

The Structure, Thermal and Magnetic Properties of Hexaaquairon(II) bis[bis(*N*-salicylideneglycinato)ferrate(III)] Dihydrate

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The title compound, $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6][\text{Fe}^{\text{III}}(\text{C}_9\text{H}_7\text{NO}_3)_2]_2 \cdot 2\text{H}_2\text{O}$, crystallizes in the monoclinic space group $P2_1/c$ with $a = 18.164(7)$, $b = 12.188(6)$, $c = 9.501(4)$ Å, $\beta = 90.44(3)^\circ$ and $Z = 2$. The structure was refined to $R = 0.056$ and $R_w = 0.078$ for 1913 reflections with $F_o \geq 5\sigma(F_o)$. The compound consists of an iron(II) complex cation, two iron(III) complex anions and two discrete water molecules. The iron(III) atoms are surrounded octahedrally by two Schiff base ligands, both coordinated through the N atom and two O atoms. Fe–N and Fe–O distances vary between 2.086(8) and 2.097(8) Å, and 1.917(8) and 2.079(7) Å, respectively. The iron(II) atom is situated in the symmetry centre and has octahedral coordination geometry formed by six water molecules. The Fe–O_w distances are 2.113(7), 2.121(7) and 2.124(7) Å. These six water molecules are joined by hydrogen-bonding interactions to the complex anions and to the water molecules of the crystal.

The synthesis of an iron-salicylaldehydeglycine compound (dark red) was first reported by Rây and Mukherjee.¹ They noted that iron, though used in the form of a ferrous salt, condensed with salicylaldehyde and glycine to give a binuclear ferric *N*-salicylideneglycinato complex. In a later study, evidence for the presence of two different iron environments was provided by Mössbauer and IR spectra of the reaction product.² As part of our systematic investigation of the complexes formed between transition metals and amino acid Schiff base ligands we synthesized the title compound from equimolar amounts of starting components and isolated suitable crystals for X-ray analysis.

Experimental

An ethanolic solution of salicylaldehyde (0.02 mol) was treated with glycine (0.02 mol) and water, and the mixture was warmed on a water-bath until all the glycine had dissolved. To this solution, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.02 mol) in water was slowly added with stirring. Dark red crystals gradually separated upon evaporation, and were filtered off, washed, and dried in air.

The space group $P2_1/c$ was confirmed from systematic absences and by the unit cell parameters found by the least-squares method from 21 centred reflections. Intensities were checked by measurement of two reference reflections (203̄, 117) after every 98 measurements. Lorentz and polarization corrections were applied but no absorption correction. The positions of the Fe atoms were found by direct methods using the XRAY 76 system,³ and those of other non-hydrogen atoms from subsequently derived electron density maps. H atoms were located from a difference Fourier map. Full-matrix least-squares anisotropic refine-

ment (H atoms isotropically) gave $R = 0.056$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/(85.0 + |F_o| + 0.003|F_o|^2)$. Av. and max $\Delta/\sigma = 0.2$ and 0.93, respectively; final difference Fourier map peaks = $0.57 \text{ e } \text{Å}^{-3}$. Atomic scattering factors for non-hydrogen atoms⁴ and H atoms⁵ were included. An anomalous dispersion correction was applied for Fe.⁶ Crystal and diffraction data are given in Table 1, and lists of calculated and observed structure factors as well as H-atom coordinates and other supplementary material are available from the authors on request. TG and DTG curves were obtained using a Mettler TA 3000

Table 1. Crystal and diffraction data.

| | |
|---|--------------------|
| M_r | 1020.30 |
| Space group | $P2_1/c$ |
| $a/\text{Å}$ | 18.164(7) |
| $b/\text{Å}$ | 12.188(6) |
| $c/\text{Å}$ | 9.501(4) |
| β/deg | 90.44(3) |
| $V/\text{Å}^3$ | 2103.3 |
| Z | 2 |
| $D_{\text{measd.}}/\text{Mg m}^{-3}$ | 1.59 |
| $D_{\text{calcd.}}/\text{Mg m}^{-3}$ | 1.611 |
| $F(000)$ | 1052 |
| 2θ range/ $^\circ$ | 5.0–55.0 |
| Measd. reflections | 4267 |
| Significant reflections ($F_o > 5\sigma(F_o)$) | 1913 |
| μ/cm^{-1} | 11.4 |
| Final R value ($\sum F_o - F_c /\sum F_o $) | 0.056 |
| Final R_w value ($[\sum w(F_o - F_c)^2/\sum w F_o ^2]^{1/2}$) | 0.078 |
| Diffractometer | Nicolet P 3 |
| Monochromator | Graphite |
| Radiation | $\text{MoK}\alpha$ |
| Scan type | ω -scan |
| Scan speed/ $^\circ \text{min}^{-1}$ | 2.0–25.0 |

system. The sample (10.29 mg) was heated in a dynamic nitrogen atmosphere at a rate of $10^{\circ}\text{C min}^{-1}$ to 900°C . The magnetic susceptibility of the compound was measured in the temperature range 93–293 K using a Newport Gouy balance system. Copper(II) sulphate pentahydrate (Merck AG) was used as standard. The data were corrected for diamagnetism using Pascal's constants.

