

Crystal and Molecular Structure of Dimeric [2,2'-(1,2-Diaminoethane)bis(2-methyl-3-butanone oximato)]copper(II) Perchlorate

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The crystal structure of dimeric [2,2'-(1,2-diaminoethane)bis(2-methyl-3-butanone oximato)]copper(II) perchlorate, $[\text{Cu}(\text{EnAO-H})_2(\text{ClO}_4)_2]$, has been determined from three-dimensional X-ray data collected with a scintillation counter. The crystals are monoclinic ($P2_1/c$) with two dimeric cations per unit cell of dimensions $a = 11.441$ (2) Å, $b = 12.992$ (2) Å, $c = 12.640$ (2) Å, and $\beta = 110.20$ (1)°. The calculated density of 1.584 (1) g/cm³ is in good agreement with the flotation density of 1.57 (1) g/cm³. The structure was solved by direct methods and refined by full-matrix least squares to $R(F) = 0.056$ using 2121 reflections with $F_o^2 > 2.0\sigma(F_o^2)$. The structure consists of discrete perchlorate ions and centrosymmetric dimeric copper complex ions. The copper(II) atom is in a distorted square-pyramidal coordination which is completed by four nitrogen atoms in the base from one ligand while the axial position is occupied by the bridging oxime oxygen atom of the ligand from the other half of the dimer. The important bond distances are Cu-O = 2.185 (4) Å, average Cu-N(oxime) = 1.941 (3) Å, average Cu-N(amine) = 1.995 (16) Å, and O...O = 2.698 (6) Å for the intramolecular hydrogen bond.

Introduction

The α -amine oxime metal complexes allow a comprehensive structural study of the variation in hydrogen bonding with O...O distance for short hydrogen bonds. The O...O distance can be varied either by changing the ligand, e.g., bis(2-amino-2-methyl-3-butanone oximato)nickel(II) ion¹ (O...O = 2.420 (3) Å) and 2,2'-(1,2-diaminoethane)bis(2-methyl-3-butanone oximato)nickel(II) ion² (O...O = 2.478 (5) Å), or by changing the size of the metal ion, e.g., from Ni(II) to Cu(II). In the present study the copper(II) complex of the latter ligand was chosen for comparison with the nickel complex and with a previously studied³ copper(II) complex with a 1,3-diaminopropane group in place of the present 1,2-diaminoethane group. In the previous copper complex³ the O...O distance was 2.46 (2) Å. The 1,2-diaminoethane group opposite the O...O hydrogen bond was expected to lengthen the hydrogen bond.

Experimental Section

Crystal Preparation. The compound $[\text{Cu}(\text{EnAO-H})]\text{ClO}_4$, $[\text{Cu}(\text{C}_{12}\text{H}_{25}\text{N}_4\text{O}_2)]\text{ClO}_4$, was prepared as described by Murmann.⁴ The wine red prismatic crystals were obtained by recrystallization from water. The perchlorate salt was used because suitable single crystals could not be obtained for halide or nitrate salts.

X-ray Data. 2,2'-(1,2-Diaminoethane)bis(2-methyl-3-butanone oximato)copper(II) perchlorate crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.441$ (2) Å, $b = 12.992$ (2), $c = 12.640$ (2) Å, and $\beta = 110.20$ (1)°. There are two dimers, $[\text{Cu}(\text{EnAO-H})_2(\text{ClO}_4)_2]$, in the unit cell, giving a calculated density of 1.584 (1) g/cm³ compared with the flotation density of 1.57 (1) g/cm³. A crystal of approximate dimensions 0.17 × 0.36 × 0.38 mm was mounted with the 122 direction nearly coincident with the ϕ axis of the Picker four-angle programmed diffractometer used to collect the intensity data. The above cell dimensions and the orientation of the crystal on the diffractometer were determined by a least-squares fit⁵ of the setting angles for 18 reflections which were carefully centered manually using a narrow-vertical slit in front of the detector at a low takeoff angle. Mo $K\alpha$ radiation filtered through Nb foil was used for the data collection. A takeoff angle of 2.5° was used for the intensity measurements which were obtained with a scintillation detector using the θ - 2θ scan technique (1° of $2\theta/\text{min}$). The receiving aperture was about 0.3 × 0.3 mm and was positioned 27 cm from the crystal. A variable scan width (0.90–1.20° of 2θ), to account for the α_1 - α_2 splitting, was used to measure the intensities of reflections to a maximum 2θ of 45°. Twenty-second background counts were obtained at each end of each scan. Attenuators were used to maintain the maximum rate count below 10000 counts/s which is within the linear range of the detector. The intensities of 3584 reflections including extinctions were measured. The systematic extinction of odd l for $h0l$ and odd k for $0k0$ verified the choice of space group $P2_1/c$. Three standards were measured after every 50 reflections and showed a linear

