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Preparation and Structural and Magnetic Characterization of β-Di-μ-hydroxo-bis[2-(2-dimethylaminoethyl)pyridine]dicopper(II) Perchlorate

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β-Di-μ-hydroxo-bis[2-(2-dimethylaminoethyl)pyridine]dicopper(II) perchlorate, $[Cu(C_9N_2H_{14})OH]_2(ClO_4)_2$, has been prepared by the reaction of copper(II) perchlorate hexahydrate with 2-(2-dimethylaminoethyl)pyridine (DMAEP) in ethanol-ether solution; this choice of solvent represses the formation of the triclinic α form of this complex. The crystal structure of the complex has been determined from three-dimensional X-ray data collected by counter methods. The material crystallizes in the monoclinic space group $P2_1/c$ with two dimeric formula units in a cell of dimensions $a = 7.266$ (3), $b = 16.500$ (9), $c = 10.851$ (4) Å, and $\beta = 82.43$ (3)°. The observed and calculated densities are 1.68 (3) and 1.70 g cm^{-3}, respectively. The structure has been refined by full-matrix least-squares methods to a final R factor of 0.032 for 1896 intensities. The complex consists of pairs of copper atoms linked by two hydroxo bridges. The coordination geometry at each copper atom is roughly tetragonal pyramidal, the basal plane consisting of the bridging oxygen atoms and the nitrogen atoms of the DMAEP ligand while the axial site is occupied by an oxygen atom from the anion. It is this unidentate perchlorate coordination which is the most striking difference between this complex and the triclinic α isomer. The epr spectrum of the complex has been interpreted to give $|D| = 0.43$ cm^{-1} and an average $g = 2.03$. The magnetic susceptibility of the complex shows a broad maximum at approximately 175°K. The data obey the Bleaney-Bowers expression for exchange-coupled pairs of copper(II) ions and yield a $2J$ value of -201 cm^{-1} with $g = 2.03$. The structural and magnetic data are consistent with those of structurally similar hydroxo-bridged copper(II) complexes.

Introduction

As a part of our continuing endeavors[1-14] to correlate the structural and magnetic properties of magnetically condensed systems, we have recently investigated the properties of several dihydroxo-bridged copper(II) and chromium(III) dimers[3,7,8,10-12,14] and have shown that there is an inverse correlation between the value of the exchange integral, J, and the Cu-O-Cu bridging angle.[12] The reported preparations[15] of copper(II) complexes with N-substituted 2-(2-aminoethyl)pyridines of this type have enabled us to continue these efforts. On the basis of magnetic and spectral data, Uhlig and coworkers[15] postulated that these complexes should be considered to be dimers of the type $[CuL(OH)]_2^{2+}$, and we have confirmed this for the cases of $[Cu(EAEP)OH]_2[ClO_4]_2$, where EAEP is 2-(2-ethylaminoethyl)pyridine,[8] and α-$[Cu(DMAEP)OH]_2[ClO_4]_2$, where DMAEP is 2-(2-dimethylaminoethyl)pyridine.[14] The initial magnetic susceptibility measurements of Uhlig and coworkers also suggested that there may be significant structural differences between the di- and monosubstituted ligand complexes since the α-dimethyl complex exhibits Curie-Weiss behavior above 80°K with $\Theta = -5°$ while the methyl- and isopropyl-substituted complexes each demonstrate a susceptibility maximum at temperatures greater than 100°K.[15] This observation is consistent with the results of our recent structural investigations of $[Cu(EAEP)OH]_2[ClO_4]_2$ and α-$[Cu(DMAEP)OH]_2[ClO_4]_2$ as minor dissimilarities in the hydroxo-bridge geometry and major differences in anion coordination between these two complexes were found; our recent magnetic measurements on these compounds also tend to confirm these earlier findings.[7,16]

In the course of our investigation of the triclinic α-$[Cu(DMAEP)OH]_2[ClO_4]_2$, a monoclinic crystalline form of this complex was discovered. Uhlig and coworkers[15] reported only one form of this material, and from a comparison of the magnetic behavior of the two isomers it is evident that the material which they reported was the triclinic α form; the

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monoclinic β form, therefore, has not been reported previously. Considering the major structural and magnetic differences between $[Cu(EAEP)OH]_2[ClO_4]_2$ and α-$[Cu(DMAEP)OH]_2[ClO_4]_2$, it was felt that characterization of the second DMAEP complex would be of great importance in our efforts to gain a better understanding of the relationship between structural changes and magnetic behavior and, also, of the coordination preferences of the perchlorate group in transition metal complexes. Hence, we report here the structural and magnetic properties of the monoclinic β-di-μ-hydroxo-bis[2-(2-dimethylaminoethyl)pyridine]dicopper(II) perchlorate, β-$[Cu(DMAEP)OH]_2(ClO_4)_2$.

Experimental Section

Epr Measurements. The X-band epr spectrum of a powdered sample of the complex was obtained using a Varian E-3 spectrometer and a JEOL ME 3X spectrometer. The transition fields were corrected for a spectrometer frequency of 9.36 GHz. A modulation frequency of 100 kHz was used in each case. The spectrum was recorded at 77°K using a quartz liquid nitrogen insertion dewar. A Magnion G-502 precision gaussmeter, a Hewlett-Packard 52452 frequency counter, and a DPPH sample were used to calibrate the magnetic fields and klystron frequencies.

Bulk Magnetic Susceptibility Measurements. The magnetic susceptibilities of two powdered samples of β-$[Cu(DMAEP)OH]_2[ClO_4]_2$ were measured using a Foner-type[17] vibrating-sample magnetometer. The reproducibility of the data was excellent. The measurements were made at temperatures in the range 4.2–300°K and at magnetic field strengths of 10 and 15 kG. No magnetic field dependence of the data was observed. The magnetic field strengths were calibrated by nuclear resonance techniques as above. The temperatures were measured with a calibrated Ga/As diode. Mercury tetrathiocyanatocobaltate(II) was used as a susceptibility standard.[18] The susceptibilities were corrected for the diamagnetism of the substituent atoms using Pascal's constants[19] and for the TIP of copper(II) (estimated to be 60×10^{-6} cgsu/Cu atom[20]).

