Crystal structure of tris(1,10-phenanthroline-*N*,*N*')iron(II) suberate tetradecahydrate, $[Fe(C_{12}H_8N_2)_3](C_8H_{12}O_4) \cdot 14H_2O$

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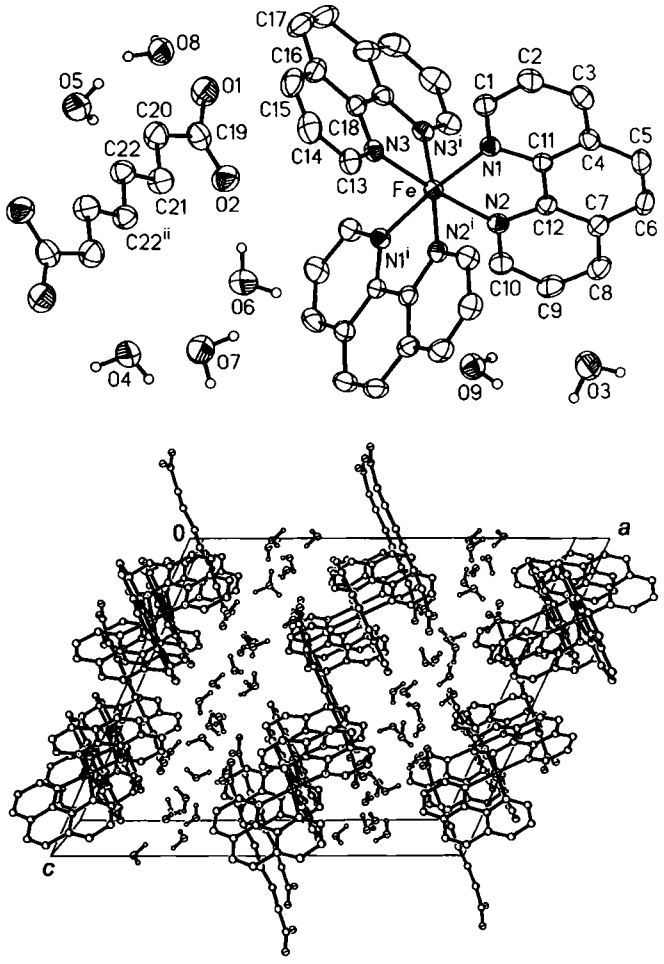

Abstract

$C_{44}H_{64}FeN_6O_{18}$, monoclinic, *C*12/*c*1 (no. 15), $a = 23.318(5)$ Å, $b = 12.097(2)$ Å, $c = 19.446(4)$ Å, $\beta = 114.34(3)°$, $V = 4997.8$ Å^3, $Z = 4$, $R_{gt}(F) = 0.049$, $wR_{ref}(F^2) = 0.128$, $T = 296$ K.

Source of material

Red crystals of the title compound were obtained by hydrothermal reaction of $FeCl_3 \cdot 6H_2O$ (1.00 mmol, 0.27 g), 1,10-phenanthroline monohydrate (1.00 mmol, 0.20 g), suberic acid (3.00 mmol, 0.65 g), NaOH (3.00 mmol, 0.12 g) and water (15 ml) in a 23 ml Teflon-lined autoclave at 170 °C for 120 h (yield 75% based on the initial phenanthroline amount).

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Discussion

The magnetic measurement indicated that the initial trivalent Fe^{3+} cation of $3d^5$ configuration is reduced to divalent Fe^{2+} cation of $3d^6$ configuration with all electron paired ($\chi_m = -690\ 10^{-6}$ cm^3 mol^{-1}). Reducing agent is obviously suberic acid which could be oxidized or chlorinated.

