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Polynuclear Complexes with Hydrogen-Bonded Bridges. Dinuclear Complex of *N*,*N*′-Bis(2-hydroxyethyl)-2,4-pentanediimine with Copper(II)

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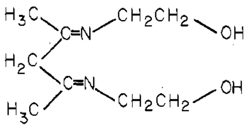
A copper(II) compound of formula $[Cu(DiimH)]_2$, where DiimH represents the dianion of the diimine Schiff base formed by the condensation of 2-aminoethanol with 2,4-pentanedione, has been synthesized and studied by magnetic, spectroscopic, and x-ray diffraction methods. The structure consists of discrete centrosymmetric dimers containing planar four-coordinate copper atoms (Cu–Cu = 4.99 (1) Å) and hydrogen bonds between the alkoxide oxygen atoms. Osmometric measurements show the hydrogen bonds to persist in chloroform solution, indicative of strong hydrogen bonding. The magnetic moment of the complex drops from 1.69 μ_B/g-atom of Cu at 298 K to 0.62 μ_B at 39 K. The antiferromagnetic coupling ($J = -94$ cm^{-1}) and the Cu–Cu distance suggest superexchange through the hydrogen bridges. The EPR spectra of powdered samples of the compound indicate a most likely g value of 2.0694 ± 0.0005 for the excited triplet state. Numerical analysis of the temperature dependence of the relative EPR absorption intensity confirmed the antiferromagnetic nature of the superexchange ($J_{EPR} = -90.4 \pm 2.8$ cm^{-1}). In addition the EPR spectra at 34.3 GHz resolved the two distinct axial sites which have essentially the same J but with slightly different **g** tensors ($\Delta g_{\parallel} \simeq 0.05$). The metal atoms are planar-coordinated by two nitrogens (Cu–N = 1.887 (11)–1.920 (12) Å) and by two oxygens (Cu–O = 1.941 (9)–1.955 (9) Å). The O–O′ distances in the bridge (2.31 (1), 2.33 (1) Å) are among the shortest reported for hydrogen-bonded oxygen atoms. Crystal data for $[Cu(DiimH)]_2$ are as follows: $P\bar{1}$, $a = 9.554$ (3) Å, $b = 13.025$ (4) Å, $c = 11.662$ (3) Å, $\alpha = 131.29$ (1)°, $\beta = 98.02$ (3)°, $\gamma = 94.31$ (1)°, $Z = 2$ dimers per unit cell, $\rho_{obsd} = 1.56$ g cm^{-3}, $\rho_{calcd} = 1.56$ g cm^{-3}, $R = 0.046$ and $R_w = 0.035$ for 1272 diffractometric reflections with $I \geq 3.3\sigma(I)$.

Introduction

In an earlier paper, we reported[1] the preparation of a cobalt(III) complex of the tetradentate ligand I (hereafter referred to as $DiimH_3$). The ligand, formed by the condensation of 2-aminoethanol with 2,4-pentanedione, contains three ionizable protons and can form neutral 1:1 complexes with trivalent metal ions. In the case of the cobalt(III) complex, the tetradentate ligand occupies four planar coordination positions and the remaining two octahedral positions are occupied by the amine nitrogens of two neutral 2-aminoethanol groups. There is an infinite network of hydrogen bonding involving the oxygens of the tetradentate ligand and the alcohol groups of the 2-aminoethanol ligands.



I

With divalent metal ions, only two protons are lost from I (the dianionic ligand is hereafter referred to as DiimH) in forming neutral complexes and the remaining proton would be expected to participate in hydrogen bonding.[2] Since the tetradentate ligand could occupy four coplanar coordination positions with the alcohol and alkoxide oxygens in adjacent positions, cooperative hydrogen bonding similar to that observed in carboxylic acid dimers is a distinct possibility for these complexes. In a recent paper,[3] we reported the first structure to show cooperative hydrogen bonding in transition metal complexes; in $CoNi(Eta)_3(EtaH)_3X_2$ (where EtaH represents 2-aminoethanol, Eta represents the anion of 2-aminoethanol, and X represents a halide), two tris chelates in a mutually cis configuration are hydrogen bonded through their oxygen faces into a dimeric unit. The hydrogen-bonded oxygen–oxygen distance of 2.51 Å indicates fairly strong bonding and the presence of three such interactions is probably sufficient to maintain the dimeric species in solution. Preparations have been reported[4–6] for $[Ni_2(Eta)_2(EtaH)_4]X_2$, $[Co_2(Eta)_3(EtaH)_3]X_3$ and $[Cr_2(Eta)_3(EtaH)_3]X_3$; although the structures have not been investigated, these compounds probably contain similar dinuclear cations held together by hydrogen bonds. Hydrogen-bonded dimers have also been reported[7] for a series of compounds with the formula $[Cu_2(tren)_2X_2](BPh_4)_2$ (where tren represents 2,2′,2″-triaminotriethylamine) for X = NCO, Cl, and CN. The dimers are held together by a pair of hydrogen bonds from tren N–H to anion X of adjacent complexes. The hydrogen-bond distances are 2.94 Å (O–N), 3.368 Å (Cl–N), and 3.047 Å (N–N) for X = NCO, Cl, and CN, respectively.

