tions at hand, Scheme I, or a minor variant thereof, would appear to be the preferred path.

The exact structural requirements governing catalytic activity of metals in epoxidation remain, in part, elusive. Relevant to the view that a substitution-labile metal center is necessary[2c] are recent reports that dioxomolybdenum(VI) β-diketonates are stereochemically labile, although net exchange with external diketone is slow.[19] Participation by the metal in one-electron redox reactions under epoxidation conditions precludes the selectivity observed and should lead instead to mixtures of products typical of radical oxidations;[20] although the two metals found to be most effective have accessible oxidation states, V(IV) and Mo(V), one unit below maximum, neither state is expected to exist in significant quantity under the strongly oxidizing conditions used.

(18) These small rate differences in epoxidations may be compared, for example, to rate differences observed in the 1,3 addition of picryl azide: A. S. Bailey and J. E. White, *J. Chem. Soc. B*, 819 (1966). With the latter, which reacts through a five-membered ring transition state, the specific rate for cyclohexene (in $CHCl_3$ at 25°) is $^1/_{50}$th the value for cyclooctene and $^1/_{64}$th that for cyclopentene. The highly strained olefin norbornene reacts 8000 times as rapidly as does cyclohexene with this reagent, whereas the corresponding ratio of epoxidation rates using $MoO_5 \cdot PO(NMe_2)_3$ is only 1.94.[14]

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As to the role of positive charge at the metal center, it is apparent that this factor must be kept within bounds. Thus boron(III) and titanium(IV), d^0 systems which are known to form peroxy complexes, are ineffective as epoxidation catalysts, presumably because polarization of the O-O bond is not sufficiently severe to allow heterolysis under the action of nucleophilic olefin. At the other end of the scale are such strongly oxidizing positive centers as Cr(VI), Se(VI), Mn(VII), and Os(VIII). Any catalytic action by these species would, in large part, be overshadowed by the ease with which they are reduced by hydroperoxide, by olefin, or by both. Between these extremes are the active d^0 systems, Mo(VI) and V(V); but why Mo(VI) is the more reactive of the two and why both are superior to W(VI), despite the effectiveness of the latter center in hydroxylic solvents,[21] remain puzzling points.

Registry No. $VO(acac)_2$, 3153-26-2; $VO(dpm)_2$, 16901-82-9; $VO(hfac)_2$, 15819-88-2; $VO(tfac)_2$, 32040-15-6; $MoO_2(acac)_2$, 17524-05-9; $(BuO)_3VO$, 1801-76-9; *t*-BuO_2H, 110-05-4; *t*-BuOH, 75-65-0; cyclohexene, 110-83-8; cyclooctene, 931-88-4.

Acknowledgments. The authors are grateful to Professors Henry Kuska, Thomas Pinnavaia, Harold Kwart, and William Movius for valuable discussions.

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Structural and Magnetic Properties of Di-μ-hydroxo-tetraglycinatodichromium(III)

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The crystal and molecular structure of di-μ-hydroxo-tetraglycinatodichromium(III), $[Cr(gly)_2OH]_2$, has been determined from three-dimensional single-crystal X-ray data obtained on an automatic four-circle diffractometer using Mo Kα radiation. The complex crystallizes in the space group C_{2h}^5-$P2_1/n$ of the monoclinic system with cell constants $a = 5.691$ (3), $b = 16.920$ (9), $c = 7.900$ (4) Å, and $\beta = 79.90$ (3)°. The observed density is 1.89 (2) g cm^{-3} and that calculated based on two dimeric formula units in the cell is 1.898 g cm^{-3}. A total of 775 independent intensities greater than twice their estimated standard deviations were used in the least-squares refinement and the final value of the conventional R factor (on F) is 0.040. The structure consists of well-separated dimeric pairs of octahedrally coordinated chromium atoms linked by two hydroxo bridges. The Cr-O-Cr-O unit is strictly planar with Cr-Cr and O-O separations of 2.974 (2) and 2.575 (6) Å and a Cr-O-Cr bridging angle of 98.2 (2)°. The two independent bridging Cr-O distances of 1.966 (4) and 1.968 (4) Å are essentially the same. Each glycinate ligand is coordinated through nitrogen and oxygen, the average Cr-O and Cr-N distances being 1.973 (4) and 2.064 (6) Å, respectively. The magnetic susceptibility data show a maximum at 20°K, which suggests that the ground state is a singlet with $2J = -8.4$ cm^{-1} and $g = 1.95$. Inclusion of biquadratic exchange leads to values of $2J = -3.8$ cm^{-1} and $j = 0.37$ cm^{-1}. The room-temperature epr spectrum is also reported. The magnetic properties of the complex are consistent with those found for copper(II) dimers with similar bridging geometry.

