Crystal structure of μ_2-oxo-bis-μ_2-formato-bis(tris(pyrazolyl)-methane)diiron(III) perchlorate, $C_{22}H_{22}Cl_2Fe_2N_{12}O_{13}$

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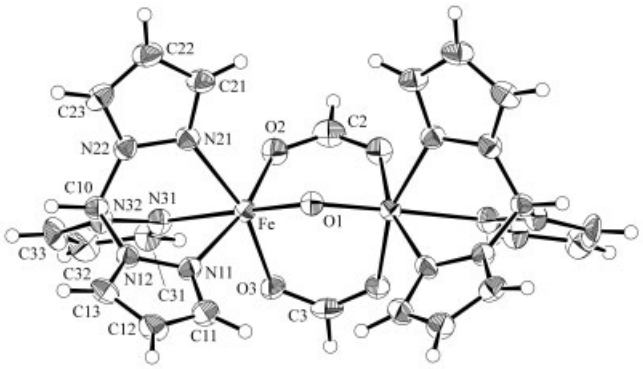

Abstract

$C_{11}H_{11}ClFeN_6O_{6.50}$, orthorhombic, *Pnnm* (No. 58), $a = 12.733(6)$ Å, $b = 15.315(9)$ Å, $c = 16.260(5)$ Å, $V = 3170.8$ Å^3, $Z = 8$, $R_{gt}(F) = 0.058$, $wR_{ref}(F^2) = 0.200$, $T = 293$ K.

Source of material

The complex was prepared as in [1]. IR spectroscopy: ν(CO) = 1570 cm^{-1}.

Discussion

This complex was investigated as a part of an extensive study [1] aimed at preparing oxo-bridged compounds of iron(III), containing the facial-tridentate ligand tris(pyrazolyl)methane, in order to compare the results to those on analogous systems containing tris(pyrazolyl)hydridoborate or triazacyclonane (tacn) end groups [2]. Such compounds are good models for non-heme iron proteins such as hemerythrins and usually contain acetate- and oxo-bridging ligands. The source of formate in the present work is not certain, but probably emanates from partial breakdown of the tridentate pz_3CH ligand, at the CH group, rather than to any carbon dioxide fixing reaction. The latter way of forming μ-formato μ-oxo iron dimers has recently been established [3]. In the present case, the complex was isolated as green crystals from MeCN solutions containing the $[Fe(III)(pz_3CH)_2](ClO_4)_3$ monomer [4]. It can also be made directly by reacting iron(III) perchlorate, ligand and sodium formate.

The dinuclear cation has mirror symmetry so that O1, C2 and C3 atoms lie on the plane; there are two perchlorate anions completing the asymmetric unit, each of which lies on a mirror plane; some residual disorder is noted as evidenced in the asymmetric anisotropic displacement parameters. The Fe atom exists in a disorted octahedral geometry defined by three nitrogen atoms of the tridentate ligand, two oxygen atoms of the bridging formates, and one oxygen of the bridging oxo group. The Fe–O1–Fe' angle of 121.9(4)° and the Fe—O1 distance of 1.765(4) Å are typical of these triply bridged Fe(III) compounds [1]. Magnetic studies revealed a μ (per Fe) of 1.68 μB and a J value of –123 cm^{-1} which is typical of such species [2].

Table 1. Data collection and handling.

Crystal:	green hexagonal, size 0.15 × 0.15 × 0.32 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.64 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC6R, $\omega/2\theta$
$2\theta_{max}$:	50.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3269, 3005
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1454
$N(param)_{refined}$:	245
Programs:	teXsan [5], SHELXS-86 [6], SHELXL-97 [7], DIFABS [8], PLATON [9], ORTEPII [10]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4*g*	0.1287	0.4612	1/2	0.084
H(3)	4*g*	–0.1141	0.7345	1/2	0.084
H(10)	8*h*	0.2435	0.7495	0.1664	0.110
H(11)	8*h*	0.1358	0.9046	0.4241	0.084
H(12)	8*h*	0.2016	1.0045	0.3165	0.084
H(13)	8*h*	0.2494	0.9149	0.1971	0.084
H(21)	8*h*	0.3908	0.5931	0.4118	0.084
H(22)	8*h*	0.5157	0.6017	0.2974	0.084
H(23)	8*h*	0.4270	0.6786	0.1837	0.084
H(31)	8*h*	–0.0490	0.5827	0.2946	0.084
H(32)	8*h*	–0.0690	0.5948	0.1443	0.084
H(33)	8*h*	0.0846	0.6788	0.0960	0.084

