		2.538 (2)[a]		2.526 (2)[a]
Cu(11)-N(111)	1.998 (5)	Cu(21)-N(211)	2.001 (5)	Cu(12)-N(121)	2.012 (5)	Cu(22)-N(221)	1.999 (5)
Cu(11)-N(115)	2.028 (5)	Cu(21)-N(215)	2.025 (5)	Cu(12)-N(125)	2.029 (5)	Cu(22)-N(225)	2.032 (5)
Cu(11)-N(119)	2.009 (5)	Cu(21)-N(219)	2.011 (5)	Cu(12)-N(129)	1.995 (5)	Cu(22)-N(229)	2.006 (5)
Cu(11)-O(10)	2.072 (7)	Cu(21)-O(20)	2.081 (8)	Cu(12)-O(10)	2.067 (8)	Cu(22)-O(20)	2.081 (9)
Cu(11)-O(21)	2.026 (10)	Cu(21)-O(11)	2.037 (10)	Cu(12)-O(22)	2.056 (10)	Cu(22)-O(12)	2.044 (10)
Cu(11)···OW(16)	3.460 (13)	Cu(21)···OW(26)	3.190 (6)				
			3.214 (6)[a]				
N(111)-C(112)	1.483 (8)	N(211)-C(212)	1.480 (8)	N(121)-C(122)	1.468 (8)	N(221)-C(222)	1.479 (8)
C(112)-C(113)	1.505 (9)	C(212)-C(213)	1.493 (8)	C(122)-C(123)	1.506 (10)	C(222)-C(223)	1.513 (9)
C(113)-C(114)	1.499 (10)	C(213)-C(214)	1.511 (9)	C(123)-C(124)	1.499 (10)	C(223)-C(224)	1.502 (9)
C(114)-N(115)	1.480 (8)	C(214)-N(215)	1.480 (7)	C(124)-N(125)	1.482 (8)	C(224)-N(225)	1.499 (8)
N(115)-C(116)	1.504 (9)	N(215)-C(216)	1.486 (8)	N(125)-C(126)	1.481 (8)	N(225)-C(226)	1.488 (8)
C(116)-C(117)	1.513 (10)	C(216)-C(217)	1.516 (9)	C(126)-C(127)	1.514 (9)	C(226)-C(227)	1.494 (9)
C(117)-C(118)	1.485 (10)	C(217)-C(218)	1.502 (9)	C(127)-C(128)	1.519 (9)	C(227)-C(228)	1.514 (9)
C(118)-N(119)	1.472 (8)	C(218)-N(219)	1.460 (8)	C(128)-N(129)	1.473 (8)	C(228)-N(229)	1.475 (8)
C(1)-O(10)	1.403 (10)	C(1)-O(20)	1.419 (10)				
C(1)-O(21)	1.222 (11)	C(1)-O(11)	1.252 (11)	C(1)-O(22)	1.211 (10)	C(1)-O(12)	1.213 (10)
Cl(10)-Cu(11)-N(111)	104.8 (2)	Cl(20)-Cu(21)-N(211)	106.1 (1)	Cl(10)-Cu(12)-N(121)	104.0 (2)	Cl(20)-Cu(22)-N(221)	103.7 (1)
Cl(10)-Cu(11)-N(115)	93.4 (2)	Cl(20)-Cu(21)-N(215)	92.7 (1)	Cl(10)-Cu(12)-N(125)	93.4 (1)	Cl(20)-Cu(22)-N(225)	94.4 (1)
Cl(10)-Cu(11)-N(119)	102.9 (2)	Cl(20)-Cu(21)-N(219)	100.7 (2)	Cl(10)-Cu(12)-N(129)	104.8 (2)	Cl(20)-Cu(22)-N(229)	104.0 (1)