decrease in intensity with time of 12% during the data collection period. The intensities were corrected for this effect.

Background and L_p corrections were made using the usual equations. Absorption corrections based on the crystal dimensions and faces (100, $\bar{1}00$, 011, $0\bar{1}\bar{1}$, $0\bar{1}1$, and $01\bar{1}$) were also applied ($\mu = 14.7 \text{ cm}^{-1}$). The range of transmission factors was 0.63–0.81. Equivalent and duplicate measurements were averaged to give 2319 independent reflections of which the 2121 reflections with $F_o^2 > 2.0\sigma(F_o^2)$ were used for the structure solution and refinement. The agreement factor, $\sum |F^2 - F_{av}^2| / \sum F^2$, was 0.024.

Determination and Refinement of the Structure. Most of the nonhydrogen atoms were located from the first E map obtained using the phasing for the set of the highest figure of merit from MULTAN.⁶ The other atoms were located from subsequent Fourier and difference Fourier syntheses. Considerable difficulty was encountered in locating and refining the perchlorate oxygen atoms which are undergoing rather extensive thermal motion; however, four definite peaks in the difference electron density maps were evident. Refinement of positional and anisotropic thermal parameters for the nonhydrogen atoms with the hydrogen atoms in near "ideal" positions⁷ converged with $R = \sum |F_o^2 - kF_c^2| / \sum F_o^2 = 0.089$ and $R_w = [\sum w(F_o^2 - kF_c^2)^2 / \sum wF_o^4]^{1/2} = 0.150$ where $w = 1/\sigma^2(F_o^2)$. The standard deviations (σ) were the following: for $F_o^2 < 26.5$, $\sigma^2(F_o^2) = 1.56F_o^2 - 0.0549F_o^4$; for $26.5 \leq F_o^2 < 85.0$, $\sigma^2(F_o^2) = 0.409F_o^2 - 0.00232F_o^4$; for $85.0 \leq F_o^2 < 275.2$, $\sigma^2(F_o^2) = 0.223F_o^2 - 0.000455F_o^4$; for $275.2 \leq F_o^2 < 1175.5$, $\sigma^2(F_o^2) = 0.102F_o^2 - 0.000009F_o^4$; and for $F_o^2 \geq 1175.5$, $\sigma^2(F_o^2) = 0.085F_o^2$. This weighting scheme was chosen to make $\Delta F^2/\sigma(F_o^2)$ nearly independent of F_o . The standard deviation of an observation of unit weight was 1.44. On the last cycle of refinement the maximum shift of any of the 217 variables was less than 20% of its standard deviation. A final difference Fourier showed residuals of about $1 \text{ e}/\text{Å}^3$ in the vicinity of the copper atom and the perchlorate oxygen atoms. The scattering factors for C, N, and O were taken from Ibers;^{7a} those of Cu and Cl from Cromer and Waber;^{7b} and those of H from Stewart.^{7c} Anomalous scattering effects of Cu and Cl^{7d} were included in F_c .^{7e} Inclusion of a secondary extinction parameter⁸ in the refinement brought no significant improvement so extinction effects were not included in the final refinement. The rather high agreement factors are probably due to the difficulty in treating the poorly resolved perchlorate oxygen atoms whose thermal parameters are extremely large. The observed and calculated structure factors ($\times 10$) and the hydrogen atom positions are available.⁹ The final positional and thermal parameters for the nonhydrogen atoms are in Tables I and II, respectively.

