

Molecular Structure and Magnetic Properties of μ -Dihydroxo-bis[4-dimethylamino-2,6-pyridine-dicarboxylatoaquoiron(III)] Dihydrate, $[(\text{CH}_3)_2\text{NC}_7\text{H}_2\text{NO}_4(\text{H}_2\text{O})\text{FeOH}]_2 \cdot 2\text{H}_2\text{O}$

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Abstract: The crystal and molecular structure of the title complex has been determined from single-crystal three-dimensional x-ray data collected by counter methods. $[(\text{CH}_3)_2\text{NC}_7\text{H}_2\text{NO}_4(\text{H}_2\text{O})\text{FeOH}]_2 \cdot 2\text{H}_2\text{O}$ crystallizes as red-brown prisms in space group $C2/m$ with $Z = 2$; $a = 13.538$ (5), $b = 10.758$ (6), $c = 9.331$ (3) Å; $\beta = 114.74$ (3)°; $d_{\text{calcd}} = 1.706$, $d_{\text{obsd}} = 1.72$ (1) g/cm³. Least-squares refinement of 907 reflections having $I \geq 3\sigma(I)$ gave a conventional R factor of 0.068. The structure consists of discrete centrosymmetric dimeric units in which two crystallographically equivalent Fe(III) ions are bridged by two OH groups. The distorted octahedral NO_5 donor set is composed of the bridging OH ions, one H_2O molecule, and a tridentate pyridinedicarboxylate ligand. Structural parameters of the planar $\text{Fe}_2(\text{OH})_2^{4+}$ unit include Fe-O bond distances of 1.937 (6) and 1.986 (9) Å, an Fe-O-Fe bridging angle of 105.3 (4)°, and an Fe...Fe separation of 3.118 (3) Å. Comparisons are drawn between the coordination geometry of the title complex and those previously observed for $\text{Fe}_2(\text{OH})_2^{4+}$ complexes of related ligands having either OH or H as the 4-ring substituents. The antiferromagnetism of the title complex is reflected by a gradual decrease of μ_{eff} from 4.94 μ_{B} (per Fe) at 301 K to 2.90 μ_{B} at 78 K. Magnetic susceptibilities over this temperature range are well described by the spin-spin model for $H = -2J\bar{S}_1\bar{S}_2$ with $S_1 = S_2 = 5/2$, $-J = 11.7$ (4) cm⁻¹, and $g = 2.0$. In contrast to the behavior of $\text{Cu}_2(\text{OH})_2^{2+}$ and $\text{Cr}_2(\text{OH})_2^{4+}$ units, spin-spin coupling within $\text{Fe}_2(\text{OH})_2^{4+}$ units is not strongly dependent on the M-OH-M bridging angles.

Introduction

Structural, magnetic, and related features of polynuclear clusters containing Fe(III) ions bridged by oxygen-donor ligands have considerable relevance to the bioinorganic chemistry of Fe(III).^{2,3} Examples of one of the simplest of such clusters, the $\text{Fe}_2(\text{OH})_2^{4+}$ unit, are surprisingly uncommon. We have structurally characterized two $\text{Fe}_2(\text{OH})_2^{4+}$ units whose six-coordinate Fe(III) ions were ligated further by tridentate 4-R-2,6-pyridinedicarboxylates (R = H, OH) and one H_2O molecule.⁴ Unfortunately, the $\text{Fe}_2(\text{OH})_2^{4+}$ units in both complexes exhibited nearly identical Fe-O distances and Fe-O-Fe bridging angles. This result served to obscure the effect, if any, that the variations of these structural parameters might have on the magnetic properties of the $\text{Fe}_2(\text{OH})_2^{4+}$ unit. Other workers have reported substantial structural/magnetic variations for dihydroxo-bridged dimers of Cr(III)⁵ and Cu(II).⁶ Crystallographic studies of the Fe(III) complexes with R = H, OH revealed that the pyridine N donor was trans to one of the bridging OH groups.⁴ With a view toward obtaining complexes of $\text{Fe}_2(\text{OH})_2^{4+}$ units which structurally were perturbed relative to those for R = H, OH, we prepared complexes of ligands substituted specifically to achieve either an increase (R = $(\text{CH}_3)_2\text{N}$) or decrease (R = Cl) in the basicity of the pyridine N donor.⁷ Strong variations in the basicity of the N donor were expected to change the lengths of the Fe-N bond and ultimately perturb the structure of the $\text{Fe}_2(\text{OH})_2^{4+}$ unit. As described elsewhere, the 4-chloro substituted complex turned out to be the first example of an oxo-bridged Fe(III) dimer having a strictly linear Fe_2O^{4+} unit.⁸ In contrast, the 4-dimethylamino complex did contain a $\text{Fe}_2(\text{OH})_2^{4+}$ unit which was perturbed in a most useful manner relative to the previously characterized $\text{Fe}_2(\text{OH})_2^{4+}$ species. We report here the synthesis, crystal structure, and magnetic susceptibilities over the 78–300 K temperature range of the 4-dimethylamino derivative.

