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# Magnetic Exchange Interaction via a Bridging Carbonate Anion: Crystal and Molecular Structure of $\mu$-Carbonato-bis(2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene)dicopper(II) Perchlorate

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The title compound, which exhibits complete diamagnetism in the range 100–300 K, crystallizes as the DMF solvate in the orthorhombic space group *Iba*2, with $a = 16.19$ (1) Å, $b = 16.67$ (1) Å, $c = 15.43$ (1) Å, and $Z = 4$. A total of 1895 reflections were measured by using counter methods, of which 1230 were considered as observed (Mo K$\alpha$ radiation, $\lambda_{\alpha_1} = 0.70926$ Å). Full-matrix, least-squares refinement of the determined model gave a final $R$ of 0.052 (227 variables). The dimeric cation exhibits a novel mode of carbonate bridging, with the carbonate acting as a symmetrical, bidentate ligand to both metal ions (Cu–O = 2.041 (1) and 2.028 (5) Å). The dimer has a crystallographic twofold axis of symmetry which passes through the carbon and one oxygen atom of the carbonate bridge (the angle subtended at the common oxygen by the copper atoms is 176.6 (2)°). The geometry about each metal most closely approximates a square pyramid with the carbonate oxygen atoms and two nitrogen donors (N1 and N3) of the triaza macrocyle forming the basal plane and the third nitrogen donor (N2) the apex. The relationship of this geometry and that of the dimer to the unusual magnetic behavior is discussed.

## Introduction

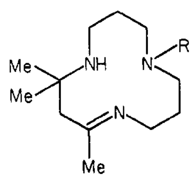
Rapidly increasing efforts have been directed toward obtaining a full understanding of the correlation between the magnetic and structural aspects in ligand-bridged polynuclear transition-metal clusters which exhibit ferromagnetic or antiferromagnetic coupling.[1-3] Attention has been focused on discrete dimers of Cu(II), not only because they are abundant[4] but also because they represent the simplest of systems and offer results which are more readily interpreted in terms of current theories of magnetic exchange interation.[5-9]

In addition to the information such studies may give toward understanding the nature of orbital interactions and to extending the predictive use of magnetic susceptibility data, a special interest in Cu(II) systems lies in the fact that the type III active sites in blue copper proteins are considered to comprise some kind of spin-paired Cu(II) dimer.[10,11]

In establishing the criteria which determine the size and sign of $J$ (the exchange integral, obtained in fitting measured magnetic behavior to that predicted by theoretical expressions), we recognize two areas of study. In systematically combining structural and magnetic data, Hodgson has found correlations between magnetic behavior and (for instance) bridging angles in dimers containing hydroxo and halogen bridges.[1] The other area is the application of molecular orbital theory in describing exchange interaction. Of particular interest are efforts to extend such studies to dimers containing bridging polyatomic anions.[7-9] As always, the studies rely heavily on experimental correlations similar to those already established, and future theoretical developments will rely on additional structural and magnetic data.

This point is clearly illustrated by two examples: in the first, subtle changes in the metal ion geometry and ligand structure in a pair of closely related Cu(II) dimers give complete diamagnetism via exchange interaction in one case and the normal magnetic behavior of a Cu(II) monomer in the other.[12] The second example concerns the structure and magnetism of a pair of oxalate-bridged Ni(II) and Cu(II) macrocylic complexes.[13] In the nickel(II) complex, the geometry about the metal ion is nearly octahedral, the bridging within the dimer is symmetrical, and antiferromagnetic coupling is observed. For the Cu(II) complex the geometry is square pyramidal, the bridging is asymmetrical, and no exchange interaction is evident. Some success has been made in interpreting the latter example in terms of orbital energies and overlap.[9]

Reaction of the polyamine bis(4-azaheptane-1,7-diamine) coordinated to Ni(II) or Cu(II) with acetone yields complexes of the macrocyclic ligand I.[14] The macrocylic system was



