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Crystal and Molecular Structure of (2-Oximino-11-oximinato-3,10-dimethyl-4,9-diazadodeca-3,9-diene)copper(II) Perchlorate

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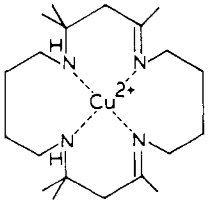
[Cu(Me$_4$OHO[15]teteneN$_4$)](ClO$_4$), (C$_{12}$H$_{21}$N$_4$O$_2$Cu)(ClO$_4$), crystallizes in the space group $P2_1/n$ with a = 6.490 (2) Å, b = 21.727 (5) Å, c = 12.398 (4) Å, β = 96.58 (3)°, and Z = 4. The structure was anisotropically refined to R_F = 0.037 and R_{wF} = 0.045 for 1445 unique reflections having intensities greater than $3\sigma(I)$. Each cupric ion is bound to four imine nitrogen atoms of one ligand and to the oximinato oxygen (O1) of an adjacent complex, forming a dimeric structure. The coordination geometry is square pyramidal distorted toward trigonal bipyramidal. The ligand is cyclic by reason of hydrogen bonding between the oxime hydrogen (on O2) and the oximinato oxygen (O1). Variable-temperature magnetic measurements between 75 and 300 K indicate that there is very little magnetic exchange between the two Cu(II) atoms of the dimer.

Introduction

The present study was undertaken as part of an investigation of the effects of large chelate rings on the geometries of copper(II) complexes. The presence of two 7-membered chelate rings in the macrocyclic complex ([5*S*(*R*),10*R*(*S*)]-2,4,4,11,11,13-hexamethyl-1,5,10,14-tetraazacyclooctadeca-1,13-diene)copper(II) perchlorate, [Cu(*cis*-[18]dieneN$_4$)](ClO$_4$)$_2$ (**1**), causes the complex to assume a geometry intermediate between square planar and tetrahedral.[1,2] the dihedral angle between the N1–Cu–N2 and N3–Cu–N4 planes in this complex is 36.6°. A structural isomer of this complex ([5*R*(*S*),14*R*(*S*)]-2,4,4,11,13,13-hexamethyl-1,5,10,14-tetraazacyclooctadeca-1,10-diene)copper(II) perchlorate, [Cu(*trans*-[18]dieneN$_4$)](ClO$_4$)$_2$, is nearly square planar.[2,3] The implication is that 7-membered chelate rings are effective in producing distortions from square-planar geometry when they involve a four-carbon bridge between imine nitrogens as in structure **2**.



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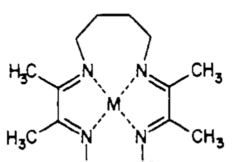

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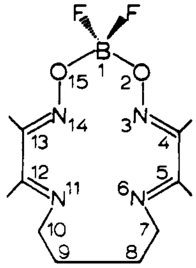
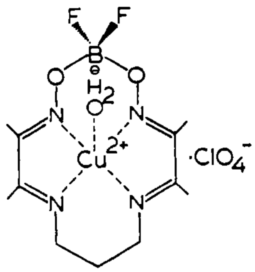
An attempt to test this hypothesis with the cupric complex of 1,1-difluoro-4,5,12,13-tetramethyl-1-bora-3,6,11,14-tetraaza-2,15-dioxacyclopentadeca-3,5,11,13-tetraenate (**3**) was unsuccessful because the copper(II) ion bound water to form a distorted pyramidal complex.[4] However, some interesting spectral differences were observed between this complex and a similar copper(II) complex of the macrocyclic ligand (1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxacyclotetondeca-3,5,10,12-tetraene (cyclops, **4**, Me$_4$F$_2$BO$_2$[14]teteneN$_4$). This latter complex also has a square-pyramidal geometry about the copper(II) ion with water in the apical position.[8]



3



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Visible spectral data for **3** with various axial ligands did not follow the usual spectrochemical series. Axial ligands which bind strongly to Cu(II) were found to pull it further from the basal nitrogen plane, reducing the crystal field splitting caused by these donors. The perturbed spectrochemical series found for **3** is different from that observed for the copper(II) complexes of the analogous 14-membered macrocycle. The differences are attributed to geometrical distortions resulting from the presence of the 7-membered ring in the 15-membered macrocycles.

