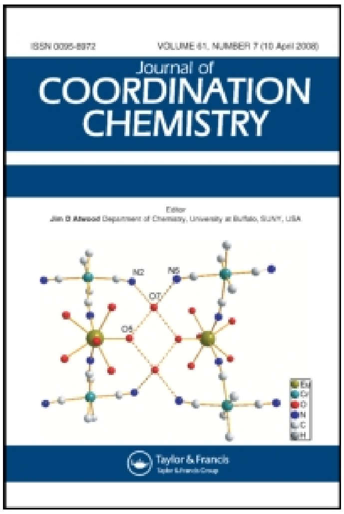

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MACROBICYCLIC d-METAL TRIS-DIOXIMATES OBTAINED BY CROSS-LINKING WITH p-BLOCK ELEMENTS. PART X. THE FIRST CRYSTAL AND MOLECULAR STRUCTURE OF CLATHROCHELATE TRIS-DIOXIMATES WITH NONSYMMETRICAL DIOXIMES: *mer* ISOMERS OF AN IRON(II) COMPLEX WITH A MACROBICYCLIC PHENYLBORON PHENYLGLYOXIMATE LIGAND

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Single crystals of the $FePhm_3(BC_6H_5)_2 \cdot BF_3$ complex contain two *mer* isomers with different orientations of phenyl substituents in dioxime fragments have been obtained by the template cross-linking of three phenylglyoximate (H_2Phm) molecules with two phenylboric acid molecules in the presence of boron trifluoride. They crystallize in space group $P\bar{1}$, $a = 13.962(5)$, $b = 13.519(2)$, $c = 12.343(6)$ Å, $\alpha = 63.63(7)$, $\beta = 100.78(4)$, $\gamma = 79.88(7)°$, $V = 1959.9$ Å^3, $Z = 2$. The structure has been determined by X-ray methods. The trigonal prismatic coordination polyhedron formed by six nitrogen atoms of the macrobicyclic ligand has a distortion angle of 21.8°. The Fe–N bond length (1.91 Å) and the bite angle (39.2°) are typical for clathrochelate tris-dioximates of iron(II). A comparison between the value of quadrupole splitting in Mössbauer (^{57}Fe) spectra obtained experimentally and its calculated value has been made.

Keywords: Iron, macrobicyclic complexes, X-ray structure, Mössbauer spectra

INTRODUCTION

X-ray structure data for a considerable number of macrocyclic iron(II) and cobalt(III) tris-dioxamates make it possible to obtain information on the spatial and electronic structure of compounds of this type, to elucidate the main relations of their formation and to discern the connection between structure and spectroscopic parameters.[1–7] At the same time, all data available concern compounds with

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symmetrical dioximes. Our attempts to produce crystals of complexes with nonsymmetrical dioximate fragments suitable for X-ray structure analysis have failed up to the present. In most cases, very fine crystals or glassy amorphous phases separated out during both synthesis and recrystallization. This was primarily due to the fact that the low symmetry molecules of these clathrochelate complexes pack loosely in the crystal lattice and also to the presence of at least two (*fac* and *mer*) isomers in solution, their ratio depending significantly on the nature of the nonsymmetrical α-dioxime. We have unexpectedly managed to obtain for the first time crystals of a macrobicyclic iron(II) tris-dioximate with phenylglyoxime; the study of its structure was the goal of the investigation reported below.

EXPERIMENTAL

Crystals with the composition $FePhm_3(BC_6H_5)_2 \cdot BF_3$ (A) were isolated in an attempt to produce a complex with different cross-linking fragments in one molecule.

A methanol solution containing the expected semiclathrochelate complex $Fe(HPhm)_3(BC_6H_5)^+$ was treated with an excess of $BF_3 \cdot (C_2H_5)_2O$. Over several days, orange-yellow crystals precipitated, one of which was chosen for X-ray structure analysis. This analysis showed the compound to be a boron-trifluoride solvate of a macrobicyclic iron(II) phenylglyoximate with identical phenylboron cross-linking groups.

