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Copper(II) Complexes with Bridging Oxime Groups. 2. Structure and Properties of a Complex of a Tetradentate Dioxime–Diimine Ligand[1]

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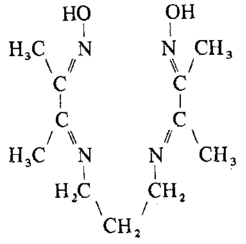
The structure has been determined by a single-crystal x-ray diffraction study for the copper(II) complex of the anion of 3,9-dimethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioxime (represented L in formulas). The structure of the compound $Cu(L)(ClO_4)\cdot{}^1/_2CH_3OH$ consists of perchlorate anions and infinite-chain anions. Each copper atom is coordinated to a tetradentate ligand through four coplanar nitrogen atoms (Cu–N distances range from 1.937 to 1.961 Å) and each copper atom is also coordinated to an oxime oxygen of the adjacent unit (Cu–O distances of 2.491 and 2.493 Å) to form singly bridged, zigzag chains. The methanol molecules are also weakly coordinated in axial positions of half of the copper atoms. Crystal data are as follows: space group $P\bar{1}$; $Z = 4$ formula units; $a = 6.897$ (3), $b = 12.023$ (4), and $c = 22.646$ (7) Å; $\alpha = 100.81$ (3), $\beta = 98.69$ (3), and $\gamma = 106.73$ (3)°; $\rho_{calcd} = 1.61$ and $\rho_{obsd} = 1.60$ (2) g cm^{-3}; $R = 0.060$ and $R_w = 0.068$ for 4383 reflections with $I \geq 3\sigma(I)$.

Introduction

In reviewing polynuclear complexes of first-row transition metal ions with oxime groups as bridging ligands, it was noted that some of the copper(II) complexes contained relatively weak bridges. Although the M–O distances in some of the oxime-bridged complexes are in the 1.9–2.0-Å range,[2-4] the Cu–O distances for the weakly bound compounds are 2.13[5] and 2.30 Å;[6,7] in the weakly bound compounds, only one of each ligand's two oxime groups is deprotonated and the bridging oxime groups also serve as hydrogen-bond acceptors for intramolecular hydrogen bonding. These compounds can be thought of as four-coordinate monomers joined into dimers by weak Cu–O interactions. It is of interest that these compounds exhibit normal magnetic moments[5-8] at room temperature while the other oxime-bridged copper(II) complexes show antiferromagnetic coupling and have greatly reduced magnetic moments at room temperature.[2-4]

It is also interesting that the structure[9,10] of the nickel(II) complex of dimethylglyoxime does not show bridging oxime groups like the copper(II) complex; although the monomeric units in the two structures are very similar, the nickel(II) complexes stack in such a way as to give short nickel–nickel distances (3.245 Å) within an infinite chain.

In order to reach a better understanding of the relationship between structures and properties of oxime-bridged complexes, we have prepared and studied copper(II) complexes with tetradentate ligands that would be expected to form stable four-coordinate complexes. One of the ligands investigated was 3,9-dimethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioxime, I, which results from the condensation of 1 mol of 1,3-diaminopropane with 2 mol of 2,3-butanedione monoxime. Crystals of a copper(II) complex of I, $Cu(L)(ClO_4)\cdot{}^1/_2CH_3OH$, have been investigated and found to contain infinite chains of complexes connected by weak oxime bridges; the preparation and crystal structure of that compound are reported in this paper.



I

Experimental Section

Preparation of $Cu(L)(ClO_4)\cdot{}^1/_2CH_3OH$. Ten millimoles of 1,3-diaminopropane was added slowly to 20 mmol of diacetyl monoxime in 25 mL of methanol. This mixture was stirred and refluxed for 1 h. To this hot solution was slowly added with rapid stirring 10 mmol of cupric perchlorate hexahydrate. After partial evaporation of the methanol, cooling the solution yielded wine red prisms. Anal. Calcd for $Cu(C_{11}H_{19}N_4O_2)(ClO_4)\cdot{}^1/_2CH_3OH$: C, 33.00; H, 5.03; N, 13.38; Cl, 8.48. Found: C, 32.48; H, 4.98; N, 13.79; Cl, 8.63.

Magnetic Studies. The magnetic susceptibility of the complex was obtained at 93 and 298 K by the Faraday method. The system was calibrated with $Hg(Co(SCN)_4)$ and corrected for the diamagnetism of the quartz bucket. Values for the diamagnetic correction were taken from Figgis and Lewis.[11] Values of 1.71 and 1.77 μ_B/g-atom of copper were obtained at 93 and 298 K, respectively.

Crystallographic Data Collection. A wine red crystal with approximate dimensions 0.3 × 0.3 × 0.6 mm was mounted on a glass fiber using epoxy cement such that the longest crystal dimension (c axis) was approximately parallel to the fiber axis.