Visible spectral data for the nonmacrocycle complexes (2-oximino-11-oximato-3,10-dimethyl-4,9-diazadodeca-3,9-diene)copper(II) with different anions were similar to those of the complexes of **3**. Therefore, it was of interest to determine

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[1] Martin, J. W. L.; Timmons, J. H.; Martell, A. E.; Rudolf, P.; Clearfield, A.; Willis, C. J. *J. Chem. Soc., Chem. Commun.* **1979**, 999.

[2] Timmons, J. H.; Rudolf, P.; Martell, A. E.; Martin, J. W. L.; Clearfield, A. *Inorg. Chem.* **1980**, *19*, 2331.

[3] Timmons, J. H.; Martin, J. W. L.; Rudolf, P.; Clearfield, A.; Martell, A. E. *Cryst. Struct. Commun.* **1979**, *8*, 937.

[4] Martin, J. W. L.; Timmons, J. H.; Martell, A. E.; Rudolf, P.; Clearfield, A., submitted for publication in *Inorg. Chem.*

0020-1669/81/1320-3056$01.25/0

the structure of one of them for structural comparisons. The results of such a study of the perchlorate $[Cu(Me_4OHO[15]teteneN_4)](ClO_4)$ is reported here.

Experimental Section

Dark crystals of the complex were grown slowly from a methanol/ethanol mixed solvent after preparation by previously published methods.[4] The crystal selected was roughly cylindrical with a length of 0.16 mm, the end faces having six edges with alternating lengths of 0.05 and 0.06 mm. The crystal was mounted with the glass fiber parallel to the long axis. A CAD-4 automated diffractometer with graphite-monochromated Mo $K\alpha_1$ radiation ($\lambda = 0.070930$ Å) was used to obtain intensity data. Unit cell dimensions determined from least-squares treatment of 25 reflections obtained at medium and high angles are $a = 6.480$ (2) Å, $b = 21.727$ (5) Å, $c = 12.398$ (4) Å, $\beta = 96.58$ (3)°, $V = 1737$ (2) Å^3, and $Z = 4$. The space group was determined to be $P2_1/n$ on the basis of systematic absences in the subsequently collected data: $h0l$ with $h + l = 2n + 1$ and $0k0$ with $k = 2n + 1$.

Intensity data were collected by the θ–2θ scan method. Scanning speeds ranged from approximately 20°/min for the most intense reflections to approximately 2°/min for the weakest. The angular scan width was $A + 0.347 \tan \theta_{\lambda_{\alpha 2}}$, where $\theta_{\lambda_{\alpha 2}}$ is determined from the formula

$$\theta_{\lambda_{\alpha 2}} = \theta_{\lambda_{\alpha 1}} + \frac{\lambda_{\alpha_2} - \lambda_{\alpha_1}}{\lambda_{\alpha_1}} \frac{360}{2} \tan \theta_{\lambda_{\alpha 1}}$$

and A depends on the crystal mosaic spread and on the divergence of the primary beam. A for this structure was 0.70. The scan was extended on each side of the peak by 25% for background determination. Reflections were collected up to $2\theta = 45°$. Three standard reflections scanned approximately every 150 reflections were used to place the intensity data on a common scale; systematic variation in these standards was not observed. Reflection intensities were calculated[5] from peak and background measurements as $I = S(C - RB)$ where S = scan rate, C = total integrated peak count, B = total background count, and R = the ratio of the scan time for the peak to the scan time for the background. The estimated error was calculated as $\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$; p is dependent on the diffractometer used and has a value of 0.05 in the present instance. Of 2336 reflections originally collected, 1445 unique ones with $I > 3\sigma(I)$ were used in refinement. Neutral-atom scattering factors[6] were used, and the metal atom was corrected for anomalous dispersion. Corrections for absorption were unnecessary because of the low absorption coefficient; $\mu = 15.0$.

Solution and Refinement. The copper atom position was determined by Patterson methods using three-dimensional maps. All nonhydrogen atom positions and the position of H1 (bound to O2) were determined by difference Fourier methods. Nonhydrogen atoms were refined anisotropically. Although the data/parameter ratio was low, the low R index and the small error in an observation of unit weight indicated that further data collection was unnecessary. Remaining hydrogen atom positions were calculated and included as a fixed contribution in the final cycles of least-squares refinement. Recalculation of their positions followed by refinement was continued until no further improvement in the R index resulted.