Unit cell parameters and intensities of 2204 unique reflections were measured with an automated CAD4 diffractometer (in the range up to $2\theta_{max} = 45°$ by $\theta/2\theta$ scanning, using filtered Mo-K_α radiation). Crystals are triclinic, $a = 13.962(5)$, $b = 13.519(2)$, $c = 12.343(6)$ Å, $\alpha = 68.63(7)°$, $\beta = 100.78(4)°$, $\gamma = 79.88(7)°$, $V = 1959.9(1)$ Å^3, space group $P\bar{1}$, $Z = 2$. The structure was solved by the direct method and refined in the isotropic approximation for all non-hydrogen atoms (anisotropic for the iron atom), using 1224 reflections with $I > 3\sigma(I)$. H atom positions were determined from a difference synthesis and refined with fixed temperature factors. The final disagreement factors are $R = 0.067$, $R_w = 0.068$ (the weight is $1/(\sigma(F) + 0.001867 \cdot F^2)$), GOF = 1.29. The final atomic coordinates, selected bond lengths and bond angles are given in Tables I and II.

Mössbauer data were recorded as described[2] previously.

TABLE I
Atomic coordinates (× 10^4) and temperature factors (Å^2 × 10^3) for the complex

Atom	*x/a*	*y/b*	*z/c*	*U**
Fe	250(2)	2177(2)	784(3)	52(1)
O(1)	−251(8)	4118(9)	1238(10)	56(3)
O(2)	−1671(9)	3957(10)	−111(11)	63(3)
O(3)	−1077(8)	2626(9)	2177(10)	60(3)
O(4)	1006(8)	−57(9)	991(10)	61(3)
O(5)	1180(9)	1573(9)	−836(11)	61(3)
O(6	2312(8)	849(9)	1302(11)	61(3)
N(1)	−470(10)	1807(11)	1989(12)	50(4)

TABLE I
Continued

Atoms	*x/a*	*y/b*	*z/c*	*U**
N(2)	354(11)	599(12)	1291(13)	60(4)
N(3)	1693(9)	1704(10)	1409(12)	47(4)
N(4)	491(11)	3338(11)	1202(13)	57(4)
N(5)	−1001(10)	3310(12)	−398(14)	56(4)
N(6)	409(12)	2319(12)	−781(15)	60(4)
C(1)	−2045(13)	4681(14)	1357(15)	50(5)
C(2)	−2960(18)	4497(19)	1432(21)	94(7)
C(3)	−3706(19)	5289(22)	1525(23)	113(8)
C(4)	−3438(20)	6222(20)	1583(22)	103(7)
C(5)	−2584(19)	6429(18)	1464(20)	84(7)
C(6)	−1858(15)	5651(17)	1348(18)	74(6)
C(7)	2518(15)	−333(16)	228(17)	61(5)
C(8)	2368(15)	−1320(16)	308(18)	72(6)
C(9)	3055(17)	−2038(17)	67(20)	85(6)
C(10)	3876(18)	−1748(20)	−252(21)	93(7)
C(11)	4033(18)	−698(20)	−434(22)	104(7)
C(12)	3347(17)	−41(18)	−145(20)	89(7)
C(13)	−1241(14)	366(15)	3329(17)	61(5)
C(14)	−1749(16)	−392(17)	3238(19)	80(6)
C(15)	−2299(20)	−850(22)	4084(26)	120(8)
C(16)	−2357(17)	−535(19)	4967(22)	95(7)
C(17)	−1867(18)	180(19)	5084(21)	98(7)
C(18)	−1319(17)	668(18)	4258(21)	92(6)
C(19)	3234(15)	2191(16)	2082(17)	66(5)
C(20)	3950(19)	1147(20)	2738(22)	97(7)
C(21)	5016(22)	995(24)	3158(26)	128(9)
C(22)	5295(20)	1975(26)	2839(25)	121(8)
C(23)	4651(25)	2973(28)	2264(29)	142(10)
C(24)	3556(20)	3152(20)	1881(22)	111(8)
C(25)	−626(13)	773(15)	2526(16)	59(5)
C(26)	−33(13)	63(15)	2141(17)	61(5)
C(27)	2187(13)	2313(13)	1760(15)	51(5)
C(28)	1408(13)	3232(13)	1674(15)	46(4)
C(29)	−1138(14)	3643(16)	−1593(19)	65(5)
C(30)	−305(15)	2962(16)	−1767(19)	60(5)
C(31)	−410(23)	3091(24)	−3033(28)	54(9)
C(32)	−1373(30)	3211(32)	−3778(40)	107(13)
C(33)	−1517(31)	3400(33)	−5072(38)	117(13)
C(34)	−639(37)	3517(36)	−5429(43)	128(15)
C(35)	277(38)	3462(40)	−4857(49)	152(16)
C(36)	406(27)	3145(28)	−3494(34)	84(11)
B(1)	−1213(18)	3827(19)	1139(22)	61(7)
B(2)	1722(16)	500(17)	397(20)	53(6)
C(31)a	−1927(39)	4534(41)	−2696(47)	110(15)
C(32)a	−2894(66)	4833(68)	−2801(75)	168(28)
C(33)a	−3706(59)	5801(68)	−4018(82)	188(26)
C(34)a	−3481(63)	6291(64)	−5077(74)	189(27)
C(35)a	−2503(55)	6027(56)	−4875(64)	150(21)
C(36)a	−1755(60)	5271(68)	−3873(81)	194(28)
B(3)	−5415(91)	7576(99)	−6720(101)	215(37)
F(1)	−6202(59)	7765(62)	−5900(68)	394(33)
F(2)	−4665(52)	8106(56)	−7026(60)	329(26)
F(3)	−5498(52)	6475(66)	−6520(64)	351(30)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalised *U*(*i*, *j*) tensor.