Unit cell parameters and the orientation matrix were determined on a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochromator (Bragg 2θ angle 12.2°) using Mo Kα radiation at a takeoff angle of 6.5°. Fifteen reflections whose 2θ values ranged from 25.3 to 10.7° were machine-centered and used in least-squares refinement of the lattice parameters and orientation matrix. Unit cell parameters obtained were[12] $a = 6.897$ (3) Å, $b = 12.023$ (4) Å, $c = 22.646$ (7) Å, $\alpha = 100.81$ (3)°, $\beta = 98.69$ (3)°, $\gamma = 106.73$ (3)°, and $V = 1724$ (1) Å^3. The triclinic space group $P\bar{1}$ was assumed and the successful refinement of the structure has confirmed this choice. The calculated density of 1.61 g cm^{-3} for 4 formula units per unit cell agrees with the experimental density of 1.60 g cm^{-3} measured by the flotation method using a mixture of carbon tetrachloride and 1,2-dibromo-1,1-dichloroethane. From ω scans of several low 2θ angle reflections, peak widths at half-height of less than 0.25° indicated a satisfactory mosaic spread for the crystal.

Intensity data were collected using θ–2θ scans with x-ray source and monochromator settings identical with those used for determination of the unit cell parameters. A variable scan rate from 5.0 to 29.3° min^{-1} was used and a scan width of 2° was sufficient to collect all of the peak intensity. Stationary background counts were measured at the beginning (bgd1) and at the end (bgd2) of each scan with the total background time equal to scan time. No significant fluctuations were observed in the intensities of three standard reflections (0,3,–5; 1,4,–1; 2,2,–4) monitored every 100 reflections. Intensities were calculated by subtracting the background counts from total scan counts (CT)

$$I = \mathrm{CT} - (\mathrm{bgd1} + \mathrm{bgd2})$$

The intensities were assigned standard deviations according to the formula

$$\sigma(I) = [\mathrm{CT} + (\mathrm{bgd1} + \mathrm{bgd2})]^{1/2}$$

From a total of 6291 reflections collected in a complete hemisphere ($\pm h, \pm k, +l$) of data out to $2\theta = 50°$, 4383 were accepted as statistically above background on the basis that I was greater than $3\sigma(I)$. Lorentz and polarization corrections were made in the usual way.

The ten crystal faces were identified by optical means as the following (perpendicular distances in millimeters from the crystal

Table I. Final Positional and Thermal Parameters[a] for $Cu(L)(ClO_4)\cdot{}^1/_2CH_3OH$

Unit A