With the dianion of ligand I and metal ions that form square-planar complexes, it should be possible to form dimers with two hydrogen bonds maintaining the dimeric structure. To investigate that possibility, we have prepared and studied the complexes of copper(II) and nickel(II) with ligand I and in this paper we report the synthesis, crystal structure, and magnetic properties of the neutral, dimeric complex $[Cu(DiimH)]_2$. The temperature dependence of the magnetic susceptibility and the electron paramagnetic resonance (EPR) of this compound are particularly interesting since they confirm the dimeric Cu(II)–Cu(II) configuration through excellent agreement with the theory of Bleaney and Bowers[8] for two exchanged coupled spin $^1/_2$ ions. A preliminary communication of part of this work has appeared;[2] the corresponding nickel compound has also been investigated and found to be isostructural with the copper compound.[9]

Experimental Section

Preparations. To a mixture of 50 ml of 2-aminoethanol and 25 ml of 2,4-pentanedione were added 10 mmol of potassium hydroxide and 10 mmol of the cupric acetate monohydrate. The resulting solution was heated gently until a green precipitate started to form on the sides of the vessel and the mixture was then allowed to stand overnight before the green needles were collected by filtration. The product was recrystallized from toluene. Anal. Calcd for $CuC_9H_{12}N_2O_2$: C, 43.62; H, 6.52; N, 11.31. Found: C, 44.42; H, 6.73; N, 11.35.

Magnetic Susceptibility. The magnetic susceptibilities were measured on a Faraday balance using $HgCo(CNS)_4$ as a calibrant. A description of the balance adapted for operation in the temperature range 15–300 K can be found elsewhere.[10] Diamagnetic corrections were made using published atomic values.[11] The magnetic susceptibility of the copper compound was determined at temperatures from 39 to 298 K. The observed susceptibilities and moments are presented in Table I.

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Table I. Variable-Temperature Magnetic Susceptibility Data for $[Cu(DiimH)]_2$

T, K	$10^3\chi_M$,[a] cgsu		μ_{eff}/	T, K	$10^3\chi_M$,[a] cgsu		μ_{eff}/
	Obsd	Calcd	Cu, μ_B		Obsd	Calcd	Cu, μ_B
297.5	2.385	2.418	1.68	91.3	4.773	4.739	1.32
260.9	2.682	2.683	1.67	78.5	4.733	4.736	1.22
235.9	2.885	2.898	1.65	62.6	4.367	4.375	1.05
202.7	3.212	3.238	1.61	54.5	3.876	3.928	0.91
193.1	3.381	3.350	1.62	47.5	3.306	3.343	0.79
144.5	4.054	4.018	1.53	43.0	2.905	2.863	0.71
100.7	4.649	4.658	1.37	39.1	2.429	2.391	0.62

[a] Molar paramagnetic susceptibility corrected for diamagnetism of compound.

Osmometric Measurements. Molecular weights were determined with a Mechrolab vapor pressure osmometer using chloroform as solvent at 37 °C. Values obtained at concentrations from 0.03 to 0.08 fw/l. for both the copper and nickel compounds were within 5% of the values calculated for dimers.

Electron Paramagnetic Resonance. The differential EPR absorption spectra of powdered samples were studied using three different spectrometers. The X-band (ca. 9.6 GHz) spectra were recorded at room temperature with a Bruker ER10 system. Th ku-band (ca. 13.8 GHz) and ka-band (ca. 34.3 GHz) spectra were obtained with homodyne spectrometer systems constructed from component parts. Both of these spectrometers utilized the same Varian V-3900 Mark I Fieldial 12-in. magnet system and the same cryogenic Dewar system. The most accurate g values were determined by measuring the ku-band spectrometer frequency and the frequency of a proton NMR gaussmeter at the same time.

The investigation of the temperature dependence of the EPR intensity spectra carried out at ku band was facilitated by a two-channel analog-to-digital converter system which recorded the lock-in detected EPR signal and the magnetic sweep field as X-Y pairs on paper tape. The spectrum of the excited-state triplet of $[Cu(DiimH)]_2$ was numerically compared with the "standard" doublet spectrum of a reference sample of DPPH (2,2-diphenyl-1-picrylhydrazyl) corresponding to baths of liquid He, liquid N_2, and CO_2 and to room temperature. The temperature of the sample cavity was measured with a digital thermocouple thermometer and a resistance thermometer. The numerical analysis of the digitalized spectra was carried out with an IBM 371/155 computer. The numerical treatment of the data included smoothing by Lagrangian interpolation, baseline correction, closure of the first integral, and subsequent determination of the total absorption intensity by a second numerical integration. A computer plot of a raw X-Y pair data file is illustrated in Figure I.

Crystallographic Data Collection for $[Cu(DiimH)]_2$. A crystal of $[Cu(DiimH)]_2$ having dimensions 0.093 × 0.178 × 0.835 mm was mounted on a glass fiber with the long dimension tilted approximately 45° to the spindle axis. This orientation was chosen because it corresponded to an extinction direction. Space group photographs indicated a triclinic cell. Sixteen reflections, manually centered on an automated Picker four-circle diffractometer, were used to refine cell parameters by a least-squares procedure. The parameters of the reduced primitive cell are $a = 9.554$ (3) Å, $b = 13.025$ (4) Å, $c = 11.662$ (3) Å, $\alpha = 131.29$ (1)°, $\beta = 98.02$ (3)°, $\gamma = 94.31$ (1)°, and $V = 1050.16$ Å^3. The calculated density (1.56 g cm^{-3}) and observed density (1.56 g cm^{-3}, by the flotation method using a mixture of n-heptane and carbon tetrachloride) agree well and are consistent with two dimers per cell.