Introduction

From recent crystallographic and magnetic studies[2-5] in our laboratory on dihydroxo-bridged copper complexes of the type $[CuL(OH)]_2^{2+}$ we have been able to conclude that the value of $2J$ is systematically related to the Cu-O-Cu bridging angle (φ), $2J$ decreasing as φ increases and the interaction changing from ferromagnetic to antiferromagnetic at φ values between 96 and 99°. It is of great interest to test this hypothesis to see if a similar relationship will hold for bridging systems involving atoms other than copper. Hence, we have undertaken the study of bridged systems involving chromium.

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The binuclear chromium complex $[Cr(gly)_2OH]_2$, where gly = $NH_4C_2O_2^-$, first reported by Ley and Ficken[6] in 1912 has been studied by Earnshaw and Lewis.[7] They have reported the magnetic susceptibility variation for the complex in the temperature range 306-80°K, and although they did not observe the maximum in susceptibility, they were able to conclude that an antiferromagnetic interaction existed and that the value of $2J$ (the singlet-triplet splitting) is -8 cm^{-1}. This low value of the magnitude of $2J$ caused us to anticipate that the value of ϕ, the Cr-O-Cr bridging angle, would be near that critical value at which the change from a ferromagnetic to an antiferromagnetic interaction occurs.[8] Hence, we have undertaken the complete structural investigation of di-μ-hydroxo-tetraglycinatodichromium(III). Since the previous workers were unable to observe the susceptibility maximum, we have also studied the low-temperature magnetic susceptibility and the room-temperature epr of this complex. The results of this study are presented herein.

Collection and Reduction of the X-Ray Data

Pale orange crystals of $[Cr(gly)_2OH]_2$ were prepared by the procedure of Earnshaw and Lewis.[7] Precession and Weissenberg photography indicated that the crystals belong to the monoclinic system. The systematic absences which were observed are $0k0$ for k odd and $h0l$ for $h + l$ odd, which strongly suggests that the space group is C_{2h}^5-$P2_1/n$, an alternate setting of the conventional space group $P2_1/c$ with equivalent positions: (x, y, z), $(\bar{x}, \bar{y}, \bar{z})$, $(^1/_2 - x, ^1/_2 + y, ^1/_2 - z)$, $(^1/_2 + x, ^1/_2 - y, ^1/_2 + z)$. The cell constants, obtained by the least-squares procedure described previously,[4] are $a = 5.691$ (3), $b = 16.920$ (9), $c = 7.900$ (4) Å, and $\beta = 79.90$ (3)°; these observations were made at 23° with the wavelength assumed as λ(Mo Kα_1) 0.7093 Å. A density of 1.898 g cm^{-3} calculated for two dimeric formula units in the cell agrees well with the value 1.89 (2) g cm^{-3} obtained by flotation in dichloromethane-dibromoethane solution.

Diffraction data were collected from a parallelpiped crystal with faces (001), (00$\bar{1}$), (010), (0$\bar{1}$0), (100), and ($\bar{1}$00); the separations between opposite faces were as follows: (001) and (00$\bar{1}$), 0.007 cm; (010) and (0$\bar{1}$0), 0.002 cm; (100) and ($\bar{1}$00), 0.034 cm. The crystal was mounted approximately normal to the (100) planes, and data were collected on a Picker four-circle automatic diffractometer using Mo Kα radiation in the manner previously described.[9] A single form (hkl) of the data was collected to a value of $2\theta = 45°$, a total of 800 independent intensities being recorded. There were very few intensities above background at values of $2\theta > 45°$.

Data processing was carried out as described by Corfield, Doedens, and Ibers,[10] using our program DATAPRC.[11,12] The value of p in the expression[13]

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

was chosen as 0.030. An absorption correction was deemed unnecessary owing to the extremely small size of the crystal and the relatively low absorption coefficient for these atoms and Mo Kα radiation of 16.6 cm^{-1}. Of the 800 independent intensities, 530 were greater than 3 times their estimated standard deviations, and 775 exceeded twice their estimated standard deviations.