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.3876 (1)	−0.4115 (1)	0.2558 (1)	0.0275 (2)	0.0098 (1)	0.0016 (1)	0.0094 (1)	0.0021 (1)	0.0014 (1)
Cl	0.1634 (3)	−0.2596 (2)	−0.0692 (1)	0.0392 (6)	0.0100 (2)	0.0028 (1)	0.0060 (3)	0.0031 (1)	0.0009 (1)
O1	0.0904 (6)	−0.2890 (4)	0.2280 (2)	0.0210 (11)	0.0086 (4)	0.0020 (1)	0.0099 (6)	0.0023 (3)	0.0011 (1)
N1	0.2108 (7)	−0.3490 (4)	0.2053 (2)	0.0250 (12)	0.0070 (4)	0.0014 (1)	0.0050 (6)	0.0014 (3)	0.0008 (2)
N2	0.4476 (7)	−0.4685 (4)	0.1765 (2)	0.0231 (12)	0.0077 (5)	0.0019 (1)	0.0059 (6)	0.0021 (3)	0.0004 (2)
N3	0.5376 (7)	−0.4876 (4)	0.3073 (2)	0.0226 (13)	0.0075 (5)	0.0028 (1)	0.0063 (6)	0.0016 (3)	0.0018 (2)
N4	0.2896 (7)	−0.3754 (4)	0.3305 (2)	0.0229 (12)	0.0072 (4)	0.0017 (1)	0.0050 (6)	0.0016 (3)	0.0010 (2)
C1	0.0727 (12)	−0.3407 (7)	0.1101 (2)	0.0458 (24)	0.0131 (8)	0.0018 (1)	0.0119 (11)	0.0009 (5)	0.0015 (3)
C2	0.2060 (8)	−0.3734 (5)	0.1474 (2)	0.0224 (15)	0.0062 (5)	0.0018 (1)	0.0026 (7)	0.0010 (3)	0.0008 (2)
C3	0.3511 (9)	−0.4425 (5)	0.1319 (3)	0.0240 (15)	0.0064 (5)	0.0018 (1)	0.0022 (7)	0.0023 (4)	0.0001 (2)
C4	0.3698 (13)	−0.4719 (8)	0.0663 (3)	0.0445 (24)	0.0157 (9)	0.0016 (1)	0.0116 (12)	0.0030 (5)	0.0006 (3)
C5	0.5925 (10)	−0.5349 (7)	0.1707 (3)	0.0299 (19)	0.0121 (8)	0.0030 (2)	0.0096 (10)	0.0035 (5)	0.0008 (3)
C6	0.5859 (15)	−0.6125 (8)	0.2148 (5)	0.0511 (30)	0.0134 (10)	0.0045 (3)	0.0158 (14)	0.0054 (7)	0.0019 (4)
C7	0.6712 (11)	−0.5515 (7)	0.2829 (3)	0.0480 (26)	0.0153 (9)	0.0020 (2)	0.0109 (12)	0.0035 (5)	0.0025 (3)
C8	0.5859 (14)	−0.5351 (9)	0.4087 (4)	0.0377 (20)	0.0116 (7)	0.0031 (2)	0.0114 (10)	0.0027 (5)	0.0020 (3)
C9	0.5017 (9)	−0.4804 (5)	0.3613 (3)	0.0498 (28)	0.0177 (11)	0.0031 (2)	0.0160 (14)	0.0025 (6)	0.0042 (4)
C10	0.3582 (9)	−0.4121 (5)	0.3763 (2)	0.0238 (15)	0.0075 (6)	0.0021 (1)	0.0033 (7)	0.0007 (4)	0.0016 (2)
C11	0.3016 (13)	−0.3908 (8)	0.4372 (3)	0.0279 (16)	0.0067 (5)	0.0016 (1)	0.0031 (7)	0.0010 (3)	0.0011 (2)
O3	0.270 (2)	−0.189 (1)	−0.101 (1)	0.101 (1)	0.023 (1)	0.007 (1)	0.000 (2)	0.014 (1)	0.005 (1)
O4	0.035 (2)	−0.350 (1)	−0.113 (1)	0.100 (5)	0.030 (2)	0.010 (1)	−0.017 (3)	0.009 (2)	−0.001 (1)
O5	0.084 (3)	−0.208 (1)	−0.027 (1)	0.222 (11)	0.034 (2)	0.009 (1)	0.066 (4)	0.033 (2)	0.009 (1)
O6	0.247 (3)	−0.334 (2)	−0.046 (1)	0.245 (13)	0.055 (3)	0.007 (1)	0.099 (6)	0.020 (2)	0.011 (1)
O(sol)	0.089 (2)	−0.618 (1)	0.228 (1)	0.035 (3)	0.015 (1)	0.003 (1)	−0.000 (1)	0.000 (1)	0.002 (1)
C(sol)	0.063 (2)	0.289 (2)	0.256 (1)	0.034 (5)	0.013 (2)	0.005 (1)	0.005 (2)	0.001 (1)	0.004 (1)