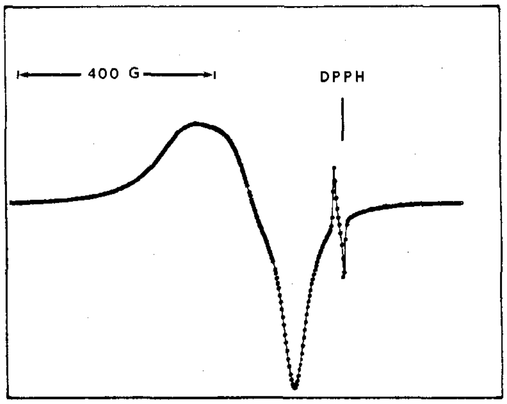

Figure 1. Computer plot of a raw X-Y pair data file of the EPR spectrum of the excited triplet state of dimeric Cu(II)-Cu(II) in $[Cu(DiimH)]_2$ at 86 K and 13.8 GHz. The center field was 4.72 kG. The distorted spectrum of a reference sample of DPPH is noted.

Intensities were measured with a scintillation counter mounted 16 cm from the crystal by the θ–2θ scan technique to a 2θ limit of 50°, using a takeoff angle of 1.6° and a scan rate of 1° min^{-1}. A symmetric scan of 2° was taken about the calculated position and stationary-background counts of 20 s were taken at the beginning (bgd1) and at the end (bgd2) of the scan. Copper attenuators, calibrated as described previously,[12] were used in the collection of data. A total of 2289 reflections were collected. Corrected intensities (I) were obtained by subtracting 3 times the actual measured background from the total integrated peak count (CT) i.e.

$$I = \mathrm{CT} - 3(\mathrm{bgd1} + \mathrm{bgd2})$$

The factor of 3 in the calculation arises from the peak scan time being 3 times as long as the total background count time. The corrected intensities were assigned standard deviations according to the formula[13]

$$\sigma(I) = [\mathrm{CT} + 0.25(t_c/t_b)^2(\mathrm{bgd1} + \mathrm{bgd2}) + (pI)^2]^{1/2}$$

where t_c is the scan time, t_b is the counting time of each background (either bgd1 or bgd2), and p is an "ignorance factor" included to avoid overweighting very strong reflections. A total of 1272 reflections were accepted as statistically above background on the basis that $\sigma(I)/I$ be less than 0.33 with p set at 0.02. Two standard reflections, $(\bar{3}3\bar{2})$ and $(\bar{2}\bar{2}\bar{1})$, were checked at intervals of 50 reflections and showed no significant variation during data collection. The intensities were corrected for Lorentz and polarization effects. The six bounding faces of the crystal were identified as (101), $(\bar{1}0\bar{1})$, $(\bar{1}01)$, $(01\bar{1})$, $(0\bar{1}1)$, and $(1\bar{2}1)$. Absorption corrections were applied by the Gaussian quadrature method; transmission coefficients ranged from 1.20 to 1.73.

Solution and Refinement of the Structure. Computations were carried out on a Burroughs B5500 computer and on a Univac 1108 computer. Programs employed included modified versions of F. L. Carter's program for calculating diffractometer settings, Zalkin's FORDAP Fourier summation program, the Busing–Martin–Levy XFLS and ORFFE least-squares and function and error programs, the Ibers rigid-body refinement modification of XFLS, the Johnson ORTEP thermal ellipsoid plotting program, the ABSORB absorption correction program from Stewart's X-RAY 72 system, and various locally written programs. Cromer and Waber's scattering factors were used for all nonhydrogen atoms[14] and Stewart's hydrogen scattering factors were employed.[15] The copper scattering factor was corrected for the real and imaginary anomalous scattering components using Cromer's dispersion factors.[16]

With four formula units per unit cell in space group $P\bar{1}$, the asymmetric unit consists of two formula units. Coordinates for two independent pairs of copper atoms were obtained from a three-dimensional Patterson function; one pair was near the inversion center at (0, 0, 0) and the other pair was near the inversion center at ($^1/_2$, $^1/_2$, $^1/_2$). An electron density calculation, phased on the copper coordinates, revealed the positions of all remaining nonhydrogen atoms. Full-matrix least-squares refinement of a scale factor, coordinates of all nonhydrogen atoms, anisotropic temperature factors for the copper atoms, and isotropic temperature factors for all other atoms was carried out using a weighting scheme based on counting statistics ($w = 4I/\sigma(I)^2$) and minimizing $w(|F_o| - |F_c|)^2$; the refinement converged to a weighted residual, $R_2 = \{\sum_i w_i(|F_o| - |F_c|)^2/\sum_i w_i \cdot (|F_o|)^2\}^{1/2}$, of 0.064 and a conventional residual, $R_1 = ((||F_o| - |F_c||)/\sum|F_o|)$, of 0.079.

