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The Ferric Chloride α-di-imine System. Part V. X-ray Structure Determination of Tris(1,10-phenanthroline)iron(II)μ-oxo-bis(trichloroiron(III))·DMF

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Introduction

The title compound is to our knowledge the second example of the novel binuclear $Cl_3Fe-O-FeCl_3^{2-}$ anion to be characterized by X-rays. It is obtained as a trace crystalline byproduct in the preparation of *mer*-[Fe(phen)Cl_3·DMF] under less than anhydrous conditions. Its structure is presented in this note.

Experimental

The crystal data for the red complex, tris(1,10-phenanthroline)iron(II)μ-oxo-bis(trichloroiron(III))·DMF, are collected in Table I. Three-dimensional intensity data were collected with a Syntex $P2_1$ automated diffractometer using Mo(Kα)monochromatized radiation. Several strong reflections were given zero weighting in the refinement. Lorentz and polarization corrections were applied to the data and absorption corrections were not made. Anomalous dispersion corrections for the iron and chlorine ions were included in both structure refinements.

TABLE I. Crystal Data for the Red Complex, Tris(1,10-phenanthroline)iron(II) μ-oxo-bis(trichloroiron(III))·DMF.

	Red complex
	$P2_1/a$
Space group cell dimensions	a = 20.773(6) Å b = 13.218(3) Å c = 15.478(4) Å β = 94.06(2)° V = 4239(2) Å^3
Calculated density	1.60 g/cc
Observed density (floatation)	1.58 g/cc
Range of data	2θmax = 40°
Total reflections	3746
Observed reflections [a]	2246

[a] $I \geqslant 1.5\sigma(I)$.

Solution and Refinement of the Structure

Tris(1,10-phenanthroline)iron(II)μ-oxo-bis(trichloroiron(III))·DMF

This structure was solved by the use of direct methods programs in the XRAY 76 program system. The program SINGEN, using the 970 highest E-values, generated 51,981 triples. The program PHASE generated a consistent set of 50 high E-values which was used as a basis set to phase the remaining reflections. These phases were used in a Fourier synthesis E-map from which were located the three iron and six chlorine atom positions. These positions were refined isotropically using least-squares to given an R-value of 0.26. Subsequent Fourier maps revealed the phenanthroline rings and oxygen bridge positions. Isotropic refinement converged to 0.16. Anisotropic refinement of the heavy atoms gave an R-value of 0.12 which was followed by another Fourier synthesis that revealed a solvent molecule of DMF. Population parameter refinement showed the DMF atoms to have occupancies of 0.55 to 1.0. The slightly lower calculated molecular weight using the observed density is in agreement with this observation. Partial loss of this molecule of solvation is apparent. The use of calculated hydrogen positions for the phenanthroline groups and $1/\sigma_{F_0^2}$ weighting resulted in final unweighted and weighted R-values of 0.102 and 0.055 respectively. The application of Hamilton's R-test [1] indicated that the initial structure was the correct structure to within 99.5% confidence.

The atomic scattering factors for iron, chlorine, nitrogen, carbon and oxygen were taken from Cromer and Mann [2] and those for hydrogen from Stewart *et al.* [3]. The XRAY 76 [4] computer program system was used throughout for data processing, structure determination and least-squares refinement. All drawings were made using the ORTEP [5] program. Observed and calculated structure factors are given in supplementary Table 1A.

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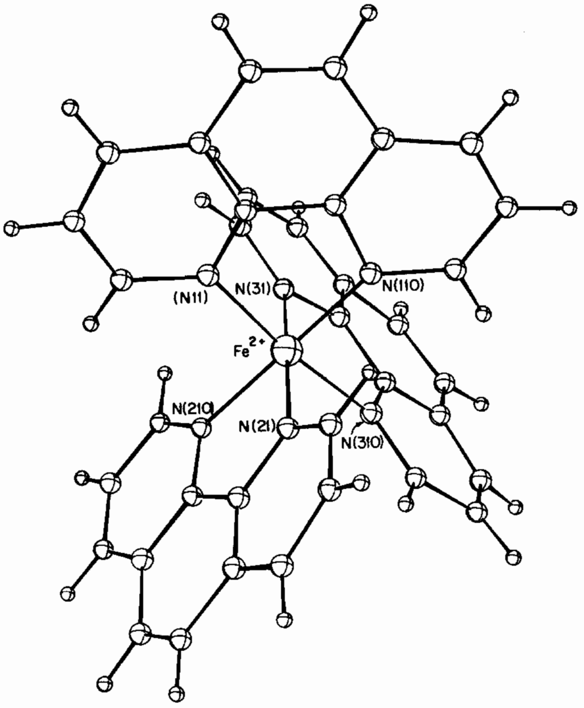

Fig. 1. View of the local coordination environment of tris(1,10-phenanthroline)iron(II) cation.