Crystallographic Data Collection and Reduction. Small, dark-blue crystals of β-$[Cu(DMAEP)OH]_2(ClO_4)_2$, essentially uncontaminated with the α form, can be obtained by mixing equimolar quantities of copper(II) perchlorate hexahydrate and DMAEP in ethanol–ether. *Anal.* Calcd for $CuN_2C_9ClO_5H_{15}$: C, 32.64; H, 4.53; N, 8.58. Found: C, 32.84; H, 4.52; N, 8.46. Crystals which were more suitable for X-ray diffraction study were obtained by the method described previously,[14] which results in the precipitation of both forms of the complex. Preliminary precession and Weissenberg photographs indicated that the needle-like crystals belong to the monoclinic system, and the systematic absences observed ($0k0$ for k odd and $h0l$ for l odd) indicate that the space group is $P2_1/c$,-C_{2h}^5. The cell constants obtained by the least-squares procedure of Busing and Levy[21] on 12 independent reflections are $a = 7.266$ (3), $b = 16.500$ (9), $c = 10.851$ (4) Å, and $\beta = 82.43$ (3)°, the observations being made at 20° and with Mo Kα radiation with an assumed wavelength of 0.7093 Å. The calculated density of 1.70 g cm^{-3} for two dimeric units per cell agrees well with the experimental density of 1.68 (3) g cm^{-3} obtained by flotation in dichloromethane–iodomethane solution.

Cell constants and diffraction data were obtained from an approximately cylindrical crystal with a length of 0.064 cm and a mean diameter of 0.008 cm. The crystal was mounted approximately perpendicular to the (100) planes and data were collected on a Picker four-circle automatic diffractometer equipped with a graphite monochromator in the manner previously described.[22] A total scan range for each reflection of from 0.75° below the calculated Kα_1 peak position to 0.75° above the calculated Kα_2 peak position was maintained, with a take-off angle of 1.0°. The scan rate for the data collection was varied, a rate of 1.0°/min being used for all reflections with $2\theta < 30°$ and a rate of 0.5°/min being used for all reflections with $2\theta \geqslant 30°$. Stationary background counts for 20 and 40 sec for $2\theta < 30°$ and $2\theta \geqslant 30°$, respectively, were recorded at each end of the scan. Two separate scale factors were used in the refinement of the structure (*vide infra*), the data with $2\theta < 30°$ being assigned scale factor S_1 and those with $2\theta \geqslant 30°$ being assigned scale factor S_2. The ratio $S_2{:}S_1$ should, of course, be $\sqrt{2}{:}1$, since these scale factors are on F; it is encouraging to note that this ratio was observed to be 1.404:1, which gives a measure of the internal consistency of the data set.

A single form ($-h$, $+k$, $\pm l$) of the data was collected out to a value of $2\theta(\mathrm{Mo}) = 50°$, above which there were few intensities greater than background. Data processing was carried out as described by Corfield, Doedens, and Ibers,[23] the value of p in the expression[24]

$$\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2]^{1/2}$$

being chosen as 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects using the expression[25]

$$1/Lp = 2 \sin 2\theta/(\cos^2 2\theta_m + \cos^2 2\theta)$$

where θ_m is the monochromator angle. No absorption correction was applied to the data; the absorption coefficient, μ, for these atoms and Mo Kα radiation is 20.0 cm^{-1}, and Bond[26] has shown that for a cylindrical sample of the dimensions of our crystal the transmission coefficients remain constant for all values of $\theta < 90°$. Of the 2570 data recorded, 1896 had intensities greater than three times their estimated standard deviations; only these reflections were used in the solution and refinement of the structure.

Solution and Refinement of the Structure

Examination of the three-dimensional Patterson[27] function revealed the position of the independent copper atom. Two cycles of full-matrix least-squares refinement, using those reflections whose intensities were greater than three times their estimated standard deviations, were run on this position. All least-squares refinements in this analysis were carried out on F, the function minimized being $\Sigma w \cdot (|F_o| - |F_c|)^2$ and the weights w being taken as $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c, the atomic scattering factors for Cu and Cl were taken from Cromer and Waber,[28] those for C, O, and N from Ibers,[29] and that for H from Stewart, Davidson, and Simpson.[30] The effects of anomalous dispersion of copper and chlorine were included in the calculations of F_c,[31] the values of $\Delta f'$ and $\Delta f''$ being taken from Cromer.[32] After the two cycles of refinement the usual agreement factors $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_2 = \Sigma(w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2)^{1/2}$ were 0.485 and 0.573, respectively. The remaining nonhydrogen atoms were located by two sequences of difference Fourier synthesis followed by least-squares refinement. The final values of R_1 and R_2 after isotropic refinement of all nonhydrogen atoms were 0.096 and 0.118, respectively.

The addition of anisotropic refinement for all nonhydrogen atoms reduced the values of R_1 and R_2 to 0.043 and 0.061 after two further cycles of least-squares refinement. At this time a difference Fourier map revealed the positions of all anticipated hydrogen atoms, with an average peak height of 0.6 e Å^{-3}. Several additional cycles of least-squares refinement varying all atomic positional parameters and utilizing anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms resulted in values of R_1 and R_2 of 0.032 and 0.039. An examination of $|F_o|$ and $|F_c|$

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for the most intense low order reflections suggested no correction for secondary extinction was necessary and none was made. Examination of the values of R_2 showed a dependence on sin θ which suggested that our weighting scheme was inappropriate. Accordingly, the weights were modified by multiplying the weights, w, for data with $2\theta < 20°$ by 0.39, which significantly reduced the dependence of R_2 on sin θ. A final cycle of least-squares refinement, in which no parameter shift was greater than 0.25 times its estimated standard deviation, resulted in values of 0.032 and 0.038 for R_1 and R_2, and the refinement was considered converged. A final difference Fourier map revelaed no peak larger than 0.6 e Å^{-3}, and only three peaks in excess of 0.35 e Å^{-3}. Of these three peaks, whose height ranged from 0.54 to 0.58 e Å^{-3}, one was in the vicinity of the copper atom and two were close to atom O(4) of the perchlorate group. A structure factor calculation using those reflections whose intensities are less than three times their estimated standard deviations demonstrated that none of these "unobserved" data have values of $|F_o - F_c| > 5.0\sigma(F_o)$. The positional and thermal parameters obtained from the final least-squares calculation, along with their associated standard deviations as estimated from the inverse matrix, are presented in Tables I and II. A compilation of observed and calculated structure factors is also available.[33]