R values were calculated[5] as $R_F = [\sum(||F_o| - |F_c||)/\sum|F_o|]$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. Reflections were weighted as $w = 1/\sigma^2(F_o) = 4F_o^2/[\sigma(F_o)^2]^2$ where $\sigma(F_o)^2 = [\sigma^2(I) + (pI)^2]^{1/2}/Lp$. The function minimized was $\sum w(|F_o| - |F_c|)^2$. Final R values were $R_F = 0.037$ and $R_{wF} = 0.045$, and the error in an observation of unit weight was 1.237.

Magnetic Susceptibility Determinations. Magnetic susceptibility measurements were obtained by the Faraday method using a Cahn Model RG electrobalance and an Alfa Model 7500W electromagnet. Measurements were taken at variable field strengths from 1.5 to 8.8 kG and agreed within ●1%. Mercury(II) (tetrathiocyanato)cobaltate(II) was used as a magnetic susceptibility standard.[7]

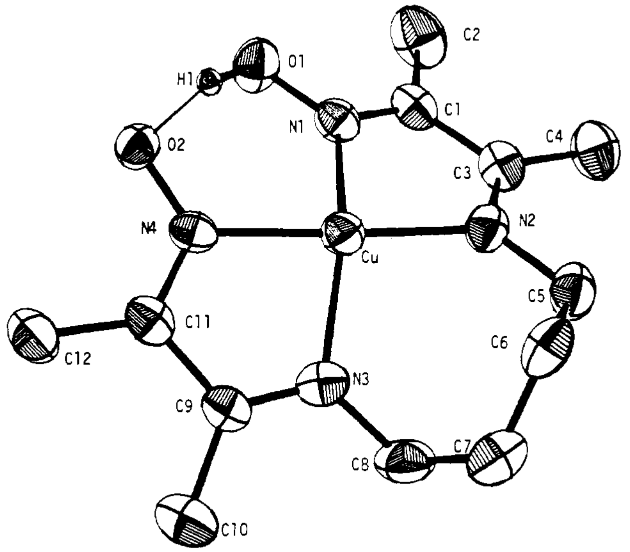

Figure 1. Perspective view of the coordination sphere about the copper(II) ion illustrating the distorted square-pyramidal geometry and the cyclic nature of the ligand resulting from the hydrogen bonding O2-H1---O1.

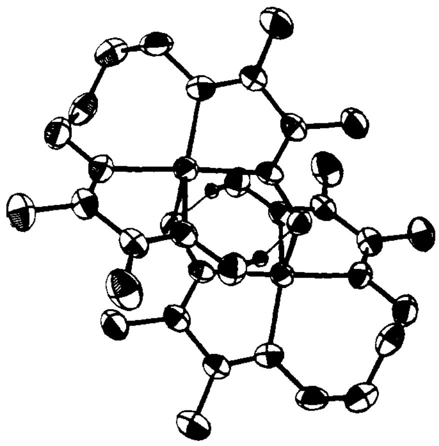

Figure 2. Perspective view of the structure of the dimeric species.

Results

The structure is dimeric with two macrocyclic complexes joined by two Cu–O1 bonds. The structure is essentially square pyramidal but is distorted somewhat toward a trigonal-bipyramidal structure. The base of the square pyramid is not planar, as indicated by the least-squares plane in Table I. The dihedral angle between N1–Cu–N2 and N3–Cu–N4 planes is 29.5°, and the angle between N2–Cu–N3 and N1–Cu–N4 plane is 31.1° (Table I). These effects must be attributed mainly to the large chelate ring, which effectively precludes planarity of the nitrogen atoms. Details of the reasons for this supposition are presented in the Discussion. Positional and thermal parameters for the atoms are given in Table II. Important bond distances and angles are given in Table III. Figure 1 illustrates the coordination sphere about the metal ion with the oxygen from the other molecule missing. A perspective view of the complete dimeric structure is provided in Figure 2.

Figure 2 indicates that Cu, O1, and N1 and Cu′, O1′, and N1′ form a 6-membered ring having a chair configuration. The Cu–Cu distance is 3.91 (1) Å. Variable-temperature magnetic susceptability measurements were performed to investigate the possibility of magnetic exchange between the

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(5) All calculations were preformed on a PDP11 computer using programs from: "Enraf-Nonius Structure Determination Package (SDP)"; Enraf-Nonius: Delft, Holland, 1975; revised, 1977.

(6) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(7) Figgis, B. N.; Nyholm, R. S. *J. Chem. Soc.* **1958**, 4190.