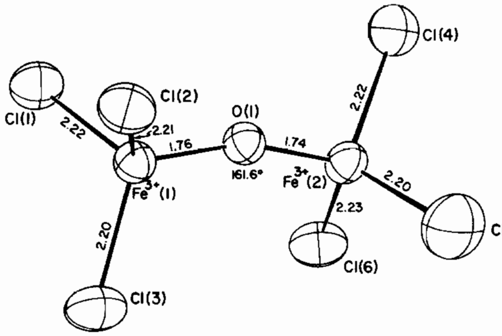

Fig. 2. View of the local coordination environment of μ-oxobis(trichloroferrate(III)) anion.

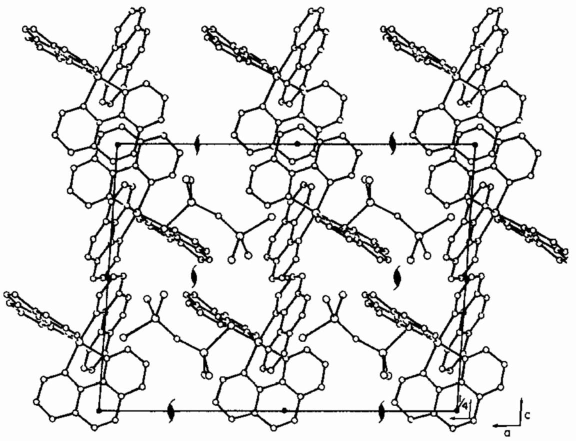

Fig. 3. Packing diagram for tris(1,10-phenanthroline)iron(II) μ-oxo-bis(trichloroferrate(III)) viewed along the *b* axis.

Description of the Structure

The molecular structure of the red tris(1,10-phenanthroline)iron(II)μ-oxobis(trichloroiron(III))· DMF is an ionic arrangement with distinct cationic and anionic sites. The cation, anion and molecular

TABLE II. Positional and Thermal Parameters[a] of Non-Hydrogen Atoms in Tris(1,10-phenanthroline)iron(II) μ-oxo-bis(trichloroiron(III))·DMF.

Atom	*X*	*Y*	*Z*	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe^{3+}(1)	0.2820(1)	0.1235(2)	0.7831(2)	4.2(2)	4.9(2)	5.1(2)	−0.2(2)	−0.5(2)	−0.2(2)
Fe^{3+}(2)	0.1397(1)	0.1481(2)	0.6552(2)	4.2(2)	4.0(2)	4.9(2)	0.0(2)	0.3(2)	0.0(2)
Cl(1)	0.3529(3)	0.1174(4)	0.6823(4)	8.8(5)	4.5(4)	7.4(5)	0.3(4)	3.4(4)	0.7(4)
Cl(2)	0.2885(3)	−0.0140(4)	0.8648(4)	7.2(4)	6.9(5)	7.1(5)	−1.1(4)	1.0(4)	1.6(4)
Cl(3)	0.3012(3)	0.2564(5)	0.8669(4)	13.2(6)	7.7(5)	9.1(5)	−2.8(5)	3.0(5)	−3.4(4)
Cl(4)	0.1126(3)	0.0087(4)	0.5816(4)	7.4(4)	3.6(4)	8.4(5)	0.2(4)	0.3(4)	−0.2(4)
Cl(5)	0.1590(3)	0.2715(4)	0.5647(4)	8.6(5)	4.7(4)	8.1(5)	−1.0(4)	3.9(4)	0.2(4)
Cl(6)	0.0556(2)	0.1959(4)	0.7276(3)	7.2(4)	5.9(4)	6.1(4)	0.6(4)	2.4(3)	0.8(4)
O(1)	0.2040(6)	0.1246(10)	0.7307(9)	7.2(4)					
Fe^{2+}(3)	0.5685(1)	0.2917(2)	0.2572(2)	3.9(2)	3.0(2)	3.2(2)	−0.2(2)	0.3(1)	0.0(2)
Phenanthroline 1									
N(11)	0.5262(6)	0.2639(11)	0.3638(9)	3.6(4)					
C(12)	0.5201(8)	0.3252(12)	0.4332(11)	3.1(5)					