Discussion

The structure of the compound is shown in Fig. 1. Atomic parameters are listed in Table 2 and bond lengths and angles in Table 3. The structure contains a complex cation situated in the symmetry centre, and two complex anions which are hydrogen-bonded to the cation. Two discrete water molecules complete the structure. The interatomic distances and angles of the compound agree well with literature values^{7–9} and are especially comparable with the values for $[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6][\text{Co}^{\text{III}}(\text{sal-gly})_2]_2 \cdot 2\text{H}_2\text{O}$.¹⁰ One of the tridentate ligands is notably bent, and Fe(1) thus deviates $0.57(2)$ Å from the calculated plane through the benzene ring.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent temperature factors (Å^2).

| | x | y | z | B_{eq}^a |
|-------|----------|-----------|----------|-------------------|
| Fe(1) | 2341(1) | 284(1) | 3799(2) | 2.07 |
| Fe(2) | 0 | 5000 | 5000 | 1.92 |
| O(1) | 2890(4) | 312(5) | 2058(7) | 2.95 |
| O(2) | 1628(4) | -212(6) | 5377(7) | 2.95 |
| O(3) | 715(4) | -1350(6) | 5972(8) | 3.60 |
| O(4) | 3204(4) | 5(5) | 4914(8) | 3.30 |
| O(5) | 1487(4) | 1065(5) | 2744(8) | 2.87 |
| O(6) | 862(4) | 2606(6) | 2381(8) | 3.21 |
| O(7) | 21(4) | 3283(6) | 5310(7) | 3.02 |
| O(8) | 1142(4) | 5190(6) | 5417(7) | 2.84 |
| O(9) | 265(4) | 4719(6) | 2856(7) | 3.03 |
| O(10) | -2156(5) | 273(9) | 1752(9) | 4.87 |
| N(1) | 1997(4) | -1268(6) | 3147(8) | 2.05 |
| N(2) | 2373(4) | 1872(6) | 4646(8) | 2.13 |
| C(1) | 3172(6) | -487(8) | 1299(10) | 2.52 |
| C(2) | 3749(6) | -276(11) | 343(11) | 3.54 |
| C(3) | 4068(7) | -1099(12) | -420(13) | 4.35 |
| C(4) | 3823(7) | -2155(10) | -313(12) | 3.96 |
| C(5) | 3267(6) | -2406(9) | 602(12) | 3.26 |
| C(6) | 2933(6) | -1581(8) | 1421(11) | 2.46 |
| C(7) | 2322(6) | -1893(7) | 2276(11) | 2.45 |
| C(8) | 1327(6) | -1679(9) | 3832(11) | 2.99 |
| C(9) | 1213(6) | -1050(8) | 5177(11) | 2.61 |
| C(10) | 3632(5) | 600(8) | 5708(11) | 2.60 |
| C(11) | 4307(6) | 180(11) | 6224(13) | 4.00 |
| C(12) | 4767(7) | 785(13) | 7075(15) | 4.79 |
| C(13) | 4565(7) | 1817(12) | 7522(16) | 5.05 |
| C(14) | 3930(7) | 2279(10) | 7007(14) | 4.05 |
| C(15) | 3458(5) | 1699(8) | 6108(11) | 2.37 |
| C(16) | 2830(6) | 2271(9) | 5547(11) | 2.88 |
| C(17) | 1771(6) | 2604(10) | 4165(13) | 3.55 |
| C(18) | 1341(5) | 2052(8) | 2994(10) | 2.09 |

$$^a B_{\text{eq}} = \frac{1}{3} \sum \sum \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