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	8*h*	0.14630(9)	0.68277(7)	0.40510(6)	0.0326(6)	0.0356(6)	0.0309(5)	0.0024(6)	0.0004(5)	–0.0015(5)
Cl(1)	4*g*	0.1472(3)	0.8702(2)	0	0.058(2)	0.042(2)	0.044(2)	0.005(2)	0	0
Cl(2)	4*g*	0.2986(3)	0.5894(2)	0	0.082(3)	0.040(2)	0.043(2)	0.020(2)	0	0
O(1)	4*g*	0.2021(6)	0.7141(5)	1/2	0.029(4)	0.038(4)	0.036(4)	–0.005(4)	0	0
O(2)	8*h*	0.1286(5)	0.5562(4)	0.4318(3)	0.049(4)	0.039(3)	0.046(3)	–0.006(3)	0.001(3)	0.002(3)
O(3)	8*h*	–0.0036(4)	0.7095(4)	0.4317(3)	0.032(3)	0.066(4)	0.039(3)	0.012(3)	0.001(3)	–0.003(3)
O(11)	4*g*	0.118(1)	0.9536(8)	0	0.21(2)	0.047(8)	0.24(2)	0.06(1)	0	0
O(12)	4*g*	0.060(1)	0.8119(9)	0	0.10(1)	0.12(1)	0.14(1)	–0.032(9)	0	0
O(13)	8*h*	0.2096(8)	0.8511(7)	–0.0664(4)	0.146(8)	0.133(8)	0.058(4)	–0.010(7)	0.038(5)	–0.018(5)
O(21)	4*g*	0.225(1)	0.5207(7)	0	0.19(2)	0.066(8)	0.101(8)	–0.065(9)	0	0
O(22)	4*g*	0.397(1)	0.553(1)	0	0.11(1)	0.14(1)	0.20(2)	0.08(1)	0	0
O(23)	8*h*	0.2868(8)	0.6400(5)	–0.0686(4)	0.176(9)	0.084(6)	0.066(4)	–0.016(6)	–0.033(5)	0.038(4)
N(11)	8*h*	0.1642(5)	0.8065(4)	0.3455(4)	0.052(5)	0.031(4)	0.034(3)	0.004(3)	0.002(3)	–0.006(3)
N(12)	8*h*	0.2017(5)	0.8124(4)	0.2679(4)	0.042(4)	0.030(4)	0.035(3)	–0.001(3)	0.001(3)	0.002(3)
N(21)	8*h*	0.2884(5)	0.6573(4)	0.3399(4)	0.031(4)	0.040(4)	0.041(3)	0.000(3)	0.000(3)	0.003(3)
N(22)	8*h*	0.3011(5)	0.6849(4)	0.2620(4)	0.040(4)	0.036(4)	0.037(3)	–0.003(4)	0.008(3)	0.002(3)
N(31)	8*h*	0.0819(5)	0.6516(4)	0.2854(4)	0.042(5)	0.038(4)	0.040(4)	–0.005(4)	–0.002(3)	–0.004(3)
N(32)	8*h*	0.1268(5)	0.6830(4)	0.2161(3)	0.033(4)	0.041(4)	0.034(3)	–0.010(3)	–0.001(3)	–0.002(3)
C(2)	4*g*	0.129(1)	0.5219(8)	1/2	0.06(1)	0.025(7)	0.073(9)	–0.010(6)	0	0
C(3)	4*g*	–0.044(1)	0.7186(8)	1/2	0.031(7)	0.056(9)	0.072(9)	0.015(7)	0	0
C(10)	8*h*	0.2200(7)	0.7339(5)	0.2219(4)	0.047(6)	0.028(5)	0.038(4)	0.003(4)	0.002(4)	–0.002(4)
C(11)	8*h*	0.1598(8)	0.8878(5)	0.3725(5)	0.072(7)	0.035(5)	0.046(4)	0.007(5)	–0.004(5)	–0.010(4)
C(12)	8*h*	0.1962(8)	0.9441(5)	0.3124(5)	0.073(7)	0.027(5)	0.055(5)	0.001(5)	–0.010(5)	–0.002(4)
C(13)	8*h*	0.2224(7)	0.8952(5)	0.2469(5)	0.044(6)	0.033(5)	0.053(5)	–0.005(4)	–0.010(4)	0.008(4)
C(21)	8*h*	0.3777(7)	0.6191(6)	0.3611(5)	0.033(5)	0.048(6)	0.057(5)	0.004(4)	0.002(4)	0.003(5)
C(22)	8*h*	0.4475(7)	0.6235(6)	0.2977(5)	0.039(6)	0.051(6)	0.068(6)	0.006(5)	0.012(5)	0.005(5)
C(23)	8*h*	0.3988(7)	0.6656(5)	0.2350(5)	0.040(5)	0.042(6)	0.057(5)	–0.008(4)	0.017(4)	–0.004(4)
C(31)	8*h*	–0.0025(7)	0.6117(6)	0.2600(5)	0.044(6)	0.053(6)	0.046(5)	–0.009(5)	0.000(4)	–0.002(4)
C(32)	8*h*	–0.0148(8)	0.6175(6)	0.1761(6)	0.057(7)	0.065(7)	0.063(6)	–0.017(6)	–0.020(5)	–0.010(5)
C(33)	8*h*	0.0694(8)	0.6636(6)	0.1501(5)	0.074(7)	0.059(6)	0.033(4)	–0.007(6)	–0.026(5)	–0.008(4)

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