A difference electron density map showed residual features, indicative of anisotropic thermal motion, in the vicinity of the oxygen atoms and the carbon atoms (C6–C9) of the 2-aminoethanol portions of the ligands. Anisotropic thermal parameters of these atoms were varied in subsequent least-squares refinements. Methine and methylene hydrogens were inserted in periodically updated calculated positions of idealized geometry (C–H = 0.95 Å; H–C–H, C–C–H, N–C–H, and O–C–H = 109.5 or 120.0°). The four CH_3 groups were included as rigid groups of C_{3v} symmetry (H–C–H = 109.5°; C–H = 0.95 Å); three positional and three angular parameters, plus an overall

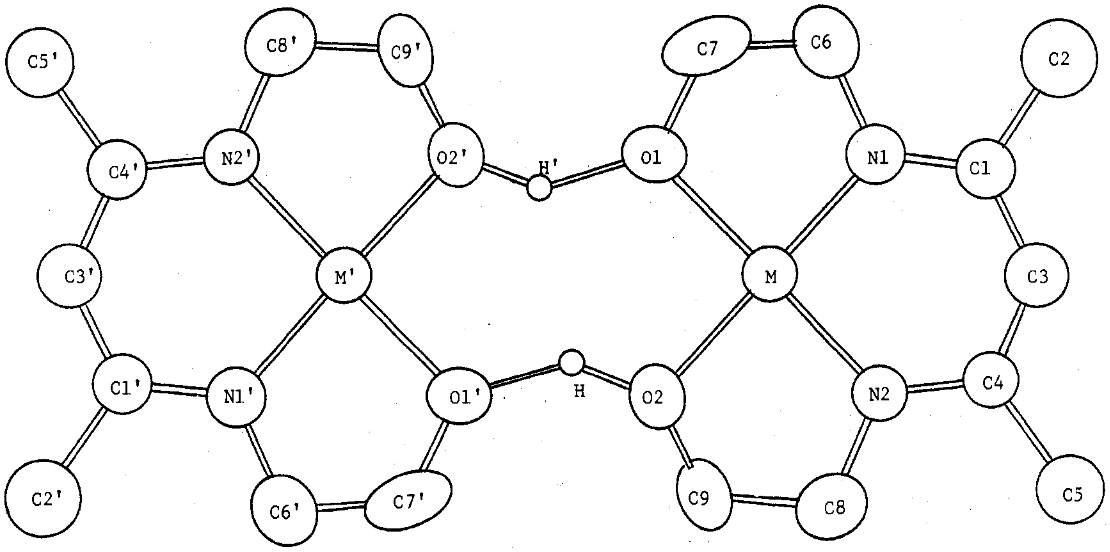

Figure 2. ORTEP drawing of the molecular structure of $[Cu(DiimH)]_2$, unit A.

temperature factor, were refined for each group. These refinements, including all atoms except the hydrogens bound to oxygens, reduced R_1 to 0.0494 and R_2 to 0.0376. A difference electron density map contained as the two highest peaks features quite reasonable for hydrogens bridging the alkoxide groups. The peak maxima lie nearly on a line and symmetrically between the oxygen atoms. A final least-squares refinement, in which the coordinates of the bridging hydrogens were allowed to vary but their temperature factors were fixed with $B = 5.0$ Å^2, gave the final residuals, $R_1 = 0.0468$ and $R_2 = 0.0357$ (1272 observations, 201 variables). The maximum parameter shift in the final cycle was 0.20σ (x coordinate for C9A) and a final difference Fourier synthesis contained no peak greater than 0.30 e/Å^3. Final atomic coordinates and thermal parameters are given in Tables II and III. A table of observed and calculated structure amplitudes is available as supplementary material.

Discussion

The asymmetric unit consists of two copper atoms and two tetradentate ligands; corresponding bond distances and bond angles within the two crystallographically independent metal–ligand units show only small differences. Interatomic distances, with their estimated standard deviations included in parentheses, are collected in Table IV; bond angles, with esd's, are given in Table V.

The square-planar coordination of each copper atom, as indicated in Figure 2, is provided by a tetradentate diimine ligand. Coordination of the two nitrogens of the ligand forms a six-membered chelate ring and further coordination of each oxygen forms a five-membered chelate ring containing a nitrogen and an oxygen. The planarity of the coordination is indicated, Table VI, by the unweighted least-squares plane of the coordinated nitrogen and oxygen atoms and by the distances of the copper, nitrogen, and oxygen atoms from this plane. The greatest deviations of coordinated atoms from these planes are 0.013 and 0.008 Å for the two units; the metal atom deviations from these planes are 0.004 and 0.002 Å.

It is interesting that the tetradentate ligand forms neutral complexes with trivalent cobalt(III) and with divalent nickel(II) and copper(II). In the cobalt(III) complex, protons from both alcohol groups and from the central carbon of the six-membered ring (C3) are removed. With the divalent metal atoms, two protons are lost and comparison of the two C–C bond lengths in the six-membered chelate ring to those of 2,4-pentanedionato chelates indicates multibond character and a delocalized π system. Both of these effects indicate the loss of a proton from the central carbon of the six-membered ring (C3), and the remaining proton is, thus, one of the alcohol protons. These indications of the proton position are further supported by the NMR spectrum of the nickel compound which contains peaks that can be assigned to two methyl groups (τ 8.20), two $-CH_2-CH_2-$ groups (τ 6.95), and a C–H group (τ 4.53). A very broad signal at τ −1.83 can be assigned to a hydrogen-bonded O–H group.