Discussion

The structure consists of discrete binuclear copper(II) complex positive ions and perchlorate counterions. The binuclear complex has each copper atom in near square-pyramidal five-coordination. The two oxime nitrogen atoms and the two amine nitrogen atoms of one α -amine oxime ligand are in a near square-planar arrangement about the copper atom while one oxime oxygen atom of the other α -amine oxime

Table I. Positional Parameters^a for [Cu(EnAO-H)]₂(ClO₄)₂

	x	y	z
Cu	0.0606 (1)	0.0768 (1)	0.1368 (1)
Cl	-0.2467 (2)	-0.0514 (1)	0.3553 (2)
O(1)	-0.0377 (3)	0.0890 (3)	-0.1081 (3)
O(2)	0.2119 (3)	0.0998 (3)	-0.0082 (3)
O(3)	-0.1889 (7)	-0.0580 (6)	0.2754 (6)
O(4)	-0.3255 (17)	-0.1208 (10)	0.3552 (13)
O(5)	-0.2908 (9)	0.0481 (7)	0.3614 (9)
O(6)	-0.1487 (13)	-0.0414 (12)	0.4655 (8)
N(1)	-0.0577 (4)	0.1132 (3)	-0.0104 (3)
N(2)	0.2113 (4)	0.0970 (4)	0.1022 (4)
N(3)	-0.0754 (4)	0.1223 (3)	0.1892 (3)
N(4)	0.1789 (4)	0.0986 (4)	0.2952 (4)
C(1)	-0.1587 (4)	0.1565 (4)	-0.0129 (4)
C(2)	0.3139 (5)	0.1134 (5)	0.1805 (5)
C(3)	-0.1621 (4)	0.1915 (4)	0.1017 (4)
C(4)	0.3114 (5)	0.1069 (5)	0.2999 (5)
C(5)	-0.2636 (5)	0.1820 (5)	-0.1172 (5)
C(6)	0.4313 (6)	0.1345 (7)	0.1596 (6)
C(7)	-0.2921 (5)	0.1812 (5)	0.1063 (5)
C(8)	-0.1175 (6)	0.3029 (5)	0.1164 (5)
C(9)	0.3806 (6)	0.1987 (6)	0.3714 (6)
C(10)	0.3743 (6)	0.0061 (6)	0.3520 (5)
C(11)	-0.0146 (5)	0.1629 (4)	0.3064 (4)
C(12)	0.1195 (5)	0.1888 (5)	0.3256 (5)

^a Standard deviations from the least-squares refinement are included in parentheses in this table and other portions of the paper.

ligand occupies the apical position of the square pyramid (Figure 1). A center of symmetry relates the two halves of the dimer. This arrangement leads to some rather close contacts between the two α -amine oxime ligands (e.g., N(1)–N(1)' = 3.20 Å, O(1)–N(1)' = 3.03 Å, and O(1)–N(2)' = 3.14 Å). The copper atom is out of the plane of the four nitrogen atoms toward the coordinated oxime oxygen atom as is usually observed for square-pyramidal Cu complexes. There is no close contact to the copper in the position trans to the coordinated oxime oxygen atom. The perchlorate oxygens are all more than 3.8 Å from the copper atom.

