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Preparation and Properties of Iron(III)–Amino Acid Complexes. 2. The Crystal and Molecular Structure of Monoclinic Tri-μ_3-oxo-triaquohexakis(glycine)triiron(III) Perchlorate

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Abstract: The crystal and molecular structure of tri-μ_3-oxo-triaquohexakis(glycine)triiron(III) perchlorate, $[Fe_3O(C_2H_5O_2N)_6(H_2O)_3](ClO_4)_7$, has been determined using single crystal x-ray techniques and refined by full matrix least squares to a conventional R factor of 0.074. The dark red-brown prismatic crystals of monoclinic space group $P2_1$ have unit cell dimensions $a = 19.26$ (2), $b = 15.61$ (1), $c = 16.69$ (2) Å, and $\beta = 100.71$ (6)°. The structure is similar to that of basic iron acetate, $[Fe_3O(CH_3COO)_6 \cdot 3H_2O]ClO_4$, with a trimeric unit having an oxygen atom at the center. The remaining coordination sites of each iron are occupied by four carboxylate oxygens from bridging glycines and a single water molecule.

The study of non-heme iron proteins has been of great interest in recent years. In an effort to study model systems for certain of these iron-containing proteins, we have prepared several iron amino acid complexes. The absorption spectra and Mössbauer and room temperature magnetics of these complexes have shown that these properties resemble those of ferritin.[2] Preliminary x-ray studies have indicated the presence of Fe_3O^{7+} clusters. The results of a detailed magnetic study done at a wide range of temperature are in agreement with the proposed trimeric iron structure.[3] To further elucidate the

Table I. Atomic Coordinates[a]