I

L1, R = H
L2, R = Me

proposed from the properties of the complexes and confirmed by X-ray crystal analysis of $Ni(L1)(NCS)_2$.[15] The macrocycles were also found to form a number of dinuclear compounds with five-coordinate copper(II) and nickel(II), with di-$\mu$-hydroxo, $\mu$-oxalato, $\mu$-carbonato, and other bridging groups. Several of these dimers exhibit spin pairing via exchange interaction, and the $\mu$-carbonato $[Cu(L2)]_2CO_3(ClO_4)_2$ is completely spin paired, showing only a small, residual, temperature-independent magnetism over the range 100–300 K.[18] Examples of such behavior are very rare for Cu(II) dimers,[12,16,17] and a complete structural characterization is

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clearly desirable in order to establish the exact geometrical conditions which give rise to this magnetic behavior. A note summarizing the results of this investigation has been published,[18] and full experimental and structural details are presented here.

## Experimental Section

A sample of the title compound was supplied by Professor Neil Curtis (Victoria University of Wellington, Wellington, New Zealand), and large, dark green, elongated plates were grown by slow evaporation of a 1:1 dimethylformamide (DMF)/2-propanol solvent mixture. A fragment of approximate dimensions 0.6 × 0.1 × 0.2 mm was selected and mounted for the purposes of photographic investigation, with the needle axis approximately coincident with the spindle axis of the cameras. Cu radiation ($\lambda = 1.5418$ Å) was used to obtain Weissenberg photographs of the *hk*0 and *hk*1 layers, together with precession photographs of the 0*kl*, 1*kl*, *h*0*l*, and *h*1*l* layers which established orthorhombic *mm*2 Laue symmetry, with systematic absences (*hkl*, $h + k + l = 2n + 1$; *h*0*l*, $h = 2n + 1$; 0*kl*, $k = 2n + 1$) consistent with the space groups *Iba*2 and *Ibam* (the former was indicated by the structure analysis).

Accurate cell dimensions were determined from counter measurement of 12 of the strongest reflections having $2\theta > 25°$ using a Picker FACS-1 computer-controlled, four-circle diffractometer (Mo K$\alpha$ radiation, $\lambda = 0.709\,26$ Å). Crystal data are as follows: $Cu_2Cl_2O_{12}N_7C_{30}H_{59}$; formula weight 907.8; space group *Iba*2; cell dimensions $a = 16.19$ (1) Å, $b = 16.67$ (1) Å, $c = 15.43$ (1) Å, $V = 4164$ Å$^3$; measured density (flotation) 1.35 (2) g mL$^{-1}$ ($Z = 4$), calculated density 1.34 g mL$^{-1}$ ($\mu$(Mo K$\alpha$) = 7.0 cm$^{-1}$, $T = 22$ (±1) °C).

Intensity data for the unique set of reflections with $2\theta < 50°$ were collected by using a $\theta$-$2\theta$ scan of base width 1.5° (increased to allow for dispersion), at a scan speed of 2°/min, with graphite-monochromatized Mo K$\alpha$ radiation, $\lambda_{\alpha_1} = 0.709\,26$ Å. Background counts were made at each scan limit. Two reflections used as standards were measured after every 100 reflections in order to monitor instrumental stability and crystal alignment; their variation was ±4% over the entire data collection. Measured intensities were corrected for Lorentz and polarization effects; absorption was neglected since it was estimated to introduce a maximum error of ±1.5% in $I$, the net count. A total of 1895 reflections were measured, of which 1230 were considered as observed (i.e., greater than $2.3\sigma_I$, where $\sigma_I = [\mathrm{TC} + (t_s/t_b)^2(B_1 + B_2) + (kI)^2]^{1/2}$; TC is the total count, $B_1$ and $B_2$ are background counts at either end of the scan range, $t_s$ is the scan time, $t_b$ is the total background count time, $k$ is a constant set to 0.03, and $I$ is the net count).