Table I. Least-Squares Planes through Selected Atoms

(a) Deviations from the Planes[a]

plane 1	*N1* (−0.217)	*N2* (0.201)	*N3* (−0.201)	*N4* (0.217)	Cu (−0.296)
plane 2	*N1* (0.000)	*N2* (0.000)	*Cu* (0.000)		
plane 3	*N2* (0.000)	*N3* (0.000)	*Cu* (0.000)		
plane 4	*N3* (0.000)	*N4* (0.000)	*Cu* (0.000)		
plane 5	*N4* (0.000)	*N1* (0.000)	*Cu* (0.000)		

(b) Equations of the Planes[b]

plane	A	B	C	D	χ^2
1	−0.7001	0.1919	−0.6878	−2.2463	10219
2	−0.7577	0.3813	−0.5296	−1.6918	
3	−0.8227	0.3139	−0.4740	−1.4682	
4	−0.5845	−0.0050	−0.8114	−3.2735	
5	−0.5444	0.0367	−0.8380	−3.3780	

(c) Dihedral Angles between Planes

planes	angle, deg
2–4	29.5
3–5	31.1

[a] Planes were calculated with use of the italicized atoms. All atoms were weighted equally. The number in parentheses is the distance (Å) of the atom from the plane. Esd's are ~0.003 Å. [b] The equation is of the form $AX + BY + CZ - D = 0$.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Cu	0.0076 (1)	0.03282 (3)	0.35372 (5)	0.0195 (2)	0.00120 (1)	0.00458 (4)	0.0000 (1)	0.0031 (1)	−0.00012 (5)
Cl	−0.2827 (3)	0.16759 (8)	0.0520 (1)	0.0321 (5)	0.00297 (4)	0.0068 (1)	0.0005 (3)	0.0033 (4)	−0.0004 (1)
O1	−0.2530 (5)	−0.0221 (1)	0.5024 (3)	0.0170 (9)	0.00157 (9)	0.0050 (2)	−0.0000 (5)	0.0046 (8)	−0.0000 (3)
O2	−0.2973 (6)	0.0970 (2)	0.4809 (3)	0.0222 (11)	0.00166 (9)	0.0082 (3)	0.0016 (5)	0.0109 (9)	0.0001 (3)
O3	−0.1295 (10)	0.2029 (4)	0.0126 (5)	0.0869 (23)	0.00980 (29)	0.0159 (5)	−0.0273 (13)	0.0498 (16)	−0.0080 (7)
O4	−0.3611 (9)	0.2026 (2)	0.1316 (4)	0.0611 (19)	0.00415 (16)	0.0147 (4)	−0.0086 (9)	0.0357 (14)	−0.0052 (5)
O5	−0.2053 (11)	0.1137 (3)	0.0961 (5)	0.1033 (28)	0.00527 (17)	0.0145 (6)	0.0283 (11)	−0.0212 (22)	0.0017 (5)
O6	−0.4287 (9)	0.1544 (3)	−0.0338 (5)	0.0696 (23)	0.00438 (18)	0.0183 (6)	0.0089 (11)	−0.0421 (18)	−0.0054 (5)
N1	−0.1634 (6)	−0.0306 (2)	0.4117 (3)	0.016 (1)	0.00137 (9)	0.0041 (3)	0.0010 (6)	−0.0013 (9)	−0.0006 (3)
N2	0.0237 (7)	−0.0313 (2)	0.2417 (3)	0.021 (1)	0.00166 (10)	0.0045 (3)	0.0019 (7)	0.0018 (10)	−0.0003 (3)
N3	0.1505 (7)	0.1036 (2)	0.2937 (3)	0.017 (1)	0.00171 (11)	0.0048 (3)	−0.0004 (6)	0.0024 (10)	0.0007 (3)
N4	−0.1426 (7)	0.1020 (2)	0.4151 (3)	0.017 (1)	0.00133 (10)	0.0054 (3)	0.0005 (6)	0.0010 (11)	−0.0004 (3)
C1	−0.1785 (8)	−0.0824 (2)	0.3604 (4)	0.013 (1)	0.0015 (1)	0.0060 (4)	0.0004 (7)	−0.002 (1)	−0.0006 (4)
C2	−0.2994 (9)	−0.1362 (3)	0.3929 (5)	0.026 (2)	0.0017 (1)	0.0084 (5)	−0.0031 (9)	0.005 (2)	−0.0016 (5)
C3	−0.0738 (8)	−0.0811 (2)	0.2605 (4)	0.019 (2)	0.0016 (1)	0.0051 (4)	−0.0007 (8)	−0.000 (1)	−0.0009 (4)
C4	−0.0903 (11)	−0.1365 (3)	0.1891 (6)	0.045 (2)	0.0025 (2)	0.0115 (6)	−0.0066 (11)	0.015 (2)	−0.0052 (6)
C5	0.1138 (10)	−0.0187 (3)	0.1410 (4)	0.033 (2)	0.0023 (2)	0.0039 (4)	−0.0002 (9)	0.002 (1)	−0.0012 (4)
C6	0.3477 (10)	−0.0116 (3)	0.1593 (5)	0.029 (2)	0.0029 (2)	0.0059 (4)	0.0011 (10)	0.009 (2)	−0.0004 (5)
C7	0.4294 (9)	0.0351 (3)	0.2429 (5)	0.019 (2)	0.0026 (2)	0.0070 (4)	0.0024 (9)	0.010 (1)	0.0013 (5)
C8	0.3316 (9)	0.0988 (3)	0.2323 (4)	0.022 (2)	0.0026 (2)	0.0055 (4)	−0.0036 (9)	0.002 (1)	0.0013 (5)
C9	0.0747 (8)	0.1563 (2)	0.3126 (4)	0.019 (2)	0.0015 (1)	0.0052 (4)	0.0001 (8)	−0.003 (1)	0.0015 (4)
C10	0.1499 (10)	0.2162 (3)	0.2749 (5)	0.031 (2)	0.0017 (1)	0.0089 (5)	−0.0020 (9)	0.004 (2)	0.0015 (5)
C11	−0.1025 (8)	0.1560 (2)	0.3811 (4)	0.020 (2)	0.0014 (1)	0.0059 (4)	−0.0005 (8)	−0.001 (1)	−0.0002 (4)
C12	−0.2128 (11)	0.2124 (3)	0.4106 (6)	0.032 (2)	0.0017 (1)	0.0121 (6)	0.0015 (9)	0.003 (2)	−0.0002 (5)