Description of the Structure

The structure consists of dimeric [Cu(DMAEP)OH]$_2^{2+}$ units and weakly bound unidentate perchlorate groups. The geometry at the copper atoms, as shown in Figure 1, may be best described as two adjoining tetragonal pyramids with a common edge defined by the two bridging hydroxyl oxygen atoms. This geometry is not unusual as it is also observed in both the nitrate[34] and sulfate[35] salts of [Cu(bipy)OH]$_2^{2+}$ and in [Cu(EAEP)OH]$_2$[ClO$_4$]$_2$[8] where the fifth coordination site of each copper is also filled by an anion or solvent molecule, but is different from the four-coordinate and six-coordinate geometries observed in [Cu(tmen)OH]$_2$Br$_2$, where tmen is tetramethylethylenediamine,[36] and α-[Cu(DMAEP)OH]$_2$-[ClO$_4$]$_2$,[14] respectively.

The "basal plane" of each pyramidal unit, consisting of a copper atom, two hydroxyl oxygen atoms, and the two coordinating nitrogen atoms from a DMAEP ligand, is essentially planar, with the largest deviation from the best least-squares planes being 0.08 Å. The geometry at the copper atom is, however, unusual inasmuch as the metal is not significantly displaced from the basal plane; in most tetragonal pyramidal transition metal complexes the metal lies above the plane in the direction of the axial ligand, the displacement of the metal from the plane usually being in the range of 0.1 to 0.2 Å.[37-39] Necessarily, as imposed by the inversion center, the dimeric plane composed of Cu, Cu$'$, O(1), O(1)$'$, N(1), N(2), N(1)$'$, and N(2)$'$ is also essentially planar with a largest deviation from the best least-squares plane of 0.09 Å. This planarity was also observed in [Cu(EAEP)OH]$_2$[ClO$_4$]$_2$, α-[Cu(DMAEP)OH]$_2$[ClO$_4$]$_2$, [Cu(bipy)OH][NO$_3$]$_2$, and [Cu(tmen)OH]$_2$Br$_2$ but not in [Cu(bipy)OH]$_2$[SO$_4$]·5H$_2$O, which contains a dihedral angle of 7.9° between pyramidal units. The bond lengths and angles for this portion of the complex, as given in Tables III and IV, are consistent with those in similar complexes,[8,14,34-36] the Cu-Cu$'$ separation being 2.935 (1) Å and the Cu-O(1) and Cu-O(1)$'$ bond lengths being 1.900 (3) and 1.919 (3) Å. The bond angles of 100.4 (1) and 79.6 (1)° for Cu-O(1)-Cu$'$ and O(1)-Cu-O(1)$'$, respectively, are also in the range of those found in previously investigated[8,14,34-36] di-μ-hydroxo copper(II) complexes. The Cu-N(1) and Cu-N(2) bond lengths are normal[4,6,13] with values of 2.003 (3) and 2.066 (3) Å, the copper to pyridine nitrogen bond length being slightly shorter than that of the copper to amine nitrogen.

The data suggest that there may be hydrogen bonding involving the bridging hydroxo group. The sum of the van der Waals radii of O and H is given by Pauling[40] as 2.60 Å and by Bondi[41] as 2.72 Å. The OH· · ·O(3) (where OH is the hydroxyl hydrogen atom) separation of 2.48 Å observed here is shorter than these values; using a more reasonable O(1)-OH distance of 1.02 Å (instead of our observed value of 0.56 Å)

Table I. Positional Parameters for β-[Cu(DMAEP)OH]$_2$(ClO$_4$)$_2$

Atom	x	y	z
Cu	−0.03313 (6)	−0.05035 (2)	0.11221 (3)
Cl	−0.36525 (13)	0.12000 (5)	0.15305 (9)
O(1)	−0.1301 (5)	−0.0333 (2)	−0.0400 (2)
O(2)	−0.2444 (5)	0.0736 (2)	0.2184 (3)
O(3)	−0.4900 (5)	0.0649 (2)	0.1074 (3)
O(4)	−0.4587 (8)	0.1763 (3)	0.2338 (5)
O(5)	−0.2578 (6)	0.1584 (2)	0.0499 (3)
N(1)	0.0913 (4)	−0.0527 (2)	0.2662 (2)
C(1)	0.1470 (6)	0.0175 (3)	0.3110 (3)
C(2)	0.2359 (7)	0.0217 (4)	0.4147 (4)
C(3)	0.2687 (6)	−0.0492 (4)	0.4750 (4)
C(4)	0.2136 (6)	−0.1213 (3)	0.4297 (4)
C(5)	0.1249 (5)	−0.1223 (2)	0.3238 (3)
C(6)	0.0549 (6)	−0.1979 (3)	0.2721 (4)
C(7)	−0.1547 (6)	−0.1931 (3)	0.2704 (4)
N(2)	−0.2040 (4)	−0.1484 (2)	0.1614 (2)
C(9)	−0.4000 (6)	−0.1218 (3)	0.1886 (4)
C(8)	−0.1925 (8)	−0.2093 (3)	0.0546 (4)
OH	−0.207 (6)	−0.028 (2)	−0.042 (4)
H(1)	0.120 (6)	0.063 (3)	0.275 (4)
H(2)	0.271 (8)	0.070 (3)	0.439 (5)
H(3)	0.314 (9)	−0.051 (3)	0.544 (5)
H(4)	0.239 (6)	−0.174 (3)	0.464 (4)
H(61)	0.079 (6)	−0.240 (3)	0.319 (4)
H(62)	0.099 (6)	−0.208 (3)	0.192 (4)
H(71)	−0.212 (6)	−0.164 (2)	0.343 (4)
H(72)	−0.200 (7)	−0.246 (3)	0.268 (4)
H(81)	−0.070 (8)	−0.222 (3)	0.042 (4)
H(82)	−0.269 (7)	−0.245 (3)	0.076 (4)
H(83)	−0.212 (8)	−0.176 (3)	−0.021 (5)
H(91)	−0.478 (8)	−0.168 (3)	0.216 (4)
H(92)	−0.416 (7)	−0.088 (3)	0.253 (4)
H(93)	−0.447 (10)	−0.098 (4)	0.115 (6)