Experimental Section

1. Preparation of the Ligand and Title Complex. The protonated ligand, 4-dimethylamino-2,6-pyridinedicarboxylic acid, was prepared⁹ from the reaction (140 °C, 14 h) of 4-chloro-2,6-pyridinedicarboxylic acid dimethyl ester (8 g) with 35 mL of 20% aqueous $(\text{CH}_3)_2\text{NH}$ in a stainless steel bomb. The reaction mixture was removed from the bomb tube and neutralized with concentrated HCl. The crude ligand was collected by filtration, and further purified by reprecipitation (three times) with HCl from ammoniacal solution. Following recrystallization from water, the white, crystalline product (5 g) melted at 267 °C (lit.¹⁰ 248 °C dec).

The essentially water-insoluble title complex was prepared in crystalline form by the urea hydrolysis technique. In a typical experiment, 2.5 mmol each of the ligand, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and urea were dissolved in 120 mL of hot distilled H_2O . Following filtration through a 0.22- μm pore size membrane, the solution was maintained at 90 °C for 2 days. The resulting red-brown prisms were collected by filtration, thoroughly washed with distilled H_2O , and dried in air at 25 °C; the yield was 0.65 g (82%).

Anal. Calcd for $\text{C}_9\text{H}_{13}\text{N}_2\text{O}_7\text{Fe}$: C, 34.09; H, 4.11; N, 8.84. Found: C, 33.91; H, 4.07; N, 9.05.

2. Magnetic Measurements. Variable temperature magnetic susceptibility studies were performed with a Faraday balance of standard design that was calibrated with $\text{HgCo}(\text{SCN})_4$. A diamagnetic correction of -164×10^6 cgsu per Fe(III) was estimated from Pascal's constants.¹¹

3. Collection of Diffraction Data. A crystal approximately $0.5 \times 0.15 \times 0.1$ mm was mounted along the long dimension (a axis) in a sealed capillary. Preliminary Weissenberg and precession photographs indicated a monoclinic system with the systematic absence hkl , $h + k = 2n + 1$. Three space groups, $C2/m$, Cm , and $C2$, are consistent with this condition.

Unit cell constants (Table I) were determined by a least-squares fit of 15 moderately intense high-angle reflections centered accurately on a Syntex P2₁ autodiffractometer using graphite monochromated $\text{Mo K}\alpha$ radiation. With two $[(\text{CH}_3)_2\text{NC}_7\text{H}_2\text{NO}_4(\text{H}_2\text{O})\text{FeOH}]_2 \cdot 2\text{H}_2\text{O}$ moieties per unit cell, the calculated density agreed well with the value observed by flotation in a $\text{CH}_2\text{Cl}_2/\text{CBr}_4$ mixture.

Table I. Crystal Data

| | | | |
|---|------------|-------------------------------|-----------------------|
| a , Å | 13.538 (5) | Z | 2 |
| b , Å | 10.758 (6) | Extinction | $hkl, h + k = 2n + 1$ |
| c , Å | 9.331 (3) | Space group | $C2/m$ |
| β , deg | 114.74 (3) | μ , cm^{-1} | 12.9 |
| V , Å ³ | 1234.25 | λ , Å | 0.71069 |
| d_{obsd} , g/cm^3 | 1.72 (1) | Temp, °C | 22 ± 1 |
| d_{calcd} , g/cm^3 | 1.706 | Mol wt, g/mol | 634.13 |

Intensity data were collected at 22 ± 1 °C using a θ - 2θ scan to a maximum of $2\theta = 60^\circ$. Each scan covered a range of 0.65° below $K\alpha_1$ and 0.75° above $K\alpha_2$ for the calculated peak position. A scan rate of $3.91 \text{ deg min}^{-1}$ was used with stationary background counts taken before and after each scan. The total time for background counting was equal to the scan time and was equally distributed before and after the peak.

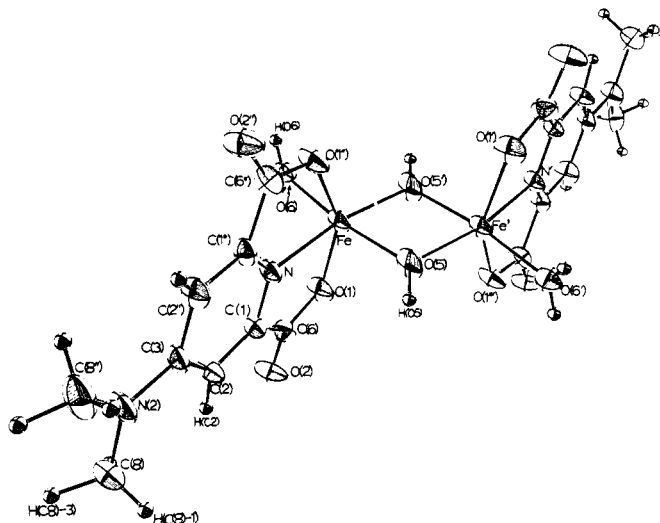
Three standard reflections were recorded after every 47 reflections; they showed random variations of $\pm 2\%$ but no significant trend. A total of 907 reflections with $I \geq 3\sigma(I)$ out of a possible 1963 were considered observed and used in the structure solution and refinement. Intensities I and $\sigma(I)$ were calculated from