TABLE II
Selected bond lengths (Å) and bond angles (deg.) for the complex

Bond lengths			
Fe-N(1)	1.88(2)	Fe-N(2)	1.91(2)
Fe-N(3)	1.89(1)	Fe-N(4)	1.92(2)
Fe-N(5)	1.91(1)	Fe-N(6)	1.91(2)
O(1)-N(4)	1.36(2)	O(1)-B(1)	1.46(3)
O(2)-N(5)	1.37(2)	O(2)-B(1)	1.47(3)
O(3)-N(1)	1.40(2)	O(3)-B(1)	1.50(2)
O(4)-N(2)	1.37(2)	O(4)-B(2)	1.47(3)
O(5)-N(6)	1.37(2)	O(5)-B(2)	1.49(2)
O(6)-N(3)	1.39(2)	O(6)-B(2)	1.55(3)
N(1)-C(25)	1.33(2)	N(2)-C(26)	1.26(3)
N(3)-C(26)	1.32(3)	N(4)-C(28)	1.26(2)
N(5)-C(29)	1.30(3)	N(6)-C(30)	1.24(2)
C(1)-C(2)	1.35(3)	C(1)-C(6)	1.38(3)
C(1)-B(1)	1.64(3)	C(2)-C(3)	1.42(4)
C(3)-C(4)	1.40(5)	C(4)-3(5)	1.29(4)
C(5)-C(6)	1.40(4)		
Bond angles			
N(1)-Fe-N(2)	78.0(7)	N(1)-Fe-N(3)	117.2(6)
N(2)-Fe-N(3)	86.6(6)	N(1)-Fe-N(4)	85.8(7)
N(2)-Fe-N(4)	150.0(6)	N(3)-Fe-N(4)	78.3(7)
N(1)-Fe-N(5)	86.0(6)	N(2)-Fe-N(5)	117.6(7)
N(3)-Fe-N(5)	150.3(6)	N(4)-Fe-N(5)	85.8(7)
N(1)-Fe-N(5)	149.8(8)	N(2)-Fe-N(6)	86.2(7)
N(3)-Fe-N(6)	87.0(7)	N(4)-Fe-N(6)	118.4(7)
N(5)-Fe-N(6)	78.7(7)	N(4)-O(1)-B(1)	111.0(16)
N(5)-O(2)-B(1)	110.9(13)	N(1)-O(3)-B(1)	110.0(15)
N(2)-O(4)-B(2)	114.5(15)	N(6)-O(5)-B(2)	114.0(15)
N(3)-O(6)-B(2)	112.9(12)	Fe-N(1)-O(3)	124.1(9)
Fe-N(1)-C(25)	120.8(15)	O(3)-N(1)-C(25)	113.5(15)
Fe-N(2)-O(4)	123.3(11)	Fe-N(2)-C(26)	118.5(16)
O(4)-N(2)-C(26)	116.7(15)	Fe-N(3)-O(6)	123.2(11)
Fe-N(3)-C(27)	121.5(11)	O(6)-N(3)-C(27)	114.1(13)
Fe-N(4)-O(1)	124.3(12)	Fe-N(4)-C(28)	116.1(14)
O(1)-N(4)-C(28)	118.4(18)	Fe-N(5)-O(2)	124.2(12)
Fe-N(5)-C(29)	117.8(14)	O(2)-N(5)-C(29)	116.7(12)
Fe-N(6)-O(5)	122.8(9)	Fe-N(6)-C(30)	118.7(17)
O(5)-N(6)-C(30)	117.1(20)	C(2)-C(1)-C(6)	119.4(21)
C(2)-C(1)-B(1)	120.3(21)	C(6)-C(1)-B(1)	120.1(19)