Being isostructural with $[M(phen)_3](C_8H_{12}O_4) \cdot 14H_2O$ (M = Co [1] and Zn [2], the title compound consists of divalent $[Fe(phen)_3]^{2+}$ complex cations, suberate anions and lattice water molecules (figure, top). The lattice H_2O molecules are involved in extensive hydrogen bonding interactions. According to the hydrogen bonding fashions, the seven crystallographically distinct lattice water molecules are classified into three groups. Three water molecules (O3, O4, O6) are each hydrogen-bonded to three neighbors by donating two hydrogen atoms and accepting one hydrogen atom. As far as the O5, O8 and O9 water molecules are concerned, each donates one hydrogen atom and accepts two hydrogen atoms to form hydrogen bonds to three neighbors. The O7 water molecule as donor and acceptor is engaged in two hydrogen bonds to two neighbors. As a result, the water molecules are hydrogen bonded into a 2D network containing rhombic ($R^4_4(8)$), pentagonal ($R^3_5(10)$), hexagonal ($R^6_6(12)$) and decagonal ($R^9_{12}(20)$) water clusters [3]. On the other hand, such 2D network can be visualized as the hydrogen bonded chains in the ...$R^6_6(12)$–$R^3_5(10)$–$R^4_4(8)$–$R^3_5(10)$–$R^6_6(12)$... sequence along [010] interconnected by the O7 water molecules. Additionally, the O7, O8 and O9 water molecules are hydrogen bonded to the carboxylate oxygen atoms of the suberate anions to generate the 3D anionic framework with three different types of channels propagating in the [001], [010], [01$\bar{1}$] directions.

Both the cation and the anion sit on a twofold axis (which passes through Fe and dissects the C17—C12^i, C18—C18^i (cation) and C22—C22^{ii} (anion) bond). Within the $[Fe(phen)_3]^{2+}$ complex cations, the Fe atom is in a slightly distorted octahedral coordination defined by six nitrogen atoms of the three phenanthroline ligands with the Fe—N bond distances averaged to 1.978 Å and *transoid* and *cisoid* N–Fe–N bond angles in the regions of 174.9° – 175.1° and 82.3° – 96.1°, respectively. The present Fe—N bond distances are practically identical to the value of 1.977 Å found in $[Fe(phen)_3](ttcH_2)(ClO_4) \cdot 2CH_3OH \cdot 2H_2O$ [4]. Along [001], the complex cations are lined up to form columnar chains with the phenanthroline ligands containing N1 atoms engaged in face-to-face π-π stacking interactions with mean interplanar distance of 3.34 Å (figure, bottom). The pillared suberate anions with normal bonding values are sandwiched between two phenanthroline ligands belonging to different chains with the methylene hydrogen atoms directed to the aromatic plane, indicating weak C–H···π interactions (mean C–H···π distance of 3.52 Å).

Table 1. Data collection and handling.

Crystal:	red block, size 0.10 × 0.14 × 0.17 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.79 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6756, 5740
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4110
$N(param)_{refined}$:	313
Programs:	SHELXS-97 [5], SHELXL-97 [6]

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

Atom	Site	x	y	z	U_{iso}
H(1)	8*f*	0.6204	0.7487	0.7491	0.061
H(2)	8*f*	0.6866	0.7150	0.6902	0.061
H(3)	8*f*	0.6666	0.5714	0.6065	0.061
H(5)	8*f*	0.5953	0.4072	0.5392	0.061
H(6)	8*f*	0.5078	0.3067	0.5184	0.061
H(8)	8*f*	0.4098	0.2726	0.5457	0.061
H(9)	8*f*	0.3517	0.3273	0.6106	0.061
H(10)	8*f*	0.3823	0.4767	0.6902	0.061
H(13)	8*f*	0.6074	0.6846	0.9080	0.061
H(14)	8*f*	0.6548	0.8436	0.9721	0.061
H(15)	8*f*	0.6202	1.0141	0.9193	0.061
H(17)	8*f*	0.5410	1.1253	0.8060	0.061
H(20A)	8*f*	0.4268	1.1391	0.8382	0.061
H(20B)	8*f*	0.3720	1.1329	0.8647	0.061
H(21A)	8*f*	0.4010	0.9579	0.9121	0.061
H(21B)	8*f*	0.4493	0.9487	0.8753	0.061
H(22A)	8*f*	0.5126	1.0842	0.9581	0.061
H(22B)	8*f*	0.4641	1.0960	0.9942	0.061
H(3A)	8*f*	0.2928	0.1449	0.4959	0.050
H(3B)	8*f*	0.2966	0.1368	0.4301	0.067
H(4A)	8*f*	0.2866	0.5955	0.5251	0.050
H(4B)	8*f*	0.2851	0.5151	0.4779	0.070
H(5A)	8*f*	0.7301	0.4111	0.8082	0.081
H(5B)	8*f*	0.7928	0.4502	0.8219	0.068
H(6A)	8*f*	0.7381	0.6931	0.8745	0.078
H(6B)	8*f*	0.7445	0.5757	0.8761	0.089
H(7A)	8*f*	0.6762	0.3187	0.7033	0.050
H(7B)	8*f*	0.6657	0.2668	0.7562	0.050
H(8A)	8*f*	0.7714	0.8611	0.8934	0.050
H(8B)	8*f*	0.7275	0.8692	0.8212	0.093
H(9A)	8*f*	0.2612	0.3147	0.4342	0.050
H(9B)	8*f*	0.2168	0.3772	0.3857	0.050