atom	x	y	z	atom	x	y	z
H1[b]	−0.2930 (0)	−0.0566 (0)	0.5000 (0)	H12	0.5740 (0)	0.0398 (0)	0.2384 (0)
H2	−0.3533 (0)	−0.1272 (0)	0.4592 (0)	H13	0.4091 (0)	0.0194 (0)	0.3124 (0)
H3	−0.4107 (0)	−0.1443 (0)	0.3379 (0)	H14	0.2886 (0)	0.1068 (0)	0.1579 (0)
H4	−0.2117 (0)	−0.1712 (0)	0.4020 (0)	H15	0.4321 (0)	0.1285 (0)	0.2595 (0)
H5	−0.0164 (0)	−0.1294 (0)	0.1287 (0)	H16	0.2610 (0)	0.2093 (0)	0.2327 (0)
H6	−0.0328 (0)	−0.1709 (0)	0.2292 (0)	H17	0.0398 (0)	0.2365 (0)	0.2318 (0)
H7	−0.2319 (0)	−0.1441 (0)	0.1650 (0)	H18	0.1964 (0)	0.2409 (0)	0.3359 (0)
H8	0.0557 (0)	0.0184 (0)	0.1103 (0)	H19	−0.3185 (0)	0.2014 (0)	0.4540 (0)
H9	0.0809 (0)	−0.0517 (0)	0.0918 (0)	H20	−0.1172 (0)	0.2395 (0)	0.4501 (0)
H10	0.3936 (0)	−0.0003 (0)	0.0921 (0)	H21	−0.2732 (0)	0.2322 (0)	0.3463 (0)
H11	0.4046 (0)	−0.0505 (0)	0.1815 (0)				

[a] The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$. [b] $B = 3.5000$ (0) Å^2 for all hydrogen atoms.

copper(II) ions. The results indicate that little magnetic exchange occurs. The magnetic moment (μ_{eff}) is slightly below a spin-only value and is very similar to that observed for chloro(2-oximino-11-oximinato-3,10-dimethyl-4,9-diazadodeca-3,9-diene)copper(II),[4] in which the chloride ion should occupy the apical position.

Discussion

Fortunately, the analogous oxime complex with a trimethylene rather than a tetramethylenebridge has been structurally characterized.[8] It is thus possible to determine which geometric effects are due to the large chelate ring. The five-coordinate copper(II) complex [Cu(Me$_4$OHO[14]tetene-N$_4$)(H$_2$O)]ClO$_4$·H$_2$O incorporates a nearly planar quadridentate ligand bound to a copper atom very close to the basal

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(8) Anderson, O. P.; Packard, A. B. *Inorg. Chem.* **1979**, *18*, 1940.