RESULTS AND DISCUSSION

The template cross-linking on an iron(II) ion of three phenylglyoxime molecules with two phenylboric acid molecules gives rise to a mixture of isomers which differ in the position of substituents in dioxime relative to the plane passing through the middle of C–C bonds in chelate rings and through the central iron atom (Figure 1). In a *fac* isomer, three identical substituents in dioxime fragments lie on one side of this plane, and in a *mer* isomer two substituents are on one side of the plane and the third on the other side. A purely statistical approach to complex formation leads to the conclusion that the *fac* isomer to *mer* isomer ratio must be 1:3. According to thin-layer silica gel chromatography data (eluant : chloroform-hexane, 1:7), a similar ratio of the isomers is observed in the case of the compound with methylglyoxime, $FeMm_3(BC_6H_5)_2$. For the $FePhm_3(C_6H_5)_2$ complex, chromatographic analysis showed a higher ratio for these isomers. This may be due to steric hindrance, observed in the case of the *fac* isomer owing to the repulsion between bulky phenyl substituents. Both isomers can be easily detected in the solution using NMR (^{13}C) spectroscopy. The signals from both types of azomethine carbon atoms consist of three lines. The least intense lines, which are at high field, belong to the *fac* isomer. The most intense middle lines relate to the type of azomethine carbon atoms on the *mer* isomer whose percentage in the molecule is higher. The third signal is due to azomethine carbon atoms of the other type in the same isomer.

X-ray structure analysis has shown that in the crystal lattice there are only molecules of *mer* isomers of two types, with different orientations of phenyl substituent in dioxime fragments. The inner coordination sphere of the central iron(II) ion is actually the same. The coordination polyhedron, intermediate between a trigonal prism and a trigonal antiprism, has a distortion angle φ of 21.8° (Figure 2).

The value of this angle for the $FePhm_3(BF)_2$ complex was estimated[2] from the quadrupole splitting (QS) value in Mössbauer (^{57}Fe) spectra (0.44 mm/s) to be 22–24°. The replacement of substituents in the cross-linking group does not usually affect the distortion angle value. QS in the spectrum of the compound