## Structural Determination

The positions of the unique copper and chlorine atoms were determined from a three-dimensional Patterson synthesis based on all the observed data, and these were refined together with a scale factor to give a residual, $R = 0.447$, where $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. A Fourier synthesis on $F_o$ with phases from $F_c$ gave the positions of the light atoms coordinated to the copper and the perchlorate oxygen atoms. Several cycles of full-matrix least-squares refinement and subsequent electron density difference maps gave the positions of all other light atoms in the macrocycle and the complete carbonate anion. With $R = 0.085$, it was clear that the perchlorate anion was disordered (large oxygen atom anisotropic thermal motion parameters) and that two of these atoms could be better described as "split atoms" (O11, O12 and O13, O14) each assigned an occupancy of 0.5. Furthermore, an array of small but significant peaks on, or close to, the twofold axis of symmetry was observed in the electron density difference map. Careful inspection of the angles and distances around these peaks revealed a satisfactory picture of a dimethylformamide solvent molecule of crystallization disordered about the twofold axis, the nitrogen and oxygen atoms lying on the axis, and the carbon atom of one of the methyl groups being best described as two split atoms (C14, C14′). Hydrogen atom positions were also determined from the electron density difference maps or, in the case of some methyl hydrogens, were calculated. Subsequent refinement of the positions of the nonhydrogen atoms, all of which were assigned anisotropic thermal motion parameters (except for the DMF solvent molecule atoms and the split perchlorate oxygen atoms), gave a final $R$ of 0.052 (227 variables). The only outstanding features were found in a final electron density difference map near the metal ion and the perchlorate anion (0.2 ± 0.07 e Å$^{-3}$). In the early stages of the refinement, unit weights were used; in the later stages, weights = $1/\sigma_F^2$ were used, where $\sigma_F = \sigma_I/(Lp(2F_o))$. A table of the measured and calculated structure factors (×10), together with hydrogen atom coordinates, is available (see the paragraph at the end of this paper regarding supplementary material). Atomic positional coordinates are listed in Table I, and thermal motion parameters are shown in Table II. Atomic scattering factors, with corrections for anomalous dispersion applied to the copper and chlorine atoms, were taken from ref 19. Computer programs used in this determination have been listed previously.[20]

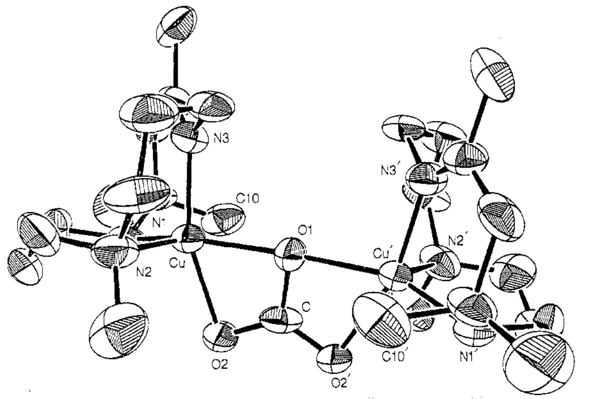

**Figure 1.** A perspective view of the $[Cu(L2)]_2CO_3^{2+}$ cation, showing thermal motion ellipsoids (50%) and labeling.

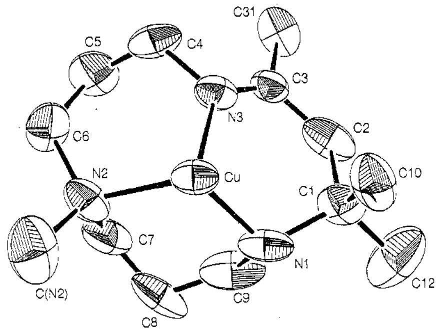

**Figure 2.** A view along the direction from the carbonate carbon atom to the copper atom of the macrocyclic ligand L2 as it occurs in the $[Cu(L2)]_2CO_3^{2+}$ cation.

## Discussion

**Description of the Structure.** The unit cell comprises four discrete L2–Cu–CO$_3$–Cu–L2 dimeric cations, eight perchlorate anions, and four DMF molecules of solvation, all well separated and affording no unusually short interionic or intermolecular contacts. A complete list of bond lengths and angles is given in Table III, a perspective view of the dimer, showing the labeling employed, is given in Figure 1, and a view of the macrocyclic ligand is given in Figure 2.

The coordination sphere of each copper atom contains the three nitrogen atoms of the macrocycle and two oxygen atoms of the bridging carbonate anion. The halves of the dimer are related by a crystallographic twofold axis of symmetry which passes through one oxygen (O1) and the carbon atom (C) of the carbonate bridge.