The crystal structure (Figure 2) is stabilized by weak interionic hydrogen bonds between perchlorate oxygens and amine hydrogens and by van der Waals forces. Perchlorate oxygens O(3) and O(6) are involved in hydrogen bonds (O(3)–N(3) = 3.06 Å, H(N3)–O(3) = 2.14 Å, N(3)–H-

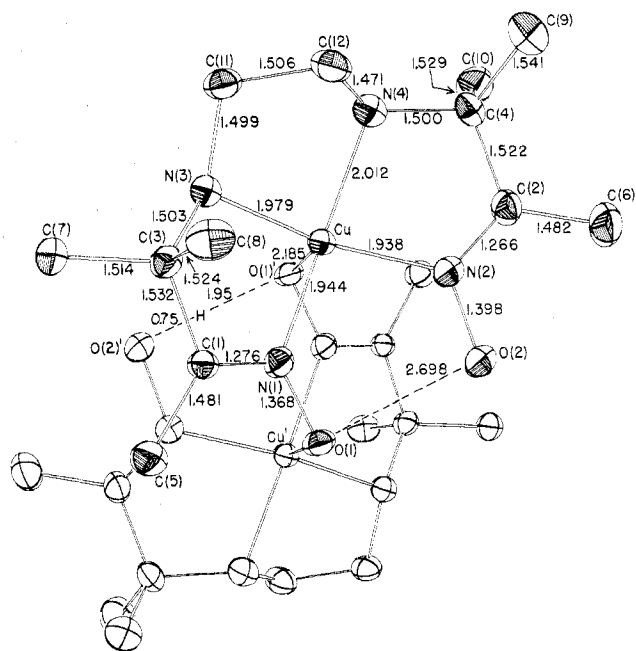


Figure 1. Perspective view of the dimeric [2,2'-(1,2-diaminoethane)bis(2-methyl-3-butanone oximato)]copper(II) ion, [Cu(EnAO-H)]₂(ClO₄)₂, showing the atom labeling and bond distances. The shaded atoms in half of the dimer are related to the unshaded atoms by a center of symmetry midway between the copper atoms. Standard deviations are the following: Cu–O and Cu–N, ± 0.004 Å; C–N and N–O, ± 0.005 – 0.007 Å; C–C, ± 0.007 – 0.009 Å.

(N3)–O(3) = 157°, O(6)–N(4) = 3.25 Å, H(N4)–O(6) = 2.51 Å, and N(4)–H(N4)–O(6) = 133°. These are considered hydrogen bonds under criteria which require a reasonable X–H...Y angle as well as a shorter than normal X...Y distance. The shorter interionic contacts are given in Table III.

Square-pyramidal five-coordination for Cu(II) is not uncommon. For example, when the perchlorate salt of the copper(II) complex of a similar tetradentate amine oxime ligand, differing only in that it has a propylene rather than ethylene bridge between the amine nitrogens, was studied,³ a five-coordinate monomeric complex was found with the fifth