Table III. Bond Distances (Å) and Bond Angles (Deg) and Their Estimated Standard Deviations

	A. Bond Distances		
Cu-O1′	2.264 (3)	Cl-O3	1.387 (6)
Cu-N1	1.957 (4)	Cl-O4	1.388 (5)
Cu-N2	1.978 (4)	Cl-O4	1.364 (5)
Cu-N3	1.985 (4)	Cl-O6	1.371 (5)
Cu-N4	1.990 (5)		
O1-N1	1.336 (5)	O2-N4	1.368 (5)
N1-C1	1.291 (6)	N4-C11	1.282 (6)
C1-C2	1.488 (7)	C11-C12	1.487 (8)
C1-C3	1.480 (7)	C11-9	1.506 (7)
C3-C4	1.490 (7)	C9-C10	1.486 (7)
C3-N2	1.288 (6)	C9-N3	1.277 (6)
N2-C5	1.464 (7)	N3-C8	1.475 (7)
C5-C6	1.517 (8)	C8-C7	1.521 (8)
C6-C7	1.503 (8)		
O2-H1	0.907 (3)	O1-H1	1.730 (3)
	B. Bond Angles		
O1′-Cu-N1	90.9 (1)	N1-Cu-N3	173.0 (2)
O1′-Cu-N2	113.1 (1)	N1-Cu-N4	93.9 (2)
O1′-Cu-N3	93.3 (1)	N2-Cu-N3	102.6 (2)
O1′-Cu-N4	96.2 (2)	N2-Cu-N4	150.2 (2)
N1-Cu-N2	80.8 (2)	N3-Cu-N4	80.1 (2)
O3-Cl-O4	106.5 (4)	O4-Cl-O5	109.5 (4)
O3-Cl-O5	111.7 (5)	O4-Cl-O6	112.8 (4)
O3-Cl-O6	107.6 (4)	O5-Cl-O6	108.8 (4)
Cu-N1-O1	122.1 (3)	Cu-N4-O2	126.3 (3)
Cu-N1-C1	116.6 (4)	Cu-N4-C11	116.0 (4)
Cu-N2-C3	11.35 (3)	Cu-N3-C9	114.8 (4)
Cu-N2-C5	121.7 (3)	Cu-N3-C8	124.9 (4)
Cu-O1′-N1′	108.3 (2)		
O1-N1-C1	121.3 (4)	O2-N4-C11	117.4 (4)
N1-C1-C2	124.3 (5)	N4-C11-C12	123.5 (5)
N1-C1-Ce	112.3 (5)	N4-C11-C9	112.7 (5)
C2-C1-C3	123.3 (5)	C12-C11-C9	123.8 (5)
C1-C3-C4	118.2 (5)	C11-C9-C10	118.7 (5)
C1-C3-N2	116.7 (4)	C11-C9-N3	115.8 (5)
C4-C3-N2	125.1 (5)	C10-C9-N3	125.5 (5)
C3-N2-C5	124.3 (4)	C9-N3-C8	120.3 (5)
N2-C5-C6	112.4 (4)	Ne-C8-C7	111.7 (4)
C5-C6-C7	116.1 (5)	C8-C7-C6	116.4 (5)
N4-O2-H1	103.3 (3)	H1-O1-N1	101.6 (3)
O2-H1-O1	163.3 (4)		

coordination plane of a square pyramid.[8] The fifth coordination site is occupied by a water molecule at a normal bonding distance.[8] The structure of [Cu(Me$_4$OHO[14]teteneN$_4$)]Cl)$_4$·$^1/_2$CH$_3$OH has also been described and consists of perchlorate anions and infinite chain cations.[9] The asymmetric unit contains copper atoms bound in two different environments. About each of these copper atoms the four nitrogen atoms of the ligand Me$_4$OHO[14]teteneN$_4$ are close to planar, with deviations of up to 0.029 Å from the mean plane giving a slight tetrahedral distortion. The metal ion is at an average distance of 0.127 Å from the basal N$_4$ plane of the ligand. The structure incorporates both weak methanol bridges and stronger oxime bridges between the copper atoms which are in a distorted octahedral geometry.[9]