Solution and Refinement of the Structure

The position of the independent chromium atom was determined from a three-dimensional Patterson function. Three cycles of least-squares refinement on this position using variable isotropic thermal parameters were run, yielding values for the usual agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2)^{1/2}$ of 0.426 and 0.487, respectively. All least-squares refinements in this analysis were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ 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 Cr and Cl were taken from Cromer and Waber,[14] that for H was taken from Stewart, Davidson, and Simpson,[15] and those for O, N, and C were taken from Ibers.[16] The effects of anomalous dispersion were included in the calculations of F_c,[17] the values of $\Delta f'$ and $\Delta f''$ being taken from Cromer.[18] Only the 530 independent intensities which were greater than 3 times their estimated standard deviations were used in the initial refinement of the structure.

Two sets of least-squares refinements and difference Fourier syntheses revealed the positions of all of the nonhydrogen atoms. Three cycles of least-squares refinement using variable anisotropic thermal parameters yielded values of 0.044 and 0.054 for R_1 and R_2, respectively. A difference Fourier synthesis revealed the locations of all of the ligand hydrogen atoms and two cycles of least-squares calculations using variable isotropic thermal parameters for the hydrogen atoms gave values of 0.030 and 0.034 for R_1 and R_2, respectively, using the 530 independent intensities greater than 3σ and values of 0.041 and 0.040 for R_1 and R_2, respectively, using the 775 independent intensities greater than 2σ. The largest peak in a difference Fourier map at this stage was within 1.0 Å of the bridging oxygen atom and was interpreted as indicating the position of the hydrogen atom of the bridging hydroxyl group. Two cycles of least-squares calculations were run including the hydroxyl hydrogen atom; the coordinates were fixed, but a variable isotropic thermal parameter was used. The resulting values of R_1 and R_2 for the data greater than 2σ were 0.040 and 0.037, respectively.

A final difference Fourier map showed no peaks greater than 0.35 e Å^{-3}, indicating conclusively that the formulation of the material as a monohydrate by the earlier workers[6,7] was incorrect. The formulation of the complex as an anhydrous material is also consistent with the density and with the elemental analysis.

In the last least-squares refinement the greatest shift in any parameter was 0.1 times its estimated standard deviation, which is taken as evidence that the refinement had converged. The value of R_2 showed no dependence on sin θ or on $|F_o|$, which indicates that the choice of $p = 0.030$ is essentially correct. Examination of the final values of $|F_o|$ and $|F_c|$ suggest to us that no correction for secondary extinction is necessary. The positional and thermal parameters derived from the last cycle of least-squares refinement, along with their standard deviations as estimated from the inverse matrix, are given in Table I. A table of observed and calculated structure amplitudes is available.[19]

Description of Structure

The structure consists of well-separated $[Cr(gly)_2OH]_2$ dimeric units as shown in Figure 1. The coordination around each Cr atom is roughly octahedral and the Cr-O-Cr-O bridging unit is strictly planar, there being an inversion center in the middle of the dimer. The Cr-Cr and O-O separations in the bridging unit are 2.974 (2) and 2.575 (6) Å, respectively, and the essential similarity of the two independent bridging Cr-O bond lengths of 1.966 (4) and 1.968 (4) Å demonstrates that the oxygen atoms are symmetrically bound to the two Cr atoms. The Cr-O-Cr angle in the bridge is 98.2 (2)° while the O-Cr-O angle is (necessarily) 81.8 (2)°. These values for the metal-metal separation and the geometry of the bridging unit are similar to those found

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(19) This table will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-342.