The five-coordinate geometry about each copper atom can be estimated by inspection of the angles subtended at the

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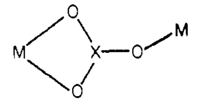
**Table I.** Fractional Atomic Coordinates ($\times 10^4$; $\times 10^5$ for Cu) in $\{[Cu(L2)]_2CO_3\}(ClO_4)_2 \cdot DMF$[a]

| atom | | *x* | *y* | *z* |
|---|---|---|---|---|
| Cu | | 9407 (6) | 8142 (5) | 5813 |
| O1 | | 0 | 0 | 542 (7) |
| O2 | | 519 (4) | 460 (3) | 1759 (4) |
| N1 | | 1232 (5) | 1930 (5) | 890 (4) |
| N2 | | 2123 (4) | 171 (4) | 587 (7) |
| N3 | | 984 (5) | 1015 (4) | −670 (5) |
| C1 | | 624 (6) | 2469 (6) | 425 (5) |
| C2 | | 809 (6) | 2448 (7) | −553 (6) |
| C3 | | 914 (6) | 1681 (6) | −1035 (5) |
| C4 | | 1133 (6) | 275 (6) | −1157 (5) |
| C5 | | 2000 (7) | −22 (7) | −1050 (2) |
| C6 | | 2189 (8) | −382 (8) | −207 (7) |
| C7 | | 2786 (5) | 777 (6) | 558 (11) |
| C8 | | 2674 (6) | 1475 (7) | 1146 (7) |
| C9 | | 2132 (8) | 2097 (7) | 795 (7) |
| C10 | | −242 (6) | 2183 (5) | 640 (9) |
| C12 | | 756 (8) | 3333 (6) | 734 (11) |
| C31 | | 953 (7) | 1819 (6) | −1988 (7) |
| C(N2) | | 2182 (8) | −309 (9) | 1356 (10) |
| C | | 0 | 0 | 1398 (8) |
| perchlorate anion | Cl | 1643 (2) | 2643 (3) | 3324 (2) |
| | C11$^b$ | 1426 (21) | 1935 (19) | 3028 (2) |
| | O12$^b$ | 1048 (11) | 2375 (11) | 2881 (11) |
| | O13$^b$ | 1894 (15) | 3383 (14) | 2840 (18) |
| | O14$^b$ | 2114 (15) | 3056 (16) | 2716 (17) |
| | O15 | 1396 (10) | 3079 (10) | 3991 (10) |
| | O16 | 2269 (13) | 2190 (10) | 3607 (16) |
| DMF | N | 0 | 5000 | 3051 (15) |
| | O | 0 | 5000 | 4483 (29) |
| | C13 | 726 (23) | 5141 (24) | 2645 (27) |
| | C14$^b$ | −75 (29) | 560 (29) | 321 (35) |
| | C14$^b$ | −16 (30) | 415 (29) | 300 (35) |
| | C15 | 502 (27) | 5061 (30) | 3848 (34) |

[a] Least-squares estimated errors are given in parentheses. [b] Split atoms, each assigned an occupancy of 0.5.

central atom by the metal–ligand bonds. The "best" square pyramid has basal angles XCuX in the cyclic sequence X = O1, O2, N1, and N3 of 65.3, 98.0, 93.9, and 96.4°, with apex–base angles N2CuX in the same sequence of 109.0, 98.5, 105.6, and 93.2°. The "best" trigonal pyramid on the other hand had equatorial angles XCuX in the sequence X = O1, N1, and N2 of 144.2, 109.0, and 104.5°, with apex–equatorial angles N3CuX of 96.4, 93.2, and 93.9° and O2CuX of 65.3, 98.5, and 98.0° and with a trans angle of 160.7°. Clearly, the choice is a difficult one and is not important in the sense that any explanation requires irregularity; we prefer the square pyramid, with N2 axial. The axial Cu–N2 distance of 2.195 (7) Å is longer than the Cu–N1 or Cu–N3 distance of 1.977 (7) and 1.961 (7) Å, respectively. Furthermore, as a consequence of the conformation adopted by the triaza macrocycle L2, there is a long contact (2.95 (2) Å) from the metal atom to a ligand methyl carbon atom (C10). Very similar structural behavior occurs in $Ni(L1)(NCS)_2$,[15] where the Ni···methyl carbon distance is 2.92 Å. Indeed, the entire ligand configurations and conformations in both complexes are very similar, with the two saturated chelate rings adopting chair conformations and the conformation of the imine chelate ring being determined by the planarity of the imine group.