$$I = (P - LB - RB)SR \text{ and } \sigma(I) = (P + LB + RB)^{1/2}SR$$

where P is the peak count, LB is the "left" background count, RB is the "right" background, and SR is the scan rate. All intensities were corrected for decay by computing average decay factors using the three standard reflections. The data were corrected for Lorentz and polarization effects; the polarization correction for the parallel-parallel mode of the $P2_1$ diffractometer was chosen assuming the monochromator crystal to be 50% perfect and 50% mosaic. An estimate of the scale factor was then obtained using Wilson's method and absorption corrections were applied. Transmission factors ranged from 0.819 to 0.886 using a linear absorption coefficient of 12.9 cm^{-1} for Mo $K\alpha$ radiation.

4. Solution and Refinement of the Structure.¹² The structure was solved by the heavy atom method, assuming the space group to be $C2/m$, and refined using full-matrix least-squares techniques. The presence of two $[(\text{CH}_3)_2\text{NC}_7\text{H}_2\text{NO}_4\text{Fe}(\text{OH})]_2$ dimers per unit cell requires that each dimer exhibit $2/m$ point symmetry in $C2/m$.

Approximate coordinates for the unique iron atom were obtained from a normal sharpened Patterson map. A difference map, based on phases determined from the iron coordinates, revealed the remaining nonhydrogen atoms except for the lattice water oxygen atom [O(9)], which was located in a subsequent difference map. With all nonhy-

**Figure 1.** Molecular structure of the title complex showing the atom numbering scheme. Lattice oxygen atoms have been omitted for clarity.

drogen scattering matter present, the initial agreement factor $R_F = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ was 0.269.

Refinement was initiated using atomic scattering factors from Cromer and Waber.¹³ All atoms were treated as neutral species. Both real and imaginary parts of the anomalous dispersion corrections were applied to iron.¹⁴ Initial refinement was based on F^2 and weights were set according to $w = 1/\sigma^2$ with $\sigma(F_o^2) = (Lp)^{-1}(\sigma^2(I) + (0.03I)^2)^{1/2}$. Several refinement cycles, the last few of which utilized anisotropic thermal parameters for all atoms, reduced R_F to 0.081.

Further refinement was based on F with a weighting scheme chosen by an analysis of variance to make $|\Delta F|/\sigma$ independent of $|F_o|$. This led to the following assignments for $\sigma(F_o)$:

$$\begin{aligned} \sigma(F_o) &= 2.24 + 0.011|F_o| & |F_o| \leq 41.1 \\ \sigma(F_o) &= 1.88 + 0.029|F_o| & |F_o| > 41.1 \end{aligned}$$

After two refinement cycles, a difference map revealed the coordinates of all unique hydrogen atoms except those of the hydroxyl group and the lattice water molecule. The position of the former was obscured by the relatively high residual electron density in the iron coordination sphere; coordinates were calculated for the hydroxyl hydrogen atom and subsequently refined. Because of the large temperature factor of

Table II. Fractional Atomic Coordinates^a and Thermal Parameters^b for the Title Complex