Table II. Final Positional and Isotropic Thermal Parameters for $[Cu(DiimH)]_2$

Atom	x	y	z	B, Å^2
		Unit A		
Cu	0.1453 (2)	−0.0016 (2)	−0.1629 (2)	*a*
O1	0.156 (1)	−0.076 (1)	−0.064 (1)	*a*
O2	−0.0050 (8)	0.0967 (8)	−0.0642 (10)	*a*
N1	0.2914 (9)	−0.0969 (9)	−0.2553 (10)	3.9 (2)
N2	0.1291 (9)	0.0711 (9)	−0.2611 (10)	3.7 (2)
C1	0.346 (1)	−0.100 (1)	−0.354 (1)	4.0 (2)
C2	0.462 (1)	−0.191 (1)	−0.427 (1)	6.7 (3)
C3	0.311 (1)	−0.023 (1)	−0.392 (2)	4.7 (4)
C4	0.217 (1)	0.059 (1)	−0.349 (1)	3.6 (2)
C5	0.203 (1)	0.147 (1)	−0.393 (1)	5.1 (3)
C6	0.331 (1)	−0.180 (1)	−0.221 (2)	*a*
C7	0.272 (2)	−0.140 (2)	−0.091 (2)	*a*
C8	0.031 (1)	0.165 (1)	−0.209 (1)	*a*
C9	−0.076 (1)	0.125 (1)	−0.151 (1)	*a*
H0	0.04 (1)	−0.07 (1)	0.00 (1)	*b*
		Unit B		
Cu	−0.3642 (2)	0.4983 (2)	0.3313 (2)	*a*
O1	−0.5631 (8)	0.4220 (9)	0.2991 (11)	*a*
O2	−0.3120 (10)	0.5882 (10)	0.5518 (9)	*a*
N1	−0.4187 (10)	0.4100 (9)	0.1144 (10)	3.8 (2)
N2	−0.1677 (9)	0.5738 (9)	0.3681 (11)	3.3 (2)
C1	−0.330 (1)	0.405 (1)	0.039 (1)	3.8 (3)
C2	−0.385 (1)	0.319 (1)	−0.142 (1)	5.5 (3)
C3	−0.181 (1)	0.470 (1)	0.106 (2)	3.7 (4)
C4	−0.108 (1)	0.548 (1)	0.264 (1)	3.7 (3)
C5	0.057 (1)	0.603 (1)	0.302 (1)	5.9 (3)
C6	−0.568 (1)	0.330 (1)	0.036 (1)	*a*
C7	−0.643 (1)	0.363 (2)	0.156 (2)	*a*
C8	−0.085 (1)	0.655 (1)	0.528 (1)	*a*
C9	−0.180 (2)	0.683 (2)	0.629 (2)	*a*
H0	−0.60 (1)	0.42 (1)	0.38 (1)	*b*

[a] Refined anisotropically. [b] Temperature factor fixed with $B = 5.0$ Å^2.

Although the separation of the two copper atoms of the asymmetric unit is large (ca. 8 Å), each metal atom of the asymmetric unit is related by symmetry to another metal atom in the unit cell. These symmetry-related metal atoms form dimeric units about inversion centers at (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$) with metal–metal distances of ca. 5.0 Å. The closest approach involving nonhydrogen atoms of the two complexes

Table III. Thermal Parameters for Anisotropically Refined[a] Atoms for $[Cu(DiimH)]_2$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
			Unit A			
Cu	0.0102 (3)	0.0099 (3)	0.0141 (4)	0.0027 (2)	0.0035 (3)	0.0083 (3)
O1	0.018 (2)	0.028 (2)	0.034 (2)	0.014 (1)	0.014 (2)	0.027 (2)
O2	0.014 (1)	0.019 (2)	0.019 (2)	0.008 (1)	0.009 (1)	0.016 (1)
C6	0.014 (2)	0.019 (2)	0.021 (3)	0.006 (2)	0.007 (2)	0.015 (2)
C7	0.025 (3)	0.032 (3)	0.043 (5)	0.013 (3)	0.011 (3)	0.034 (4)
C8	0.019 (2)	0.012 (2)	0.018 (3)	0.005 (2)	0.006 (2)	0.010 (2)
C9	0.018 (2)	0.018 (2)	0.016 (2)	0.008 (2)	0.009 (2)	0.012 (2)
			Unit B			
Cu	0.0093 (3)	0.0108 (3)	0.0114 (3)	−0.005 (2)	0.0013 (2)	0.0068 (3)
O1	0.009 (1)	0.023 (2)	0.015 (2)	−0.005 (1)	0.000 (1)	0.013 (1)
O2	0.014 (1)	0.024 (2)	0.012 (2)	−0.008 (1)	−0.002 (1)	0.011 (1)
C6	0.012 (2)	0.016 (2)	0.014 (2)	−0.001 (2)	0.003 (2)	0.009 (2)
C7	0.013 (2)	0.040 (4)	0.022 (3)	−0.002 (2)	−0.001 (3)	0.023 (3)
C8	0.010 (2)	0.017 (2)	0.017 (3)	0.001 (2)	0.004 (2)	0.011 (2)
C9	0.020 (3)	0.021 (3)	0.017 (3)	−0.008 (2)	−0.005 (2)	0.012 (2)

[a] The form of the thermal ellipsoid expression is $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl]$.