(continued on facing page)

TABLE II. *(continued)*

Atom	*X*	*Y*	*Z*	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(13)	0.4839(8)	0.2930(15)	0.5028(11)	4.1(6)					
C(14)	0.4586(8)	0.1981(15)	0.5039(12)	5.2(6)					
C(15)	0.4429(9)	0.0336(15)	0.4293(12)	5.2(6)					
C(16)	0.4514(9)	−0.0258(15)	0.3623(13)	5.5(7)					
C(17)	0.4964(10)	−0.0447(15)	0.2133(13)	6.0(7)					
C(18)	0.5277(10)	−0.0040(17)	0.1501(14)	7.1(8)					
C(19)	0.5497(9)	0.9068(15)	0.1594(12)	4.8(6)					
N(110)	0.5403(6)	0.1532(10)	0.2288(9)	3.6(4)					
C(111)	0.5087(8)	0.1099(13)	0.2944(11)	3.1(5)					
C(112)	0.5003(8)	0.1711(13)	0.3666(11)	3.2(5)					
C(113)	0.4663(8)	0.1358(14)	0.4369(11)	3.9(6)					
C(114)	0.4828(8)	0.0051(14)	0.2874(11)	4.5(6)					
Phenanthroline 2									
N(21)	0.6014(7)	0.3103(10)	0.1420(9)	3.6(4)					
C(22)	0.6593(8)	0.2977(14)	0.1172(11)	4.1(6)					
C(23)	0.6761(9)	0.3105(14)	0.0310(13)	5.5(6)					
C(24)	0.6272(9)	0.3337(15)	−0.0319(12)	5.6(7)					
C(25)	0.5091(11)	0.3731(15)	−0.0634(12)	6.1(7)					
C(26)	0.4529(10)	0.3856(17)	−0.0337(15)	7.3(7)					
C(27)	0.3817(10)	0.4008(15)	0.0896(13)	5.7(6)					
C(28)	0.3786(9)	0.3917(14)	0.1749(13)	4.6(6)					
C(29)	0.4306(9)	0.3633(14)	0.2272(12)	4.3(6)					
N(210)	0.4874(6)	0.3443(10)	0.1973(8)	2.9(4)					
C(211)	0.4940(8)	0.3524(13)	0.1109(11)	3.5(5)					
C(212)	0.5550(8)	0.3352(13)	0.0786(11)	3.3(5)					
C(213)	0.5650(9)	0.3476(14)	−0.0107(13)	4.5(6)					
C(214)	0.4388(9)	0.3810(14)	0.0537(13)	4.7(6)					
Phenanthroline 3									
N(31)	0.6504(6)	0.2444(10)	0.3118(8)	3.1(4)					
C(32)	0.6767(9)	0.1527(15)	0.3218(2)	4.8(6)					
C(33)	0.7364(8)	0.1304(14)	0.3664(12)	4.6(6)					
C(34)	0.7713(9)	0.2077(16)	0.4001(12)	4.6(6)					
C(35)	0.7795(9)	0.3928(16)	0.4359(12)	5.6(6)					
C(36)	0.7551(10)	0.4866(15)	0.4265(13)	6.7(7)					
C(37)	0.6652(10)	0.5977(16)	0.3573(12)	5.7(7)					
C(38)	0.6087(9)	0.6046(15)	0.3108(12)	4.6(6)					
Atom									
C(39)	0.5766(9)	0.5168(15)	0.2826(12)	4.4(6)					
N(310)	0.6018(7)	0.4228(11)	0.2948(9)	3.4(4)					
C(311)	0.6591(8)	0.4210(13)	0.3381(11)	2.9(5)					
C(312)	0.6879(8)	0.3209(12)	0.3502(10)	3.1(5)					
C(313)	0.7478(9)	0.3065(15)	0.3979(11)	4.1(6)					
C(314)	0.6958(9)	0.5056(15)	0.3735(12)	4.2(6)					
DMF[c]									
O(41)	0.1007(18)	0.4145(28)	0.9533(24)	6.3[d]					
C(42)	0.6591(12)	0.0421(20)	0.8951(17)	7.6					
N(43)	0.8260(9)	0.4634(16)	0.1553(13)	7.6					
C(44)	0.3683(10)	0.1007(17)	0.0891(14)	7.6					
C(45)	0.8299(10)	0.3495(17)	0.2287(13)	6.3					