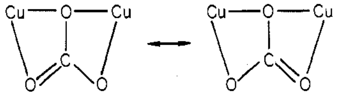
Previous structural studies[21-29] have shown various possible bonding modes for carbonate and nitrate ligands. The predominant bridging mode approximates



X = N, C

and is found for carbonate in complex dimers of a variety of metal ions: $Cu(NH_3)_2CO_3$,[22] $Co(NH_3)_4CO_3Br$,[26] $Pt(PPh_3)CO_3$,[27] $(Mo(CO)(PMe_2Ph)_3CO_3)_2$,[28] and $Rh_2(CO_3)(PPh_3)_5 \cdot C_6H_6$.[29] The mode of bridging of the carbonate ion in the present complex is completely novel; it acts (within experimental error) as a symmetrical bidentate ligand to both copper atoms, with Cu–O1 = 2.041 (1) Å, Cu–O2 = 2.028 (5) Å, CuO1Cu = 176.6 (0.2)° and O1CuO2 = 65.3 (0.3)°.

The range of C–O bond lengths in these complexes is from 1.245 (3)[22] to 1.36 (2)[24] Å, the distance in each case depending largely on the interaction with the metal ion, which is affected in some cases by the other ligands in the coordination sphere. Where bond lengths are accurate enough to show it, the C–O length decreases as the metal–oxygen interaction decreases; e.g., in $Cu(NH_3)_2CO_3$,[22] the Cu–O and respective C–O distances are 2.303 (2) and 1.245 (3), 1.989 (2) and 1.299 (3), and 1.986 (2) and 1.307 (3) Å. In $[Cu(L2)]_2CO_3^{2+}$, the unusual $CO_3^{2-}$ bridging results in corresponding distances of 2.028 (1) and 1.27 (1) Å for O2 and 2.041 (5) and 1.32 (1) Å for O1 and could be considered to reflect a certain stabilization of two of three possible resonance forms:



The C–O lengths in free carbonate as found in calcite[30] are 1.294 (4) Å. The copper–oxygen distances lie to the high end of a range of $Cu^{II}$–O lengths of 1.88–2.04 Å found in carbonate, carboxylato, and β-diketonato complexes.[22] A recent report[31] describes the only other structurally characterized $Cu–CO_3–Cu$ system exhibiting an entirely similar bridging unit. μ-Carbonato-dichlorobis(*N*,*N*,*N′*,*N′*-tetramethyl-1,3-propanediamine)dicopper(II) has Cu–O1 = 2.153 Å, Cu–O2 = 1.978 Å, and CuO1Cu = 170.3° and is diamagnetic, with no detectable ESR spectrum at 77 K.

In all the carbonato complexes, the bridging anion is essentially planar (exactly planar in the present case), and it is observed that, when bound as a bidentate ligand, the four-membered ring formation causes the OCO angle to decrease from 120° to an average of 116°[29] (116.1 (0.6)° in $[Cu(L2)]_2CO_3^{2+}$).

**Exchange Interaction.** The points remaining for discussion are clear: the title compound exhibits a novel mode of bridging for the carbonate anion, and it also displays a magnetic property (diamagnetism as a result of exchange interaction via the bridging anion), which is very rare. A simple interpretation is immediately possible by recognizing the very nearly linear CuO1Cu (176.6 (0.2)°) arrangement in the dimeric unit. Such a geometry is considered to provide an effective route for exchange interaction, and experimental confirmation lies in the structure of the diamagnetic $[(NH_3)_5CrOCr(NH_3)]_5^{4+}$

