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Crystal structure of bis(1,10-phenanthroline-1κN,1$\kappa N'$)tetrachloro-1κCl,2$\kappa^3 Cl$-μ-oxo-1:2$\kappa^2 O$-diiron(III) trichloromethane solvate, $[FeCl(C_{12}H_8N_4)_2]O(FeCl_3) \cdot CHCl_3$, *a dinuclear iron(III) complex with an unsymmetrical μ-oxo bridge*

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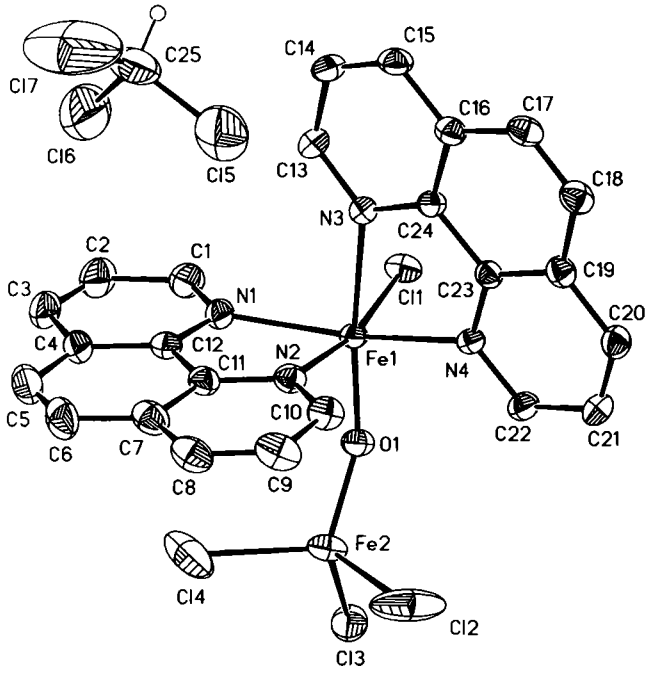

Abstract

$C_{25}H_{17}Cl_7Fe_2N_4O$, triclinic, $P\bar{1}$ (no. 2), $a = 8.014(2)$ Å, $b = 11.822(2)$ Å, $c = 15.795(3)$ Å, $\alpha = 94.26(3)°$, $\beta = 93.87(3)°$, $\gamma = 98.53(3)°$, $V = 1471.1$ Å^3, $Z = 2$, $R_{gt}(F) = 0.066$, $wR_{ref}(F^2) = 0.171$, $T = 293$ K.

Source of material

To a solution of 1,10-phenanthroline (1.0 mmol), 1-adamantanecarboxylic acid (1.0 mmol) in ethanol (25 mL) was added a solution of iron(III) chloride (1.0 mmol) in ethanol (10 mL). The resulting solution was boiled under reflux for ca. 2 h, then concentrated until crystallization was observed. The red solid was filtered, dried and recrystallized from chloroform giving dark red single crystals suitable for X-ray diffraction analysis.

Discussion

Polynuclear iron(III) clusters have attracted considerable attention in bioinorganic chemistry due to their presence in the protein ferritin and the related material hemosiderin. Several synthetic Fe-O-Fe μ-oxo diiron(III) complexes show catalyze-like activity and catalysts for alkane oxidation. The title structure consists of $[(FeCl_3)(\mu\text{-oxo})(FeCl(phen)_2)]$ complexes and $CHCl_3$ solvent molecules. The $[FeCl_3]$ and $[FeCl(phen)_2]$ fragments are connected by an unsymmetrical μ-oxo bridge in the dinuclear iron(III) complex, with distances of Fe1—O1 of 1.812(3) Å and Fe2—O1 of 1.747(3) Å which are somewhat longer than the shortest known Fe—O bond of 1.709 Å [1], but comparable to 1.824(3) Å and 1.771(1) Å in $[Fe_2Cl_4O(C_7H_{12}N_2)_4]$ [2]. The bond angle Fe1–O1–Fe2 of 149.5(2)° is less than respective one of 168.50(8)° in $[Fe_2Cl_4O(C_7H_{12}N_2)_4]$ [2]. The bond lengths to the donor atoms lie in the ranges 2.209(2) Å – 2.320(2) Å for Fe—Cl as well as in the ranges 2.143(4) Å – 2.251(4) Å for Fe—N, which are longer than those found for $[Fe(phen)_3][(\mu\text{-oxo})Fe_2Cl_6] \cdot DMF$ [3]. The non-bonded Fe1···Fe2 distance in the title complex is 3.434(1) Å.

Table 1. Data collection and handling.