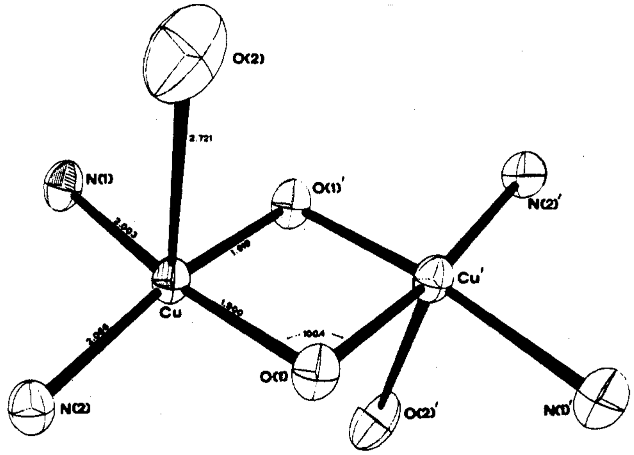

Figure 1. View of the coordination geometry around the copper atoms in β-[Cu(DMAEP)OH]$_2$(ClO$_4$)$_2$.

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Table II. Thermal Parameters for β-$[Cu(DMAEP)OH]_2(ClO_4)_2$

Atom	β_{11}[a] or B, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.00897 (11)	0.00269 (2)	0.00459 (5)	−0.00087 (3)	−0.00159 (4)	0.00077 (2)
C1	0.01204 (21)	0.00314 (4)	0.01042 (10)	0.00005 (6)	−0.00286 (11)	−0.00040 (4)
O(1)	0.0066 (6)	0.0034 (1)	0.0060 (2)	−0.0012 (2)	−0.0020 (3)	0.0010 (1)
O(2)	0.0185 (8)	0.0074 (2)	0.0086 (3)	0.0029 (3)	−0.0048 (4)	−0.0001 (2)
O(3)	0.0193 (9)	0.0052 (1)	0.0174 (4)	−0.0038 (3)	−0.0099 (5)	0.0014 (2)
O(4)	0.0393 (15)	0.0062 (2)	0.0289 (8)	0.0050 (5)	0.0048 (9)	−0.0054 (3)
O(5)	0.0289 (10)	0.0051 (1)	0.0132 (4)	−0.0042 (3)	−0.0035 (5)	0.0022 (2)
N(1)	0.0111 (7)	0.0038 (1)	0.0051 (2)	−0.0001 (2)	−0.0018 (3)	0.0009 (1)
C(1)	0.0148 (9)	0.0040 (2)	0.0058 (3)	−0.0006 (3)	−0.0021 (4)	0.0003 (2)
C(2)	0.0163 (10)	0.0061 (2)	0.0067 (4)	−0.0015 (4)	−0.0023 (5)	−0.0013 (2)
C(3)	0.0139 (9)	0.0083 (3)	0.0055 (3)	−0.0005 (4)	−0.0034 (4)	0.0012 (3)
C(4)	0.0118 (9)	0.0065 (2)	0.0068 (3)	−0.0004 (4)	−0.0022 (4)	0.0028 (2)
C(5)	0.0090 (8)	0.0046 (2)	0.0053 (3)	0.0004 (3)	−0.0003 (4)	0.0015 (2)
C(6)	0.0178 (10)	0.0035 (2)	0.0084 (4)	0.0009 (3)	−0.0025 (5)	0.0019 (2)
C(7)	0.0162 (9)	0.0031 (1)	0.0073 (3)	−0.0007 (3)	−0.0005 (4)	0.0015 (2)
N(2)	0.0110 (6)	0.0027 (1)	0.0057 (2)	−0.0005 (2)	−0.0003 (3)	0.0006 (1)
C(8)	0.0210 (11)	0.0029 (2)	0.0080 (4)	−0.0011 (4)	−0.0010 (5)	−0.0004 (2)
C(9)	0.0114 (9)	0.0034 (2)	0.0094 (4)	−0.0004 (3)	0.0002 (5)	0.0002 (2)
OH	1.2 (10)					
H(1)	3.2 (9)					
H(2)	4.9 (11)					
H(3)	6.1 (13)					
H(4)	3.7 (9)					
H(61)	3.7 (9)					
H(62)	3.9 (10)					
H(71)	3.4 (8)					
H(72)	4.4 (10)					
H(81)	4.4 (10)					
H(82)	4.4 (10)					
H(83)	5.3 (11)					
H(91)	4.9 (10)					
H(92)	4.2 (10)					
H(93)	8.3 (16)					

[a] The form of the anisotropic thermal ellipsoid 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 III. Internuclear Distances in β-$[Cu(DMEAP)OH]_2(ClO_4)_2$