Cl(10)-Cu(11)-O(10)	71.7 (2)	Cl(20)-Cu(21)-O(20)	70.7 (2)	Cl(10)-Cu(12)-O(10)	71.8 (2)	Cl(20)-Cu(22)-O(20)	71.6 (2)
Cl(10)-Cu(11)-O(21)	114.0 (3)	Cl(20)-Cu(21)-O(11)	113.5 (3)	Cl(10)-Cu(12)-O(22)	113.0 (3)	Cl(20)-Cu(22)-O(12)	112.7 (3)
Cl(10)-Cu(11)···OW(16)	144.8 (2)	Cl(20)-Cu(21)···OW(26)	155.9 (1)				
N(111)-Cu(11)-N(115)	92.3 (2)	N(211)-Cu(21)-N(215)	92.7 (2)	N(121)-Cu(12)-N(125)	91.4 (2)	N(221)-Cu(22)-N(225)	91.6 (2)
N(111)-Cu(11)-N(119)	151.6 (2)	N(211)-Cu(21)-N(219)	152.3 (2)	N(121)-Cu(12)-N(129)	150.6 (2)	N(221)-Cu(22)-N(229)	151.5 (2)
N(111)-Cu(11)-O(10)	91.4 (3)	N(211)-Cu(21)-O(20)	91.6 (3)	N(121)-Cu(12)-O(10)	92.0 (3)	N(221)-Cu(22)-O(20)	92.1 (3)
N(111)-Cu(11)-O(21)	82.6 (3)	N(211)-Cu(21)-O(11)	82.4 (3)	N(121)-Cu(12)-O(22)	81.1 (3)	N(221)-Cu(22)-O(12)	82.8 (3)
N(111)-Cu(11)···OW(16)	90.2 (3)	N(211)-Cu(21)···OW(26)	85.9 (2)				
N(115)-Cu(11)-N(119)	92.5 (2)	N(215)-Cu(21)-N(219)	93.3 (2)	N(125)-Cu(12)-N(129)	92.8 (2)	N(225)-Cu(22)-N(229)	92.9 (2)
N(115)-Cu(11)-O(10)	165.2 (3)	N(215)-Cu(21)-O(20)	163.4 (3)	N(125)-Cu(12)-O(10)	165.2 (3)	N(225)-Cu(22)-O(20)	166.0 (3)
N(115)-Cu(11)-O(21)	152.5 (3)	N(215)-Cu(21)-O(11)	153.7 (3)	N(125)-Cu(12)-O(22)	153.5 (3)	N(225)-Cu(22)-O(12)	152.9 (3)
N(115)-Cu(11)···OW(16)	53.6 (3)	N(215)-Cu(21)···OW(26)	65.4 (2)				
N(119)-Cu(11)-O(10)	91.1 (3)	N(219)-Cu(21)-O(20)	90.4 (3)	N(129)-Cu(12)-O(10)	91.2 (3)	N(229)-Cu(22)-O(20)	90.3 (3)
N(119)-Cu(11)-O(21)	80.3 (3)	N(219)-Cu(21)-O(11)	80.3 (3)	N(129)-Cu(12)-O(22)	82.2 (3)	N(229)-Cu(22)-O(12)	80.5 (3)
N(119)-Cu(11)···OW(16)	70.5 (3)	N(219)-Cu(21)···OW(26)	72.2 (2)				
O(10)-Cu(11)···OW(16)	140.8 (3)	O(20)-Cu(21)···OW(26)	130.9 (3)				
O(21)-Cu(11)···OW(16)	99.3 (4)	O(11)-Cu(21)···OW(26)	88.4 (3)				
Cu(11)-Cl(10)-Cu(12)	92.77 (8)	Cu(21)-Cl(20)-Cu(22)	93.39 (8)	Cu(11)-O(10)-Cu(12)	123.7 (4)	Cu(21)-O(20)-Cu(22)	124.3 (4)