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**Table II.** Thermal Motion Parameters ($10^3$ Å$^2$; $10^4$ Å$^2$ for Cu)

| atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Cu | 568 (5) | 589 (5) | 316 (4) | −140 (5) | 12 (9) | 12 (8) |
| O1 | 58 (5) | 56 (4) | 41 (5) | −21 (4) | 0 | 0 |
| O2 | 67 (4) | 70 (4) | 30 (3) | −22 (4) | 0 (3) | 6 (3) |
| N1 | 76 (5) | 84 (6) | 30 (4) | −23 (5) | −6 (4) | 1 (4) |
| N2 | 9 (4) | 81 (5) | 43 (4) | 5 (4) | 0 (7) | 22 (7) |
| N3 | 55 (5) | 69 (6) | 37 (4) | −1 (4) | −3 (4) | −1 (4) |
| C1 | 81 (7) | 68 (6) | 33 (7) | −1 (5) | 6 (5) | 14 (5) |
| C2 | 64 (7) | 100 (8) | 50 (6) | −15 (6) | −6 (5) | 33 (6) |
| C3 | 56 (6) | 66 (6) | 35 (5) | 5 (5) | −7 (5) | 2 (5) |
| C4 | 91 (9) | 87 (8) | 28 (5) | −17 (6) | 9 (5) | −15 (5) |
| C5 | 98 (9) | 102 (8) | 49 (6) | 13 (8) | 16 (7) | −3 (6) |
| C6 | 112 (10) | 72 (9) | 38 (7) | 22 (8) | 24 (7) | 0 (6) |
| C7 | 55 (5) | 117 (7) | 60 (6) | 3 (6) | −18 (9) | −2 (9) |
| C8 | 40 (7) | 140 (12) | 60 (7) | −9 (7) | −18 (5) | 33 (7) |
| C9 | 89 (8) | 107 (8) | 59 (9) | −66 (7) | −2 (7) | −5 (6) |
| C10 | 77 (7) | 82 (6) | 71 (7) | 24 (5) | 14 (9) | 33 (8) |
| C12 | 179 (12) | 66 (6) | 110 (12) | −9 (7) | 32 (13) | −22 (9) |
| C31 | 60 (6) | 84 (7) | 74 (7) | 0 (6) | 17 (6) | 35 (6) |
| C(N2) | 76 (10) | 104 (14) | 113 (12) | 30 (10) | 26 (9) | 20 (10) |
| C | 80 (11) | 46 (8) | 29 (8) | 4 (8) | 0 | 0 |
| O13 | 260 (5) | 285 (17) | 139 (10) | −114 (14) | 43 (11) | −115 (12) |
| O14 | 280 (2) | 241 (18) | 415 (29) | −98 (15) | −254 (23) | 122 (18) |

| atom | $U$ | atom | $U$ | atom | $U$ |
|---|---|---|---|---|---|
| O11 | 189 (12) | N | 114 (4) | C14 | 129 (21) |
| O11′ | 132 (9) | O | 153 (14) | C14′ | 127 (23) |
| O12 | 86 (5) | C13 | 174 (15) | C15 | 208 (19) |
| O12′ | 122 (8) | | | | |

**Table III.** Bond Distances (Å) and Angles (Deg) in $\{[Cu(L2)]_2CO_3\}(ClO_4)_2 \cdot HCON(CH_3)_2$

| Distances | | | |
|---|---|---|---|
| Cu–N1 | 1.978 (8) | C2–C3 | 1.49 (1) |
| Cu–N2 | 2.195 (7) | C3–C31 | 1.49 (1) |
| Cu–N3 | 1.961 (7) | C4–C5 | 1.50 (1) |
| Cu–O1 | 2.041 (1) | C5–C6 | 1.47 (1) |
| Cu–O2 | 2.028 (5) | C7–C8 | 1.49 (1) |
| N1–C1 | 1.51 (1) | C8–C9 | 1.46 (1) |
| N1–C9 | 1.49 (1) | C–O1 | 1.32 (1) |
| N2–C6 | 1.54 (1) | C–O2 | 1.27 (1) |
| N2–C7 | 1.48 (1) | N–C13 | 1.35 (4) |
| N2–C(N2) | 1.43 (1) | N–C14 | 1.59 (5) |
| N3–C3 | 1.25 (1) | N–C14′ | 1.48 (4) |
| N3–C4 | 1.47 (1) | N–C15 | 1.49 (4) |
| C1–C10 | 1.52 (1) | C15–O | 1.28 (4) |
| C1–C12 | 1.53 (1) | mean Cl–O | 1.35 |
| C1–C2 | 1.54 (1) | | |