Atoms	Dist, Å	Atoms	Dist, Å
Cu–Cu′	2.935 (1)	C(7)–N(2)	1.477 (5)
Cu–O(1)	1.900 (3)	N(2)–C(8)	1.471 (5)
Cu–O(1)′	1.919 (3)	N(2)–C(9)	1.482 (5)
Cu–O(2)	2.721 (4)	C(1)–H(1)	0.88 (4)
Cu–N(1)	2.003 (3)	C(2)–H(2)	0.88 (5)
Cu–N(2)	2.066 (3)	C(3)–H(3)	0.86 (6)
Cl–O(2)	1.422 (3)	C(4)–H(4)	0.97 (4)
Cl–O(3)	1.419 (3)	C(6)–H(61)	0.89 (5)
Cl–O(4)	1.390 (4)	C(6)–H(62)	0.90 (5)
Cl–O(5)	1.427 (4)	C(7)–H(71)	0.97 (4)
N(1)–C(1)	1.339 (5)	C(7)–H(72)	0.93 (5)
C(1)–C(2)	1.372 (6)	C(8)–H(81)	0.93 (6)
C(2)–C(3)	1.378 (7)	C(8)–H(82)	0.89 (5)
C(3)–C(4)	1.367 (7)	C(8)–H(83)	0.97 (5)
C(4)–C(5)	1.390 (6)	C(9)–H(91)	0.98 (5)
C(5)–C(6)	1.486 (6)	C(9)–H(92)	0.89 (5)
C(5)–N(1)	1.344 (5)	C(9)–H(93)	0.99 (7)
C(6)–C(7)	1.528 (7)	O(1)–OH	0.56 (9)

Table IV. Internuclear Angles in β-$[Cu(DMEAP)OH]_2(ClO_4)_2$

Atoms	Angles, deg	Atoms	Angles, deg
Cu–O(1)–Cu	100.4 (1)	O(4)–Cl–O(5)	111.7 (3)
O(1)–Cu–O(1)	79.6 (1)	Cu–O(2)–Cl	123.0 (1)
O(1)–Cu–N(2)	93.5 (1)	C(1)–N(1)–C(5)	119.2 (3)
O(1)–Cu–O(2)	90.2 (1)	N(1)–C(1)–C(2)	122.6 (4)
O(1)–Cu–N(1)	171.2 (2)	C(1)–C(2)–C(3)	118.5 (5)
O(1)′–Cu–N(1)	91.8 (1)	C(2)–C(3)–C(4)	119.4 (4)
O(1)′–Cu–O(2)	85.2 (1)	C(3)–C(4)–C(5)	119.8 (4)
O(1)′–Cu–N(2)	170.7 (2)	C(4)–C(5)–N(1)	120.5 (4)
N(1)–Cu–N(2)	95.2 (1)	C(4)–C(5)–C(6)	122.8 (4)
N(1)–Cu–O(2)	87.3 (1)	N(1)–C(5)–C(6)	116.7 (3)
N(2)–Cu–O(2)	101.1 (1)	C(5)–C(6)–C(7)	110.6 (4)
O(1)′–Cu–N(1)	91.8 (1)	C(6)–C(7)–N(2)	112.5 (3)
O(1)′–Cu–O(2)	85.2 (1)	C(7)–N(2)–C(8)	109.0 (3)
O(2)–Cl–O(3)	107.1 (2)	C(7)–N(2)–C(9)	108.5 (3)
O(2)–Cl–O(4)	109.1 (3)	C(8)–N(2)–C(9)	107.1 (3)
O(2)–Cl–O(5)	108.7 (2)	Cu–O(1)–OH	122 (4)
O(3)–Cl–O(4)	111.5 (3)	Cu′–O(1)–OH	115 (4)
O(3)–Cl–O(5)	108.7 (2)		

we calculate an O(3)· · ·OH separation of 2.09 Å with an associated O(1)–OH· · ·O(3) angle of 147°. Hence, an application of the criterion[42] that a hydrogen bond exists if both the A–H and H· · ·B (here A = O(1) and B = O(3)) distances are less than the sums of their van der Waals radii leads to the conclusion that there is an O(1)–OH· · ·O(3) hydrogen bond between the bridging hydroxo group and the perchlorate. The O(1)· · ·O(3) separation of 2.993 Å is less than twice the van der Waals radius of O as given by Bondi (3.02 Å), although slightly greater than the corresponding value given by Pauling (2.80 Å).

Examination of the solid state infrared spectrum of the complex, however, leads to a different conclusion. The spectrum shows a strong, sharp band at 3580 cm^{-1}, which appears to be much more similar to the value of 3620 cm^{-1} normally attributed[43] to free hydroxyl groups than to the broad band centered near 3320 cm^{-1} which usually results[43] from hydrogen-bonded hydroxyl groups. Hence, we conclude that any hydrogen bonding which is present in this system must be very weak.

The geometry of the DMAEP ligand, which can be seen in Figure 2, is similar to that of other chelating aminoethylpyridines[6,8,13,14,44-47] with five atoms of the ligand, N(1), C(5),

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(43) J. C. D. Brand and G. Eglinton, "Applications of Spectroscopy to Organic Chemistry," Oldbourne Press, London, 1965, p 136.

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(46) D. L. Lewis and D. J. Hodgson, *Inorg. Chem.*, 12, 2935 (1973).

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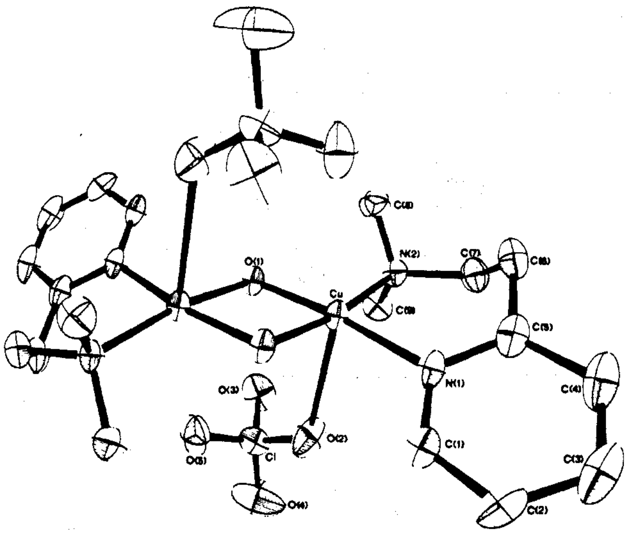

Figure 2. View of the dimeric unit in β-[Cu(DMAEP)OH]$_2$(ClO$_4$)$_2$. Thermal ellipsoids are drawn at the 40% probability level and hydrogen atoms are omitted for clarity.