Atom	x	y	z	Atom	x	y	z
H5A	0.61	−0.58	0.13	H6B	0.42	−0.70	0.21
H5B	0.73	−0.48	0.18	H7A	0.82	−0.48	0.29
H6A	0.67	−0.68	0.20	H7B	0.70	−0.60	0.31

Unit B

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.0433 (1)	−0.0884 (1)	0.2442 (1)	0.0187 (2)	0.0098 (1)	0.0016 (1)	0.0016 (1)	0.0011 (1)	0.0014 (1)
Cl	0.0078 (3)	0.2404 (2)	0.4308 (1)	0.0358 (5)	0.0099 (2)	0.0028 (1)	0.0047 (3)	0.0008 (1)	0.0009 (1)
O1	−0.3486 (6)	−0.2109 (4)	0.2720 (2)	0.0200 (10)	0.0200 (4)	0.0021 (1)	0.0004 (5)	0.0013 (2)	0.0012 (2)
O2	−0.3695 (6)	−0.1895 (4)	0.1645 (2)	0.0210 (10)	0.0106 (4)	0.0023 (1)	0.0002 (5)	0.0004 (2)	0.0017 (2)
N1	−0.1456 (7)	−0.1507 (4)	0.2947 (2)	0.0217 (12)	0.0072 (4)	0.0015 (1)	0.0028 (6)	0.0009 (3)	0.0008 (2)
N2	0.2385 (6)	−0.0314 (4)	0.3237 (2)	0.0181 (11)	0.0079 (5)	0.0019 (1)	0.0026 (6)	0.0006 (3)	0.0004 (2)
N3	0.2182 (7)	−0.0124 (4)	0.1927 (2)	0.0202 (12)	0.0076 (5)	0.0028 (1)	0.0031 (6)	0.0030 (3)	0.0018 (2)
N4	−0.1652 (7)	−0.1242 (4)	0.1693 (2)	0.0221 (12)	0.0075 (4)	0.0017 (1)	0.0036 (6)	0.0015 (3)	0.0012 (2)
C1	−0.1874 (12)	−0.1595 (7)	0.3996 (3)	0.0392 (22)	0.0128 (8)	0.0019 (2)	0.0024 (10)	0.0034 (5)	0.0015 (3)
C2	−0.0679 (8)	−0.1265 (5)	0.3526 (2)	0.0253 (15)	0.0065 (5)	0.0017 (1)	0.0051 (7)	0.0019 (3)	0.0010 (2)
C3	0.1614 (8)	−0.0573 (5)	0.3683 (3)	0.0232 (15)	0.0070 (5)	0.0017 (1)	0.0041 (7)	0.0000 (3)	0.0003 (2)
C4	0.2751 (11)	−0.0286 (8)	0.4337 (3)	0.0351 (21)	0.0150 (9)	0.0016 (1)	0.0052 (11)	−0.0005 (41)	0.0007 (3)
C5	0.4572 (10)	0.0361 (7)	0.3296 (3)	0.0213 (16)	0.0123 (8)	0.0028 (2)	0.0028 (9)	0.0011 (4)	0.0008 (3)
C6	0.4846 (12)	0.1120 (9)	0.2856 (5)	0.0270 (21)	0.0161 (11)	0.0044 (3)	0.0000 (11)	0.0010 (6)	0.0027 (5)
C7	0.4400 (10)	0.0507 (7)	0.2166 (4)	0.0243 (18)	0.0112 (7)	0.0034 (2)	0.0026 (9)	0.0022 (5)	0.0024 (3)
C8	0.2124 (13)	0.0343 (9)	0.0911 (4)	0.0423 (25)	0.0180 (11)	0.0030 (2)	0.0058 (13)	0.0047 (6)	0.0040 (4)
C9	0.1210 (9)	−0.0194 (5)	0.1387 (3)	0.0299 (17)	0.0074 (6)	0.0021 (1)	0.0058 (8)	0.0033 (4)	0.0016 (2)
C10	−0.1066 (9)	−0.0877 (5)	0.1239 (3)	0.0292 (17)	0.0065 (5)	0.0017 (1)	0.0045 (7)	0.0018 (4)	0.0011 (2)
C11	−0.2448 (12)	−0.1092 (8)	0.0627 (3)	0.0434 (24)	0.0147 (9)	0.0020 (2)	0.0065 (12)	0.0010 (5)	0.0025 (3)
O3	−0.058 (2)	0.312 (1)	0.399 (1)	0.113 (5)	0.023 (1)	0.008 (1)	0.029 (2)	−0.002 (1)	0.004 (1)
O4	0.001 (3)	0.150 (1)	0.386 (1)	0.146 (8)	0.027 (2)	0.011 (1)	0.040 (3)	0.002 (2)	−0.001 (1)
O5	0.182 (2)	0.290 (1)	0.473 (1)	0.087 (4)	0.034 (2)	0.010 (1)	−0.023 (2)	−0.015 (1)	0.009 (1)
O6	−0.125 (2)	0.163 (2)	0.453 (1)	0.084 (5)	0.055 (3)	0.008 (1)	−0.034 (3)	−0.003 (1)	0.011 (1)
O(sol)	−0.022 (2)	0.118 (1)	0.272 (1)	0.057 (4)	0.017 (1)	0.003 (1)	0.019 (3)	0.006 (1)	0.002 (1)
C(sol)	0.018 (3)	0.215 (2)	0.244 (1)	0.049 (6)	0.014 (2)	0.004 (1)	0.013 (3)	0.008 (1)	0.005 (1)

Atom	x	y	z	Atom	x	y	z
H5A	0.55	0.08	0.37	H6B	0.66	0.18	0.30
H5B	0.52	0.00	0.31	H7A	0.51	−0.02	0.22
H5A	0.39	0.18	0.30	H7B	0.48	0.12	0.20

[a] For hydrogen atoms $B_{\text{iso}} = 5.0$ A^2.

center to the faces are given in parentheses): $\{\bar{1}\bar{1}0\}$ (1.67), $\{011\}$ (0.164), $\{0\bar{1}1\}$ (0.181), $\{1\bar{2}\bar{1}\}$ (0.127), $\{001\}$ (0.322). Absorption corrections were calculated by the Gaussian quadrature method;[13] corrections to F^2 ranged from 1.20 to 1.40.

Solution and Refinement of Structure. All computations were carried out on a CDC Cyber 70/74 computer. Programs used include Zalkin's FORDAP Fourier summation program, Ibers' NUCLS5 modification of the Busing–Martin–Levy ORFLS full-matrix least-squares program, the Busing–Martin–Levy ORFFE function and error program, Johnson's ORTEPII plotting program, Stewart's ABSORB absorption correction program from the X-ray 72 system, the software package for the Syntex $P2_1$ diffractometer, and the various locally written programs.

In structure factor calculations, the scattering factors for all atoms except hydrogen were taken from Cromer and Waber's tabulation;[14] Stewart's hydrogen atom scattering factors were used.[15] In all cases, neutral-atom scattering factors were used. The scattering factors of the copper and chlorine atoms were corrected for the real and imaginary anomalous dispersion components using the dispersion factors

Table II. Selected Interatomic Distances (Å) and Angles (deg) of $Cu(L)(ClO_4)\cdot{}^1/_2CH_3OH$