	x/a	y/b	z/c		x/a	y/b	z/c
Fe1	0.5647 (2)	0.3064	0.3528 (2)	ON1	0.8281 (27)	0.9041 (39)	0.0726 (35)
Fe2	0.5675 (3)	0.1533 (3)	0.2175 (3)	ON2	0.7563 (37)	0.8800 (37)	0.9509 (45)
Fe3	0.4175 (2)	0.2074 (3)	0.2707 (2)	ON3	0.7432 (28)	0.8528 (32)	0.0837 (25)
Fe4	0.0723 (2)	0.6390 (3)	0.3397 (2)	ON4	0.7386 (37)	0.9726 (45)	0.0024 (54)
Fe5	−0.0844 (2)	0.7107 (3)	0.2490 (2)	OX1	0.5157 (9)	0.2239 (12)	0.2793 (10)
Fe6	0.0597 (2)	0.7874 (3)	0.1967 (2)	OX2	0.0165 (8)	0.7115 (12)	0.2633 (9)
ClA	0.8661 (7)	0.2552 (9)	0.0900 (7)	O1	0.6267 (10)	0.3533 (12)	0.2758 (11)
ClB	0.8402 (6)	0.2281 (7)	0.3634 (7)	O2	0.6326 (12)	0.2484 (15)	0.1882 (13)
ClC	0.3443 (5)	0.7413 (6)	0.3171 (7)	O3	0.6401 (11)	0.2192 (14)	0.4085 (12)
ClD	0.2301 (4)	0.3831 (5)	0.3635 (5)	O4	0.6364 (12)	0.1175 (15)	0.3132 (14)
ClE	0.1112 (5)	0.1453 (6)	0.2844 (5)	O5	0.5104 (12)	0.0449 (15)	0.2245 (14)
ClF	0.4937 (8)	0.4378 (10)	0.0474 (7)	O6	0.4170 (12)	0.0791 (15)	0.2862 (14)
ClG	0.2641 (11)	0.0195 (12)	0.1087 (9)	O7	0.5001 (12)	0.1777 (14)	0.1113 (13)
ClH	0.4799 (5)	0.5315 (6)	0.4903 (3)	O8	0.3963 (11)	0.1943 (15)	0.1469 (12)
ClI	0.7362 (4)	0.8642 (5)	0.3639 (5)	O9	0.3953 (11)	0.3334 (13)	0.2572 (12)
ClJ	0.7537 (4)	0.5443 (5)	0.3970 (5)	O10	0.4948 (10)	0.4020 (12)	0.3048 (10)
ClK	0.0074 (7)	0.5104 (8)	0.0264 (9)	O11	0.4126 (9)	0.2144 (12)	0.3913 (10)
ClL	0.0005 (4)	0.9422 (5)	0.4756 (4)	O12	0.5077 (9)	0.2926 (13)	0.4410 (10)
ClM	0.5841 (4)	0.6790 (6)	0.2152 (6)	O13	0.6177 (11)	0.3953 (14)	0.4351 (12)
ClN	0.7625 (10)	0.9117 (12)	0.0314 (12)	O14	0.6220 (12)	0.0808 (15)	0.1486 (13)
OA1	0.8373 (24)	0.3236 (34)	0.1032 (33)	O15	0.3055 (10)	0.1931 (14)	0.2586 (11)
OA2	0.8886 (17)	0.2579 (26)	0.0171 (16)	O16	0.0226 (9)	0.6649 (11)	0.4304 (10)
OA3	0.9161 (21)	0.2431 (21)	0.1597 (24)	O17	−0.0836 (10)	0.7120 (13)	0.3693 (10)
OA4	0.8182 (40)	0.1902 (44)	0.0921 (25)	O18	0.0116 (10)	0.5338 (12)	0.3060 (11)
OB1	0.8849 (60)	0.1704 (46)	0.3432 (40)	O19	−0.0910 (9)	0.5844 (12)	0.2465 (10)
OB2	0.8896 (31)	0.2647 (45)	0.3991 (39)	O20	−0.0979 (10)	0.8411 (12)	0.2491 (11)
OB3	0.8120 (24)	0.2193 (51)	0.4309 (24)	O21	−0.0048 (10)	0.8905 (13)	0.2065 (11)
OB4	0.7973 (22)	0.2649 (29)	0.3071 (23)	O22	−0.1022 (9)	0.7092 (13)	0.1268 (11)
OC1	0.4127 (14)	0.7410 (17)	0.2943 (22)	O23	−0.0064 (11)	0.7538 (13)	0.0899 (11)
OC2	0.3453 (18)	0.7762 (22)	0.3983 (20)	O24	0.1292 (10)	0.7002 (14)	0.1757 (11)
OC3	0.2947 (20)	0.7934 (28)	0.2726 (27)	O25	0.1369 (9)	0.5935 (11)	0.2670 (10)
OC4	0.3148 (24)	0.6569 (24)	0.3122 (22)	O26	0.1243 (10)	0.8366 (12)	0.2952 (11)
OD1	0.1600 (12)	0.3903 (13)	0.3791 (12)	O27	0.1440 (9)	0.7286 (11)	0.3840 (10)
OD2	0.2741 (14)	0.4600 (17)	0.3807 (17)	O28	0.1302 (8)	0.5602 (11)	0.4329 (9)
OD3	0.2658 (16)	0.3180 (17)	0.4111 (16)	O29	−0.1949 (10)	0.7093 (14)	0.2336 (11)
OD4	0.2330 (14)	0.3648 (22)	0.2812 (15)	O30	0.1089 (10)	0.8698 (13)	0.1256 (12)