C(6), C(7), and N(2), forming a six-membered "boat" ring with Cu. The atoms forming the base of the "boat" [N(1), N(2), C(5), and C(7)] are approximately planar with an average deviation from the best least-squares plane of 0.11 Å, while Cu and C(6) are displaced from this plane by 0.43 and 0.75 Å, respectively. This C(6) displacement is very similar to that in [Cu(EAEP)OH]$_2$[ClO$_4$]$_2$[8] and α-[Cu(DMAEP)OH]$_2$[ClO$_4$]$_2$,[14] and the Cu displacement is approximately intermediate between the values of 0.57 and 0.33 Å observed in the same complexes. These values show that the DMAEP "boat" is somewhat "flatter" than that in the ethyl-substituted complex but "deeper" than that of the α form of the dimethyl-substituted complex. These observations are consistent with the various modes of perchlorate coordination observed, with the greater "flattening" present in the α-DMAEP complex allowing six-coordinate geometry at the copper atom whereas the β-DMAEP and EAEP complexes are five coordinate with the substituted AEP ligand partially inhibiting coordination at the sixth coordination site.

The interaction between the perchlorate anion and the copper atom is clearly weak, the Cu-O(2) separation being 2.721 (4) Å, and may best be described as what Hathaway and coworkers[48] have called semicoordination. The geometry of the perchlorate group is essentially tetrahedral with Cl-O bond lengths ranging from 1.391 (4) to 1.427 (4) Å and O-Cl-O bond angles of 107.1 (3) to 111.6 (3)°. The bond lengths and angles which involve atom O(4) are apparently inconsistent with those not involving O(4), since those involving O(4) have mean values of 1.391 (4) Å and 110.8 (4)° while the others have mean values of 1.423 (4) Å and 108.2 (3)°. This anomaly cannot be ascribed to the effects of the perchlorate coordination since coordination is only through O(2); it may be, however, that our description of the thermal motion of atom O(4) is inadequate, as evidenced by the two small residual peaks in the final difference Fourier in the vicinity of this atom (*vide supra*). Moreover, the application of an independent model "correction" for the thermal motions of the perchlorate atoms[49] leads to a reversal of the "uncorrected" trend, with Cl-O(4) becoming the longest of the four Cl-O bonds rather than the shortest. These observations tend to confirm that the observed apparent deviation from tetrahedral geometry is an artifact of the thermal model and is probably not significant. This nonperturbation from tetrahedral geometry is consistent with earlier observation of "semicoordinated" anions.[8,47,48]

It is evident that the principal difference between the α and β forms of [Cu(DMAEP)OH]$_2$(ClO$_4$)$_2$, therefore, involves the nature of the interaction between the perchlorate anion and the cation. A comparison of these two structures, along with those of the related complexes [Cu(EAEP)OH]$_2$[ClO$_4$]$_2$[8] and Cu(AEP)$_2$(ClO$_4$)$_2$,[47] gives an indication of the varying modes of perchlorate coordination which we have observed in these related aminoethylpyridine complexes of copper(II). It is noteworthy that in both the present structure and in that of [Cu(EAEP)OH][ClO$_4$]$_2$ a second oxygen atom (O(5) in the present example) appears to approach the sixth coordination site of the second copper atom (see Figure 2), although the Cu-O(5) separation of 3.12 Å is much too large for any interaction to be postulated. As described previously, closer approach to the sixth coordination site in either complex appears to be sterically hindered by the DMAEP ligand. An examination of Table V, in which the relevant parameters concerning the perchlorate coordination in these four complexes are compared with those observed in Cu(bipy)$_2$(ClO$_4$)$_2$ [bipy = 2,2′-bipyridine][50] and in [Cu(bipyram)$_2$](ClO$_4$)$_2$ [bipyram = 2,2′-bipyridylamine],[51] demonstrates the remarkable coordinating versatility of the perchlorate anion.

Magnetic Properties

The X-band epr spectrum of the complex is shown in Figure 3. The spectrum can be interpreted in terms of the axial effective spin Hamiltonian given in eq 1. The triplet state

$$\mathcal{H} = \mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S} + D[S_z^2 - {}^1/_3 S(S+1)] \qquad (1)$$

($\Delta m_s = 1$) resonance fields of a randomly oriented sample calculated from eq 1 are given by[52]

$$\begin{aligned} (H_\perp)_1^2 &= (1/g_\perp\beta)^2[h\nu(h\nu - D)] \\ (H_\perp)_2^2 &= (1/g_\perp\beta)^2[h\nu(h\nu + D)] \\ (H_{||})_1 &= (1/g_{||}\beta)|h\nu - D| \\ (H_{||})_2 &= (1/g_{||}\beta)(h\nu + D) \end{aligned} \qquad (2)$$

It is concluded that D is greater than $h\nu$ since assignment of $(H_\perp)_1$ to any of the absorptions leads to unreasonable g values. Hence, $(H_\perp)_1$ is not observed. By assigning $(H_{||})_1$ = 1200 G, $(H_{||})_2$ = 7550 G, and $(H_\perp)_2$ = 5150 G, we obtain $|D|$ = 0.43 cm^{-1}, $g_{||}$ = 2.10, and $g_\perp$ = 2.00. This yields an average value of g = 2.03 according to $\langle g\rangle = {}^1/_3 g_{||} + {}^2/_3 g_\perp$. However, the observed resonance positions are dipolar broadened sufficiently to prevent determination of extremely precise values for the parameters in eq 2. The resonance at 3200 G is assigned to a doublet state transition which is due to the presence of a small amount of monomeric impurity. The detection of such impurities has been reported in similar systems.[3,7,53]

The temperature variation of the magnetic susceptibility of

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(48) D. S. Brown, J. D. Lee, B. G. A. Melsom, B. J. Hathaway, I. M. Procter, and A. A. G. Tomlinson, *Chem. Commun.*, 369 (1967).