Distances			Angles		
Atoms	Unit A	Unit B	Atoms	Unit A	Unit B
Cu-N1	1.947 (5)	1.944 (5)	N1-Cu-N2	81.6 (2)	81.4 (2)
Cu-N2	1.947 (5)	1.949 (5)	N2-Cu-N3	100.2 (2)	100.5 (2)
Cu-N3	1.961 (5)	1.960 (5)	N3-Cu-N4	80.6 (2)	80.4 (2)
Cu-N4	1.937 (5)	1.940 (5)	N4-Cu-N1	96.7 (2)	96.8 (2)
Cu-O1′	2.493 (4)	2.491 (4)	O1′-Cu-N1	84.4 (2)	84.5 (2)
Cu-O(sol)	2.624 (10)	2.625 (11)	O1′-Cu-N2	91.8 (2)	91.9 (2)
N1-O1	1.344 (6)	1.345 (6)	O1′-Cu-N3	101.5 (2)	101.5 (2)
N4-O2	1.369 (6)	1.373 (6)	O1′-Cu-N4	96.4 (2)	96.6 (2)
C2-N1	1.282 (7)	1.282 (7)	O1-N1-C2	120.6 (4)	120.8 (4)
C10-N4	1.280 (7)	1.267 (7)	O1-N1-Cu	123.2 (3)	123.1 (3)
C3-N2	1.263 (7)	1.259 (7)	Cu-N1-C2	116.1 (4)	116.0 (4)
C4-N3	1.277 (8)	1.278 (8)	N1-C2-C1	125.0 (5)	124.7 (5)
C5-N2	1.454 (8)	1.465 (8)	N1-C2-C3	111.8 (5)	112.2 (5)
C7-N3	1.465 (8)	1.461 (8)	C1-C2-C3	123.2 (5)	123.1 (5)
C1-C2	1.487 (8)	1.487 (8)	C2-C3-C4	117.8 (5)	118.1 (5)
C10-C11	1.485 (9)	1.491 (9)	C2-C3-N2	116.1 (5)	115.6 (5)
C2-C3	1.513 (8)	1.510 (8)	C4-C3-N2	126.2 (5)	126.4 (5)
C9-C10	1.496 (9)	1.500 (9)	C3-N2-Cu	114.3 (4)	114.8 (4)
C3-C4	1.497 (9)	1.493 (8)	C3-N2-C5	124.0 (5)	123.8 (5)
C8-C9	1.490 (9)	1.487 (9)	Cu-N2-C5	121.6 (4)	121.4 (4)
C(sol)-O(sol)	1.368 (20)	1.412 (20)	N2-C5-C6	111.7 (6)	111.9 (5)
CuA-CuB	5.129 (4)		C5-C6-C7	117.8 (7)	118.3 (8)
CuA-CuB′	5.122 (4)		C6-C7-N3	111.1 (6)	110.8 (6)
Cl-O3	1.349 (8)	1.342 (8)	C7-N3-C8	95.0 (4)	95.0 (4)
Cl-O4	1.311 (13)	1.326 (13)	C7-N3-Cu	121.1 (4)	121.2 (4)
Cl-O5	1.323 (9)	1.313 (9)	Cu-N3-C9	114.7 (4)	114.6 (4)
Cl-O6	1.349 (10)	1.340 (9)	N3-C9-C8	126.0 (6)	126.2 (6)
			N3-C9-C10	115.3 (5)	115.2 (5)
			C8-C9-C10	118.6 (6)	118.6 (5)
			C9-C10-C11	123.6 (5)	123.2 (5)
			C9-C10-N4	111.9 (5)	112.0 (5)
			C11-C10-N4	124.5 (6)	124.8 (5)
			C10-N4-Cu	117.4 (4)	117.7 (4)
			C10-N4-O2	119.4 (4)	119.6 (4)
			Cu-N4-O2	123.1 (3)	122.6 (3)
			Cu′-O1-N1	141.7 (3)	141.7 (3)
			O(sol)-Cu-N1	89.7 (3)	89.3 (3)
			O(sol)-Cu-N2	85.1 (3)	85.0 (3)
			O(sol)-Cu-N3	84.5 (3)	84.8 (3)
			O(sol)-Cu-N4	86.4 (3)	86.3 (3)
			O3-Cl-O4	102.4 (9)	102.1 (9)
			O3-Cl-O5	116.9 (8)	116.8 (8)
			O3-Cl-O6	119.1 (10)	120.4 (10)
			O4-Cl-O5	117.5 (11)	117.0 (11)
			O4-Cl-O6	90.7 (12)	89.1 (12)
			O5-Cl-O6	107.7 (8)	108.2 (7)
			O(sol)-Cu-O1	173.7 (2)	173.4 (3)
			C(sol)-O(sol)-Cu	130.1 (9)	130.6

tabulated by Cromer.[16] The agreement factors are defined in the usual way as

$$R = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$$

and

$$R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$$

In all least-squares refinements, the quantity minimized was $\sum(|F_o| - |F_c|)^2$.

Two sets of copper atoms were located from a three-dimensional Patterson synthesis and a structure factor calculation based on the copper atoms gave $R = 0.46$. All nonhydrogen atoms except solvent molecules and perchlorate oxygens were located in a difference Fourier map and included in structure factor calculations; R was equal to 0.19. Introduction of the perchlorate oxygens and refinement of anisotropic thermal parameters for 12 atoms lowered R to 0.11. Final refinement, including two solvent molecules with multipliers of 0.5, 12 hydrogen atoms in fixed positions, and anisotropic thermal parameters for all nonhydrogen atoms gave $R = 0.060$ and $R_w = 0.068$.

Residual electron density was observed in the vicinity of solvent molecules and C6. The largest shift in the final refinement was 2.7 standard deviations for the z coordinate of the methanol carbon in unit B.