| Atom | x | y | z | β_{11} or B , Å ² | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|-----------|----------|----------|-----------|--------------------------------------|--------------|--------------|--------------|--------------|--------------|
| Fe | 1247 (1) | 0 | 454 (2) | 29 (1) | 59 (1) | 41 (1) | 0 | -5 (1) | 0 |
| O(5) | 151 (5) | 0 | 1352 (8) | 34 (4) | 119 (9) | 41 (8) | 0 | -10 (5) | 0 |
| O(6) | 2153 (5) | 0 | -818 (7) | 44 (4) | 56 (6) | 82 (10) | 0 | 19 (5) | 0 |
| O(9) | 980 (10) | 0 | 4719 (13) | 125 (9) | 407 (29) | 156 (19) | 0 | 78 (11) | 0 |
| N(1) | 2516 (6) | 0 | 2636 (8) | 28 (4) | 49 (7) | 51 (9) | 0 | -2 (5) | 0 |
| N(2) | 4807 (7) | 0 | 7265 (9) | 34 (5) | 88 (8) | 49 (9) | 0 | -10 (6) | 0 |
| C(3) | 4026 (7) | 0 | 5752 (10) | 24 (5) | 81 (10) | 47 (11) | 0 | 1 (6) | 0 |
| O(1) | 1649 (4) | 1856 (5) | 924 (5) | 51 (3) | 63 (4) | 62 (6) | 9 (3) | -3 (4) | 10 (4) |
| O(2) | 2706 (4) | 3233 (5) | 2712 (6) | 83 (4) | 48 (4) | 86 (7) | -7 (4) | 21 (4) | -1 (4) |
| C(1) | 2868 (5) | 1080 (6) | 3389 (7) | 29 (3) | 57 (6) | 58 (7) | -2 (4) | 11 (4) | -8 (5) |
| C(2) | 3637 (6) | 1130 (7) | 4925 (7) | 43 (4) | 62 (6) | 57 (8) | -9 (5) | 3 (5) | -17 (6) |
| C(6) | 2396 (5) | 2159 (7) | 2287 (7) | 44 (4) | 59 (7) | 69 (8) | 4 (5) | 17 (5) | -8 (6) |
| C(8) | 5172 (6) | 1170 (9) | 8124 (8) | 44 (5) | 118 (9) | 72 (9) | -1 (6) | 2 (6) | -29 (8) |
| H(O(5)) | 34 (9) | 0 | 228 (13) | 1.33 | | | | | |
| H(O(6)) | 226 (7) | 67 (8) | -113 (9) | 1.33 | | | | | |
| H(C(2)) | 380 (7) | 187 (8) | 538 (9) | 1.33 | | | | | |
| H(C(8)-1) | 467 (7) | 155 (8) | 844 (9) | 1.33 | | | | | |
| H(C(8)-2) | 533 (6) | 181 (8) | 750 (9) | 1.33 | | | | | |
| H(C(8)-3) | 596 (6) | 107 (8) | 898 (8) | 1.33 | | | | | |

^a Nonhydrogen coordinates are $\times 10^4$; hydrogen coordinates are $\times 10^3$. The atom numbering scheme has been chosen to be consistent with that reported previously for related $\text{Fe}_2(\text{OH})_2^{4+}$ derivatives; see ref 4. ^b 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. Bond Distances (Å)^a and Angles (deg) in the Title Complex and Related $Fe_2(OH)_2^{4+}$ Complexes