Cu(11)-N(111)-C(112)	120.4 (4)	Cu(21)-N(211)-C(212)	119.1 (4)	Cu(12)-N(121)-C(122)	119.4 (4)	Cu(22)-N(221)-C(222)	119.9 (4)
N(111)-C(112)-C(113)	110.2 (5)	N(211)-C(212)-C(213)	110.8 (5)	N(121)-C(122)-C(123)	109.8 (6)	N(221)-C(222)-C(223)	110.5 (5)
C(112)-C(113)-C(114)	114.3 (6)	C(212)-C(213)-C(214)	113.9 (5)	C(122)-C(123)-C(124)	114.3 (6)	C(222)-C(223)-C(224)	113.8 (6)
C(113)-C(114)-N(115)	114.0 (6)	C(213)-C(214)-N(215)	113.6 (5)	C(123)-C(124)-N(125)	113.7 (6)	C(223)-C(224)-N(225)	113.7 (5)
C(114)-N(115)-Cu(11)	114.5 (4)	C(214)-N(215)-Cu(21)	114.6 (3)	C(124)-N(125)-Cu(12)	114.8 (4)	C(224)-N(225)-Cu(22)	114.0 (4)
C(114)-N(115)-C(116)	108.4 (5)	C(214)-N(215)-C(216)	109.2 (5)	C(124)-N(125)-C(126)	108.1 (5)	C(224)-N(225)-C(226)	107.9 (5)
Cu(11)-N(115)-C(116)	113.5 (4)	Cu(21)-N(215)-C(216)	114.5 (4)	Cu(12)-N(125)-C(126)	115.1 (4)	Cu(22)-N(225)-C(226)	114.8 (4)
N(115)-C(116)-C(117)	113.2 (6)	N(215)-C(216)-C(217)	113.1 (5)	N(125)-C(126)-C(127)	114.2 (5)	N(225)-C(226)-C(227)	114.1 (5)
C(116)-C(117)-C(118)	114.1 (6)	C(216)-C(217)-C(218)	113.8 (5)	C(126)-C(127)-C(128)	113.7 (6)	C(226)-C(227)-C(228)	114.4 (6)
C(117)-C(118)-N(119)	110.8 (6)	C(217)-C(218)-N(219)	111.1 (5)	C(127)-C(128)-N(129)	110.0 (5)	C(227)-C(228)-N(229)	109.9 (5)
C(118)-N(119)-Cu(11)	119.8 (4)	C(128)-N(219)-Cu(21)	121.2 (4)	C(128)-N(129)-Cu(12)	119.2 (4)	C(228)-N(229)-Cu(22)	119.4 (4)
Cu(11)-O(10)-C(1)	117.3 (6)	Cu(21)-O(20)-C(1)	117.6 (6)	Cu(12)-O(10)-C(1)	119.1 (5)	Cu(22)-O(20)-C(1)	118.1 (6)
Cu(11)-O(21)-C(1)	132.2 (8)	Cu(21)-O(11)-C(1)	131.3 (8)	Cu(12)-O(22)-C(1)	132.6 (8)	Cu(22)-O(12)-C(1)	134.5 (8)
O(20)-C(1)-O(21)	111.3 (9)	O(10)-C(1)-O(11)	112.3 (8)	O(20)-C(1)-O(22)	113.6 (8)	O(10)-C(1)-O(12)	113.2 (8)
O(21)-C(1)-O(22)	135.1 (10)	O(11)-C(1)-O(12)	134.5 (10)				