OE1	0.0559 (15)	0.2077 (21)	0.2993 (19)	C1	0.6465 (15)	0.3233 (19)	0.2154 (17)
OE2	0.1685 (13)	0.1495 (22)	0.3488 (14)	C2	0.6895 (17)	0.3811 (22)	0.1709 (19)
OE3	0.0867 (27)	0.0591 (18)	0.2877 (31)	C3	0.6523 (14)	0.1443 (20)	0.3825 (16)
OE4	0.1310 (17)	0.1731 (19)	0.2117 (14)	C4	0.6983 (18)	0.0869 (23)	0.4464 (21)
OF1	0.4767 (40)	0.3550 (43)	0.0000 (35)	C5	0.4636 (17)	0.0246 (21)	0.2606 (19)
OF2	0.5091 (24)	0.4211 (38)	0.1208 (22)	C6	0.4469 (16)	−0.0661 (24)	0.2758 (22)
OF3	0.5881 (23)	0.4932 (35)	0.0202 (36)	C7	0.4394 (16)	0.1859 (19)	0.1007 (17)
OF4	0.4687 (38)	0.5039 (39)	0.0200 (44)	C8	0.4008 (21)	0.1837 (26)	0.0070 (22)
OG1	0.2543 (34)	−0.0154 (25)	0.1988 (35)	C9	0.4316 (17)	0.4011 (21)	0.2701 (19)
OG2	0.3428 (20)	0.0002 (29)	0.0783 (24)	C10	0.3963 (17)	0.4782 (22)	0.2485 (19)
OG3	0.2496 (17)	0.1090 (19)	0.1122 (20)	C11	0.4502 (15)	0.2529 (18)	0.4459 (16)
OG4	0.2090 (34)	−0.0287 (33)	0.0459 (24)	C12	0.4319 (17)	0.2653 (21)	0.5271 (18)
OH1	0.4241 (13)	0.4835 (18)	0.4520 (17)	C13	−0.0385 (15)	0.6900 (18)	0.4301 (16)
OH2	0.5173 (15)	0.5672 (20)	0.4329 (20)	C14	−0.0597 (15)	0.6978 (19)	0.5175 (17)
OH3	0.5346 (25)	0.4725 (25)	0.5368 (24)	C15	−0.0525 (15)	0.5298 (19)	0.2741 (17)
OH4	0.4600 (13)	0.5869 (22)	0.5472 (18)	C16	−0.0864 (16)	0.4333 (19)	0.2637 (17)
OI1	0.7405 (13)	0.8683 (15)	0.2766 (15)	C17	−0.0598 (16)	0.9003 (19)	0.2302 (17)
OI2	0.7513 (13)	0.7779 (17)	0.3889 (16)	C18	−0.0805 (17)	0.9922 (21)	0.2285 (19)
OI3	0.6707 (13)	0.8904 (17)	0.3784 (18)	C19	−0.0676 (16)	0.7275 (20)	0.0738 (18)
OI4	0.8005 (12)	0.9066 (15)	0.4122 (14)	C20	−0.0993 (17)	0.7232 (22)	−0.0105 (19)
OJ1	0.7766 (22)	0.5623 (22)	0.3205 (19)	C21	0.1525 (14)	0.6277 (19)	0.2043 (16)
OJ2	0.6746 (18)	0.5527 (23)	0.3872 (26)	C22	0.1995 (16)	0.5791 (20)	0.1630 (18)
OJ3	0.7895 (18)	0.5903 (18)	0.4581 (16)	C23	0.1499 (13)	0.8057 (17)	0.3593 (15)
OJ4	0.7639 (16)	0.4565 (15)	0.4075 (20)	C24	0.1936 (15)	0.8686 (19)	0.4297 (17)
OK1	0.0428 (29)	0.5236 (30)	0.0967 (28)	N1	0.6817 (17)	0.4680 (22)	0.1905 (19)
OK2	−0.0607 (25)	0.5355 (34)	0.0739 (26)	N2	0.7170 (15)	0.1282 (21)	0.5203 (18)
OK3	−0.0214 (44)	0.5451 (31)	−0.0521 (28)	N3	0.4733 (20)	−0.1254 (26)	0.2144 (22)
OK4	0.0031 (30)	0.4226 (20)	0.0064 (23)	N4	0.3241 (18)	0.1934 (24)	−0.0080 (20)
OL1	0.0154 (14)	0.8864 (23)	0.4145 (15)	N5	0.4409 (16)	0.5517 (20)	0.2521 (18)
OL2	−0.0304 (12)	0.8928 (15)	0.5318 (13)	N6	0.3654 (12)	0.2104 (18)	0.5309 (14)
OL3	0.0620 (15)	0.9796 (17)	0.5186 (20)	N7	0.8761 (11)	0.7466 (15)	0.5098 (12)
OL4	−0.0457 (14)	0.0096 (16)	0.4431 (14)	N8	−0.0220 (13)	0.3705 (16)	0.2906 (14)
OM1	0.6410 (14)	0.6974 (24)	0.1819 (15)	N9	−0.1335 (18)	−0.0008 (23)	0.2738 (20)
OM2	0.5867 (12)	0.7220 (20)	0.2890 (15)	N10	−0.0496 (14)	0.7253 (18)	−0.0660 (16)
OM3	0.5257 (13)	0.7118 (19)	0.1586 (14)	N11	0.2059 (14)	0.6113 (18)	0.0839 (16)
OM4	0.5816 (13)	0.5869 (14)	0.2136 (21)	N12	0.1901 (16)	0.9510 (21)	0.4014 (18)