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[a] Estimated standard deviations are given in parentheses and refer to the least significant digits. [b] The anisotropic temperature factors are multiplied by 100 and are of the form $T = \exp[-2\pi^2(U11(ha^*)^2 + \ldots + 2U12(hka^*b^*) + \ldots]$. [c] Occupancy of these atoms at these positional parameters ranged from 0.55 to 1.0. [d] The isotropic temperature factors for the DMF atoms were fixed at the indicated values.

TABLE III. Calculated Hydrogen Positional Parameters[a] for Tris(1,10-phenanthroline)iron(II) μ-oxo-bis(trichloroiron(III))•DMF.

Atom	X	Y	Z
Phenanthroline 1			
H(12)	0.5410	0.3934	0.4350
H(13)	0.4773	0.3408	0.5518
H(14)	0.4345	0.1748	0.5540
H(15)	0.4182	0.0064	0.4781
H(16)	0.4341	−0.0970	0.3649
H(17)	0.4815	−0.1157	0.2060
H(18)	0.5362	−0.0432	0.0969
H(19)	0.5743	0.1281	0.1127
Phenanthroline 2			
H(22)	0.6944	0.2786	0.1622
H(23)	0.7223	0.3034	0.0158
H(24)	0.6379	0.3403	−0.0940
H(25)	0.5130	0.3818	−0.1272
H(26)	0.4166	0.4008	−0.0766
H(27)	0.3425	0.4211	0.0523
H(28)	0.3366	0.4055	0.2024
H(29)	0.4267	0.3567	0.2907
Phenanthroline 3			
H(32)	0.6517	0.0948	0.2941
H(33)	0.7523	0.0595	0.3730
H(34)	0.8158	0.1944	0.4272
H(35)	0.8212	0.3831	0.4705
H(36)	0.7776	0.5444	0.4565
H(37)	0.6870	0.6603	0.3808
H(38)	0.5899	0.6725	0.2963
H(39)	0.5328	0.5232	0.2519

[a] The hydrogen atom thermal parameters were given a fixed isotropic value of U = 0.0633.

packing diagrams are shown in Figs. 1, 2 and 3, respectively. Positional and thermal parameters of the non-hydrogen atoms are given in Table II while those for the calculated hydrogen atoms are given in Table III. Bond distances and angles with standard deviations are in Table IV.

The average phenanthroline bite angle is 82.6° and the Fe^{2+}–N bond distances range from 1.94 to 1.99 Å which agrees well with the average value of 1.97 Å found in the tris(1,10-phenanthroline)iron(II) cation investigated by Zalkin *et al.* [6]. All phenanthroline rings are nearly planar with a maximum deviation of 0.04 Å. The rings are nearly perpendicular to each other with a 92.2° angle between each pair of planes.

To our knowledge, this is only the second example of a μ-oxo-bis(trichloroferrate(III)) anion reported in the literature. The Fe^{3+}–O bond distances in the present compound (average value of 1.75 Å) agree with those reported by Nelson *et al.* [7] as found for pyridinium μ-oxo-bis(trichloroferrate(III))–pyridine (1.75 Å). Fe^{3+}–Cl bond distances in the red compound (2.20–2.23 Å) are also in agreement with those reported by Nelson (2.21–2.22 Å) while the Fe–O–Fe bond angle is slightly larger in the present compound (161.6°) than that found by Nelson (155.6°).

It is interesting that this compound contains spin-iron(III) and low-spin iron(II) together. However, the phenanthroline and chloro ligands sufficiently insulate the iron sites from each other to prevent any type of charge transfer interaction between Fe^{2+} and Fe^{3+}. The Fe^{2+} and Fe^{3+} ions are well separated with the ferrous site 10.6 Å from the Fe^{3+}(1)–O–Fe^{3+} (2) plane. The red color of the complex is undoubtedly due primarily to the presence of the low-spin Fe(phen)$_3^{2+}$ chromophore.