Table I. Positional and Thermal Parameters for $[(gly)_2CrOH]_2$

(a) Positions of Nonhydrogen Atoms

Atom	x	y	z	β_{11} [a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	−0.0202 (2)	0.0726 (1)	0.1026 (1)	0.0123 (3)	0.0014 (1)	0.0048 (2)	0.0001 (1)	0.0019 (2)	0.0000 (1)
O1	0.0969 (6)	0.1018 (2)	0.3449 (5)	0.0135 (13)	0.0019 (2)	0.0044 (8)	−0.0008 (4)	0.0011 (9)	−0.0003 (3)
O2	−0.1531 (6)	0.0286 (2)	−0.1246 (5)	0.0119 (15)	0.0016 (2)	0.0036 (7)	0.0000 (4)	0.0011 (8)	0.0000 (3)
O3	0.2475 (6)	0.1252 (2)	0.0204 (5)	0.0116 (13)	0.0014 (2)	0.0070 (8)	0.0009 (4)	0.0018 (8)	0.0012 (3)
O4	0.0060 (8)	0.1058 (2)	−0.3931 (6)	0.0367 (19)	0.0026 (2)	0.0048 (9)	−0.0015 (5)	0.0025 (10)	−0.0003 (4)
O5	−0.1487 (7)	0.2725 (2)	0.3735 (5)	0.0186 (15)	0.0025 (2)	0.0115 (9)	0.0020 (5)	0.0008 (10)	−0.0025 (4)
N1	−0.3038 (11)	0.0297 (4)	0.2066 (8)	0.0151 (23)	0.0025 (3)	0.0108 (12)	−0.0008 (7)	0.0035 (14)	−0.0007 (5)
N2	−0.1739 (10)	0.1822 (3)	0.0508 (8)	0.0157 (22)	0.0022 (2)	0.0060 (12)	0.0014 (6)	−0.0013 (12)	0.0001 (4)
C1	−0.0467 (11)	0.0924 (3)	0.4512 (8)	0.0245 (25)	0.0012 (3)	0.0064 (12)	0.0010 (6)	0.0007 (15)	0.0000 (4)
C2	−0.2933 (11)	0.0620 (4)	0.3805 (8)	0.0194 (24)	0.0025 (3)	0.0086 (13)	0.0005 (7)	0.0066 (14)	−0.0009 (8)
C3	0.2068 (10)	0.1914 (3)	−0.0570 (8)	0.0138 (22)	0.0015 (3)	0.0065 (11)	−0.0009 (6)	−0.0016 (13)	0.0004 (6)
C4	−0.0395 (13)	0.2269 (5)	−0.0595 (12)	0.0189 (27)	0.0024 (3)	0.0171 (19)	0.0026 (7)	0.0055 (20)	0.0031 (7)

(b) Positions of Hydrogen Atoms

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H1N1	−0.417 (11)	0.035 (4)	0.162 (9)	3.0 (2.2)	H2C2	−0.344 (11)	0.024 (4)	0.455 (9)	4.5 (1.8)
H2N1	−0.294 (11)	−0.021 (5)	0.211 (9)	3.8 (2.0)	H1C4	−0.109 (13)	0.224 (5)	−0.150 (9)	4.0 (2.4)
H1N2	−0.307 (10)	0.178 (3)	0.015 (8)	1.1 (1.5)	H2C4	−0.038 (9)	0.288 (4)	−0.011 (8)	2.9 (1.4)
H2N2	−0.173 (10)	0.200 (4)	0.149 (8)	2.2 (1.6)	HB1	0.039	0.445	0.285	4.0 (1.6)
H1C2	−0.394 (8)	0.106 (3)	0.368 (6)	0.7 (1.1)					

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

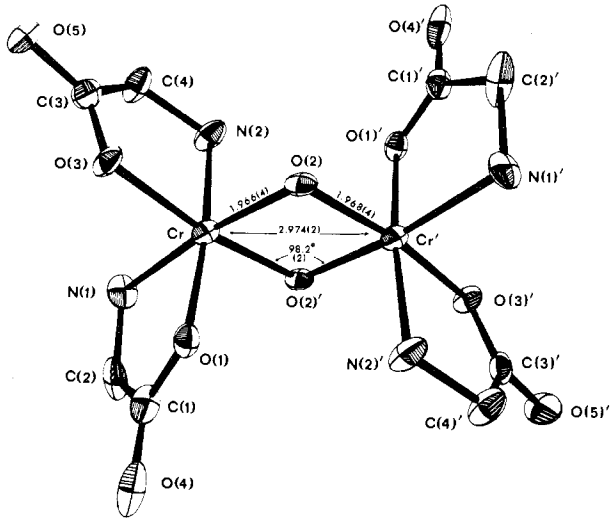

Figure 1. View of the $[Cr(gly)_2OH]_2$ molecule. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

in the Cu complexes $[Cu(bipy)OH]_2(NO_3)_2$, where bipy = 2,2′-bipyridine,[20] $[Cu(EAEP)OH]_2^{2+}$, where EAEP = 2-(2-ethylaminoethyl)pyridine,[4] and $[Cu(tmen)OH]_2^{2+}$, where tmen = tetramethylethylenediamine,[21] in which the Cu-Cu separations are 2.847, 2.917 (5), and 3.000 (4) Å, respectively, and the bridging geometry is roughly planar.