[a] Estimated standard deviations in parentheses.

Table II. Atomic Temperature Factors[a,b]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Fe1	15 (1)	34 (2)	27 (1)	0 (1)	5 (1)	1 (1)
Fe2	35 (1)	26 (2)	47 (2)	6 (1)	20 (1)	2 (2)
Fe3	18 (1)	27 (1)	30 (1)	1 (1)	7 (1)	−2 (1)
Fe4	15 (1)	18 (1)	21 (1)	0 (1)	3 (1)	1 (1)
Fe5	19 (1)	23 (1)	21 (1)	4 (1)	3 (1)	0 (1)
Fe6	17 (1)	23 (2)	22 (1)	−2 (1)	1 (1)	4 (1)
CLA	48 (5)	95 (9)	48 (5)	−29 (5)	23 (4)	−34 (6)
CLB	30 (3)	52 (6)	59 (5)	−1 (3)	5 (3)	14 (4)
CLC	39 (4)	35 (4)	70 (6)	−7 (3)	14 (3)	3 (1)
CLD	22 (2)	34 (4)	37 (3)	4 (2)	4 (2)	1 (3)
CLE	40 (3)	47 (4)	32 (4)	−5 (3)	4 (2)	8 (3)
CLF	71 (6)	92 (9)	40 (6)	40 (6)	5 (4)	4 (5)
CLG	112 (10)	104 (12)	72 (8)	−20 (9)	−3 (7)	10 (8)
CLH	30 (3)	38 (4)	58 (5)	−5 (3)	8 (3)	−12 (4)
CLI	27 (3)	27 (3)	40 (4)	2 (2)	10 (2)	4 (3)
CLJ	23 (2)	35 (4)	34 (3)	−2 (2)	7 (2)	2 (2)
CLK	67 (6)	59 (7)	77 (8)	4 (4)	−19 (5)	−24 (5)
CLL	23 (2)	32 (4)	31 (3)	−2 (2)	8 (2)	−4 (3)
CLM	24 (3)	52 (5)	53 (4)	2 (3)	7 (3)	−12 (4)
CLN	69 (8)	73 (9)	94 (10)	−3 (1)	19 (7)	4 (1)
OA1	76 (23)	124 (36)	173 (40)	22 (20)	0 (2)	−30 (30)
OA2	75 (15)	153 (32)	35 (12)	3 (10)	12 (11)	−36 (16)
OA3	76 (17)	83 (21)	91 (22)	−16 (15)	42 (17)	−31 (18)
OA4	260 (53)	250 (65)	67 (23)	−78 (51)	19 (12)	−77 (23)
OB1	489 (99)	205 (58)	178 (51)	196 (66)	29 (15)	−108 (44)
OB2	85 (28)	222 (58)	215 (50)	3 (3)	−26 (13)	159 (48)
OB3	87 (22)	537 (99)	86 (23)	−117 (39)	−8 (8)	154 (42)
OB4	80 (19)	137 (33)	86 (21)	49 (21)	−6 (6)	27 (22)
OC1	38 (10)	44 (14)	151 (24)	12 (10)	42 (13)	−12 (15)
OC2	67 (15)	81 (21)	84 (18)	−34 (15)	23 (13)	−34 (17)
OC3	60 (16)	98 (28)	171 (32)	15 (9)	5 (4)	36 (16)
OC4	146 (25)	75 (23)	92 (22)	−55 (20)	57 (19)	−47 (19)
OD1	45 (10)	33 (11)	36 (10)	−1 (4)	22 (8)	4 (2)
OD2	47 (11)	46 (14)	88 (17)	−15 (10)	25 (11)	−17 (13)
OD3	85 (16)	50 (15)	49 (13)	19 (13)	1 (1)	14 (12)
OD4	50 (11)	115 (23)	46 (13)	−1 (13)	23 (10)	−5 (5)
OE1	44 (11)	85 (19)	110 (20)	42 (14)	32 (12)	39 (17)
OE2	33 (9)	123 (22)	42 (12)	−3 (1)	16 (8)	20 (15)
OE3	132 (31)	12 (13)	216 (40)	−10 (10)	5 (2)	27 (18)
OE4	91 (16)	88 (20)	29 (10)	11 (10)	28 (10)	21 (12)
OF1	232 (56)	187 (59)	122 (36)	−37 (15)	8 (3)	−57 (39)
OF2	102 (26)	278 (61)	47 (18)	−57 (34)	27 (17)	4 (2)
OF3	63 (20)	455 (107)	202 (47)	149 (41)	−31 (24)	−128 (58)
OF4	180 (45)	114 (41)	278 (62)	−4 (3)	−86 (14)	9 (4)
OG1	208 (46)	61 (25)	190 (43)	−37 (28)	30 (30)	22 (20)
OG2	54 (16)	146 (35)	126 (27)	21 (19)	16 (16)	−44 (25)
OG3	61 (15)	46 (16)	97 (20)	−6 (12)	0 (1)	35 (14)
OG4	285 (47)	169 (42)	80 (23)	−74 (39)	74 (27)	−76 (26)
OH1	29 (8)	74 (17)	79 (16)	−22 (10)	22 (9)	−22 (14)
OH2	47 (12)	75 (19)	101 (20)	6 (12)	32 (13)	30 (16)
OH3	134 (27)	76 (24)	109 (26)	−5 (20)	44 (21)	−21 (21)
OH4	30 (9)	128 (25)	83 (18)	−18 (13)	26 (11)	70 (18)
OI1	42 (10)	39 (12)	55 (13)	0 (9)	8 (8)	6 (10)
OI2	33 (9)	56 (15)	84 (16)	3 (6)	26 (10)	15 (13)
OI3	33 (10)	55 (15)	101 (19)	3 (9)	17 (11)	−28 (14)
OI4	32 (9)	46 (13)	51 (12)	−18 (9)	5 (8)	−8 (9)
OJ1	131 (25)	74 (20)	63 (18)	0 (18)	39 (17)	11 (10)
OJ2	53 (15)	79 (22)	180 (32)	19 (15)	39 (18)	−12 (2)
OJ3	83 (16)	57 (16)	50 (14)	−22 (13)	8 (8)	−21 (12)
OJ4	59 (13)	13 (11)	128 (23)	9 (8)	−2 (10)	17 (13)
OK1	159 (32)	119 (36)	131 (30)	−2 (20)	−94 (27)	−66 (27)
OK2	52 (21)	118 (37)	168 (27)	29 (23)	99 (43)	100 (56)
OK3	289 (61)	107 (35)	89 (28)	93 (39)	22 (32)	13 (24)
OK4	204 (35)	37 (17)	79 (20)	7 (21)	9 (20)	−19 (15)
OL1	45 (11)	124 (26)	41 (12)	−1 (14)	12 (9)	−24 (15)
OL2	41 (9)	51 (14)	32 (10)	−11 (9)	14 (8)	6 (6)
OL3	39 (11)	48 (15)	115 (22)	0 (10)	12 (12)	30 (15)
OL4	47 (11)	40 (12)	47 (12)	−6 (10)	−14 (9)	−1 (1)
OM1	38 (11)	153 (26)	50 (12)	18 (15)	22 (9)	−7 (2)
OM2	32 (9)	107 (21)	46 (12)	22 (12)	10 (8)	1 (1)
OM3	35 (9)	85 (17)	48 (11)	15 (9)	−11 (8)	−40 (12)

Table II (*Continued*)