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	4*e*	½	0.63429(3)	¾	0.0299(2)	0.0331(2)	0.0324(2)	0	0.0132(2)	0
N(1)	8*f*	0.56102(8)	0.6273(2)	0.7032(1)	0.0334(9)	0.037(1)	0.0367(9)	−0.0020(8)	0.0159(7)	−0.0005(8)
N(2)	8*f*	0.45870(8)	0.5140(2)	0.67678(9)	0.0333(9)	0.037(1)	0.0369(9)	−0.0027(8)	0.0140(8)	0.0011(8)
C(1)	8*f*	0.6116(1)	0.6898(2)	0.7155(1)	0.043(1)	0.046(1)	0.052(1)	−0.013(1)	0.024(1)	−0.009(1)
C(2)	8*f*	0.6517(1)	0.6700(2)	0.6799(2)	0.046(1)	0.062(2)	0.067(2)	−0.017(1)	0.032(1)	−0.007(1)
C(3)	8*f*	0.6398(1)	0.5851(2)	0.6300(2)	0.050(1)	0.063(2)	0.059(2)	0.000(1)	0.036(1)	−0.002(1)
C(4)	8*f*	0.5869(1)	0.5185(2)	0.6145(1)	0.043(1)	0.043(1)	0.043(1)	0.006(1)	0.022(1)	0.004(1)
C(5)	8*f*	0.5700(1)	0.4261(2)	0.5640(1)	0.058(2)	0.051(2)	0.048(1)	0.008(1)	0.027(1)	−0.005(1)
C(6)	8*f*	0.5179(1)	0.3661(2)	0.5518(1)	0.063(2)	0.041(1)	0.044(1)	0.007(1)	0.021(1)	−0.008(1)
C(7)	8*f*	0.4779(1)	0.3914(2)	0.5887(1)	0.048(1)	0.034(1)	0.038(1)	0.001(1)	0.012(1)	−0.0010(9)
C(8)	8*f*	0.4225(1)	0.3328(2)	0.5783(1)	0.057(2)	0.041(1)	0.051(1)	−0.010(1)	0.015(1)	−0.009(1)
C(9)	8*f*	0.3881(1)	0.3656(2)	0.6168(2)	0.047(1)	0.048(1)	0.059(2)	−0.016(1)	0.016(1)	−0.003(1)
C(10)	8*f*	0.4069(1)	0.4559(2)	0.6650(1)	0.039(1)	0.049(1)	0.052(1)	−0.009(1)	0.020(1)	−0.004(1)
C(11)	8*f*	0.54876(9)	0.5439(2)	0.6521(1)	0.037(1)	0.033(1)	0.032(1)	0.0026(9)	0.0142(9)	0.0031(9)
C(12)	8*f*	0.4936(1)	0.4812(2)	0.6386(1)	0.037(1)	0.033(1)	0.033(1)	0.0025(9)	0.0121(9)	0.0031(9)
N(3)	8*f*	0.54523(8)	0.7564(2)	0.8172(1)	0.0349(9)	0.042(1)	0.038(1)	−0.0011(8)	0.0174(8)	−0.0043(8)
C(13)	8*f*	0.5929(1)	0.7530(2)	0.8857(1)	0.041(1)	0.057(2)	0.042(1)	−0.001(1)	0.013(1)	−0.008(1)
C(14)	8*f*	0.6216(1)	0.8488(3)	0.9247(2)	0.047(1)	0.086(2)	0.052(2)	−0.015(2)	0.013(1)	−0.025(2)
C(15)	8*f*	0.6010(1)	0.9503(3)	0.8934(2)	0.058(2)	0.062(2)	0.080(2)	−0.022(2)	0.035(2)	−0.032(2)
C(16)	8*f*	0.5511(1)	0.9577(2)	0.8225(2)	0.053(2)	0.045(1)	0.074(2)	−0.009(1)	0.037(1)	−0.016(1)
C(17)	8*f*	0.5242(1)	1.0581(2)	0.7836(2)	0.084(2)	0.035(1)	0.111(3)	−0.009(1)	0.058(2)	−0.011(1)
C(18)	8*f*	0.5251(1)	0.8578(2)	0.7866(1)	0.039(1)	0.038(1)	0.050(1)	−0.002(1)	0.026(1)	−0.004(1)
O(1)	8*f*	0.3348(1)	1.1250(2)	0.7131(1)	0.090(2)	0.068(1)	0.048(1)	0.008(1)	0.015(1)	0.003(1)
O(2)	8*f*	0.3331(1)	0.9541(2)	0.7557(1)	0.081(1)	0.060(1)	0.058(1)	0.014(1)	0.022(1)	0.006(1)
C(19)	8*f*	0.3511(1)	1.0519(3)	0.7649(2)	0.061(2)	0.069(2)	0.045(1)	0.010(2)	0.023(1)	0.003(1)
C(20)	8*f*	0.3959(1)	1.0900(3)	0.8434(2)	0.069(2)	0.061(2)	0.046(1)	0.006(2)	0.016(1)	−0.001(1)
C(21)	8*f*	0.4309(1)	0.9993(2)	0.8992(2)	0.056(2)	0.059(2)	0.052(2)	−0.002(1)	0.016(1)	0.001(1)
C(22)	8*f*	0.4826(1)	1.0440(2)	0.9712(1)	0.054(2)	0.051(2)	0.049(1)	−0.002(1)	0.019(1)	0.002(1)
O(3)	8*f*	0.31130(9)	0.1787(2)	0.4701(1)	0.071(1)	0.073(1)	0.064(1)	−0.016(1)	0.033(1)	−0.001(1)
O(4)	8*f*	0.3031(1)	0.5768(2)	0.4936(1)	0.077(1)	0.065(1)	0.058(1)	−0.006(1)	0.032(1)	−0.006(1)
O(5)	8*f*	0.7644(1)	0.4422(2)	0.8406(1)	0.096(2)	0.071(1)	0.062(1)	−0.009(1)	0.033(1)	−0.003(1)
O(6)	8*f*	0.7365(2)	0.6330(2)	0.8971(2)	0.161(3)	0.059(1)	0.112(2)	0.001(2)	0.093(2)	0.008(1)
O(7)	8*f*	0.6654(1)	0.3359(2)	0.7399(1)	0.097(2)	0.066(1)	0.069(1)	0.003(1)	0.035(1)	−0.000(1)
O(8)	8*f*	0.7616(1)	0.8357(2)	0.8498(1)	0.087(1)	0.062(1)	0.052(1)	0.005(1)	0.025(1)	0.0009(9)
O(9)	8*f*	0.24368(9)	0.3772(2)	0.4333(1)	0.073(1)	0.061(1)	0.052(1)	0.002(1)	0.0250(9)	−0.0013(9)