The bond distances and angles in the complex are shown in Tables II and III. The Cr-N distances of 2.061 (5) and 2.067 (5) Å are similar to the mean values of 2.075 (2) and 2.081 (5) Å reported for two separate complexes of tris(ethylenediamine)chromium(III)[22] and to the mean value of 2.068 (1) Å found in $Cr(gly)_3 \cdot H_2O$.[23] The Cr-O(glycinato) bond lengths of 1.970 (4) and 1.977 (4) Å compare with the values of 1.962–1.967 Å in $Cr(gly)_3 \cdot H_2O$,[23] 1.951 (7) Å in tris(acetylacetonato)chromium(III),[24] and 1.955 (9) Å in di-μ-diphenylphosphinato-acetylacetonatochromium(III).[25]

The bond lengths and angles found in the two independent glycinato ligands are similar to those found in $Cr(gly)_3 \cdot H_2O$,[23] in $Cu(gly)_2 \cdot H_2O$,[26] and, with the exception of the C-O bond lengths, in the α, β, and γ forms of glycine.[27–29]

Table II. Internuclear Separations in $[Cr(gly)_2OH]_2$ (Å)

Cr-Cr′	2.974 (2)	C2-C1	1.508 (8)	N1-H1N1	0.68 (7)
Cr-O1	1.977 (4)	C1-O4	1.235 (7)	N1-H2N1	0.86 (7)
Cr-O2	1.966 (4)	C1-O1	1.279 (7)	N2-H1N2	0.76 (6)
Cr-O2′	1.968 (4)	N2-C4	1.466 (9)	N2-H2N2	0.83 (5)
Cr-O3	1.970 (4)	C3-C4	1.522 (9)	C2-H1C2	0.93 (5)
Cr-N1	2.067 (6)	C3-O5	1.228 (7)	C2-H2C2	0.95 (7)
Cr-N2	2.061 (5)	C3-O3	1.278 (7)	C4-H1C4	0.76 (7)
N1-C2	1.470 (9)			C4-H2C4	1.10 (6)

Table III. Internuclear Angles in $[Cr(gly)_2OH]_2$ (deg)

Cr-O2-Cr′	98.2 (2)	C2-C1-O4	118.7 (5)
O2-Cr-O2′	81.8 (2)	O4-C1-O1	124.1 (6)
O1-Cr-O2	171.4 (2)	C1-O1-Cr	117.3 (3)
O1-Cr-O2′	93.1 (2)	C2-C1-O1	117.3 (6)
O1-Cr-O3	93.2 (2)	H1N1-N1-H2N1	102.1 (6.0)
O1-Cr-N2	91.6 (2)	H1N1-N1-C2	108.1 (5.0)
N1-Cr-O2	91.6 (2)	H1N1-N1-Cr	118.3 (5.0)
N1-Cr-O2′	94.2 (2)	H2N1-N1-C2	109.9 (5.0)
N1-Cr-O3	173.0 (2)	H2N1-N1-Cr	108.6 (4.0)
N1-Cr-N2	93.5 (3)	H1N2-N2-H2N2	103.0 (6.0)
O3-Cr-O2	93.8 (2)	H1N2-N2-C4	114.5 (5.0)
O3-Cr-O2′	91.0 (2)	H1N2-N2-Cr	110.3 (5.0)
O3-Cr-N2	81.6 (2)	H2N2-N2-C4	116.3 (5.0)
N2-Cr-O2	94.3 (2)	H2N2-N2-Cr	102.4 (4.0)
N2-Cr-O2′	171.5 (2)	H1C2-C2-H2C2	111.9 (7.0)
Cr-N2-C4	109.5 (3)	H1C2-C2-N1	106.1 (6.0)
N2-C4-C3	111.3 (6)	H1C2-C2-C1	106.6 (6.0)
C4-C3-O3	116.3 (5)	H2C2-C2-N1	110.8 (6.0)
C4-C3-O5	118.9 (5)	H2C2-C2-C1	110.5 (6.0)
O5-C3-O3	124.8 (5)	H1C4-C4-H2C4	111.8 (7.0)
C3-O3-Cr	117.9 (3)	H1C4-C4-N2	106.3 (6.0)
Cr-N1-C2	109.5 (3)	H1C4-C4-C3	108.1 (6.0)
N1-C2-C1	110.8 (5)	H2C4-C4-N2	104.4 (6.0)
		H2C4-C4-C3	114.3 (6.0)

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Table IV. Possible A-H···B Hydrogen Bonds

A	H	B	H···B, Å	A···B, Å	A-H···B, deg
O2	HB1	O4	1.87	2.766	175
N1	H2N1	O4	2.45	3.069	130
N2	H2N2	O5	2.14	2.958	167
N2	H1N2	O5	2.23	2.915	151

In free glycine, the two C-O distances are equal, but in $Cu(gly)_2 \cdot H_2O$, $Cr(gly)_3 \cdot H_2O$, and the present case the coordinated oxygen has a longer C-O bond than the uncoordinated carboxyl oxygen.