Final atomic positional and thermal parameters are listed in Table I, selected interatomic distances and angles are in Table II, and least-squares planes of the two molecular units of $Cu(L)(ClO_4)\cdot{}^1/_2CH_3OH$ are in Table III. An illustration of the monomeric unit appears in Figure 1 and a stereoview of the polynuclear chains appears in Figure 2. A table of calculated and observed structure factor

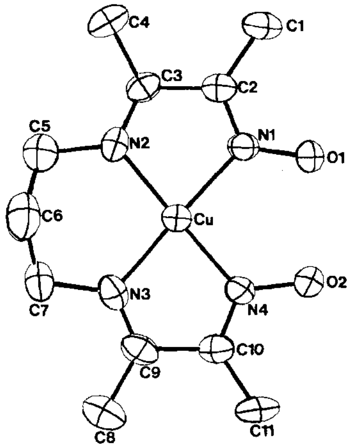


Figure 1. Monomeric unit of CuL^+ showing the numbering system for ligand atoms.

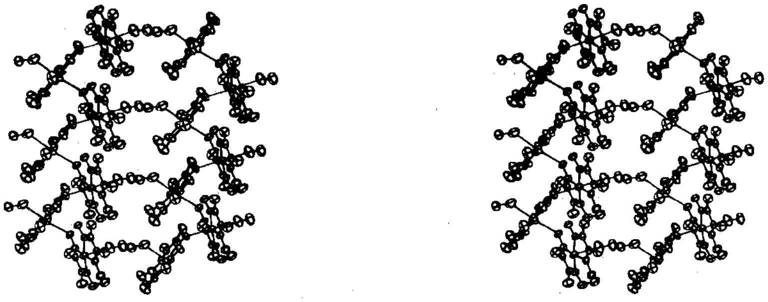


Figure 2. Stereoview of the polynuclear chains of $\mathrm{Cu(L)(ClO_4)\cdot{}^1/_2CH_3OH}$.

Table III. Least-Squares Planes within the Molecule $\mathrm{Cu(L)(ClO_4)\cdot{}^1/_2\,CH_3OH}$[a,b]

Atom	Dev, Å	Atom	Dev, Å
(a) Plane Involving Four Atoms Strongly Coordinated to Copper in Unit A			
Equation: $0.53106x + 0.84339y + 0.08166z + 2.21757 = 0$			
N1A	0.023	N4A	−0.022
N2A	−0.020	CuA	0.126
N3A	0.019		
(b) Plane Involving Four Atoms Strongly Coordinated to Copper in Unit B			
Equation: $-0.52996x + 0.84423y + 0.08009z + 0.43171 = 0$			
N1B	−0.026	N4B	0.029
N2B	0.018	CuB	−0.128
N3B	−0.016		
(c) Plane Involving the Ligand L in Unit A			
Equation: $0.53657x + 0.84148y + 0.06326z + 2.42805 = 0$			
O1A	0.165	C4A	−0.004
O2A	0.076	C5A	0.188
N1A	0.170	C6A	−0.522
N2A	0.152	C7A	−0.166
N3A	0.141	C8A	0.183
N4A	0.076	C9A	−0.198
C1A	−0.119	C10A	−0.013
C2A	0.053	C11A	−0.032
C3A	0.073	CuA	0.261
(d) Plane Involving the Ligand L in Unit B			
Equation: $0.53782x - 0.84296y + 0.01251z - 0.90593 = 0$			
O1B	0.098	C4B	−0.567
O2B	−0.173	C5B	0.029
N1B	0.138	C6B	−0.565
N2B	0.170	C7B	0.030
N3B	−0.060	C8B	0.215
N4B	−0.171	C9B	0.210
C1B	−0.590	C10B	0.164
C2B	−0.360	C11B	0.119
C3B	−0.305	CuB	0.147

[a] Direction cosines of the plane refer to the orgthogonal axis system *a, b, c**. [b] All atoms weighted at unity.

amplitudes may be obtained. [See paragraph at end of paper regarding supplementary material.]

Discussion

The two formula units of the asymmetric unit, labeled unit A and unit B in the tables, are very similar; within each formula unit the ligand is coordinated to copper, Figure 1, to form two five-membered and one six-membered chelate rings. Each five-membered chelate ring includes an oxime nitrogen and an imine nitrogen; the six-membered chelate ring includes two imine nitrogens. The four nitrogen atoms of the ligand are coplanar (maximum deviation of these four atoms from their least-squares plane is 0.03 Å in unit B and 0.02 Å in unit A) and about equidistant from the copper atom (1.937 (5)–1.961 (5) Å in unit A and 1.940 (5)–1.960 (5) Å in unit B). The copper of unit A is coordinated to an oxime oxygen of unit B (Cu–O1 distance of 2.493 (4) Å) and the copper of unit B is coordinated to an oxime oxygen of unit A translated one unit cell along the *a* axis (Cu–O1 distance of 2.491 (4) Å). This interaction with the oxime oxygen of the adjacent unit forms singly bridged infinite chains, Figure 2, with dihedral angles of approximately 70° between nitrogen planes of adjacent units. The copper atom in each unit is 0.13 Å out of the plane of the coordinated nitrogen atoms in the direction of the coordinated oxime oxygen. The methanol is more weakly coordinated (Cu–O distances for both units are 2.62 (1) Å) to complete a distorted octahedron about copper. Because of the formula of the compound, there are only sufficient methanol molecules to coordinate half of the copper atoms; furthermore, there is insufficient room between chains to accommodate a methanol coordinated to each copper—the methanol carbon positions of unit A and unit B occupy positions only 0.83 Å apart. These results suggest that the methanol molecules are disordered over two sets of positions—those coordinated to CuA and those coordinated to CuB.