| Atoms | Distance | | | Atoms | Distance | | |
|----------------|--|--------------------|---------------------|---------------------|--|--------------------|---------------------|
| | This work (R = (CH ₃) ₂ N) | R = H ₄ | R = OH ⁴ | | This work (R = (CH ₃) ₂ N) | R = H ⁴ | R = OH ⁴ |
| Fe...Fe' | 3.118 (3) | 3.089 (2) | 3.078 (2) | O(1)-Fe-O(6) | 87.4 (2) | 86.5 (2) | 86.9 (2) |
| Fe-O(1) | 2.068 (5) | 2.078 (4) | 2.064 (4) | | | 87.8 (2) | 89.8 (1) |
| | | 2.053 (5) | 2.021 (4) | O(5)-Fe-O(5') | 74.7 (4) | 76.4 (2) | 76.8 (2) |
| Fe-O(5') | 1.937 (6) | 1.938 (5) | 1.938 (4) | O(5')-Fe-O(6) | 95.8 (3) | 95.3 (2) | 93.1 (2) |
| Fe-O(5) | 1.986 (9) | 1.993 (5) | 1.989 (4) | O(5)-Fe-O(6) | 170.5 (2) | 170.7 (1) | 168.2 (2) |
| Fe-O(6) | 2.032 (9) | 2.021 (5) | 2.044 (4) | O(1)-Fe-N(1) | 75.6 (1) | 75.5 (2) | 75.7 (2) |
| Fe-N(1) | 2.043 (6) | 2.070 (6) | 2.057 (5) | | | 75.5 (2) | 75.8 (2) |
| O(1)-C(6) | 1.292 (7) | 1.261 (5) | 1.285 (7) | O(5')-Fe-N(1) | 167.3 (4) | 168.0 (2) | 168.3 (2) |
| | | 1.285 (6) | 1.272 (7) | O(5)-Fe-N(1) | 92.5 (3) | 92.3 (2) | 93.5 (2) |
| O(2)-C(6) | 1.237 (8) | 1.252 (6) | 1.231 (6) | O(6)-Fe-N(1) | 96.9 (3) | 96.3 (2) | 97.1 (2) |
| | | 1.225 (8) | 1.235 (6) | O(1)-C(6)-O(2) | 124.9 (6) | 125.9 (5) | 124.9 (5) |
| N(1)-C(1) | 1.338 (7) | 1.344 (7) | 1.330 (6) | | | 126.0 (4) | 124.8 (5) |
| | | 1.326 (8) | 1.333 (6) | O(1)-C(6)-C(1) | 114.3 (6) | 115.7 (5) | 114.1 (4) |
| C(1)-C(2) | 1.375 (7) | 1.389 (6) | 1.377 (8) | | | 114.2 (5) | 114.0 (4) |
| | | 1.379 (6) | 1.380 (8) | O(2)-C(6)-C(1) | 120.8 (5) | 118.4 (3) | 121.1 (5) |
| C(1)-C(6) | 1.504 (9) | 1.501 (8) | 1.527 (7) | | | 119.8 (4) | 121.2 (5) |
| | | 1.517 (7) | 1.522 (7) | N(1)-C(1)-C(2) | 121.9 (6) | 119.6 (3) | 122.4 (5) |
| C(2)-C(3) | 1.418 (8) | 1.393 (10) | 1.412 (7) | | | 121.6 (5) | 121.4 (4) |
| | | 1.416 (9) | 1.417 (7) | N(1)-C(1)-C(6) | 110.8 (5) | 111.4 (3) | 110.9 (4) |
| C(3)-N(2) | 1.365 (10) | | | | | 111.1 (3) | 110.3 (5) |
| N(2)-C(8) | 1.463 (10) | | | C(1)-N(1)-C(1'') | 120.6 (7) | 122.7 (3) | 121.4 (5) |
| C(2)-H(C(2)) | 0.88 (8) | 1.09 | 1.08 | C(1)-C(2)-C(3) | 118.7 (6) | 118.5 (5) | 117.2 (4) |
| | | 1.09 | 1.09 | | | 116.9 (6) | 117.8 (5) |
| O(5)-H(O(5)) | 0.79 (12) | 1.03 | 1.08 | C(2)-C(1)-C(6) | 127.0 (6) | 129.0 (5) | 126.7 (4) |
| O(6)-H(O(6)) | 0.81 (9) | 0.96 | 0.90 | | | 127.2 (6) | 128.3 (4) |
| | | 0.78 | 0.94 | C(2)-C(3)-C(2'') | 118.0 (7) | 120.6 (4) | 119.8 (5) |
| C(8)-H(C(8)-1) | 0.94 (10) | | | C(2)-C(3)-N(2) | 120.9 (3) | | |
| C(8)-H(C(8)-2) | 0.98 (10) | | | C(3)-N(2)-C(8) | 120.3 (4) | | |
| C(8)-H(C(8)-3) | 1.04 (6) | | | C(8)-N(2)-C(8'') | 118.7 (8) | | |
| Fe'-Fe-O(1) | 102.5 (2) | 102.9 (2) | 103.4 (1) | C(1)-C(2)-H(C(2)) | 117 (4) | 121 | 120 |
| | | 102.3 (2) | 100.5 (1) | | | 123 | 121 |
| Fe'-Fe-O(6) | 133.7 (2) | 134.0 (1) | 131.8 (1) | H(C(2))-C(2)-C(3) | 123 (5) | 121 | 122 |
| Fe-O(1)-C(6) | 118.7 (4) | 118.9 (4) | 119.4 (3) | | | 120 | 121 |
| | | 119.7 (4) | 120.6 (3) | N(2)-C(8)-H(C(8)-1) | 115 (5) | | |
| Fe-O(5)-Fe' | 105.3 (4) | 103.6 (2) | 103.2 (6) | N(2)-C(8)-H(C(8)-2) | 113 (5) | | |
| Fe-N(1)-C(1) | 119.3 (3) | 118.2 (4) | 119.6 (2) | N(2)-C(8)-H(C(8)-3) | 109 (5) | | |
| | | 119.1 (4) | 118.9 (4) | H(C(8)-1)-C(8)- | 105 (8) | | |
| Fe-N(1)-C(3) | 172.3 (5) | 176.6 (3) | 175.7 (2) | H(C(8)-2) | | | |
| O(1)-Fe-O(1'') | 149.8 (2) | 149.7 (1) | 150.6 (2) | H(C(8)-1)-C(8)- | 117 (7) | | |
| O(1)-Fe-O(5') | 105.0 (1) | 108.5 (2) | 110.5 (2) | H(C(8)-3) | | | |
| | | 101.7 (2) | 98.8 (2) | H(C(8)-2)-C(8)- | 97 (6) | | |
| O(1)-Fe-O(5) | 95.0 (2) | 92.1 (1) | 90.9 (1) | H(C(8)-3) | | | |
| | | 97.9 (2) | 97.7 (1) | | | | |

^a Primed atoms are related to unprimed atoms by a center of symmetry; doubly primed atoms are related to unprimed atoms by a mirror plane perpendicular to *b*.