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
OM4	23 (9)	25 (11)	169 (26)	−3 (1)	12 (12)	−7 (1)
ON1	82 (23)	221 (50)	176 (43)	−56 (3)	−7 (2)	35 (17)
ON2	173 (40)	131 (42)	193 (50)	−36 (14)	100 (36)	32 (19)
ON3	166 (34)	135 (35)	92 (24)	3 (2)	50 (23)	25 (15)
ON4	182 (39)	198 (52)	384 (74)	50 (14)	134 (40)	209 (61)

	β		β		β
OX1	2.3 (4)	O22	3.2 (4)	C15	2.7 (6)
OX2	1.9 (3)	O23	3.3 (4)	C16	2.8 (6)
O1	3.4 (4)	O24	3.7 (4)	C17	3.1 (6)
O2	4.4 (5)	O25	2.8 (3)	C18	3.7 (7)
O3	4.3 (3)	O26	2.8 (4)	C19	2.7 (6)
O4	4.8 (5)	O27	2.7 (4)	C20	3.4 (7)
O5	5.1 (5)	O28	1.8 (3)	C21	2.4 (6)
O6	4.0 (5)	O29	3.3 (4)	C22	3.5 (6)
O7	4.5 (5)	O30	3.7 (4)	C23	2.1 (5)
O8	4.2 (4)	C1	3.0 (6)	C24	3.4 (6)
O9	4.0 (4)	C2	4.2 (7)	N1	7.2 (7)
O10	3.0 (4)	C3	2.7 (5)	N2	5.4 (7)
O11	2.9 (4)	C4	4.8 (8)	N3	8.6 (9)
O12	2.9 (4)	C5	4.3 (6)	N4	8.0 (8)
O13	3.8 (4)	C6	5.2 (8)	N5	5.6 (7)
O14	4.3 (5)	C7	3.2 (6)	N6	4.0 (5)
O15	4.1 (4)	C8	5.4 (9)	N7	2.7 (4)
O16	2.2 (4)	C9	3.5 (7)	N8	4.0 (5)
O17	3.3 (4)	C10	4.8 (7)	N9	6.6 (8)
O18	2.6 (4)	C11	2.5 (5)	N10	4.8 (6)
O19	2.4 (4)	C12	3.1 (7)	N11	5.4 (6)
O20	3.6 (4)	C13	2.6 (6)	N12	6.4 (7)
O21	3.5 (4)	C14	3.5 (6)		

[a] For six irons and perchlorate clusters ansotropic temperature factors are applied. For all the other atoms isotropic temperature factors are applied. [b] Factors are in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{13}hl + 2\beta_{23}kl + 2\beta_{12}hk)]$.

structure of these materials we have carried out the first complete structural analysis of an iron(III) amino acid complex, $[Fe(gly)_2H_2O]_3O(ClO_4)_7$.

Experimental Section

Preparation of the Complex: $[Fe_3O(C_2H_5O_2N)_6(H_2O)_3](ClO_4)_7$. Preparation of single crystals of this complex was carried out using the procedure previously described.[2,4]

Crystal data and data collection: $[Fe_3O(C_2H_5O_2N)_6(H_2O)_3](ClO_4)_7$, mol wt = 1383.7, monoclinic, a = 19.26 (2), b = 15.61 (1), c = 16.69 (2) Å, β = 100.71 (6)°, v = 4930.3 Å^3, d_m = 1.956 g cm^{-3} (by flotation), z = 4, d_c = 1.865 g cm^{-3}; space group $P2_1$ from systematic absences: $0k0$, $k = 2n$; Mo Kα radiation, λ = 0.71069 Å, μ(Mo Kα) = 13.93 cm^{-1}.

Preliminary unit cell and space group data were obtained from Weissenberg photographs. The data were collected on a Picker four-circle automated diffractometer. The crystal used was a rectangular plate of dimensions 0.2 × 0.4 × 0.08 mm. Mo Kα radiation with a zirconium filter was used for data collection. Unit-cell dimensions were determined by least-squares fit of the angular positions of 12 independent reflections. All independent reflections to sin θ_{max} = 0.715 were sampled by use of the θ-2θ scan procedure, the 2θ being over a range of 1.5° at 1°/min. Three standard reflections were measured after every 50 reflections. The net counts of these standards were constant to within 5% over the whole data measurement period. The intensities of 11 736 lattice points were measured, of which 8437 reflections had $|F_o|/\sigma|F_o| > 3.0$ and were considered observed. Corrections for Lorentz and polarization effects were applied after subtraction of background.

Determination of the Structure. The structure was determined by heavy atom methods and refinement was carried out using full-matrix least squares.[5] A structure factor calculation based on positions of the six iron atoms located from a Patterson map gave an initial R factor of 0.45. Anomalous dispersion corrections were made for iron. Several successive least-squares and difference Fourier cycles allowed placement of all of the other non-hydrogen atoms and the agreement factor $[R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|]$ was 0.089. Examination of the difference Fourier indicated the presence of anisotropic thermal motion for the perchlorate atoms. The temperature factors for the six iron and the perchlorate atoms were converted to their anisotropic equivalents and several cycles of refinement led to a final R of 0.074. All changes in positional and thermal parameters were less than 0.2 times their estimated standard deviations for the final cycle of refinement. A final difference Fourier map showed no peaks above the expected background value. No attempt was made to locate the hydrogen atoms. Unit weights were used throughout.