TABLE IV. Bond Lengths and Angles for Non-Hydrogen Atoms[a] of Tris(1,10-phenanthroline)iron(II) μ-oxo-bis(trichloroiron(III))•DMF.

Anion			
Lengths (Å)			
Fe^{3+}(1)–O(1)	1.76(2)	Fe^{3+}(2)–O(1)	1.74(2)
Fe^{3+}(1)–Cl(1)	2.22(2)	Fe^{3+}(2)–Cl(4)	2.218(8)
Fe^{3+}(1)–Cl(2)	2.213(7)	Fe^{3+}(2)–Cl(5)	2.205(8)
Fe^{3+}(1)–Cl(3)	2.204(8)	Fe^{3+}(2)–Cl(6)	2.23(2)
Angles (°)			
Fe^{3+}(1)–O(1)–Fe^{3+}(2)	161.6(9)		
O(1)–Fe^{3+}(1)–Cl(1)	108.2(5)	O(1)–Fe^{3+}(2)–Cl(4)	110.5(5)
O(1)–Fe^{3+}(1)–Cl(2)	106.7(5)	O(1)–Fe^{3+}(2)–Cl(5)	113.2(5)
O(1)–Fe^{3+}(1)–Cl(3)	112.8(5)	O(1)–Fe^{3+}(2)–Cl(6)	107.7(5)

(continued on facing page)

TABLE IV. *(continued)*

Cl(1)–Fe^{3+}(1)–Cl(2)	110.8(2)	Cl(4)–Fe^{3+}(2)–Cl(5)	109.8(2)
Cl(1)–Fe^{3+}(1)–Cl(3)	110.0(2)	Cl(4)–Fe^{3+}(2)–Cl(6)	108.2(2)
Cl(2)–Fe^{3+}(1)–Cl(3)	108.5(2)	Cl(5)–Fe^{3+}(2)–Cl(6)	107.1(2)
Cation			
Lengths (Å)	*Phenanthroline 1*	*Phenanthroline 2*^{b}	*Phenanthroline 3*^{c}
Fe^{2+}(3)–N(11)	1.96(2)	1.97(2)	1.95(2)
Fe^{2+}(3)–N(110)	1.96(1)	1.99(2)	1.94(2)
N(11)–C(12)	1.36(2)	1.30(2)	1.33(2)
C(12)–C(13)	1.42(3)	1.41(3)	1.41(3)
C(13)–C(14)	1.36(3)	1.39(3)	1.34(3)
C(14)–C(113)	1.34(3)	1.37(3)	1.39(3)
C(113)–C(15)	1.44(3)	1.41(3)	1.42(3)
C(15)–C(16)	1.32(3)	1.30(3)	1.34(3)
C(113)–C(112)	1.42(3)	1.42(3)	1.41(3)
C(16)–C(114)	1.43(3)	1.40(3)	1.45(3)
C(114)–C(17)	1.37(3)	1.37(3)	1.39(3)
C(17)–C(18)	1.32(3)	1.33(3)	1.33(3)
C(18)–C(19)	1.41(3)	1.35(3)	1.39(3)
C(19)–N(110)	1.33(2)	1.32(2)	1.36(2)
N(110)–C(111)	1.37(2)	1.36(3)	1.32(2)
C(111)–C(114)	1.49(3)	1.45(3)	1.44(3)
C(111)–C(112)	1.40(2)	1.41(3)	1.46(2)
C(112)–N(11)	1.34(2)	1.36(2)	1.38(2)
Angles (°)			
N(11)–Fe^{2+}(3)–N(21)	172.5(6)	N(110)–Fe^{2+}(3)–N(210)	174.2(6)
N(11)–Fe^{2+}(3)–N(31)	90.2(6)	N(21)–Fe^{2+}(3)–N(31)	94.8(6)
N(11)–Fe^{2+}(3)–N(310)	94.9(6)	N(21)–Fe^{2+}(3)–N(310)	91.2(6)
N(110)–Fe^{2+}(3)–N(21)	91.8(6)	N(210)–Fe^{2+}–(3)–N(31)	177.0(6)
N(110)–Fe^{2+}(3)–N(210)	89.6(4)	N(210)–Fe^{2+}–(3)–N(310)	95.7(6)
N(110)–Fe^{2+}(3)–N(31)	92.0(6)		
	Phenanthroline 1	*Phenanthroline 2*^{d}	*Phenanthroline 3*^{e}
N(11)–Fe^{2+}(3)–N(110)	82.5(6)	82.6(5)	82.8(6)
C(12)–N(11)–C(112)	117(1)	116(1)	114(1)
N(11)–C(12)–C(13)	120(1)	124(2)	126(2)
C(12)–C(13)–C(14)	121(2)	118(2)	118(2)
C(13)–C(14)–C(113)	119(2)	121(2)	122(2)
C(14)–C(113)–C(15)	126(2)	130(2)	126(2)
C(14)–C(113)–C(112)	119(2)	115(2)	116(2)
C(15)–C(113)–C(112)	116(2)	115(2)	118(2)
C(113)–C(15)–C(16)	124(2)	123(2)	122(2)
C(15)–C(16)–C(114)	124(2)	126(2)	121(2)
C(16)–C(114)–C(17)	132(2)	129(2)	128(2)
C(16)–C(114)–C(111)	113(2)	113(2)	119(2)
C(111)–C(114)–C(17)	114(2)	118(2)	113(2)
N(11)–C(112)–C(113)	123(2)	126(2)	125(2)
N(11)–C(112)–C(111)	115(2)	113(2)	113(1)
C(113)–C(112)–C(111)	121(2)	121(2)	122(2)
C(112)–C(111)–C(114)	122(2)	121(2)	117(1)
C(112)–C(111)–N(110)	116(2)	119(2)	115(1)
N(110)–C(111)–C(114)	121(2)	119(2)	128(2)
C(114)–C(17)–C(18)	124(2)	119(2)	122(2)
C(17)–C(18)–C(19)	119(2)	122(2)	120(2)
C(18)–C(19)–N(110)	123(2)	122(2)	123(2)