[a] Interatomic distance averaged over thermal motion; second atom assumed to ride on first.

Table V. Deviation (Å) from the Least-Squares Plane[a]

$$-0.9608x + 0.2527y - 0.1143z + 1.6968 = 0$$

Cu(11)	−0.056 (1)	Cu(12)	0.022 (1)	Cu(21)	0.020 (1)
Cu(22)	0.014 (1)	Cl(10)	0.023 (3)	Cl(20)	−0.036 (2)
C(1)	−0.001 (8)	O(10)	−0.003 (9)	O(11)	−0.025 (11)
O(12)	0.052 (11)	O(20)	0.030 (10)	O(21)	0.009 (11)
O(22)	−0.049 (11)	N(115)[b]	−0.100 (6)	N(125)[b]	0.041 (6)
N(215)[b]	0.011 (6)	N(225)[b]	−0.024 (6)		

[a] The equation of the plane is referred to the orthogonal axes a, b', and c^*. [b] Not used in defining the plane.

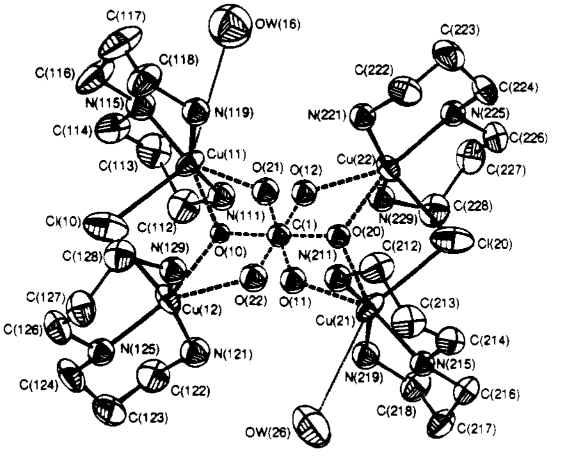
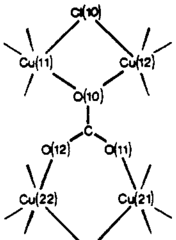
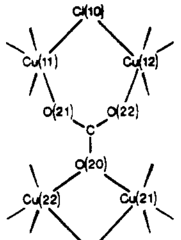


Figure 1. Projected view of the cation showing the atom labeling. The broken lines indicate the disorder of the carbonate group. In this figure and in Figure 2 the hydrogen atoms have been deleted for clarity.

the center bridging all four Cu atoms and with Cl atoms additionally bridging the two shorter sides. These atoms lie in an approximate plane (see Table V). One dpt ligand is coordinated meridionally to each Cu atom normal to this plane with N(*nm*5) in-plane. The carbonate is disordered such that a single oxygen atom alternately bridges one or the other pair of Cl-bridged Cu atoms while the other two oxygen atoms are linked to each of the remaining two Cu atoms.





Each Cu atom is five-coordinate, with the geometry depending on the mode of carbonate coordination. When the four-membered chelate ring Cu–Cl–Cu–O(*n*0) is formed, the average for angle O–Cu–Cl = 71.5 (5)° and O–Cu–N(*nm*5) = 165.0 (11)° but, when the six-membered ring Cu–Cl–Cu–O(*n*1)–C–O(*n*2) is formed, these angles average 113.3 (6) and 153.2 (6)°, respectively. In the former case the Cu atom environment is best described as being in an irregular trigonal-bipyramidal array (with O(*n*0) and N(*nm*5) axial) while the latter arrangement is closer to an irregular square pyramid (with Cl apical).

Cu(11) and Cu(21) also exhibit long contacts to water molecules OW(16) (3.46 (1) Å) and OW(26) (3.190 (6) Å), respectively (these would complete irregular octahedra). OW(16) has an occupancy of only 0.5 and has little influence on the geometry about Cu(11) (Cu(11)–Cl(10) = 2.519, Cu(12)–Cl(10) = 2.520 (2) Å), but OW(26) has a marked effect upon the molecule, causing Cu(21)–Cl(20) to lengthen to 2.549 (2) Å which, in turn, causes a shortening of Cu(22)–Cl(20) to 2.508 (2) Å.