Final positional parameters are presented in Table I. The anisotropic temperature factors for the six irons and the perchlorates and the isotropic temperature factors for all the other atoms are given in Table II. Bond distances are given in Table III, selected bond angles in Table IV, and calculations of planes are summarized in Table V. Figure 1 shows a single $[Fe_3O(gly)_6(H_2O)_3]$ unit. The observed and calculated structure factors are available in microfiche.

Discussion

Each trimeric iron unit has an oxygen at the center. The iron(III) atoms are located at the apices of an equilateral triangle with average side 3.30 (1) Å. The average distance between the central oxide atom and an iron is 1.90 (2) Å. The Fe_3O groups are planar within experimental error (Table V), the central oxygen being 0.01–0.04 Å from the plane of the three irons and the angles at this oxygen averaging 120 (1)°.

Each iron is involved with a water molecule trans to the central oxide. The average Fe–O(water) distance is 2.09 (2) Å. These oxygens are also on the plane of the Fe_3O cluster (maximum deviation 0.03 Å).

Coordination of each iron is close to octahedral, the remaining coordination sites being occupied by four carboxylate

Table III. Interatomic Distances (Å)[a]

Fe1-OX1	1.90 (2)	O4-C3	1.22 (3)
Fe2-OX1	1.91 (2)	O5-C5	1.21 (3)
Fe3-OX1	1.89 (2)	O6-C5	1.35 (3)
Fe4-OX2	1.88 (2)	O7-C7	1.18 (3)
Fe5-OX2	1.91 (2)	O8-C7	1.23 (3)
Fe6-OX2	1.91 (2)	O9-C9	1.26 (3)
Fe1-Fe2	3.29 (1)	O10-C9	1.24 (3)
Fe1-Fe3	3.30 (1)	O11-C11	1.21 (3)
Fe2-Fe3	3.29 (1)	O12-C11	1.28 (3)
Fe4-Fe5	3.31 (1)	O16-C13	1.23 (3)
Fe4-Fe6	3.30 (1)	O17-C13	1.25 (3)
Fe5-Fe6	3.29 (1)	O18-C15	1.25 (3)
Fe1-O1	2.04 (2)	O19-C15	1.18 (3)
Fe1-O3	2.08 (2)	O20-C17	1.25 (3)
Fe2-O2	2.05 (2)	O21-C17	1.21 (3)
Fe2-O4	1.96 (2)	O22-C19	1.23 (3)
Fe2-O5	2.03 (2)	O23-C19	1.23 (3)
Fe2-O7	2.03 (2)	O24-C21	1.27 (3)
Fe3-O6	2.02 (2)	O25-C21	1.26 (3)
Fe3-O8	2.04 (2)	O26-C23	1.19 (3)
Fe3-O9	2.02 (2)	O27-C23	1.28 (3)
Fe3-O11	2.04 (2)	C1-C2	1.51 (4)
Fe1-O10	2.06 (2)	C3-C4	1.54 (4)
Fe1-O12	2.00 (2)	C5-C6	1.48 (4)
Fe4-O16	1.98 (2)	C7-C8	1.60 (4)
Fe4-O18	2.03 (2)	C9-C10	1.40 (4)
Fe5-O17	2.00 (2)	C11-C12	1.48 (4)
Fe5-O19	1.98 (2)	C13-C14	1.58 (4)
Fe5-O20	2.05 (2)	C15-C16	1.62 (4)
Fe5-O22	2.00 (2)	C17-C18	1.49 (4)
Fe6-O21	2.06 (2)	C19-C20	1.43 (4)
Fe6-O23	2.05 (2)	C21-C22	1.45 (4)
Fe6-O24	1.99 (2)	C23-C24	1.62 (4)
Fe6-O26	2.03 (2)	C2-N1	1.41 (4)
Fe4-O25	2.01 (2)	C4-N2	1.38 (4)
Fe4-O27	2.00 (2)	C6-N3	1.53 (4)
Fe1-O13	2.08 (2)	C8-N4	1.46 (4)
Fe2-O14	2.03 (2)	C10-N5	1.43 (4)
Fe3-O15	2.13 (2)	C12-N6	1.55 (4)
Fe4-O28	2.13 (2)	C14-N7	1.44 (4)
Fe5-O29	2.09 (2)	C16-N8	1.56 (4)
Fe6-O30	2.09 (2)	C18-N9	1.46 (4)
O1-C1	1.23 (3)	C20-N10	1.44 (4)
O2-C1	1.26 (3)	C22-N11	1.44 (4)
O3-C3	1.28 (3)	C24-N12	1.38 (4)

[a] Estimated standard deviations in parentheses in units of the last significant figures of the parameter itself.