The carbon-hydrogen bond lengths are in the range $0.71(16)$ – $1.08(11)$ Å, and the oxygen-hydrogen lengths in the water molecules range from $0.60(8)$ to $0.98(12)$ Å. The crystal packing is illustrated in Fig. 2. In the asymmetric unit, two water O atoms of the $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ unit form hydrogen bonds with the uncoordinated O atoms of the carboxylate groups. The $\text{O}(9_w) \cdots \text{O}(3)$, $\text{O}(3) \cdots \text{H}(20)$ and $\text{O}(9_w) \cdots \text{H}(20)$ distances have the respective values $2.800(11)$, $2.08(16)$ and $0.73(16)$ Å, and the $\text{O}(9_w) \cdots \text{O}(3)$ angle is $169(16)^{\circ}$. The $\text{O}(7_w) \cdots \text{O}(6)$, $\text{O}(6) \cdots \text{H}(16)$ and $\text{O}(7_w) \cdots \text{H}(16)$ distances are $2.707(10)$, $1.95(10)$ and 0.77

Table 3. Interatomic distances (Å) and angles ($^{\circ}$).

| | | | |
|-------------------|-----------|-------------------|-----------|
| Fe(1)–O(1) | 1.938(7) | Fe(1)–O(1)–C(1) | 131.2(6) |
| Fe(1)–O(2) | 2.079(7) | Fe(1)–O(2)–C(9) | 119.5(6) |
| Fe(1)–O(4) | 1.917(8) | Fe(1)–O(4)–C(10) | 134.8(6) |
| Fe(1)–O(5) | 2.071(7) | Fe(1)–O(5)–C(18) | 120.5(6) |
| Fe(1)–N(1) | 2.086(8) | Fe(1)–N(1)–C(7) | 126.6(7) |
| Fe(1)–N(2) | 2.097(8) | Fe(1)–N(1)–C(8) | 115.1(6) |
| Fe(2)–O(7) | 2.113(7) | Fe(1)–N(2)–C(16) | 128.5(7) |
| Fe(2)–O(8) | 2.121(7) | Fe(1)–N(2)–C(17) | 114.7(6) |
| Fe(2)–O(9) | 2.124(7) | O(1)–Fe(1)–N(1) | 85.2(3) |
| O(1)–C(1) | 1.317(12) | O(1)–Fe(1)–N(2) | 107.4(3) |
| O(2)–C(9) | 1.282(13) | O(1)–Fe(1)–O(2) | 161.5(3) |
| O(3)–C(9) | 1.239(13) | O(1)–Fe(1)–O(4) | 92.9(3) |
| O(4)–C(10) | 1.300(13) | O(1)–Fe(1)–O(5) | 88.2(3) |
| O(5)–C(18) | 1.255(12) | O(2)–Fe(1)–N(1) | 76.3(3) |
| O(6)–C(18) | 1.243(12) | O(2)–Fe(1)–N(2) | 90.4(3) |
| N(1)–C(7) | 1.274(13) | O(2)–Fe(1)–O(4) | 93.5(3) |
| N(1)–C(8) | 1.472(14) | O(2)–Fe(1)–O(5) | 90.8(3) |
| N(2)–C(16) | 1.282(14) | O(4)–Fe(1)–N(1) | 104.2(3) |
| N(2)–C(17) | 1.481(14) | O(4)–Fe(1)–N(2) | 86.0(3) |
| C(1)–C(2) | 1.417(15) | O(4)–Fe(1)–O(5) | 162.9(3) |
| C(1)–C(6) | 1.407(14) | O(5)–Fe(1)–N(1) | 92.9(3) |
| C(2)–C(3) | 1.369(18) | O(5)–Fe(1)–N(2) | 77.3(3) |
| C(3)–C(4) | 1.365(19) | N(1)–Fe(1)–N(2) | 163.5(3) |
| C(4)–C(5) | 1.373(17) | O(7)–Fe(2)–O(8) | 93.7(3) |
| C(5)–C(6) | 1.411(15) | O(7)–Fe(2)–O(9) | 88.3(3) |
| C(6)–C(7) | 1.432(15) | O(8)–Fe(2)–O(9) | 88.2(3) |
| C(8)–C(9) | 1.506(15) | O(1)–C(1)–C(2) | 120.6(9) |
| C(10)–C(11) | 1.413(16) | O(1)–C(1)–C(6) | 122.3(9) |
| C(10)–C(15) | 1.428(14) | C(1)–C(2)–C(3) | 121.7(11) |
| C(11)–C(12) | 1.373(19) | C(2)–C(1)–C(6) | 117.1(9) |
| C(12)–C(13) | 1.378(21) | C(2)–C(3)–C(4) | 120.7(12) |
| C(13)–C(14) | 1.370(19) | C(3)–C(4)–C(5) | 119.9(12) |
| C(14)–C(15) | 1.398(16) | C(4)–C(5)–C(6) | 120.8(10) |
| C(15)–C(16) | 1.437(15) | C(5)–C(6)–C(1) | 119.7(10) |
| C(17)–C(18) | 1.513(15) | C(5)–C(6)–C(7) | 117.5(9) |
| C(6)–C(7)–N(1) | 125.1(9) | C(13)–C(14)–C(15) | 121.4(12) |
| C(7)–N(1)–C(8) | 118.3(8) | C(14)–C(15)–C(10) | 120.1(10) |
| C(7)–C(6)–C(1) | 122.6(9) | C(14)–C(15)–C(16) | 117.6(10) |
| N(1)–C(8)–C(9) | 108.7(8) | C(16)–C(15)–C(10) | 122.2(9) |
| O(2)–C(9)–O(3) | 125.2(10) | C(16)–N(2)–C(17) | 116.7(9) |
| O(2)–C(9)–C(8) | 116.6(9) | N(2)–C(16)–C(15) | 124.8(10) |
| O(3)–C(9)–C(8) | 118.2(9) | N(2)–C(17)–C(18) | 109.6(9) |
| O(4)–C(10)–C(11) | 120.8(10) | O(5)–C(18)–O(6) | 125.4(9) |
| O(4)–C(10)–C(15) | 123.0(9) | O(5)–C(18)–C(17) | 117.2(9) |
| C(10)–C(11)–C(12) | 122.1(12) | O(6)–C(18)–C(17) | 117.3(9) |
| C(11)–C(12)–C(13) | 120.7(12) | | |
| C(11)–C(10)–C(15) | 116.2(10) | | |
| C(12)–C(13)–C(14) | 119.3(13) | | |