Table II. Anisotropic Thermal Parameters^a for [Cu(EnAO-H)]₂(ClO₄)₂

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.0048 (1)	0.0055 (1)	0.0036 (1)	0.0004 (1)	0.0012 (1)	-0.0004 (1)
Cl	0.0141 (2)	0.0074 (1)	0.0114 (2)	0.0012 (1)	0.0072 (2)	0.0021 (1)
O(1)	0.0070 (3)	0.0049 (2)	0.0034 (2)	0.0006 (2)	0.0023 (2)	0.0001 (2)
O(2)	0.0068 (4)	0.0078 (3)	0.0049 (3)	0.0002 (3)	0.0027 (3)	0.0013 (2)
O(3)	0.0258 (10)	0.0128 (6)	0.0148 (7)	-0.0034 (6)	0.0123 (7)	-0.0008 (5)
O(4)	0.0798 (40)	0.0222 (13)	0.0487 (26)	-0.0310 (21)	0.0491 (30)	-0.0202 (16)
O(5)	0.0254 (12)	0.0134 (7)	0.0273 (13)	0.0027 (8)	0.0085 (11)	-0.0039 (8)
O(6)	0.0408 (22)	0.0372 (19)	0.0123 (9)	0.0089 (17)	-0.0007 (11)	0.0087 (11)
N(1)	0.0062 (4)	0.0044 (3)	0.0047 (3)	-0.0003 (3)	0.0022 (3)	-0.0004 (2)
N(2)	0.0066 (4)	0.0063 (3)	0.0051 (3)	0.0002 (3)	0.0022 (3)	0.0006 (3)
N(3)	0.0065 (4)	0.0051 (3)	0.0046 (3)	0.0003 (3)	0.0018 (3)	-0.0003 (2)
N(4)	0.0070 (4)	0.0065 (3)	0.0051 (3)	-0.0001 (3)	0.0014 (3)	-0.0002 (3)
C(1)	0.0056 (5)	0.0040 (3)	0.0039 (4)	-0.0003 (3)	0.0013 (3)	0.0003 (3)
C(2)	0.0060 (5)	0.0060 (4)	0.0066 (5)	0.0002 (3)	0.0018 (4)	0.0009 (3)
C(3)	0.0060 (5)	0.0052 (3)	0.0048 (4)	0.0010 (3)	0.0022 (3)	-0.0001 (3)
C(4)	0.0055 (5)	0.0066 (4)	0.0056 (4)	-0.0003 (3)	0.0007 (4)	-0.0005 (3)
C(5)	0.0071 (5)	0.0080 (5)	0.0051 (4)	0.0021 (4)	0.0015 (4)	0.0007 (3)
C(6)	0.0060 (6)	0.0126 (7)	0.0094 (6)	-0.0011 (5)	0.0019 (5)	0.0022 (5)
C(7)	0.0061 (5)	0.0090 (5)	0.0062 (4)	0.0010 (4)	0.0027 (4)	-0.0002 (4)
C(8)	0.0111 (6)	0.0048 (4)	0.0068 (5)	0.0003 (4)	0.0030 (4)	-0.0006 (3)
C(9)	0.0100 (7)	0.0103 (6)	0.0087 (6)	-0.0036 (5)	0.0020 (5)	-0.0022 (5)
C(10)	0.0085 (6)	0.0094 (6)	0.0071 (5)	0.0016 (4)	0.0013 (4)	0.0020 (4)
C(11)	0.0083 (5)	0.0063 (4)	0.0043 (4)	0.0013 (4)	0.0020 (4)	-0.0005 (3)
C(12)	0.0088 (6)	0.0064 (4)	0.0051 (4)	0.0001 (4)	0.0008 (4)	-0.0011 (3)

^a The anisotropic thermal parameters are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

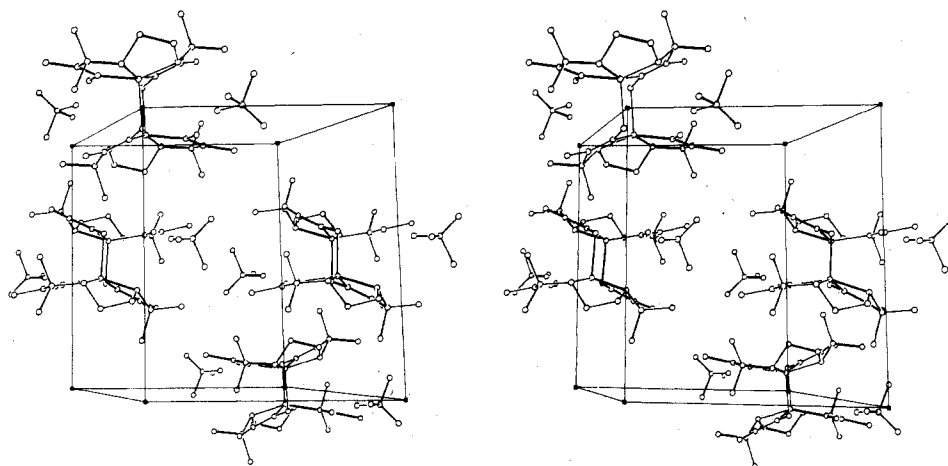


Figure 2. Stereoscopic view of the packing of the ions in the unit cell for $[\text{Cu}(\text{EnAO-H})]_2(\text{ClO}_4)_2$. The unit cell edges are shown.