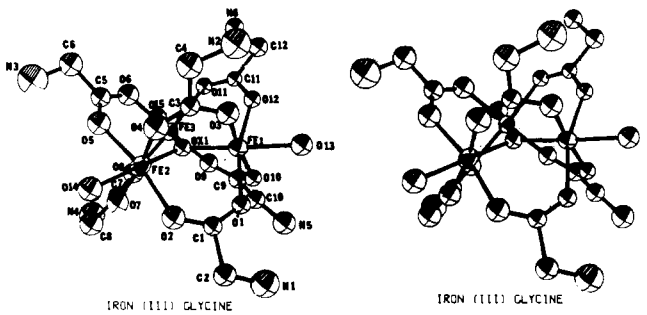

Figure 1. A view of a single $[Fe_3O(gly)_6(H_2O)_3]$ unit.

oxygens from bridging glycines. Angles at each iron show the glycine oxygens displaced from the ideal octahedral position toward the water oxygen. Each pair of iron(III) atoms is bridged by two glycine groups, one above and one below the Fe_3O plane. The average Fe-O(carboxylate oxygen) distance is 2.02 (2) Å. Each glycine ligand is close to being coplanar with the two irons it bridges (maximum deviation 0.50 Å). In

Table IV. Representative Interatomic Angles (degrees)

Fe1-OX1-Fe2	119 (1)	Fe5-O22-C19	134 (2)
Fe2-OX1-Fe3	119 (1)	Fe6-O23-C19	133 (2)
Fe3-OX1-Fe1	120 (1)	Fe6-O24-C21	135 (2)
Fe4-OX2-Fe5	120 (1)	Fe4-O25-C21	128 (2)
Fe5-OX2-Fe6	119 (1)	Fe6-O26-C23	131 (2)
Fe6-OX2-Fe4	120 (1)	Fe4-O27-C23	129 (2)
OX1-Fe1-O13	179 (1)	O1-C1-O2	124 (3)
OX1-Fe2-O14	178 (1)	O3-C3-O4	127 (3)
OX1-Fe3-O15	178 (1)	O5-C5-O6	126 (3)
OX2-Fe4-O28	176 (1)	O7-C7-O8	133 (3)
OX2-Fe5-O29	179 (1)	O9-C9-O10	126 (3)
OX2-Fe6-O30	178 (1)	O11-C11-O12	126 (3)
O13-Fe1-O1	85 (1)	O16-C13-O17	127 (3)
O13-Fe1-O3	85 (1)	O18-C15-O19	129 (3)
O13-Fe1-O10	88 (1)	O20-C17-O21	129 (2)
O13-Fe1-O12	82 (1)	O22-C19-O23	126 (3)
O14-Fe2-O2	83 (1)	O24-C21-O25	125 (3)
O14-Fe2-O4	87 (1)	O26-C23-O27	128 (3)
O14-Fe2-O5	85 (1)	O1-C1-C2	117 (3)
O14-Fe2-O7	85 (1)	O2-C1-C2	118 (3)
O15-Fe3-O6	83 (1)	O3-C3-C4	115 (3)
O15-Fe3-O8	84 (1)	O4-C3-C4	118 (3)
O15-Fe3-O9	84 (1)	O5-C5-C6	122 (3)
O15-Fe3-O11	83 (1)	O6-C5-C6	111 (3)
O28-Fe4-O16	80 (1)	O7-C7-C8	115 (3)
O28-Fe4-O18	86 (1)	O8-C7-C8	112 (3)
O28-Fe4-O25	86 (1)	O9-C9-C10	117 (3)
O28-Fe4-O27	85 (1)	O10-C9-C10	119 (3)
O29-Fe5-O17	86 (1)	O11-C11-C12	123 (3)
O29-Fe5-O19	86 (1)	O12-C11-C12	110 (3)
O29-Fe5-O20	83 (1)	O16-C13-C14	115 (2)
O29-Fe5-O22	84 (1)	O17-C13-C14	117 (2)
O30-Fe6-O21	85 (1)	O18-C15-C16	116 (2)
O30-Fe6-O23	86 (1)	O19-C15-C16	115 (2)
O30-Fe6-O24	86 (1)	O20-C17-C18	123 (3)
O30-Fe6-O26	87 (1)	O21-C17-C18	111 (2)
Fe1-O1-C1	133 (2)	O22-C19-C20	120 (3)
Fe2-O2-C1	133 (2)	O23-C19-C20	117 (3)
Fe1-O3-C3	128 (2)	O24-C21-C22	119 (3)
Fe2-O4-C3	133 (2)	O25-C21-C22	116 (3)
Fe2-O5-C5	126 (2)	O26-C23-C24	118 (2)
Fe3-O6-C5	134 (2)	O27-C23-C24	113 (2)
Fe2-O7-C7	128 (2)	C1-C2-N1	112 (3)
Fe3-O8-C7	128 (2)	C3-C4-N2	112 (3)
Fe3-O9-C9	132 (2)	C5-C6-N3	111 (3)
Fe4-O10-C9	132 (3)	C7-C8-N4	115 (3)
Fe3-O11-C11	130 (2)	C9-C10-N5	114 (3)
Fe4-O12-C11	133 (2)	C11-C12-N6	108 (2)
Fe4-O16-C13	129 (2)	C13-C14-N7	113 (3)
Fe5-O17-C13	133 (2)	C15-C16-N8	105 (2)
Fe4-O18-C15	130 (2)	C17-C18-N9	108 (3)
Fe5-O19-C15	133 (2)	C19-C20-N10	114 (3)
Fe5-O20-C17	129 (2)	C21-C22-N11	114 (3)
Fe6-O21-C17	131 (2)	C23-C24-N12	109 (2)