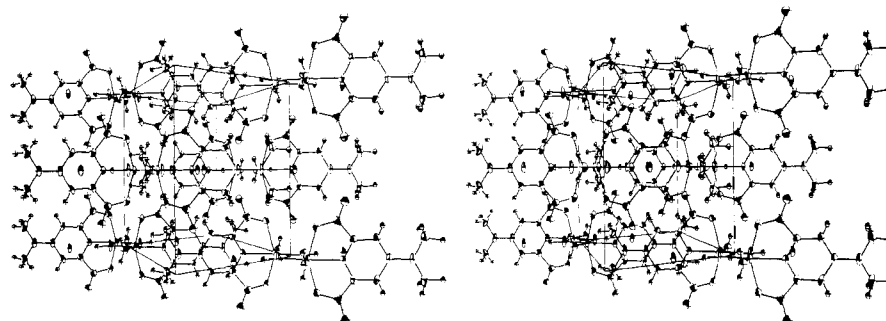


Figure 2. Stereoscopic packing diagram for the title complex viewed approximately along *a*; the *b* axis is vertical. For clarity, the thermal parameters of the lattice water oxygen atom [O(9)] have been artificially reduced.

the lattice water oxygen atom, no further attempt was made to locate the H₂O hydrogen atoms.

Several cycles of full-matrix refinement resulted in final values of R_F of 0.068 and $R_{wF} = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$, the quantity minimized, of 0.085. For the last refinement cycle, all parameter changes were within their estimated standard deviation. A final dif-

ference map showed a general background of $0.3 e/\text{\AA}^3$ and no significant features. Final atomic parameters, together with their estimated standard deviations, are given in Table II. A view of the complex, showing the atom numbering scheme, is given in Figure 1, while the unit cell contents are shown in Figure 2. A list of observed and calculated structure factors is available.¹⁵

Table IV. Least-Squares Planes and Deviations Therefrom for the Title Complex

| Plane | Equations of the Planes ^a | | | | Atoms defining plane ^b |
|-------|--------------------------------------|-----|--------|---------|---|
| | A | B | C | D | |
| I | 0.0 | 1.0 | 0.0 | 0.0 | Fe, Fe', O(5), O(5'), O(6), O(6'), N(1), N(1'), C(3), C(3'), N(2), N(2') |
| II | -0.8416 | 0.0 | 0.5401 | -0.9973 | O(1), O(1''), N(1), O(5') |
| III | 0.4621 | 0.0 | 0.8868 | 1.216 | O(1), O(1''), O(6), O(5) |
| IV | -0.9526 | 0.0 | 0.3042 | -1.577 | N(1), C(1), C(2), C(3), C(2''), C(1'') |
| V | -0.9516 | 0.0 | 0.3072 | -1.607 | N(1), C(1), C(2), C(3), C(2''), C(1'') C(6), C(6''), O(1), O(2), O(1'') O(2'') |

| Deviations from the Planes | | | | | |
|----------------------------|--------|--------|--------|--------|--------|
| | Atom | Dev, Å | | Atom | Dev, Å |
| (II) | O(1) | -0.155 | (V) | N(1) | 0.032 |
| | O(1'') | -0.155 | | C(1) | 0.054 |
| | N(1) | 0.204 | | C(2) | 0.034 |
| | O(5') | 0.106 | | C(3) | 0.056 |
| | Fe | -0.066 | | C(2'') | 0.034 |
| (III) | O(1) | 0.343 | C(1'') | 0.054 | |
| | O(1'') | 0.343 | C(6) | -0.034 | |
| | O(6) | -0.337 | C(6'') | -0.034 | |
| | O(5) | -0.350 | O(1) | 0.067 | |
| | Fe | -0.177 | O(2) | -0.165 | |
| | N(1) | -0.008 | O(1'') | 0.067 | |
| | | | O(2'') | -0.165 | |
| (IV) | C(1) | 0.012 | Fe | 0.288 | |
| | C(2) | -0.012 | N(2) | 0.006 | |
| | C(3) | 0.007 | C(8) | 0.078 | |
| | C(2'') | -0.012 | C(8'') | 0.078 | |
| | C(1'') | 0.012 | | | |

^a Equations describing the planes are of the form $AX_0 + BY_0 + CZ_0 = D$ where X_0 , Y_0 , and Z_0 are Cartesian axes coincident with bxc^* , b , and c^* directions, respectively. ^b The atoms defining plane I are strictly coplanar.

Table V. Possible Hydrogen Bonding Contact Distances

| Donor (D) | Hydrogen (H) ^a | Acceptor (A) | D-H...A | D...A ^b | H...A |
|-------------------|---------------------------|--------------|---------|--------------------|----------|
| O(6) | H(O(6)) (ii) | O(2) (iii) | 154 (8) | 2.656 (7) | 1.91 (8) |
| O(9) ^b | | O(9) (v) | | 2.912 (17) | |
| O(9) | | O(2) (iv) | | 2.992 (10) | |
| O(5) | | O(9) (i) | | 2.860 (13) | |
| O(5) | | O(6) (vi) | | 2.946 (9) | |
| O(5) | | O(1) (i) | | 2.989 (7) | |

^a i = x, y, z ; ii = x, \bar{y}, z ; iii = $1/2 - x, -1/2 + y, \bar{z}$; iv = $1/2 - x, 1/2 - y, 1 - z$; v = $\bar{x}, y, 1 - z$; vi = \bar{x}, y, \bar{z} . ^b D...A distances less than 3 Å are listed.