| Angles | | | |
|---|---|---|---|
| N1CuN2 | 104.5 (0.3) | C10C1C12 | 110.9 (0.9) |
| N1CuN3 | 93.9 (0.3) | C1C2C3 | 122.1 (0.8) |
| N1CuO1 | 144.2 (0.3) | C2C3C31 | 125.3 (0.9) |
| N1CuO2 | 98.0 (0.3) | C2C3N3 | 125.3 (0.9) |
| N2CuN3 | 93.2 (0.3) | C31C3N3 | 111.4 (0.8) |
| N2CuO1 | 109.0 (0.2) | C3N3C4 | 122.1 (0.8) |
| N2CuO2 | 98.5 (0.3) | N3C4C5 | 112.1 (0.8) |
| N3CuO1 | 96.4 (0.4) | C4C5C6 | 115.4 (0.9) |
| N3CuO2 | 160.7 (0.3) | C5C6N2 | 116.6 (0.9) |
| O1CuO2 | 65.3 (0.3) | C6N2C7 | 109.7 (0.9) |
| CuN1C1 | 106.8 (0.5) | C6N2C(N2) | 108.8 (0.7) |
| CuN1C9 | 112.7 (0.5) | C(N2)N2C7 | 111 (1) |
| CuN2C(N2) | 109.5 (0.5) | N2C7C8 | 115.4 (0.9) |
| CuN2C6 | 110.5 (0.5) | C7C8C9 | 113.7 (0.9) |
| CuN2C7 | 107.4 (0.5) | C8C9N1 | 114.7 (0.8) |
| CuN3C3 | 126.3 (0.5) | O1CO2 | 116.1 (0.6) |
| CuN3C4 | 111.5 (0.5) | O2CO2′ | 127 (1) |
| CuO1C | 88.3 (0.5) | C13NC14 | 128 (2) |
| CuO2C | 90.3 (0.4) | C13NC14′ | 107 (6) |
| CuO1Cu | 176.6 (0.2) | C13NC15 | 94 (2) |
| N1C1C10 | 108.1 (0.7) | C14NC15 | 104 (2) |
| N1C1C12 | 108.6 (0.8) | C14′NC15 | 102 (2) |
| N1C1C2 | 108.9 (0.9) | NC15O | 115 (2) |
| C2C1C10 | 112.8 (0.9) | mean OClO | 109 |
| C2C1C12 | 107.4 (0.9) | | |

cation (CrOCr = 180°).[32] However, such a mechanism would ignore the possible importance of the symmetrical bidentate coordination of the carbonate anion to both metal centers.

Several studies[7–9,33] have been made which endeavor to interpret the antiferromagnetism in copper(II) complexes by considering exchange via molecular orbitals on the bridging polyatomic anions. The most applicable of these are the qualitative discussions of Hendrickson et al.[7] and the semiempirical calculations of Hoffmann et al.[9] reported for metal centers symmetrically bridged by oxalate and squarate anions. Several of the criteria determining the extent of exchange interaction, which have been identified qualitatively and given some support quantitatively, can be recognized in the present system.

The size and type of magnetic interaction are dependent on several factors: the symmetry and energies of the metal orbitals that contain the unpaired electron density, the symmetry and energies of molecular orbitals or the bridging anion, and the extent of overlap between these two systems. The existence of a symmetrically bridging ligand in $[Cu(L2)]_2CO_3^{2+}$ immediately explains the predominance of antiferromagnetic exchange: if the unpaired electron on one copper ion is delocalized onto a carbonate molecular oribtal, and because the bridging is symmetrical, the unpaired electron on the other metal ion is delocalized onto the same orbital and only an antiferromagnetic mechanism causing spin pairing is possible.

Interpreting the magnitude of the exchange coupling requires closer inspection of the metal d orbital containing the unpaired spin and its overlap with the carbonate molecular orbitals. If square-pyramidal geometry is assumed, together with the coordinate system in II, the unpaired electron density will be found in the $d_{xy}$ orbital.