Table III. Interionic Contacts (Å) Less Than 3.5 Å Not Involving Hydrogen Atoms

O(1)-C(11)	3.44 (1)	O(4)-C(2)	3.49 (1)
O(2)-C(12)	3.40 (1)	O(6)-C(12)	3.19 (1)
O(3)-N(3) ^a	3.06 (1)	O(6)-N(4) ^a	3.25 (1)
O(3)-O(2)	3.34 (1)	O(6)-O(6)	3.39 (3)
O(3)-C(11)	3.44 (1)	O(6)-C(11)	3.25 (1)
O(4)-C(6)	3.38 (1)		

^a This is an interionic hydrogen bond.

position occupied by an oxygen atom of the perchlorate ion. The average Cu-N(amine) distance (2.00 (2) Å) in this complex compares well with that of 1.99 (1) Å in the perchlorate copper complex³ as does the Cu-N(oxime) distance of 1.941 (3) Å compared with 1.96 (1) Å in the previous study. The apical Cu-O distance of 2.185 (4) Å in this complex is, however, significantly shorter than that to the perchlorate oxygen in the perchlorate complex (2.40 (1) Å). As a result the Cu is considerably further out of the nitrogen square plane toward the apical oxygen. The N(amine)-Cu-O angles (average 107.2°) are considerably larger than the N(oxime)-Cu-O angles (average 96.8°) indicating a significant distortion of the square-pyramidal coordination. The resulting trans N-Cu-N angles (average 155.8°) also reflect the distortion from planarity. The best plane defined by the four coordinated nitrogens is defined by the equation

$$1.07(9)X + 12.9(1.0)Y - 0.24(3)Z - 1.43(12) = 0$$

The maximum deviation of any of the nitrogens from this plane is 0.032 (5) Å while the Cu is 0.40 Å from the plane. The deviations of the other ligand atoms from this plane are given in Table IV. Apparently because of the dimerization, the puckering of the tetradentate ligand is much different from that observed in the square-planar nickel(II) complex.¹⁰ In that complex all the chelate ring carbon atoms as well as the oxime oxygens are within 0.46 Å of the nitrogen plane (average deviation of 0.24 Å) and are distributed equally on each side of the plane. In this complex they deviate from the nitrogen plane by as much as 1.06 Å (average deviation of 0.44 Å), and all the atoms except the coordinated oxime oxygen are off to the side of the nitrogen plane away from the other half of the dimer. This configuration (see Figure 2) is probably necessary to minimize repulsion between the ligand atoms in the two halves of the dimer.

The geometry of the perchlorate group (Table V) is poorly defined with a range of apparent Cl-O distances from 1.27 to 1.46 Å (average 1.38 (6) Å) and a range of O-Cl-O angles from 92 to 118° (average 110(7)°). This is probably due to the high thermal motion of the oxygen atoms which have maximum root-mean-squared displacements ranging from 0.41

Table IV. Deviations of Selected Atoms (Å) from the Nitrogen Square Plane

N(1)	-0.024 (4)	C(3)	0.85
N(2)	0.028 (5)	C(4)	0.22
N(3)	0.028 (4)	C(5)	0.67
N(4)	-0.032 (5)	C(6)	0.74
Cu	-0.40	C(7)	0.58
O(1)	-0.29	C(8)	2.33
O(2)	0.09	C(9)	1.46
O(1) ^a	-2.56	C(10)	-1.03
C(1)	0.44	C(11)	0.59
C(2)	0.33	C(12)	1.06

^a The axial oxygen from the other half of the dimer.