Crystal:	dark red chunk, size 0.10 × 0.40 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	16.50 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID IP, ω
$2\theta_{max}$:	54.78°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10026, 6253
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5311
$N(param)_{refined}$:	352
Programs:	SHELXS-97 [4], SHELXL-97 [5]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.7462	0.3024	0.2065	0.067
H(2)	2*i*	0.7742	0.3400	0.0632	0.082
H(3)	2*i*	0.5422	0.3015	–0.0350	0.078
H(5)	2*i*	0.2275	0.2152	–0.0671	0.082
H(6)	2*i*	–0.0214	0.1339	–0.0183	0.081
H(8)	2*i*	–0.1868	0.0604	0.1044	0.073
H(9)	2*i*	–0.1874	0.0383	0.2491	0.077
H(10)	2*i*	0.0615	0.0911	0.3377	0.060
H(13)	2*i*	0.5160	0.4579	0.2812	0.053
H(14)	2*i*	0.4412	0.6275	0.3414	0.059
H(15)	2*i*	0.2826	0.6256	0.4590	0.055
H(17)	2*i*	0.1357	0.5059	0.5716	0.056
H(18)	2*i*	0.0706	0.3337	0.6262	0.058
H(20)	2*i*	0.1067	0.1210	0.6258	0.056
H(21)	2*i*	0.2130	–0.0357	0.5607	0.059
H(22)	2*i*	0.3616	–0.0095	0.4382	0.050
H(25)	2*i*	1.1735	0.6148	0.2157	0.134