The average Cu–N distance is shorter for the terminal N's than for N(*nm*5) (2.004 (6) Å; cf. 2.029 (5) Å), which is a common feature for dpt complex but the reverse of that observed for the bis(2-aminoethyl)amine analogues.[23] The six-membered chelate rings are in chair conformations, and all adopt the usual back-to-back arrangement.[24] Bond lengths and angles within the dpt groups are also typical of these compounds.[23-26]

The bridging nature of the carbonate group is unusual. One O atom is bonded to two Cu atoms, and the other two O atoms are each bonded to one Cu atom. The Cu–O distances are longer for the bridging O than for the other two (average 2.075 (7) Å; cf. average 2.041 (13) Å). This is also observed in $[(CuL)_2CO_3](ClO_4)_2$ (2.041 (1) Å; cf. 2.028 (5) Å,[1] $[(CuCl(tetramethyl\text{-}1,3\text{-}propanediamine))_2CO_3]$ (2.153 (1) Å; cf. 1.978 (2) Å),[13] and $[(CuCl(tetraethylethylenediamine))_2CO_3]$ (2.093 (2) Å; cf. 1.975 (3) Å)[27] and results from the sharing of the O atom electron density over two Cu–O bonds rather than one.

I is the second example of triligate–tetrametallic coordination of the carbonate group. The only other example to date is malachite (Cu(1)–O(0) = 2.055, Cu(2)–O(0) = 2.115, Cu(2)′–O(1) = 2.049, and Cu(1)″–O(2) = 1.996 (1) Å), but, in this compound, the Cu atoms are out of plane and there are also two longer contacts to a further two Cu atoms (2.641 (1) Å to O(0) and 2.510 (1) Å to O(2)).[16] The Cu–O–Cu angle is 124.0 (4)° for I compared with 94.53 (7)° for malachite.

The dimensions of the two orientations of the carbonate group could not be determined precisely as C(1) could not be

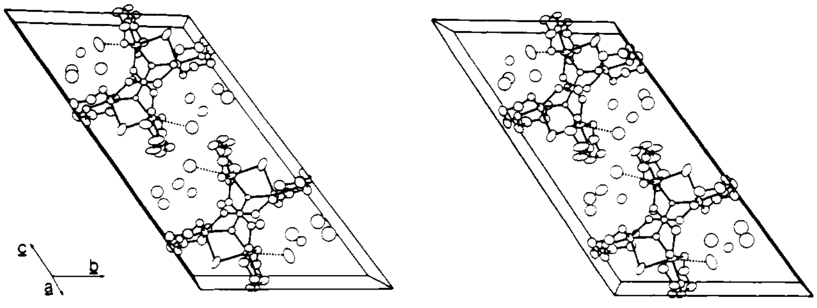


Figure 2. Molecular packing in the unit cell.

resolved into its two half-components and had to be placed at the mean position. Consequently, the listed values for distances and angles involving C(1) have little physical significance and certainly cannot be used to infer bond orders. We expect that C–O(*n*0) will have a lower bond order than the other two (O(*n*0) is involved in two Cu–O bonds rather than just one) and therefore will be longer. Valence shell replusion furthermore predicts that angle O(*n*1)–C–O(*n*2) will be larger O(*n*0)–C–O(*n*1)/O(*n*2)[7] unless there are external forces acting upon the group such as stereochemical requirements or hydrogen bonding.[4,14]

As can be seen in Figure 1, the major vibration axes of Cl(10) and Cl(20) are not normal to the Cu–Cl–Cu plane, as would be expected, but lie in plane. This suggests that the Cl atoms might be disordered to a small extent, probably in concert with the orientation of the carbonate. Cl(10) would be expected to be located further from the center for carbonate 1*n* than for carbonate 2*n* and conversely for Cl(20). Consequently, when the two orientations are superimposed, the electron density of the Cl atoms would be elongated in the direction observed. Disorder of the Cl atoms would also be expected to affect the Cu atoms slightly and, indeed, the observed thermal anisotropy of the Cu atoms is in agreement with this. It should be noted that the possible Cl disorder is at right angles to the Cu–Cu vector and so does not affect the *relative* length of Cu(21)–Cl(20) (cf. Cu(22)–Cl(20)) to any significant degree.

Acknowledgment. We are grateful for the financial support of the Natural Sciences and Engineering Research Council of Canada which made this work possible. We also wish to thank Dr. N. F. Curtis of the Victoria University of Wellington, Wellington, New Zealand, for details of unpublished work and for helpful discussion and encouragement, Dr. E. J. Yabe of the Division of Chemistry, NSERC, Ottawa, Canada, for making available the NSERC PDP-8e computer programs, and Dr. A. R. Davis, who assisted in data collection.