Table V

Bond Angles (deg) in $[\text{Cu}(\text{EnAO-H})]_2(\text{ClO}_4)_2$

N(1)-Cu-N(2)	97.5 (2)	Cu-N(4)-C(12)	99.1 (3)
N(1)-Cu-N(3)	83.1 (2)	C(4)-N(4)-C(12)	118.9 (4)
N(2)-Cu-N(4)	82.0 (2)	N(1)-C(1)-C(3)	115.2 (4)
N(3)-Cu-N(4)	87.8 (2)	N(1)-C(1)-C(5)	124.7 (4)
O(1)-Cu-N(1) ^a	94.4 (2)	C(3)-C(1)-C(5)	119.9 (4)
O(1)-Cu-N(2) ^a	99.2 (2)	N(2)-C(2)-C(4)	115.9 (5)
O(1)-Cu-N(3) ^a	106.7 (2)	N(2)-C(2)-C(6)	123.0 (5)
O(1)-Cu-N(4) ^a	107.7 (2)	C(4)-C(2)-C(6)	121.1 (5)
O(3)-Cl-O(4)	118.0 (6)	C(1)-C(3)-N(3)	107.0 (4)
O(3)-Cl-O(5)	111.7 (6)	C(1)-C(3)-C(7)	110.8 (4)
O(3)-Cl-O(6)	107.3 (6)	C(1)-C(3)-C(8)	106.3 (4)
O(4)-Cl-O(5)	112.6 (9)	N(3)-C(3)-C(7)	109.1 (4)
O(4)-Cl-O(6)	112.0 (10)	N(3)-C(3)-C(8)	111.7 (4)
O(5)-Cl-O(6)	92.2 (7)	C(7)-C(3)-C(8)	111.8 (5)
C(1)-N(1)-O(1)	120.8 (4)	C(2)-C(4)-N(4)	109.2 (4)
Cu-N(1)-O(1)	122.0 (3)	C(2)-C(4)-C(9)	110.9 (5)
Cu-N(1)-C(1)	117.1 (3)	C(2)-C(4)-C(10)	107.9 (5)
C(2)-N(2)-O(2)	117.0 (4)	N(4)-C(4)-C(9)	112.7 (5)
Cu-N(2)-C(2)	120.2 (4)	N(4)-C(4)-C(10)	105.9 (5)
Cu-N(2)-O(2)	122.7 (3)	C(9)-C(4)-C(10)	109.9 (5)
Cu-N(3)-C(3)	109.2 (3)	N(3)-C(11)-C(12)	109.7 (4)
Cu-N(3)-C(11)	106.6 (3)	N(4)-C(12)-C(11)	108.4 (5)
C(3)-N(3)-C(11)	118.7 (4)	N(2)-Cu-N(3)	154.0 (2)
Cu-N(4)-C(4)	111.9 (3)	N(1)-Cu-N(4)	157.7 (2)

Perchlorate Bond Distances (Å)

Cl-O(3)	1.27 (1)	Cl-O(5)	1.40 (1)
Cl-O(4)	1.39 (1)	Cl-O(6)	1.46 (1)

^a These nitrogen atoms are in the other half of the dimer.

to 0.79 Å. The average Cl-O distance is somewhat short (e.g., the average value in an earlier study² was 1.42 (2) Å).

The bond distances (Figure 1) and the bond angles within the amine oxime ligand (Table V) can be compared with those in the same ligand in the previously studied nickel(II) complex.¹⁰ Despite the difference in puckering of the ligand, the "ideal" tetrahedral angles are well maintained for the sp³ carbon atoms (C(3), C(4), C(11), C(12)) in both compounds.

Both compounds show deviation from tetrahedral angles about the amine nitrogens (N(3) and N(4)) with the external C–N–C angles opening to nearly 120° to facilitate the tetradentate coordination. In both cases the M–N–O angles are slightly larger ($\approx 122^\circ$) than the “ideal” 120° sp^2 angle which tends to slightly lengthen the hydrogen bond. Other bond angles in the two cases are also very similar. The bond distances in the two compounds are generally in agreement except for the oxime N–O distances (average 1.383 Å in this complex and average 1.356 Å in the Ni complex) and the adjacent N(oxime)–C distances (average 1.271 Å in this complex and average 1.288 Å in the nickel complex). The apparent shift in the multiple bonding from the N–O toward C–N bond in this complex may be a result of the longer hydrogen bond (O...O, 2.698 Å) in this complex compared with the case of the nickel complex (2.474 Å). The longer N–O distance (1.398 Å) involves the oxygen to which the hydrogen atom is bonded in a nearly covalent fashion (O–H, 0.75 Å from difference Fourier position). The other O–H distance is 1.95 Å. The hydrogen bond in this complex is much longer than that in any other α -amine oxime complex we have studied. This may be partially due to the steric requirements of the ligand with the larger Cu(II) metal but is probably also partially a result of the dimerization which involves coordination of one of the hydrogen bond oxime oxygens with the copper. Attempts are under way to obtain single crystals with some other better coordinating anion replacing the perchlorate ion in hopes of obtaining a monomer.