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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(1)	2*i*	0.46877(8)	0.18113(5)	0.31672(4)	0.0405(3)	0.0279(3)	0.0322(3)	0.0033(2)	0.0074(2)	0.0012(2)
Fe(2)	2*i*	0.41768(9)	−0.10035(6)	0.23509(5)	0.0431(4)	0.0335(4)	0.0626(4)	0.0024(3)	0.0078(3)	−0.0103(3)
Cl(1)	2*i*	0.7414(2)	0.2472(1)	0.37651(8)	0.0454(6)	0.0380(6)	0.0551(6)	0.0028(5)	−0.0008(5)	−0.0057(5)
Cl(2)	2*i*	0.2034(3)	−0.1849(2)	0.3028(2)	0.100(1)	0.055(1)	0.229(3)	−0.024(1)	0.104(2)	−0.036(1)
Cl(3)	2*i*	0.6085(2)	−0.2186(1)	0.23161(9)	0.0746(9)	0.0545(8)	0.0568(7)	0.0282(7)	0.0120(6)	0.0063(6)
Cl(4)	2*i*	0.3468(4)	−0.0743(2)	0.1012(1)	0.188(3)	0.105(2)	0.080(1)	0.092(2)	−0.064(1)	−0.043(1)
Cl(5)	2*i*	1.0336(3)	0.4443(3)	0.2484(2)	0.095(2)	0.150(2)	0.117(2)	−0.030(2)	−0.019(1)	0.005(2)
Cl(6)	2*i*	1.2423(7)	0.4925(3)	0.1166(2)	0.319(6)	0.128(3)	0.117(2)	0.055(3)	0.073(3)	0.017(2)
Cl(7)	2*i*	0.9472(9)	0.5999(4)	0.1290(5)	0.340(7)	0.122(3)	0.449(9)	0.089(4)	−0.266(7)	−0.022(4)
O(1)	2*i*	0.4917(4)	0.0325(3)	0.2913(2)	0.044(2)	0.033(2)	0.045(2)	0.003(1)	0.007(1)	−0.001(1)
N(1)	2*i*	0.5038(5)	0.2401(3)	0.1923(2)	0.052(2)	0.039(2)	0.035(2)	0.010(2)	0.011(2)	0.005(1)
N(2)	2*i*	0.2077(5)	0.1515(3)	0.2498(2)	0.039(2)	0.038(2)	0.043(2)	0.005(2)	0.006(2)	0.000(2)
N(3)	2*i*	0.4066(5)	0.3543(3)	0.3613(2)	0.043(2)	0.033(2)	0.034(2)	0.005(2)	0.004(1)	0.004(1)
N(4)	2*i*	0.3457(5)	0.1541(3)	0.4315(2)	0.045(2)	0.029(2)	0.034(2)	0.007(2)	0.006(1)	0.004(1)
C(1)	2*i*	0.6492(7)	0.2851(5)	0.1660(4)	0.060(3)	0.053(3)	0.053(3)	−0.001(2)	0.016(2)	0.006(2)
C(2)	2*i*	0.6657(9)	0.3080(6)	0.0803(4)	0.080(4)	0.068(4)	0.061(3)	0.006(3)	0.034(3)	0.014(3)
C(3)	2*i*	0.5310(9)	0.2839(5)	0.0229(4)	0.096(5)	0.059(3)	0.046(3)	0.016(3)	0.028(3)	0.013(2)
C(4)	2*i*	0.3718(8)	0.2343(5)	0.0491(3)	0.080(4)	0.048(3)	0.037(2)	0.016(3)	0.010(2)	0.003(2)
C(5)	2*i*	0.223(1)	0.2023(6)	−0.0079(4)	0.100(5)	0.070(4)	0.040(3)	0.029(4)	−0.002(3)	0.001(3)
C(6)	2*i*	0.0770(9)	0.1563(6)	0.0209(4)	0.075(4)	0.080(4)	0.047(3)	0.026(3)	−0.015(3)	0.003(3)
C(7)	2*i*	0.0618(7)	0.1376(5)	0.1081(3)	0.057(3)	0.055(3)	0.054(3)	0.019(3)	−0.008(2)	−0.007(2)
C(8)	2*i*	−0.0866(7)	0.0866(5)	0.1416(4)	0.047(3)	0.065(4)	0.067(3)	0.012(3)	−0.007(2)	−0.013(3)
C(9)	2*i*	−0.0854(7)	0.0706(6)	0.2257(4)	0.040(3)	0.069(4)	0.080(4)	0.004(3)	0.006(3)	−0.012(3)
C(10)	2*i*	0.0624(6)	0.1041(5)	0.2784(3)	0.044(3)	0.051(3)	0.055(3)	0.005(2)	0.010(2)	0.001(2)
C(11)	2*i*	0.2089(6)	0.1677(4)	0.1659(3)	0.046(2)	0.038(2)	0.040(2)	0.011(2)	0.002(2)	−0.001(2)
C(12)	2*i*	0.3656(6)	0.2166(4)	0.1352(3)	0.055(3)	0.033(2)	0.041(2)	0.009(2)	0.006(2)	0.001(2)
C(13)	2*i*	0.4511(6)	0.4549(4)	0.3302(3)	0.051(3)	0.036(2)	0.045(2)	0.003(2)	0.006(2)	0.011(2)
C(14)	2*i*	0.4072(7)	0.5566(4)	0.3660(3)	0.061(3)	0.030(2)	0.053(3)	0.002(2)	−0.002(2)	0.007(2)
C(15)	2*i*	0.3139(6)	0.5556(4)	0.4347(3)	0.054(3)	0.031(2)	0.051(3)	0.012(2)	−0.003(2)	−0.003(2)
C(16)	2*i*	0.2662(6)	0.4508(4)	0.4705(3)	0.039(2)	0.037(2)	0.039(2)	0.010(2)	−0.001(2)	−0.003(2)
C(17)	2*i*	0.1720(6)	0.4392(4)	0.5448(3)	0.048(3)	0.043(3)	0.050(3)	0.011(2)	0.009(2)	−0.008(2)
C(18)	2*i*	0.1368(6)	0.3388(5)	0.5778(3)	0.048(3)	0.052(3)	0.045(2)	0.007(2)	0.014(2)	−0.004(2)
C(19)	2*i*	0.1943(6)	0.2373(4)	0.5412(3)	0.040(2)	0.046(3)	0.036(2)	0.005(2)	0.005(2)	0.001(2)
C(20)	2*i*	0.1676(6)	0.1299(5)	0.5759(3)	0.050(3)	0.052(3)	0.038(2)	0.001(2)	0.010(2)	0.009(2)
C(21)	2*i*	0.2301(7)	0.0380(4)	0.5382(3)	0.061(3)	0.041(3)	0.046(3)	0.001(2)	0.008(2)	0.015(2)
C(22)	2*i*	0.3182(6)	0.0545(4)	0.4651(3)	0.052(3)	0.033(2)	0.043(2)	0.009(2)	0.009(2)	0.006(2)
C(23)	2*i*	0.2842(5)	0.2450(4)	0.4685(2)	0.032(2)	0.035(2)	0.031(2)	0.002(2)	0.001(2)	0.001(2)
C(24)	2*i*	0.3180(5)	0.3530(4)	0.4314(3)	0.037(2)	0.030(2)	0.036(2)	0.004(2)	0.001(2)	0.002(2)
C(25)	2*i*	1.108(1)	0.5519(7)	0.1807(6)	0.152(9)	0.067(5)	0.106(6)	0.027(5)	−0.056(6)	−0.023(4)

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