Fig. 1. A perspective view of the complex showing the atomic numbering scheme.

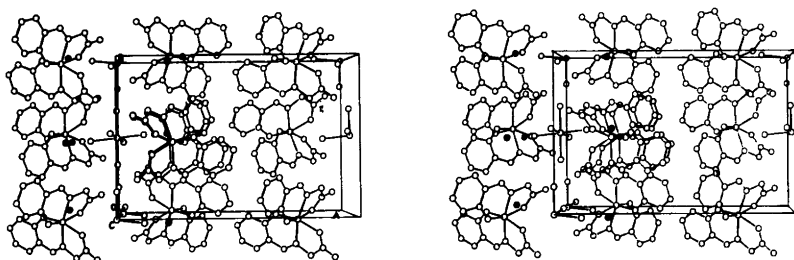
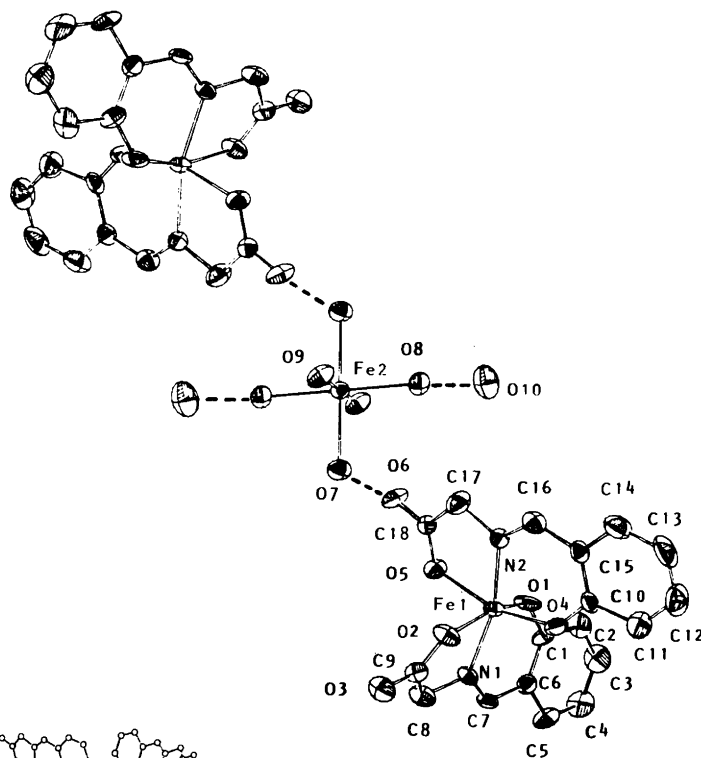


Fig. 2. Stereoview of the unit cell packing.