Table IV. Selected Interatomic Distances (Å) for $[Cu(DiimH)]_2$ Complexes

Atoms	Unit A	Unit B
M-M′	4.989 (5)	4.987 (5)
O1-O2′	2.33 (1)	2.31 (1)
O1-HO	1.38 (12)	1.08 (14)
O2-HO	1.09 (12)	1.28 (12)
M-O1	1.939 (9)	1.941 (7)
M-O2	1.954 (9)	1.953 (12)
M-N1	1.889 (10)	1.922 (13)
M-N2	1.906 (9)	1.901 (9)
O1-C7	1.38 (2)	1.35 (1)
O2-C9	1.40 (1)	1.38 (1)
C6-C7	1.46 (2)	1.48 (2)
C8-C9	1.53 (1)	1.47 (2)
N1-C6	1.44 (1)	1.45 (1)
N2-C8	1.45 (1)	1.44 (1)
N1-C1	1.31 (1)	1.28 (1)
N2-C4	1.31 (1)	1.27 (1)
C1-C2	1.58 (1)	1.57 (1)
C4-C5	1.52 (1)	1.56 (1)
C1-C3	1.39 (2)	1.41 (1)
C3-C4	1.36 (2)	1.40 (2)
HO-HO′	2.07 (21)	2.45 (20)

Table V. Selected Angles for the $[Cu(DiimH)]_2$ Complexes

Atoms	Unit A	Unit B
O1-HO-O2′	142 (9)	156 (10)
O1-M-O2	93.1 (4)	92.8 (5)
O1-M-N1	85.9 (4)	86.3 (5)
O2-M-N2	85.7 (4)	85.6 (5)
N1-M-N2	95.4 (4)	95.2 (5)
HO-O1-M	116 (4)	124 (4)
HO-O2-M	111 (6)	124 (10)
HO-O1-C7	133 (4)	126 (5)
HO-O2-C9	132 (5)	125 (5)
O1-C7-C6	117.1 (12)	119.4 (12)
O2-C9-C8	111.0 (10)	115.1 (12)
C7-C6-N1	108.9 (11)	108.6 (10)
C9-C8-N2	106.5 (9)	110.7 (10)
C6-N1-M	114.5 (8)	113.2 (8)
C8-N2-M	113.2 (7)	113.2 (7)
C6-N1-C2	120.4 (10)	121.8 (10)
C8-N2-C4	120.0 (10)	121.3 (10)
N1-C1-C2	118.0 (10)	119.7 (10)
N2-C4-C5	98.0 (10)	121.3 (10)
N1-C2-C3	122.4 (12)	124.3 (12)
N2-C4-C3	120.8 (12)	124.8 (11)
C2-C1-C3	119.0 (10)	115.9 (10)
C5-C4-C3	120.2 (10)	113.9 (10)
C1-C3-C4	130.2 (14)	125.5 (12)
C7-O1-M	109.9 (8)	110.2 (8)
C9-O2-M	108.5 (7)	110.1 (9)
C1-N1-M	124.8 (8)	124.5 (8)
C4-N2-M	126.0 (8)	125.2 (9)
M-O1-O2′	133.3 (5)	134.6 (6)
M-O2-O1′	131.6 (5)	132.1 (5)
C1-C2-H	101-120	108-113
C4-C5-H	108-111	106-111

forming a dimer are the oxygen–oxygen distances of 2.31–2.33 Å. The short oxygen–oxygen distances and the presence of one proton for each pair of oxygen atoms suggest that the dimers are held together by cooperative O–H–O hydrogen bonding. To our knowledge, these are the shortest hydrogen-bonded O–O distances known and they are very close to the F–F distance observed for the HF_2^- ion (2.26 Å). The strength of the hydrogen bonding is further indicated by the dimeric molecular weights obtained for chloroform solutions of these complexes.

Positions for the bridging hydrogen atoms were located in difference electron density maps and these positions were varied in subsequent least-squares refinements. The final positions, Figure 2, are about 1.1 Å from one oxygen and about 1.3 Å from the second. The refined positions indicate a slight bending, with O–H–O angles of about 150°, but it is difficult to say whether this effect is real (a similarly bridged structure shows linear O–H–O groups[17]).

The only significant difference in the two independent dimeric units can be expressed in terms of deviations of the dimers from planarity. The difference is apparent from the distance of one metal atom from the least-squares plane of the four atoms coordinated to the other metal atom of the same dimer, Table VI. For unit B, the distance of M′ from the coordination plane of M is only 0.224 Å; for unit A, the distance is 0.500 Å.

The magnetic moment of the compound, Table I, varies from 1.68 μ_B at room temperature to 0.62 μ_B at 39 K. Using the Bleaney–Bowers equation[8] for exchange coupled dimers

$$\chi_M = 2g^2\beta^2N/3kT\{1 + {}^1/_3 \exp(-J/kT)\}^{-1} + N\alpha$$

least-squares methods were used to obtain values of g, J, and $N\alpha$. Values of $g = 2.04$, $J = -94$ cm^{-1}, and $N\alpha = 118 \times 10^{-6}$ were obtained and the agreement between observed and calculated molar susceptibilities is indicated in Figure 3. Because of the two independent dimers, there should be two different J values and the value obtained for the best fit would be an average of these values.

Table VI. Equations for the Least-Squares Plane[a] of the Coordinated Atoms

Equations of the Least-Squares Plane for N1, N2, O1 and O2

Unit 1: $0.5327X + 0.4159Y + 0.7370Z = 0.2478$

Unit 2: $-0.4149X + 0.9030Y + 0.1117Z = 6.172$

	Distance from plane, Å			Distance from plane, Å	
Atom	Unit A	Unit B	Atom	Unit A	Unit B
O1	−0.013	−0.008	C3	0.068	−0.170
O2	0.010	0.008	C4	0.091	−0.137
N1	0.012	0.008	C5	0.348	−0.280
N2	−0.011	−0.008	C6	−0.089	−0.053
M	0.004	0.002	C7	0.186	0.158
M′	−0.500	−0.224	C8	0.101	0.015
C1	−0.018	−0.098	C9	−0.471	0.330
C2	−0.084	−0.212			

[a] The equations are referred to orthogonal axes with the orthogonal X axis coincident to a and the orthogonal Z axis coincident to c^*.