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References

1. Geraghty, M.; McCann, M.; Devereux, M.; McKee, V.: Syntheses and anti-*Candida* activity of Cobalt(II) complexes of octanedioic acid ($odaH_2$) and nonanedioic acid ($ndaH_2$); X-ray crystal structures of $[Co(phen)_3]oda \cdot 14H_2O$ and $[Co(phen)_3]nda \cdot 11.5H_2O$ (phen = 1,10-phenanthroline). Inorg. Chem. Acta **293** (1999) 160-166.
2. Wei, D.-Y.; Zheng, Y.-Q.; Lin, J.-L.: Self - assembly of Zinc Ions with Suberic Acid and Phenanthroline – Crystal Structures of five New Zinc Phenanthroline Suberato Complexes. Z. Anorg. Allg. Chem. **628** (2002) 2005-2012.
3. Etter, M. C.; McDonald, J. C.; Bernstein, J.: Graph-set analysis of hydrogen-bond patterns in organic crystals. Acta Crystallogr. B**46** (1990) 256-262.
4. Kopel, P.; Trávnicek, Z.; Zbořil, R.; Marek, J.: Synthesis, X-ray and Mössbauer study of iron(II) complexes with trithiocyanuric acid ($ttcH_3$). The X-ray structures of $[Fe(bpy)_3](ttcH) \cdot 2bpy \cdot 7H_2O$ and $[Fe(phen)_3](ttcH_2)(ClO_4) \cdot 2CH_3OH \cdot 2H_2O$. Polyhedron **23** (2004) 2193-2202.
5. Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Larger Structures. Acta Crystallogr. A**46** (1990) 467-473.
6. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.