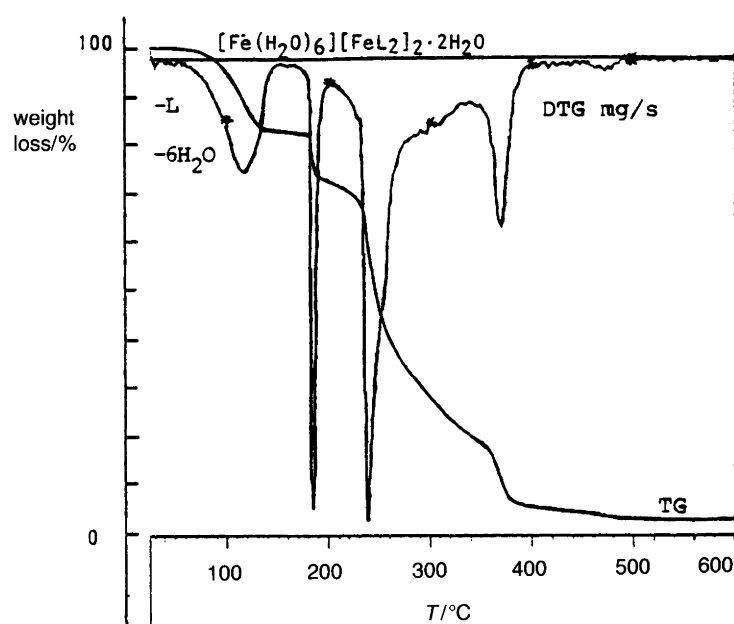


Fig. 3. Thermogravimetric curves for $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6][\text{Fe}^{\text{III}}(\text{C}_9\text{H}_7\text{NO}_3)_2]_2 \cdot 2\text{H}_2\text{O}$.

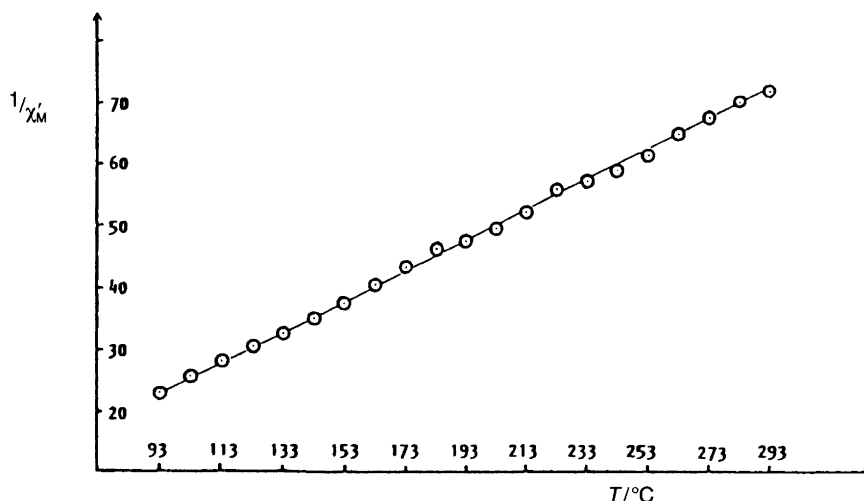


Fig. 4. $1/\chi_M'$ against temperature for $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6][\text{Fe}^{\text{III}}(\text{C}_9\text{H}_7\text{NO}_3)_2] \cdot 2\text{H}_2\text{O}$.

(10) Å, respectively. The angle O(7_w)–H(16)···O(6) is 166 (10)°. A third interaction, 2.776(11) Å in magnitude, exists between O(8_w) and the crystal water oxygen, O(10). The O(10)···H(18) and O(8_w)–H(18) distances are 1.90(26) and 0.98(26) Å, respectively, and the angle O(8_w)–H(18)···O(10) is 147(23)°. Thus, the complex cation and water of crystallization are joined with the complex anions into a hydrogen-bonded network.

The TG curve (Fig. 3) shows that the compound is thermally stable in the 20–70°C region. The overall decomposition occurs in four steps, centred in the DTG curve at 120, 185, 240 and 370°C. The first stage, corresponding to a weight loss of 17%, occurs in the temperature range 70–130°C. The weight loss is consistent with the loss of one Schiff base ligand (calc. value 17.4%). A first plateau is observed on the TG curve between 130 and 180°C, indicating the formation of a stable intermediate product. The subsequent further loss (11%) at 185°C is tentatively attributed to the elimination of six molecules of water of crystallization (calc. 10.6%). The major part of the decomposition takes place between 230 and 380°C, where the compound loses 66% of its mass in two stages. The residual weight at 500°C is only 3%, indicative of volatilization during the thermal decomposition.

The magnetic moment, μ_{eff} (293 K) = 5.64 B.M., agrees with the value of 5.58 B.M. required for the combination of one high-spin Fe(II) and two high-spin Fe(III) ions. The molar paramagnetic susceptibility, corrected for diamagne-

tism using Pascal's constants, obeys the Curie-Weiss law over the range 93–293 K, as shown in Fig. 4.

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