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Table V. Comparison of Perchlorate Coordination in Various Copper(II) Complexes

Complex	Cu coord no.	Perchlorate coord	Cu–O bond length	Cu–O–Cl bond angle	Ref
$Cu(bipy)_2(ClO_4)_2$	6	Intermolecular bidentate[a]	2.45 (2) 2.73 (2)	140 (1) 124 (1)	50
α-$[Cu(DMAEP)OH]_2(ClO_4)_2$	6	Intramolecular bidentate with additional H bonding	2.782 (2) 2.716 (3)	121.2 (1) 117.7 (1)	14
$Cu(AEP)_2(ClO_4)_2$	6	Unidentate	2.833 (2)	148.8 (1)	47
β-$[Cu(DMAEP)OH]_2(ClO_4)_2$	5	Unidentate	2.721 (4)	123.0 (2)	This work
$[Cu(EAEP)OH]_2(ClO_4)_2$	5	Unidentate	2.618 (9) 2.562 (10)	130.7 139.8	8
$Cu(bipyam)_2(ClO_4)_2$	4	None			51

[a] An additional noncoordinated perchlorate is also present in this complex.

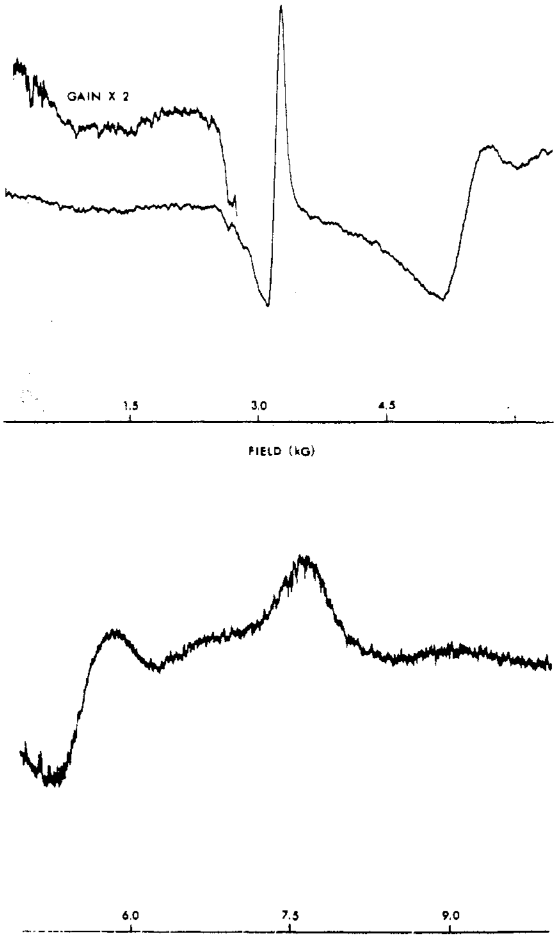

Figure 3. The X-band epr spectrum of a powdered sample of β-[Cu-(DMAEP)OH]$_2$(ClO$_4$)$_2$ from 0 to 6.5 kG taken on a Varian E-3 spectrometer (above), and the spectrum from 4.5 to 10 kG taken on a JEOL ME 3X spectrometer (below). The spectra were taken at 77°K.

the complex β-$[Cu(DMAEP)OH]_2(ClO_4)_2$ from 50 to 300°K is shown in Figure 4. A very broad maximum in susceptibility is observed centering around approximately 175°K. The data obey the Bleaney-Bowers expression,[54] eq 3, for

$$\chi_m = \frac{Ng^2\beta^2}{3kT}\,[1 + {}^1\!/_3\exp(-2J/kT)]^{-1} + N\alpha \qquad (3)$$

exchange-coupled pairs of copper(II) ions. The symbols in eq 3 have their usual meanings and the exchange energy is defined by the Hamiltonian

$$\mathcal{H} = -2J\mathbf{S}_1\cdot\mathbf{S}_2$$

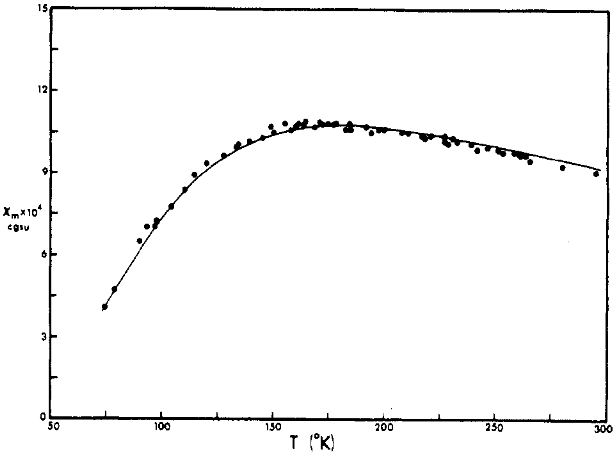

Figure 4. Plot of the inverse susceptibility of β-[Cu(DMAEP)OH]$_2$-(ClO$_4$)$_2$ per Cu atom as a function of temperature. The solid line represents the values calculated from the Bleaney–Bowers equation with $g = 2.03$ and $2J = -201$ cm^{-1}.

In order to extract the value of $\langle g\rangle$ and the singlet-triplet splitting energy, $2J$, from the bulk susceptibility data, the best fit of eq 3 to the experimental data was obtained. The minimization of the function A_{BF}, defined by eq 4, was used

$$A_{BF} = \sum_i [(\chi(\text{exptl})_i - \chi(\text{calcd})_i)T_i]^2 \qquad (4)$$

as the criterion for the best fit. The best fit values for the parameters are $\langle g\rangle = 2.00$ and $2J = -195$ cm^{-1}, where $A_{BF} = 2.1 \times 10^{-4}$. Since this value of $\langle g\rangle$ is somewhat lower than the epr g value, an additional fit was obtained by holding $\langle g\rangle$ constant at 2.03 and allowing $2J$ to vary. Although this process resulted in a larger value for A_{BF} ($= 5.7 \times 10^{-4}$), the fit to the lower temperature points was improved. With the epr g value, the best fit value of $2J$ is -201 cm^{-1}. In view of these results, a value of $\langle g\rangle = 2.03$ is probably accurate within 2% and $2J = -200 \pm 10$ cm^{-1}.