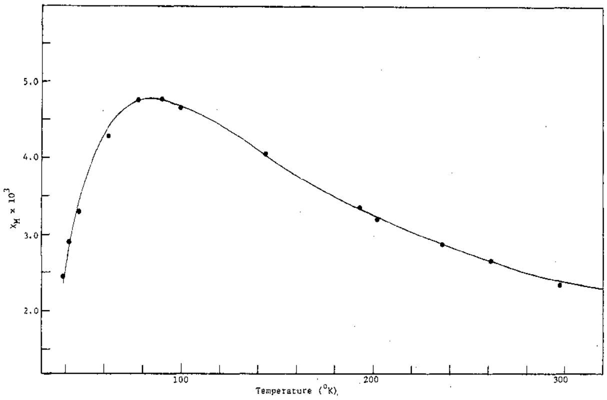

Figure 3. Experimental and calculated magnetic susceptibility data for $[Cu(DiimH)]_2$. Solid line represents values calculated for $g = 2.04$ and $J = -94$ cm^{-1}.

The X-band EPR spectrum was a single, slightly asymmetric line with a g value of approximately 2.07 and a width of about 160 G. The ku-band spectrum hinted of a more complex structure as the example shown in Figure 1 illustrates. Extending our investigation to higher frequency provided evidence for resolution of the EPR spectra of the two distinct dimeric units, as indicated in the example ka-band spectrum shown in Figure 4. The two lower field absorption edges, that is, the first two extrema in the ka-band differential EPR spectrum, correspond to the parallel g values (2.14 and 2.09 at 77 K).[18] The two high-field absorption edges, the last two extrema in the ka-band differential EPR spectrum, which are not well resolved correspond to the perpendicular g values (2.03 and 2.06 at 77 K). It is significant to note that the intensities due to the two sites were found to be essentially the same at room temperature and 77 K indicating that the two sites must have essentially the same J value. These values are consistent with the average extreme g values determined at ku band ($\langle g_\parallel \rangle = 2.125 \pm 0.001$ and $\langle g_\perp \rangle = 2.039 \pm 0.001$ at 77 K) and the most likely g value also determined at ku band ($g_0 = 2.0694 \pm 0.0005$).

The integrated EPR absorption intensity data rationalized to those of the standard reference doublet are summarized in Figure 5. The best fit of these data to the behavior predicted by Boltzmann statistics[19] for an excited-state triplet $|J|$ above a ground-state singlet, $A_T/A_D \propto 4/[3 + \exp(-J/kT)]$, gave an EPR J value of -90.4 ± 2.8 cm^{-1}. The solid line in Figure 5 indicates this fit.

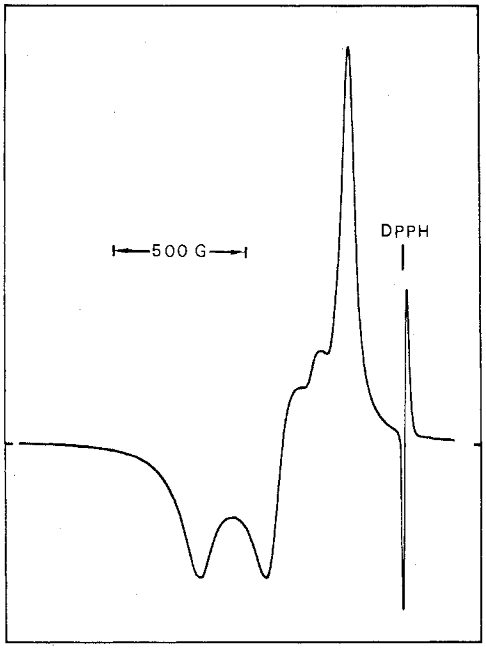

Figure 4. Chart of the EPR spectrum of the excited triplet states of dimeric Cu(II)–Cu(II) sites in $[Cu(DiimH)]_2$ at 77 K and 34.3 GHz. The center field was 11.6 kG. The distorted spectrum of a reference sample of DPPH is noted.

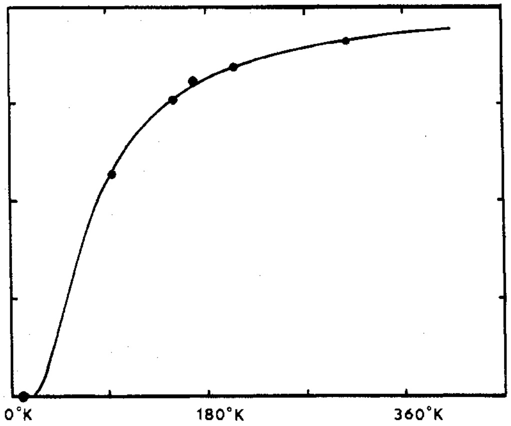

Figure 5. Temperature variation of the integrated EPR intensity of the excited triplet state of dimeric Cu(II)–Cu(II) in $[Cu(DiimH)]_2$ rationalized to that of a "standard" doublet: ●, experimental data; –, curve predicted by Boltzmann statistics for an excitation of 90.4 cm^{-1} above a ground-state singlet.