Finally, some comment on the choice of space group seems desirable. Excluding the lattice water oxygen atom, the variation in the anisotropic thermal parameters is not usually large and compares favorably with the variation reported for analogous structures $[(\text{HOC}_7\text{H}_2\text{NO}_4(\text{H}_2\text{O})\text{FeOH})_2$ and $(\text{HC}_7\text{H}_2\text{NO}_4(\text{H}_2\text{O})\text{FeOH})_2 \cdot 4\text{H}_2\text{O}]^4$ where the point symmetry of the dimers is $\bar{1}$. Further, in the present structure, the thermal ellipsoids (Figure 1) "point" in reasonable directions (i.e., approximately normal to bond axes). For these reasons, we assumed that deviations from $2/m$ point symmetry were small and did not attempt refinement in either $C2$ or Cm .

Description of the Structure. The structure consists of discrete dimeric units of point symmetry $2/m$ in which two centrosymmetrically related Fe(III) ions are bridged by two OH groups. A distorted octahedral coordination environment of each Fe(III) ion is provided by the two bridging OH groups, a water molecule, and a tridentate 2,6-pyridinedicarboxylate ligand. The limited "bite" of the latter ligand results in a reduction of the O(1)-Fe-O(1'') bond angle from the idealized value of 180° to the observed value of $149.8(2)^\circ$ (Table III). The entire $\text{Fe}_2(\text{OH})_2(\text{H}_2\text{O})_2^{4+}$ unit lies within the mirror plane (plane I, Table IV) which bisects the tridentate ligand. The two tridentate ligands lie on opposite sides of the dimeric units and are interrelated by a twofold axis along b .

Detailed comparison between the structural parameters of the three $\text{Fe}_2(\text{OH})_2^{4+}$ complexes that have been structurally characterized are given in Table III. The Fe-O(H) bond distances in all three complexes

are identical within experimental error; those of the title complex are 1.937 (6) and 1.986 (9) Å. However, the Fe-O-Fe bridging angle ($105.3(4)^\circ$) observed for the title complex is about 2° larger than those observed for the other two $\text{Fe}_2(\text{OH})_2^{4+}$ units. Consequently, the Fe...Fe separation in the title complex also is somewhat larger (~ 0.03 Å).

The basicities⁷ of the ligands used in these studies increase in the order $\text{R} = \text{H}$, $\text{R} = \text{OH}$, $\text{R} = (\text{CH}_3)_2\text{N}$; the Fe-N bond distances observed for their respective complexes are 2.070 (6), 2.057 (5), and 2.043 (6) Å. Thus, the systematic increase in electron density at the N donor site is in fact reflected by an apparent strengthening of the resulting Fe-N bond. The only structurally significant response of the $\text{Fe}_2(\text{OH})_2^{4+}$ units to this perturbation is the increase in the Fe-O-Fe angle noted above. Other structural features of the coordination geometry and ligand are unremarkable.

The gross molecular structure of the title complex is quite similar to that observed for the other two $\text{Fe}_2(\text{OH})_2^{4+}$ complexes⁴ and for a $\text{Cr}_2(\text{OH})_2^{4+}$ analogue with the $\text{R} = \text{H}$ ligand.¹⁶ Both the title complex and the $\text{Cr}_2(\text{OH})_2^{4+}$ analogue exhibit point symmetry $2/m$ while for the other two $\text{Fe}_2(\text{OH})_2^{4+}$ complexes, the point symmetry is $\bar{1}$. A structural feature of the title complex which results from this high point symmetry is plane I (Table IV). Neither of the other two $\text{Fe}_2(\text{OH})_2^{4+}$ complexes has a coordination geometry which is coplanar to this degree.

Intermolecular hydrogen bonding distances are listed in Table V.

Table VI. Magnetic Susceptibility Results for the Title Complex

| T, K | $10^6 \chi_{Fe}, \text{cgsu}$ | | $\mu_{\text{eff}} \text{ per Fe}, \mu_B^c$ | |
|--------|-------------------------------|--------------------|--|-------|
| | Obsd ^a | Calcd ^b | Obsd | Calcd |
| 301 | 10150 | 9990 | 4.94 | 4.90 |
| 222 | 11680 | 11690 | 4.55 | 4.56 |
| 174 | 12730 | 12790 | 4.21 | 4.22 |
| 138 | 13550 | 13490 | 3.87 | 3.86 |
| 99 | 13670 | 13850 | 3.29 | 3.31 |
| 78 | 13440 | 13750 | 2.90 | 2.93 |

^a Observed magnetic susceptibilities are given per Fe(III) and include a diamagnetic correction of -164×10^{-6} cgsu. ^b Calculated by the equation given in the text for $-J = 11.74 \text{ cm}^{-1}$ and $g = 2.00$. ^c Calculated using the formula $\mu_{\text{eff}}^2 = 7.998\chi_{Fe}(T)$ and the observed and calculated values of χ_{Fe} . Errors in the observed values of μ_{eff} are $\sim 0.04 \mu_B$.