Charge balance considerations dictate the loss of one proton from the ligand in forming the complex and the remaining oxime proton would be expected to form a hydrogen bond between the two oxime oxygens. The only residual electron density near the oxime oxygens in each formula unit is between the two oxygens and closer to the uncoordinated oxygen. The O1–O2 distances (2.511 (5) Å for unit A and 2.505 (5) Å for unit B) are similar to the hydrogen-bonded oxygen–oxygen distance observed in structures of other copper–oxime complexes.[5–7,17]

The magnetic moment of the compound at room temperature, 1.77 μ_B, is near the spin-only value for one unpaired electron; the moment shows little change with temperature, dropping only to 1.71 μ_B at 93 K. Because of the bridging arrangement, the pathway for spin exchange would involve the half-filled $d_{x^2-y^2}$ orbital of one copper atom, σ orbitals of nitrogen and oxygen, and the filled d_{z^2} orbital of the adjacent copper atom. In terms of both the long copper–oxygen distance and the bridging arrangement, this compound is similar to bis(dimethylglyoximato)copper(II), for which weak ferromagnetic spin coupling was observed.[8]

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Registry No. $\mathrm{Cu(L)(ClO_4)\cdot{}^1/_2CH_3OH}$, 62197-90-4; 1,3-diaminopropane, 109-76-2; diacetyl monoxime, 57-71-6.

Supplementary Material Available: Listing of structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Taken from the Ph.D. dissertation of J. H. Smith, Georgia Institute of Technology, 1976.
(2) R. Beckett and B. F. Hoskins, *J. Chem. Soc., Dalton Trans.*, 291 (1972).
(3) J. A. Bertrand, J. H. Smith, and P. G. Eller, *Inorg. Chem.*, **13**, 1649 (1974).
(4) J. A. Bertrand, J. H. Smith, and D. G. VanDerveer, *Inorg. Chem.*, preceding paper in this issue.

(5) J. W. Fraser, G. R. Hedwig, H. K. J. Powell, and W. T. Robinson, *Aust. J. Chem.*, **25**, 747 (1972).
(6) S. Bezzi, E. Bua, and G. Schiavinato, *Gazz. Chim. Ital.*, **81**, 856 (1951).
(7) A. Vaciago and L. Zamibonelli, *J. Chem. Soc. A*, 218 (1970).
(8) J. F. Villa and W. E. Hatfield, *J. Chem. Phys.*, **55**, 4758 (1971).
(9) L. E. Godycki and R. E. Rundle, *Acta Crystallogr.*, **6**, 487 (1953).
(10) D. E. Williams, G. Wohlauer, and R. E. Rundle, *J. Am. Chem. Soc.*, **81**, 755 (1959).
(11) B. N. Figgis and J. Lewis, *Mod. Coord. Chem.*, 403 (1960).
(12) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digits.
(13) P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Crystallogr.*, **18**, 1035 (1965).
(14) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1945).
(15) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(16) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(17) I. B. Bliss and E. O. Schlemper, *Inorg. Chem.*, **14**, 3037 (1975).

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Crystal Structure and Molecular Geometry of the Homogeneous Hydrogenation Catalyst $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$ and of Its Precursor $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}Cl)_2$. A Direct Comparison of $Ir(\mu\text{-}H)(\mu\text{-}Cl)Ir$ and $Ir(\mu\text{-}Cl)_2Ir$ Bridging Systems