The copper–copper distance within dimeric units (5 Å) rules out direct exchange and the copper–copper distance between dimers (8 Å) rules out cooperative lattice effects; the antiferromagnetic behavior must be due to superexchange via the bridging hydrogen atoms. Furthermore, the absence of low energy p orbitals on hydrogen rules out a π mechanism and leaves a σ pathway as the only reasonable possibility. In view of these considerations, the magnitude of the coupling constant is surprisingly large. The coupling constant is also large in comparison to the values obtained[7] for the $[Cu_2(tren)_2X_2](BPh_4)_2$ compounds; the coupling constants for those compounds were in the range of 0 to −4 cm^{-1}. Further examples of hydrogen-bonded complexes are needed to establish a relationship between the magnitudes of the coupling and the strength of the hydrogen bonding. Studies of other hydrogen-bonding species are in progress.

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Registry No. [Cu(DiimH)]$_2$, 60525-65-7; 2-aminoethanol, 141-43-5; 2,4-pentanedione, 123-54-6.

Supplementary Material Available: Listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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Bending of Linear Nitric Oxide Ligands in Four-Coordinate Transition Metal Complexes. Crystal and Molecular Structure of Dinitrosyldithioacetylacetonatocobalt(−I), Co(NO)$_2$(SacSac)

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The crystal and molecular structure of dinitrosyldithioacetylacetonato cobalt, Co(NO)$_2$(SacSac), has been determined at 294 K from three-dimensional data measured by counter methods. The compound crystallizes in the centrosymmetric monoclinic space group $C2/m$ (C_{2h}^3, No. 12) with $a = 16.565$ (2) Å, $b = 7.604$ (2) Å, $c = 8.709$ (1) Å, $\beta = 114.90$ (1)°, $V = 995.05$ Å^3, $\rho_{\text{calcd}} = 1.67$ g cm^{-3} for $Z = 4$. The structure was solved by conventional Patterson and Fourier techniques and refined by full-matrix least squares to final residuals $R = 0.040$ and $R_w = 0.040$ for 580 independent reflections with $I/\sigma(I) \geq 3.0$. The molecule has exact m symmetry with the mirror plane containing the Co(SacSac) unit. The coordination geometry around the cobalt is a slightly distorted tetrahedron. Bond distances of interest are Co–S = 2.217 (2), 2.224 (2) Å, Co–N = 1.650 (6) Å, and N–O = 1.120 (5) Å. The Co–N–O angle is 168.9 (5)° and the N–Co–N angle is 115.5 (3)°. From a comparison of the details of this structure with those of other tetracoordinate dinitrosyls containing the $\{M(NO)_2\}^{10}$ functional group, it is evident that "linear" M–N–O systems are invariably partially bent with M–N–O angles ranging from 158.9 to 178.7°. The angles N–M–N and O–M–O are found to be linearly correlated with O–M–O ≤ N–M–N ≤ 130° for M = first-row transition metal (attracto conformer) and 130° ≤ N–M–N ≤ O–M–O for M = second- and third-row transition metals (repulso conformer). The conditions and requirements leading to partial bending of "linear" nitrosyl ligands in tetracoordinate complexes are discussed.

Introduction

The nitric oxide ligand is amphoteric and can act either as a one-electron donor (NO$^-$; bent MNO) or as a three-electron donor (NO$^+$; linear MNO).[1] In order to characterize this unusual ligand property, a large number of metal–nitrosyl complexes have been studied by x-ray crystallography.[2,3] Recent interest has centered on the four-coordinate dinitrosyl complexes of the group 8 metals, especially since several have been found to promote the catalytic reduction of nitric oxide by carbon monoxide to form nitrous oxide and carbon dioxide.[4–8] To date, all such complexes have been shown to have a distorted tetrahedral coordination about the metal with M–N–O groups which are approximately linear rather than fully bent (i.e., M–N–O = 120°). This structural evidence is consistent with the nitrosyl ligands acting essentially as three-electron donors (NO$^+$) with the metal atom having, at least formally, both a closed-shell d^{10} configuration and an unusually low oxidation state (e.g., Fe(−II), Co(−I)).

Attempts to correlate structure and bonding with chemical reactivity require, as a prerequisite, both the synthesis of new four-coordinate dinitrosyls and a knowledge of the fine details of their geometrical structures. At present, relevant crystallographic data are limited to the phosphine (PPh$_3$) series M(NO)$_2$P$_2$, in which M is Fe, Ru, Os, Co$^+$, Rh$^+$, and Ir$^+$, some polynuclear bridged species containing the functional Fe(NO)$_2$ or Co(NO)$_2$ group, and the monomeric compounds Fe(NO)$_2$(f$_6$fos)[9] and Fe(NO)$_2$(CO)$_2$. Although the supporting ligands are commonly phosphines and so, to some degree, in competition with nitric oxide for π-electron density from the central metal atom, in several instances π-donating ligands such as halogens complete the coordination sphere. The binuclear complex [Fe(NO)$_2$SEt)]$_2$ provides the only example so far structurally characterized of a sulfur donor ligand completing the coordination environment.

All of the complexes possess pseudotetrahedral geometry (see Table V), but, interestingly, pronounced differences in the magnitude of the N–M–N angle are observed. It has been suggested[10] that "opening up" of the N–M–N angle can be rationalized in terms of increased repulsion between the nitrosyl ligands concomitant with increasing extent of back-bonding from the metal. The alternative molecular orbital description[3] of pseudotetrahedral dinitrosyls correlates the observed distortions from an idealized T_d geometry in these d^{10} complexes in terms of changes in metal/ligand parentage of the HOMO. Either approach leads to the expectation that larger N–M–N angles are matched with NO$^-$ character, and smaller N–M–N angles with NO$^+$ character. The more strongly reducing second- and third-row transition metals favor the former; the