A comparison of β-DMAEP with the EAEP complex reveals many similarities in the structural and magnetic properties of the two complexes. The magnetic parameters for the EAEP complex[7] are $|D| = 0.48$ cm^{-1}, $g_\parallel = 2.12$, and $g_\perp = 2.0$, which yields $\langle g\rangle = 2.04$ with $2J = -130$ cm^{-1}. In this complex, the copper-copper separation is 2.92 Å, the average Cu-O in-plane bond length is 1.92 Å, the average out-of-plane Cu-O distance (to a perchlorate oxygen) is 2.59 Å, and the mean Cu-O-Cu bond angle is 99.2°.[8]

The magnetic and structural data for the β-DMAEP complex may be compared with those of the series of structurally similar hydroxo-bridged complexes in which a near linear relationship between the bridge angle, ϕ, and the singlet-triplet splitting has been found.[12] It may be seen in Figure 5 that the singlet-triplet splitting, $2J = -200$ cm^{-1}, at $\phi = 100.4°$ is consistent with the established relationship. The

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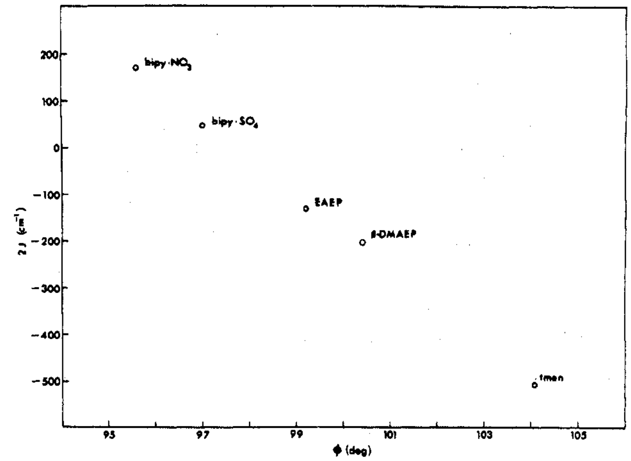

Figure 5. Plot of the Cu–O–Cu bridging angle, ϕ, *vs.* the singlet–triplet splitting, $2J$, for the five completely characterized dihydroxo-bridged copper(II) complexes.

inverse relationship between the copper-copper separation and the magnitude of the exchange energy indicates that direct exchange is not present in these systems but that superexchange *via* the bridging ligands is the mechanism responsible for the spin-spin interaction.

A comparison of the structures of the α and β forms of the DMAEP complex reveals some information which is germane to the question of the mechanism of the exchange interaction. The copper-copper separation in the α form is 2.94 Å, the mean Cu-O in-plane length is 1.94 Å, and the Cu-O-Cu bridge angle is 98.4°. Perhaps the most important difference in the two forms is that the long out-of-plane Cu-O bond in the α form is part of a bidentate perchlorato bridge.[14]

Preliminary magnetic susceptibility data[16] indicate that the exchange interaction in the α form results in a singlet ground state with $|2J|$ less than 10 cm^{-1}. Although the bridge angle correlation would predict a smaller singlet-triplet splitting for α-DMAEP than for β-DMAEP, the predicted value of $2J$ (see Figure 5) should be closer to -60 cm^{-1}. Thus, as would be expected for a superexchange mechanism, the perchlorato bridge significantly affects the exchange interaction and appears to make a positive contribution to it. This is not necessarily to say that the perchlorate bridge transmits spin-spin interactions by superexchange, but that the presence of four bridges in the α form complicates the discussion of the spin-spin coupling mechanism and removes the α form from the class of compounds which obeys the near linear $2J$ *vs.* ϕ relationship.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1013.

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Carbene Precursors and Metal Complexes. Synthesis and Structure Determination of Chloro(difluoromethyl)(*O*-chlorodifluoroacetato)carbonylbis(triphenylphosphine)iridium(III)-Benzene, $IrCl(CHF_2)(OCOCF_2Cl)(CO)(PPh_3)_2 \cdot C_6H_6$

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The complex IrCl(CHF$_2$)(OCOCF$_2$Cl)(CO)(PPh$_3$)$_2$ has been isolated as the initial product from the reaction between IrCl(CO)(PPh$_3$)$_2$ and the difluorocarbene percursor NaCF$_2$ClCOO. Its crystal and molecular structure have been determined from three-dimensional X-ray data collected by the θ-2θ scan technique and refined by least-squares methods to a discrepancy factor of 0.048 based on 3759 reflections with $F_o^2 > 5.0\sigma(F_o^2)$. The complex crystallizes in space group $P\bar{1}$ of the triclinic system with cell dimensions of $a = 18.31$ (2) Å, $b = 12.15$ (1) Å, $c = 10.92$ (1) Å, $\alpha = 106.98$ (5)°, $\beta = 94.75$ (5)°, $\gamma = 108.98$ (5)°, and $V = 2154$ Å^3. The experimental and calculated densities of 1.60 (2) and 1.60 g/cm^3 agree for $Z = 2$ with one molecule of benzene per molecule of complex. An essentially octahedral coordination geometry about the iridium is found with the difluoromethyl group and the O-coordinated chlorodifluoroacetate in trans positions. Evidence for the existence of the hydrogen atom in the proposed difluoromethyl group is discussed. The Ir–C bond length of 2.09 (2) Å indicates that the –CHF$_2$ group is coordinated solely as a σ donor. The chlorodifluoroacetate ion coordinates in monodentate fashion with an Ir–O distance of 2.12 (1) Å. Despite the monodentate coordination of the carboxylate group, the two C–O distances do not differ significantly, averaging 1.25 (2) Å. All other structural parameters are as expected for an Ir(III) octahedral complex.

Introduction

There are presently many reported examples of metal-carbene complexes, most of which have been synthesized by the conversion of coordinated carbonyl or isocyanide ligands to coordinated carbenes.[2] In addition, other carbene complexes have been synthesized by procedures ranging from sub-

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(1) (a) Brown University. (b) University of Rochester.

(2) For reviews of this area see E. O. Fischer, *Pure Appl. Chem.*, 30, 1161 (1972); F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 16, 487 (1972).