Registry No. I, 12329-65-6.

Supplementary Material Available: Tables of calculated H coordinates, deviations of Cu atoms from the planes through N atoms of dpt ligands, and structure factor amplitudes (43 pages). Ordering information is given on any current masthead page.

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Notes

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A Dodecahedral, Eight-Coordinate Chelate Complex, Tetrakis(2-mercaptopyrimidinato)tungsten(IV)

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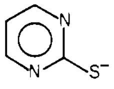
Received June 20, 1980

Considerable effort has been devoted to understanding the factors that govern ligand arrangements in eight-coordinate complexes.[1-3] One of the most common and most intensively studied polyhedra is the dodecahedron. When the ligands are chelating, and especially when they have a small bite, they tend to span the *m* edges,[4] giving a structure of the *mmmm* type, although this is not invariably the case.[5] If the chelating ligands are identical but unsymmetrical, there are six possible stereoisomers.[1] A consideration of metal–ligand σ- and π-bonding factors suggests that the π bonding will predominate[3] in determining the preferences for sites A and B.[4] It is not always easy to decide which of two ligating atoms has the greater π-donating or π-accepting ability, but for the ligand used in this work, the anion of 2-mercaptopyrimidine, **1**, it



1 (mpd⁻)

seems clear that the mercaptide sulfur atom would be the better π donor and the aromatic nitrogen atom the better π acceptor. For a d^2 metal ion, the arguments of Burdett, Hoffmann, and Fay[3] suggest that the nitrogen atoms should be found in the B positions and the sulfur atoms in the A positions.

Table I. Crystallographic Parameters

space group	*C*2/*c*	cryst size, mm	0.30 × 0.30 × 0.30
a, Å	24.991 (3)	μ, cm^{-1}	54.47
b, Å	14.611 (2)	2θ range, deg	0–45
c, Å	14.112 (2)	no. of data	2285
$\alpha = \gamma$, deg	90.0	$F_o^2 > 2.5\sigma(F_o^2)$	2008
β, deg	111.52 (1)	no. of variables	279
V, Å^3	4794 (2)	R_1	0.028
d_x, g/cm^3	1.639	R_2	0.040
Z	8	esd	0.944
fw	591.53		

We have prepared and structurally characterized an M(mpd)$_4$ molecule, where M is the d^2 species W^{IV}, and we find that the implied prediction of Burdett, Hoffmann, and Fay is obeyed.

Experimental Section

Materials. Tungsten carbonyl was purchased from Pressure Chemical Co., and 2-mercaptopyrimidine, Hmpd, was purchased from Aldrich Chemical Co., Inc. All other compounds and solvents were of reagent grade or better from commercial sources. Diglyme was dried over sodium and deoxygenated prior to use. Reactions were performed under argon by using standard Schlenk techniques.

Preparation of W(mpd)$_4\cdot{}^1/_2$(diglyme). To 30 mL of dry diglyme were added 0.352 g (1 mM) of W(CO)$_6$ and 0.444 g (4 mM) of 2-mercaptopyrimidine. The mixture was then heated under reflux for ~16 h to give a brown-violet solution. The mixture was filtered, and slow evaporation of the mother liquor gave an essentially quantitative yield of mostly microcrystalline product in which there were one or two crystals suitable for X-ray diffraction.

X-ray Crystallography. A suitable crystal was secured to the end of a thin glass fiber with epoxy cement and mounted on a Syntex P$\bar{1}$ automatic diffractometer. Procedures used for data collection as well as solution and refinement of the structure have been described

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(4) For definitions of terms such as *m* edges, *A* and *B* vertices, etc., see ref 1-3.
(5) Lewis, D. F.; Fay, R. C. *J. Chem. Soc., Chem. Commun.* **1974**, 1046.

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