In contrast to the two preceding structures the four nitrogen atoms of the tetradentate ligand in [Cu(Me$_4$OHO[15]teteneN$_4$)](ClO$_4$) are not coplanar as shown by the large deviations from the least-squares plane (plane 1, Table I) through them. This large distortion appears to be due largely to the presence of the tetramethylene linkage between imino donor-nitrogen atoms of the ligand. A similar, though smaller, tetrahedral distortion is observed in the structure of the macrocyclic complex [Cu(Me$_2$F$_2$BO$_2$[15]teteneN$_4$)(H$_2$O)](ClO$_4$),[4] whereas

Table IV. Magnetic Data on Some Copper(II)-Oxime Complexes

compd	μ_{eff}, μ_B (room temp)	μ_{eff}, μ_B (*T*, K)
[Cu(Me$_4$OHO[15]teteneN$_4$)](ClO$_4$)[a]	1.74	1.68 (73)
[Cu(Me$_4$OHO[15]teteneN$_4$)]Cl[b]	1.74	1.66 (73)
Cu(L)(ClO$_4$)·$^1/_2$CH$_3$OH[c]	1.77	1.71 (93)
Cu(LH$_2$)(ClO$_4$)$_2$[d]	1.87	1.92 (93)
Cu(DMG)Cl$_2$[e]	1.85	1.84 (90)

[a] Calculated with $\chi_L = -1.752 \times 10^{-4}$ cgsu. [b] Calculated with $\chi_L = -1.692 \times 10^{-4}$ cgsu. [c] Reference 9. [d] Reference 10. [e] Reference 14.

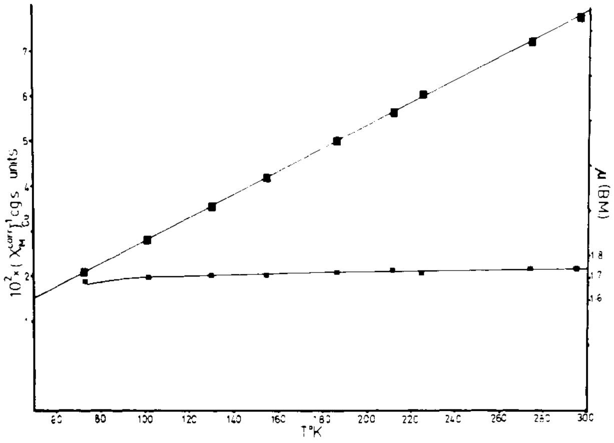

Figure 3. Effective magnetic moment (and the inverse of magnetic susceptibility) as a function of temperature for [Cu(Me$_4$OHO[15]teteneN$_4$)](ClO$_4$). The solid line obeys the Curie–Weiss relationship with $\Theta = -8.6$ K.

the four nitrogen donor atoms of the macrocyclic ligand in the complex [Cu(Me$_2$F$_2$BO$_2$[14]teteneN$_4$)(H$_2$O)](ClO$_4$) are again essentially planar.[8]

The greater degree of tetrahedral distortion of the N$_4$ plane in [Cu(Me$_4$OHO[15]teteneN$_4$)](ClO$_4$) compared to that in [Cu(Me$_2$F$_2$BO$_2$[15]teteneN$_4$)(H$_2$O)]ClO$_4$ is reasonable since the nonmacrocyclic ligand has greater flexibility. The distance between the O1 oximinato and O2 oximino atoms of the ligand in [Cu(Me$_4$OHO[15]teteneN$_4$)](ClO$_4$) is quite long at 2.613 Å compared to the analogous distance of 2.49 Å in the complex [Cu(Me$_4$OHO[14]teteneN$_4$)(H$_2$O)](ClO$_4$).[8] The increase in this distance can be explained in terms of twisting the ligand about the metal and in terms of the greater mean metal–nitrogen distance (1.98 Å compared to 1.94 Å) within the [Cu(Me$_4$OHO[15]teteneN$_4$)](ClO$_4$) complex. The magnetic results for the complex [Cu(Me$_4$OHO[15]teteneN$_4$)](ClO$_4$) and the complex [Cu(Me$_4$OHO[15]teteneN$_4$)Cl] are given in Table IV and shown by comparison to be very similar and characteristic of complexes in which very weak coupling occurs between adjacent copper(II) ions. Both of the complexes [Cu(Me$_4$OHO[15]teteneN$_4$)](ClO$_4$) and [Cu(Me$_4$OHO-[15]teteneN$_4$) give very good fits to the Curie–Weiss relationship over the 75–300 K range with Weiss constant values of −8.6 and −11.1°, respectively. Plots of $1/\chi_m$ and μ_{eff}, respectively, vs. temperature are given in Figure 3 for the complex [Cu(Me$_4$OHO[15]teteneN$_4$)]ClO$_4$.