There is evidence for hydrogen bonding in the complex, with all possible hydrogen bonds involving the carboxyl oxygen atoms (O4 and O5) of the glycinato ligands, as expected. The possible hydrogen bonds are listed in Table IV; the criterion used for inclusion in Table IV was that in order for hydrogen bonding to exist there must be *two* heavy atom-hydrogen (*i.e.*, O-H or N-H) separations less than the sum of the van der Waals radii of hydrogen and the heavy atom.[30] The van der Waals radii of H, N, and O listed by Pauling[31] are 1.2, 1.5, and 1.40 Å, respectively, while Bondi[32] gave values of 1.20, 1.55, and 1.52 Å, respectively; fortunately, there are no separations in this complex which would satisfy Bondi's criterion but fail on Pauling's.

Magnetic Properties

The spin-spin Hamiltonian $-2J\mathbf{S}_1 \cdot \mathbf{S}_2$ is routinely used for the description of the magnetic behavior of exchange-coupled metal ion pairs. Magnetically dilute chromium(III) ions in an octahedral crystal field are characterized by an orbitally nondegenerate ground state with $S = {}^3/_2$. Exchange coupling yields a manifold of levels having $S' = 0, 1, 2, 3$ with the $S' = 0$ state lowest in energy if the interaction is antiferromagnetic in nature (J negative). Ferromagnetic interactions yield an $S' = 3$ ground state (J positive). Taking note of the degeneracies of the various spin levels, the magnetic susceptibility expression is obtained by substitution of the first-order Zeeman coefficients into the Van Vleck equation.[33] The resulting expression for exchange-coupled chromium(III) ions is

$$\chi_m = \frac{2g^2N\beta^2}{kT}\left[\frac{\exp(-2J/kT) + 5\exp(-6J/kT) + 14\exp(-12J/kT)}{1 + 3\exp(-2J/kT) + 5\exp(-6J/kT) + 7\exp(-12J/kT)}\right]$$

The capability of the susceptibility expression to explain the magnetic data for $[(gly)_2Cr(OH)_2Cr(gly)_2]$ is illustrated in Figure 2, where the best least-squares fit of the experimental data to the expression is presented as the dashed line. It may be seen that only the general features of the magnetic behavior are reproduced by the simple theoretical expression with $2J \doteq -8.4$ cm^{-1} and $g = 1.95$. The deviation observed here appears to be similar to that noted for $[(NH_3)_5CrOHCr(NH_3)_5]_2Cl_3(ClO_4)_7 \cdot H_2O$ and $[(NH_3)_5CrOHCr(NH_3)_4OH]Cl_4 \cdot H_2O$ by Ikeda, Kimura, and Uryu.[34] In order to explain the experimental data, Ikeda, *et al.*, invoked a biquadratic exchange interaction represented by the term $-j(\mathbf{S}_1 \cdot \mathbf{S}_2)^2$ in the exchange Hamiltonian. Using this latter approximation the energy levels are given by

$$E(S') = -2J[S'(S'+1) - S_1(S_1+1) - S_2(S_2+1)] - j[{}^1/_2[S(S+1) - S_1(S_1+1) - S_2(S_2+1)]]^2$$

From the modified energy level arrangement the expression for the magnetic susceptibility is

$$\chi_m = \left\{\frac{g^2N\beta^2}{kT}\right\}\left\{\frac{2\exp[(-2J+16.5j)/kT] + 10\exp[(-6J+43.5j)/kT] + 28\exp[(-12J+69j)/kT]}{1.0 + 3\exp[(-2J+16.5j)/kT] + 5\exp[(-6J+43.5j)/kT] + 7\exp[(-12J+69j)/kT]}\right\}$$