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The homogeneous hydrogenation catalyst μ-chloro-μ-hydrido-dichlorobis(pentamethylcyclopentadienyl)diiridium(III), $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$, and its synthetic precursor di-μ-chloro-dichlorobis(pentamethylcyclopentadienyl)diiridium(III), $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}Cl)_2$, have each been studied by means of a single-crystal x-ray structural analysis. Crystal data are as follows. $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$: orthorhombic, space group *Pbcn*, $a = 12.493$ (2) Å, $b = 14.454$ (3) Å, $c = 12.860$ (2) Å, ρ(obsd) = 2.177 (5) and ρ(calcd) = 2.180 g cm^{-3} for mol wt 762.2, $V = 2322.1$ (7) Å^3, and $Z = 4$. The molecule has crystallographic C_2 symmetry. $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}Cl)_2$: monoclinic, space group $P2_1/c$, $a = 8.384$ (1) Å, $b = 9.278$ (1) Å, $c = 15.741$ (2) Å, $\beta = 106.52$ (1)°, ρ(obsd) = 2.259 (7) and ρ(calcd) = 2.254 g cm^{-3} for mol wt 796.7, $V = 1173.8$ (3) Å^3, and $Z = 2$. This species has crystallographic C_i symmetry. Diffraction data for each complex were collected with a Syntex $P2_1$ four-circle diffractometer (Mo Kα radiation; $2\theta(\max) = 40°$) and the structures were solved via the Syntex XTL structure determination system. Final discrepancy indices were $R_F = 4.4\%$ and $R_{wF} = 4.9\%$ for $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$ (1089 independent reflections) and $R_F = 3.3\%$ and $R_{wF} = 4.6\%$ for $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}Cl)_2$ (1095 independent reflections). Each complex is isomorphous and isostructural with its rhodium analogue. Dimensions within the central $Ir(\mu\text{-}H)(\mu\text{-}Cl)Ir'$ bridge of $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$ are as follows: Ir⋯Ir′ = 2.903 (1) Å, Ir–Cl = 2.451 (4) Å, Ir–H = 1.94 (7) Å, Ir–Cl–Ir′ = 72.65 (8)°, Ir–H–Ir′ = 96.9 (25)°, and H–Ir–Cl = 95.2 (17)°. Dimensions within the $Ir(\mu\text{-}Cl)_2Ir'$ bridge of $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}Cl)_2$ are as follows: Ir⋯Ir′ = 3.769 (1) Å, Ir–Cl = 2.449 (3) Å, 2.456 (3) Å, Ir–Cl–Ir′ = 100.45 (12)°, and Cl–Ir–Cl′ = 79.55 (12)°. These data are discussed and compared with data previously obtained for the rhodium analogues.

Introduction

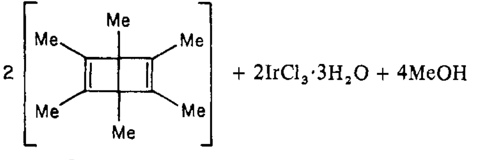
We have previously reported the results of x-ray structural analyses of $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$[1] and $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$.[2] The present structural investigations of the iridium analogues, $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$ and $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}Cl)_2$, were undertaken in order to obtain direct comparisons of $Ir(\mu_2\text{-}H)(\mu_2\text{-}Cl)Ir$ and $Ir(\mu_2\text{-}Cl)_2Ir$ bridges both with each other and with the corresponding $Rh(\mu_2\text{-}H)(\mu_2\text{-}Cl)Rh$ and $Rh(\mu_2\text{-}Cl)_2Rh$ bridges in otherwise identical molecular species. These comparisons are rendered more chemically meaningful (although less crystallographically exciting) by the discovery that $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$ is isomorphous with $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$ and that $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}Cl)_2$ is isomorphous with $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$.

All four of the above-mentioned species are implicated as powerful catalysts in homogeneous hydrogenation reactions.[3] For both iridium and rhodium, the active catalyst is the μ-chloro-μ-hydrido species. However, this can be generated in situ (under the normal experimental conditions for hydrogenation) from the di-μ-chloro complex by the heterolytic cleavage of dihydrogen (see eq 1).

$$[(\eta^5\text{-}C_5Me_5)MCl]_2(\mu\text{-}Cl)_2 + H_2 \rightarrow [(\eta^5\text{-}C_5Me_5)MCl]_2(\mu\text{-}H)(\mu\text{-}Cl) + HCl \qquad (1)$$

Experimental Section

$[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}Cl)_2$ was prepared via the method of Maitlis et al.[4] from the reaction of $IrCl_3 \cdot 3H_2O$ (Ventron) and hexamethyl(Dewar benzene) (Aldrich) in methanol (see eq 2). The product was washed with ether and recrystallized from 1,2-dichloroethane.



$$+ 2IrCl_3 \cdot 3H_2O + 4MeOH$$

$$\rightarrow [(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}Cl)_2 + 2MeCH(OMe)_2 + 2HCl + 6H_2O \qquad (2)$$

Crystals of $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$ were supplied by Professor P. M. Maitlis of Sheffield University, Sheffield, England.

Each complex is stable indefinitely in the solid state and does not decompose upon exposure to x-rays.

Collection of X-Ray Diffraction Data

1. $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$. The crystal selected for the structural investigation was a red block of maximum dimension 0.13 mm. It was mounted on a thin glass fiber, sealed into a 0.2-mm diameter thin-walled Lindemann glass capillary, and fixed into a eucentric goniometer. The crystal was centered in a random orientation (later found to be with $[\bar{4}45]$ offest by ~0.72° from coincidence with the ϕ axis) on a Syntex $P2_1$ four-circle diffractometer under the control of a NOVA 1200 computer. Axial photographs revealed D_{2h} (*mmm*) Laue symmetry, indicating that the crystal belonged to the orthorhombic crystal class.

Determination of the orientation matrix, measurement of unit cell parameters, checks on peak profile, and data collection were carried out as described previously;[5] details are given in Table I.

Examination of the complete set of intensity data revealed the systematic absences $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, and $hk0$