As with the chelidamate ($R = OH$) and dipicolinate ($R = H$) derivatives studied previously,⁴ no evidence was found for intramolecular hydrogen bonding. In the present structure, the strongest hydrogen bonds, as measured by the donor-acceptor distance, are between symmetry related carboxylate oxygen atoms and bound water molecules. Since these are not expected to perturb the structural parameters of the $Fe_2(OH)_2^{4+}$ units to any great degree, the structure may be regarded as consisting of virtually discrete and magnetically dilute dimers.

Magnetic Susceptibility. Observed magnetic susceptibilities and magnetic moments of the title complex are presented in Table VI. An antiferromagnetic exchange interaction clearly is indicated by the gradual decrease of μ_{eff} from $4.94 \mu_B$ (per Fe) at 301 K to $2.90 \mu_B$ at 78 K. The spin-spin interaction model based on the exchange Hamiltonian $H = -2J\bar{S}_1\bar{S}_2$ with $S_1 = S_2 = 5/2$ and $g = 2.00$ leads to the relationship¹¹

$$\chi \text{ (per Fe)} = \frac{1.501}{T} \left(\frac{55 + 30z^{10} + 14z^{18} + 5z^{24} + z^{28}}{11 + 9z^{10} + 7z^{18} + 5z^{24} + 3z^{28} + z^{30}} \right)$$

where $z = \exp[-J/kT]$. Fitting of the susceptibility data to this expression using a nonlinear least-squares program which minimized the quantity

$$S = \sum_{\lambda=1}^N (\mu_{\text{obsd}}^2 - \mu_{\text{calcd}}^2)^2$$

yielded a coupling constant of $-J = 11.7 \pm 0.4 \text{ cm}^{-1}$.

The observed variation of the magnetic susceptibility with temperature is well described (Table VI) by the above expression using the parameter $-J = 11.74 \text{ cm}^{-1}$.

Discussion

Three 4-substituted 2,6-pyridinedicarboxylate complexes of the $Fe_2(OH)_2^{4+}$ unit now have been characterized structurally as well as magnetically. The magnetic behavior of these complexes is well described by the $-2J^{5/2} \cdot 5/2$ model with $g = 2.00$ and $-J = 11.7 \text{ cm}^{-1}$ ($R = (CH_3)_2N$), $-J = 7.3 \text{ cm}^{-1}$ ($R = OH$), and $-J = 11.4 \text{ cm}^{-1}$ ($R = H$). The major structural difference between the three $Fe_2(OH)_2^{4+}$ units is the somewhat larger Fe-O-Fe angle exhibited by the title

complex (Table III). Such a variation in bridging angle has profound magnetic significance for $Cu_2(OH)_2^{2+}$ complexes⁶ and appears to be significant for $Cr_2(OH)_2^{4+}$ complexes.⁵ Variations in the Fe-O-Fe angle apparently have little magnetic significance for the above complexes of the $Fe_2(OH)_2^{4+}$ unit. Moreover, similar results were observed for the two Schiff-base complexes of $Fe_2(\text{alkoxo})_2^{4+}$ units which have been fully characterized by other workers.^{17,18} These dimers have Fe-O-Fe angles in the range $104.1-110.6^\circ$ and have yielded $-J$ values of $\sim 17 \text{ cm}^{-1}$. Values of $-J$ in the range $7.3-17 \text{ cm}^{-1}$ account for the magnetic behavior of the 11 $Fe_2(OH)_2^{4+}$ and $Fe_2(\text{alkoxo})_2^{4+}$ complexes studied so far. We conclude that spin-spin coupling within such units is weakly antiferromagnetic ($-J = 12 \pm 5 \text{ cm}^{-1}$) and shows no significant trends with variations in the Fe-O-Fe angle and in the chemical nature of the nonbridging ligands. A similar invariance prevails for the more strongly coupled ($-J \cong 100 \text{ cm}^{-1}$) Fe_2O^{4+} units.^{8,19}

Acknowledgments. This research was supported by the Rutgers Computing Center. We thank Dr. Albert Schweitzer and Dr. Dana Powers for their assistance in obtaining and analyzing the magnetic susceptibility data.

Supplementary Material Available: Structure factor tables for the title complex (5 pages). Ordering information is given on any current masthead page.

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