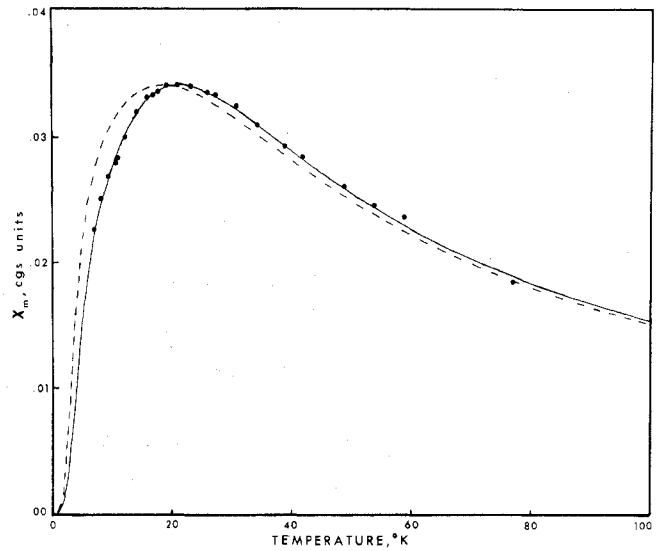

Figure 2. The temperature variation of the magnetic susceptibility of $[(gly)_2Cr(OH)_2Cr(gly)_2]$. The dashed line represents the best fit in the absence of the biquadratic exchange term, and the solid line represents the best fit including the biquadratic exchange term. The experimental data are shown as dots.

As can be seen in Figure 2, the temperature variation of the magnetic susceptibility is exactly fitted by this expression with $2J = -3.81$ cm^{-1}, $j = 0.37$ cm^{-1}, and $g = 1.95$. We emphasize that the energy level intervals are to be compared and not the $2J$ parameters which result from the fitting processes.

The room-temperature epr spectrum of a powdered sample of the complex exhibited a single broad symmetrical band at approximately $g = 2$. There was no appreciable change in either bandwidth or signal intensity upon cooling the sample to 106°K, the low-temperature limit of our variable-temperature device. This observation is in exact agreement with the results of calculations of intensities by Fournier, Landry, and Bartram[35] for exchange-coupled chromium(III) pairs having a coupling constant comparable to that obtained here.

If we further invoke the assumption[35] that $2D = g\beta(\Delta H)$, where ΔH is the observed line width, we calculate $|D| = 0.074$ cm^{-1}. It is interesting to speculate about the magnitude of the zero-field splitting. Isolated chromium ions in relatively low-symmetry environments frequently have somewhat larger D values than that observed here.[36] Since

(29) Y. Iitaka, *Acta Crystallogr.*, 14, 1 (1961).
(30) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968.
(31) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.
(32) A. Bondi, *J. Phys. Chem.*, 68, 441 (1964).
(33) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932, Chapter IX.
(34) H. Ikeda, I. Kimura, and N. Uryu, *J. Chem. Phys.*, 48, 4800 (1968).
(35) J. T. Fournier, J. R. Landry, and R. H. Bartram, *J. Chem. Phys.*, 55, 2522 (1971).
(36) See, for example, J. C. Hempel, L. O. Morgan, and W. B. Lewis, *Inorg. Chem.*, 9, 2064 (1970).

Table V. Structural and Magnetic Data for Hydroxo-Bridged Complexes

Complex	M-O-M, deg	$2J$, cm^{-1}
$[(dipy)Cu(OH)_2Cu(dipy)]SO_4 \cdot 5H_2O$	97[a]	+48[b]
$[(EAEP)Cu(OH)_2Cu(EAEP)](ClO_4)_2$	99.2 (3)[c]	−130.4[d]
$[(tmen)Cu(OH)_2Cu(tmen)]Br_2$	104.1 (2)[e]	−509[f]
$[(gly)_2Cr(OH)_2Cr(gly)_2]$	98.2 (2)[g]	−8.4[g,h]

[a] A. T. Casey, B. F. Hoskins, and F. D. Whillans, *Chem. Commun.*, 904 (1970). [b] Reference 3. [c] Reference 4. [d] Reference 5. [e] Reference 21. [f] Reference 20. [g] This work; ref 8. [h] Reference 7.

crystal field effects and dipole-dipole interactions as well as the exchange interaction contribute to the zero-field splitting, these contributions must be of opposite sign such that they are able to attenuate the overall value of the zero-field splitting.