(continued overleaf)

TABLE IV. *(continued)*

	Phenanthroline 1	*Phenanthroline 2*[d]	*Phenanthroline 3*[e]
C(19)–N(110)–C(111)	118(1)	119(1)	114(2)
Fe^{2+}(3)–N(11)–C(12)	129(1)	130(1)	133(1)
Fe^{2+}(3)–N(11)–C(112)	114(1)	114(1)	114(1)
Fe^{2+}(3)–N(110)–C(111)	112(1)	110(1)	115(1)
Fe^{2+}(3)–N(110)–C(19)	130(1)	131(1)	130(1)
Cl(3)–Fe–O	94.4(1)	C(7)–C(8)–C(9)	119.6(5)
N(1)–Fe–N(10)	76.3(2)	C(8)–C(9)–N(10)	123.2(5)
N(1)–Fe–O	164.3(2)	Fe–N(1)–C(2)	117.8(5)
N(10)–Fe–O	88.5(2)	Fe–N(1)–C(2)	126.2(4)
C(2)–N(1)–C(12)	118.0(4)	Fe–N(1)–C(12)	115.8(3)
N(1)–C(2)–C(3)	121.9(5)	Fe–N(10)–C(11)	114.3(4)
C(2)–C(3)–C(4)	119.9(6)	Fe–N(10)–C(9)	127.9(3)
C(4)–C(13)–C(5)	123.9(5)	C(15)–N–C(16)	121.3(5)
C(4)–C(14)–C(12)	116.8(5)	C(16)–N–C(17)	117.1(5)
C(5)–C(13)–C(12)	119.3(5)	C(15)–N–C(17)	121.7(5)
C(13)–C(5)–C(6)	121.0(5)	Fe–O–C(15)	127.3(4)

[a] Estimated standard deviations are given in parentheses and refer to the least significant digits. [b] Bond lengths in this column are for the analogous bond in phenanthroline 2. [c] Bond lengths in this column are for the analogous bond in phenanthroline 3. [d] Bond angles in this column are for the analogous angle in phenanthroline 2. [e] Bond angles in this column are for the analogous angle in phenanthroline 3.

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