The Cu-O1′ distance in the oxime-bridged complex [Cu(Me$_4$OHO[15]teteneN$_4$)](ClO$_4$) is quite long at 2.26 Å and is in the range observed for a number of weakly bridged copper(II) oxime dimers which have "normal" magnetic moments at room temperature.[9-11] The oxime bridging in

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$[Cu(Me_4OHO[15]teteneN_4)](ClO_4)$ is very similar to that observed in tetrakis(*N,N'*-dimethyl glyoximato)dicopper(II)[12,13] which shows evidence of weak antiferromagnetic exchange[11] at low temperatures (5–50 K). Further investigations on the effect of 7-membered and larger chelate rings on the coordination geometry and physical and chemical properties of copper(II) complexes are currently in progress.

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Registry No. $[Cu(Me_4OHO[15]teteneN_4)](ClO_4)$, 78149-30-1.

Supplementary Material Available: Tables of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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A Methylene-Bridged Metal–Metal Bond: Neutron Diffraction Study of $(\mu\text{-}CH_2)[(\eta^5\text{-}C_5H_5)Rh(CO)]_2$ at 15 K[1]

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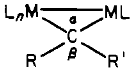
A low-temperature neutron diffraction study of $(\mu\text{-}CH_2)[(\eta^5\text{-}C_5H_5)Rh(CO)]_2$ has been carried out in order to determine the geometry of the bridging methylene group with high precision. The mean methylene C–H bond distance is found to be 1.095 (1) Å, and the H–C–H angle of 110.4 (1)° lies near the tetrahedral value. The dihedral angle between the CH_2 and Rh_2C planes is 84.1°. The cyclopentadienyl ligands are slightly distorted from an ideal pentagonal shape, reflecting the influence of the coordination about rhodium on the five-membered rings. There is no systematic displacement of the hydrogen atoms from the planes of the rings, with respect to the rhodium atom positions. Crystallographic data: space group $P\bar{1}$, $Z = 2$, $a = 7.857$ (2) Å, $b = 8.914$ (2) Å, $c = 9.319$ (2) Å, $\alpha = 74.21$ (2)°, $\beta = 81.25$ (1)°, $\gamma = 82.56$ (2)°, $T = 15$ K. The final unweighted R value based on F^2 for 3054 reflections ($(\sin\theta)/\lambda < 0.70$ Å^{-1}) is 0.036.

Introduction

Over the past 15 years, a tremendously rich chemistry has developed involving metal–carbene complexes,[5] and such complexes have been postulated as intermediates in many catalytic reaction sequences.[6] Recently, a series of novel μ-methylene complexes having structures of the type **1** has



1

been prepared and characterized.[7,8] Binuclear complexes with two[9] and three[9,10] bridging methylene groups as well as one with a single bridging methylene and two carbonyls[11] are now known, as are triosmium cluster systems with an Os–Os bond bridged by a hydride and a methylene ligand[12–14] or the dipolar $^-CH(CH_2)(P^+Me_2Ph)$.[15–17] The methylene carbon atom of the bridging ligand in **1** is highly distorted from tetrahedral geometry; a recent survey of structural parameters determined by X-ray diffraction for such compounds has indicated that

Table I. Experimental Details and Refinement Parameters

cryst wt	4.165 mg
cryst vol	2.012 mm^3 (approximately $0.5 \times 1.0 \times 4.0$ mm)
cryst boundary faces	{100}, {001}, {011}
calcd transmission range	0.832–0.910
no. of reflctns measd	3684
no. of independent reflectns (m)	3054
agreement factor for averaging	
$R_c = \Sigma\sum_{i=1}^{n'} \lvert\langle F_o^2\rangle - F_{oi}^2\rvert / \Sigma n'\langle F_o^2\rangle$	0.039
$R(F^2) = \Sigma\lvert F_o^2 - k^2F_c^2\rvert/\Sigma F_o^2$	0.036
$R_w(F^2) = [\Sigma w(F_o^2 - k^2F_c^2)^2/\Sigma wF_o^4]^{1/2}$	0.038
$S = [\Sigma w(F_o^2 - k^2F_c^2)^2/k^4(m-n)]^{1/2}$	1.24
no. of variable parameters (n)	263

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[1] Research carried out at Brookhaven National Laboratory under contract with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences.
[2] Brookhaven National Laboratory.
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[4] Karl-Winnacker Scholarship Recipient, 1979–1984.
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