We now consider the spin-spin coupling mechanism.[37] The structural data support a pseudotetrahedral geometry for the bridging oxygen atom. Thus there is an available lone pair of electrons in the nonbonding hybrid orbital on the oxygen which can interact with like pairs from the "t_{2g}" π orbitals[38] on each chromium ion. It is more difficult to account for the coupling of the remaining unpaired electron on each chromium without considering the effects of intraatomic exchange, since the in-plane π orbitals on each chromium are not advantageously oriented for a superexchange process. However, this latter process cannot be ruled out with certainty since these orbitals can mix with the σ orbitals of the bridging oxygen atom.

It is of interest to compare the structural and magnetic data for $[(gly)_2Cr(OH)_2Cr(gly)_2]$ with analogous data for hydroxo-bridged copper(II) complexes. These data are collected in Table V, where it may be seen that the singlet-triplet splittings in the copper(II) complexes correlate well with the Cu-O-Cu angle. The data for the chromium(III) complex are similar and it will be of considerable merit to characterize additional hydroxo-bridged chromium(III) and copper(II) complexes so that the structural factors which determine the magnitude of the spin-spin coupling can be identified.

(37) For an early account see P. W. Anderson, *Magnetism*, 1, Chapter 2 (1963). For a recent review see A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, 45 (1971).

(38) Specifically, with the z axis taken perpendicular to the Cr-O-Cr-O plane, these are the d_{xz}, d_{yz} orbitals.

Experimental Section

Magnetic Measurements. In the temperature range 77-296°K, magnetic susceptibilities of a powdered sample were determined using a Faraday balance.[39] A Foner-type vibrating sample magnetometer,[40] operating at a field strength of 10,000 G, was used to determine the magnetic susceptibilities in the 4.2-80°K temperature range. Mercury tetrathiocyanatocobaltate(II) was used as a magnetic susceptibility standard,[41] and diamagnetic corrections were estimated from Pascal's constants.[42]

Epr Measurements. The epr spectra of a powdered sample were obtained using a Varian V4502 X-band spectrometer equipped with a variable-temperature accessory.

Registry No. $[Cr(gly)_2OH]_2$, 36926-80-4.

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(39) W. E. Hatfield, C. S. Fountain, and R. Whyman, *Inorg. Chem.*, 5, 1855 (1966).
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Structure of π-$C_5H_5Rh(CH_2{=}CHF)_2$ and π-$C_5H_5Rh(CH_2{=}CHF)(CH_2{=}CH_2)$

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A solution of π-$C_5H_5Rh(CH_2{=}CHF)_2$ contains six isomers as a consequence of differing orientations of the vinyl fluoride ligands. Two isomers of π-$C_5H_5Rh(CH_2{=}CH_2)(CH_2{=}CHF)$ were detected. The free energy difference of the isomers is small for both compounds (<1 kcal). The energy barrier to rotation of coordinated vinyl fluoride in π-$C_5H_5Rh(CH_2{=}CHF)_2$ appears to be slightly greater than that for ethylene in π-$C_5H_5Rh(CH_2{=}CH_2)_2$.

Complexes of ethylene with rhodium(I) undergo a change of configuration through a propeller-like rotation of the ethylene ligand with the olefin-rhodium bond as its axis.[1] The energy barriers to rotation of coordinated ethylene in π-$C_5H_5Rh(C_2H_4)_2$ (15.0 ± 0.2 kcal[1b]) and some of its analogs have been evaluated,[1b,c] but, aside from data for C_2F_4 in π-$C_5H_5Rh(C_2H_4)(C_2F_4)$[1b] (no rotation detected), corresponding data for rhodium complexes of substituted olefins have not been reported. Accordingly the temperature dependence of the ^1H and ^{19}F nmr spectra of π-$C_5H_5Rh(CH_2{=}CHF)_2$ was studied.

Initiation of rapid rotation of ethylene in π-$C_5H_5Rh(C_2H_4)_2$ on raising the temperature is indicated by the nmr spectrum in the following manner. At low temperature the hydrogen of coordinated ethylene is responsible for two characteristically complex upfield absorptions centered at −2.89 and −1.00 ppm. These are attributed respectively to "outside" (H^o) and "inside" (H^i) locations (see Figure 1). At high temperatures fast rotation exchanges H^o and H^i and these absorptions broaden and, finally, coalesce.

Absorptions in the proton nmr spectrum of π-C_5H_5Rh-

(1) (a) R. Cramer, *J. Amer. Chem. Soc.*, 86, 217 (1964); (b) R. Cramer, J. B. Kline, and J. D. Roberts, *ibid.*, 91, 2519 (1969); (c) R. Cramer and J. J. Mrowca, *Inorg. Chim. Acta*, 5, 528 (1971).