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Registry No. [Cu(EnAO-H)]₂(ClO₄)₂, 68492-44-4.

Supplementary Material Available: Hydrogen atom positional parameters and a listing of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

References and Notes

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Structure of [Rh₂(CO)₂(μ-CO)(μ-Cl)((C₆H₅)₂PCH₂P(C₆H₅)₂)₂][B(C₆H₅)₄]: An “A-Frame” Complex Having a Carbonyl Ligand Coordinated in the Proposed Active Site

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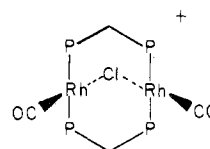
The facile, reversible reaction of the “A-frame” complex [Rh₂(CO)₂(μ-CO)(μ-Cl)((C₆H₅)₂PCH₂P(C₆H₅)₂)₂]⁺ with carbon monoxide yields the tricarbonyl species [Rh₂(CO)₂(μ-CO)(μ-Cl)((C₆H₅)₂PCH₂P(C₆H₅)₂)₂]⁺. An X-ray crystallographic study on the tricarbonyl species indicates that one carbonyl ligand is coordinated in the proposed active site of the parent “A-frame” complex, bridging the two rhodium atoms, verifying that small unsaturated molecules can coordinate at this active site. The tricarbonyl species crystallizes in the space group C_{2h}^1-P1 in a cell of dimensions $a = 14.451$ (2) Å, $b = 17.661$ (2) Å, $c = 13.726$ (1) Å, $\alpha = 102.06$ (1)°, $\beta = 95.59$ (1)°, and $\gamma = 75.56$ (1)° with $Z = 2$. On the basis of 8097 unique reflections, the structure was refined by full-matrix least-squares techniques to agreement indices of $R = 0.063$ and $R_w = 0.099$. Some relevant metrical parameters are Rh–P(av) = 2.333 (8) Å, Rh–C(terminal) = 1.831 (7) and 1.836 (7) Å, Rh–C(bridging) = 2.104 (7) and 2.034 (7) Å, Rh–Cl = 2.575 (2) and 2.607 (2) Å, C–O(terminal) = 1.139 (8) and 1.139 (8) Å, C–O(bridging) = 1.172 (8) Å, Rh–C–Rh = 86.7 (3)°, and Rh–Cl–Rh = 66.51 (4)°.

Introduction

Binuclear metal complexes in which the metals are held in close proximity are of considerable interest owing, in part, to their potential utility as simple models for multicentered metal catalysts.¹ In these binuclear complexes the metals can act independently of each other, reacting essentially as two monomeric units, or one metal center can perturb the other, thereby altering its chemistry relative to the related mononuclear metal complex. Balch and co-workers² have carried out studies in this regard, relating the chemistry at the metal centers to the distances between the metals, utilizing diphosphine and other bidentate ligands of various bite sizes bridging two square-planar Rh(I) centers.

One particularly interesting class of binuclear metal complexes having the metals in close proximity are the so-

called “A-frame” complexes.³ Several such complexes have been reported,³⁻⁷ one being [Rh₂(CO)₂(μ-Cl)(DPM)₂][BPh₄]⁴ (Ph = C₆H₅, DPM = Ph₂PCH₂PPh₂), the frame of which is diagrammed below:



In complexes of this type several coordination possibilities exist. Small molecules can coordinate in the proposed³ active site, between the two metal atoms, opposite the bridging chloro ligand, or to either or both metals on the sides of the metals remote from the active site. In any case the proximity of the