[a] Estimated standard deviations in parentheses in units of the last significant figure of the parameter itself.

the structure of glycine alone, the nitrogen is 0.436 Å out of the plane of the carbons and oxygens.[6] Consistent with the zwitterionic state of each glycine, each nitrogen also shows several close (hydrogen bonding) contacts with perchlorate oxygens, 2.9 (4) Å. All Cl-O distances fall in the range 1.2-1.7 Å with the exception of ClF-OF3, which is 2.13 Å and which was not improved by any attempts to relocate OF3.

The presence of the Fe_3O^{7+} trimeric unit has been demonstrated crystallographically in three previous cases, $[Fe_3O(CH_3COO)_6(H_2O)_3]ClO_4$,[7] $[Fe_3O(piv)_6(MeOH)_3]Cl$,[8] and $K_5[Fe_3O(SO_4)_6(H_2O)_3]\cdot 6H_2O$.[9] As can be seen from Table VI the agreement between corresponding interatomic distances and bonds is close. The most significant difference is in the slight elongation observed in the Fe-O(H_2O) bond of the

Table V. Equations of Planes of Best (Least-Squares) Fit to Selected Groups of Atoms and Distances of Various Atoms from Planes

Plane	Atoms	Equations in form $px + qy + rz = s$				Std dev	Distances of atoms from planes, Å	
		p	q	r	s			
1	Fe1, Fe2, Fe3, O13, O14, O15	0.301	−10.720	11.870	1.101	(0.02)	OX1	−0.03
2	Fe4, Fe5, Fe6, O28, O29, O30	−1.837	11.264	11.542	11.035	(0.03)	OX2	−0.01

Table VI. A Comparison of Interatomic Distances (Å) in $Fe_3O(H_2O)_3$ Units

	Fe-Fe	Fe-O (oxide)	Fe-O (H_2O)
$\{Fe_3O(CH_3COO)_6(H_2O)_3\}ClO_4$	3.29		2.08
$\{Fe_3O(piv)_6(MeOH)_3\}Cl$	3.27	1.905 (5)	
$K_5\{Fe_3O(SO_4)_6(H_2O)_3\}\cdot 6H_2O$	3.295 (5)	1.922 (3)	2.13 (1)
$\{Fe_3O(gly)_6(H_2O)_3\}(ClO_4)_7$	3.30 (1)	1.90 (2)	2.09 (2)

sulfate complex. The Fe-O-Fe bond angles of all the compounds except one show similar close agreement, 120°. In the pivalate complex the Fe-O-Fe angles are 118.5° by virtue of the fact that the central oxygen is displaced 0.24 Å to one side of the Fe_3 plane. Investigation of the effect of this displacement upon the magnetic susceptibility of the pivalate compound has considerable significance in light of the controversy surrounding the interpretation of the low-temperature magnetic data on the acetate complex[10] and the recent report of the application of an exchange Hamiltonian applicable to an isosceles triangle to the magnetic properties of $[Fe_3O(pro)_6(H_2O)_3](ClO_4)_7$.[3]

Of further interest is a comparison of the carboxylate bonding in the glycine, pivalate, and acetate complexes. Unfortunately the report on the acetate structure is incomplete; hence a direct comparison is possible only between the pivalate and glycine complexes. In the pivalate structure, where the central oxygen is displaced above the plane of the three iron atoms, those bridging pivalate groups which lie above the plane show a symmetrical bridging configuration with an O-C-O angle of 119° and the β carbon 0.37 Å from the O-C-O plane. Those bridging pivalate groups which lie below the plane of the iron atoms are unsymmetrical with a larger O-C-O angle (130°) and the β carbon 0.57 Å from the O-C-O plane. In the glycine structure the O-C-O angle averages 127.1° and the β carbon as well as the nitrogen lie on the O-C-O plane (average deviation 0.07).

The distortion of the FeO_6 octahedra is somewhat different in the two cases. In the pivalate structure, the distortion takes the form of tilting the Fe-O(carboxy) bonds beneath the plane of the three iron atoms away from that plane and toward the Fe-O(methanol) bond [O(carboxy)-Fe-O(methanol), 85-91°; O(carboxy)-Fe-O(oxide), 100-102°]. The bond angles involving the Fe-O(carboxy) bonds above the plane of the iron atoms vary from 79 to 89°. The trans O(methanol)-Fe-O(oxide) bond angle is 166°. The glycine structure shows a general distortion of the Fe-O(carboxylate) bonds toward the Fe-O(water) bond (80-88°) and away from the central oxide-Fe bond (91-98°). The trans O(water)-Fe-O(oxide) bond angles are 176-179°, relatively undistorted from the ideal 180°.

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Supplementary Material Available: a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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