From calculations on oxalate-bridged dimers,[9] it has been concluded that inspection of the highest filled ligand orbitals of the proper symmetry to interact with the metal d orbitals is all that is needed to account for the energies and symmetries of the highest, filled dimer MO's, which in turn have been shown to determine the type and extent of exchange interaction. The highest, filled carbonate MO's are the nonbonded oxygen atom lone pairs.[34]

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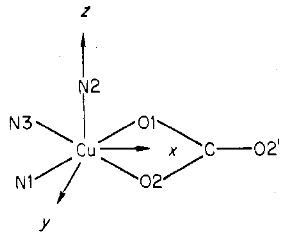
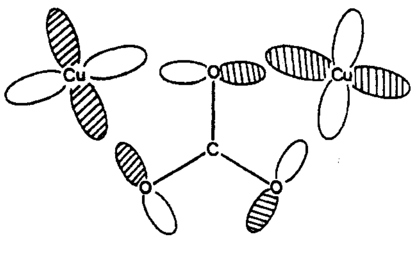


II

With these guidelines, and the geometry of the dimer, it is not a difficult task to sketch metal and carbonate orbitals which, upon overlap, would provide an effective route for strong exchange interaction (III).

It would be interesting, of course, to see if calculations of the type that were successful for the oxalate and squarate systems[9] are able not only to support the assignment above but also to give some quantitative interpretation of the observed diamagnetism resulting from exchange. Furthermore, the question as to whether consideration of the linear CuO1Cu system is sufficient to account for the diamagnetism or whether symmetrical bridging via the entire carbonate anion is the essential structural parameter will require further theoretical inspection.



III

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**Registry No.** $[[Cu(L2)]_2CO_3](ClO_4)_2 \cdot DMF$, 72784-64-6.

**Supplementary Material Available:** Listings of structure factor amplitudes and calculated hydrogen atom fractional coordinates (20 pages). Ordering information is given on any current masthead page.

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# Crystal and Molecular Structure of the Undecacoordinate Complex Pentaaquatris(nitrato)lanthanum(III) Hydrate

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The crystal and molecular structure of pentaaquatris(nitrato)lanthanum(III) hydrate, $[La(NO_3)_3(H_2O)_5] \cdot H_2O$, has been determined from 3102 reflections collected by counter methods. The complex crystallizes in the triclinic space group $P\bar{1}$ with two formula units in a cell of dimensions $a = 8.933$ (5) Å, $b = 10.723$ (4) Å, $c = 6.664$ (2) Å, $\alpha = 78.86$ (3)°, $\beta = 77.92$ (4)°, and $\gamma = 87.93$ (4)°. The structure was solved by Patterson and Fourier techniques and refined by least-squares calculations to a final conventional $R$ value of 0.038. The lanthanum atom is 11-coordinate, being bonded to three bidentate nitrate groups and five water molecules. The La–O(nitrate) and La–O(water) distances are in the ranges 2.617–2.875 and 2.526–2.668 Å, respectively. The N–O bond lengths vary between 1.219 and 1.280 Å; the shortest distances involve the noncoordinated oxygens. The sixth water molecule is outside the coordination sphere of lanthanum but participates in the network of hydrogen bonds.

## Introduction

The geometries of high-coordination polyhedra with coordination numbers (CN) exceeding 9 have not been systematically analyzed, probably because of the relatively small number of structure determinations available. There exists thus a clear need for additional X-ray studies of reasonable accuracy. A high-coordination character is likely if the central ion is large, e.g., $La^{3+}$ or $Ce^{3+}$, and the coordinating ligands are compact. The nitrate ion is a suitable ligand since, besides being relatively small, it often coordinates bidentately with a short bite. Accordingly an investigation into the nitrato complexes of trivalent lanthanum was initiated as part of a larger project concerning the structures of high-coordinate oxo complexes.[2-5]

The present paper describes the X-ray structural analysis of lanthanum nitrate hexahydrate, which is an 11-coordinate complex corresponding to the formula $[La(NO_3)_3(H_2O)_5] \cdot H_2O$.[4] According to the X-ray powder data, the cerium nitrate hexahydrate is isostructural, but the lanthanum and cerium compounds differ from the nitrate hexahydrates of the heavier lanthanoids;[6] a structural analysis carried out for the praseodymium compound has shown it to have a 10-coordinate structure $[Pr(NO_3)_3(H_2O)_4] \cdot 2H_2O$.[7]

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