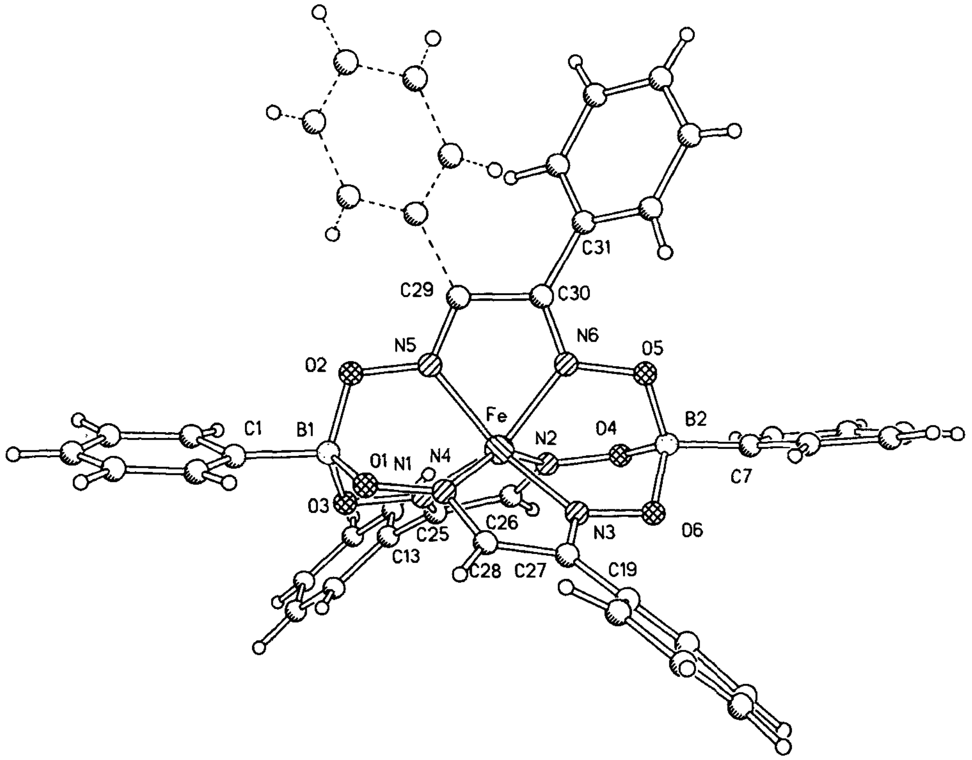

FIGURE 1 Perspective view of the $FePhm_3(BC_6H_5)_2$ molecule with the labelling scheme used.

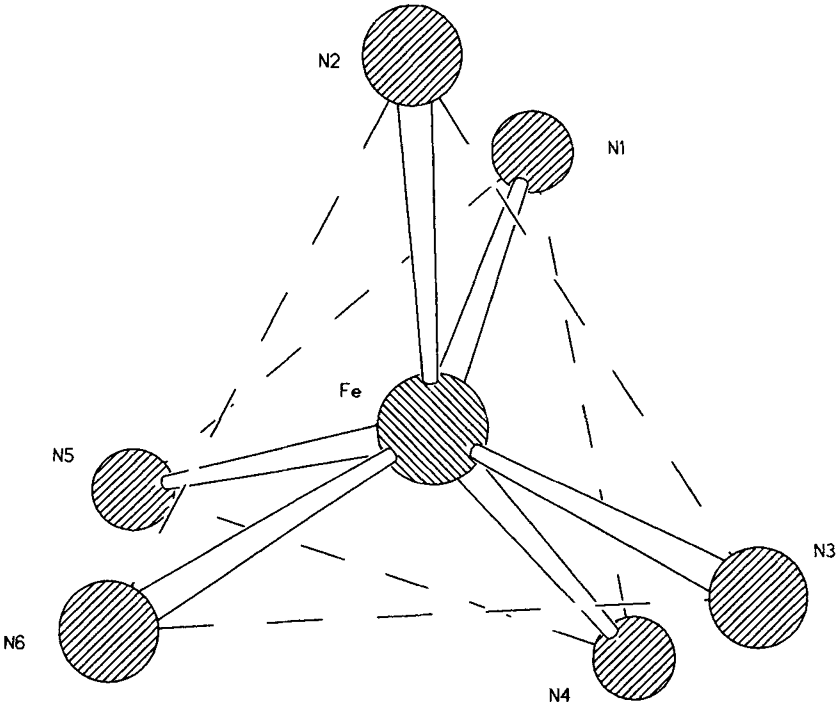

FIGURE 2 The geometry of the coordination polyhedron about the iron atom.

$FePhm_3(BC_6H_5)_2$ does not actually differ from the predicted[2] QS value for macrobicyclic boron-containing phenylglyoximate complexes. The QS values can be calculated for a complex using an equation containing geometrical parameters, found from X-ray structure data and the partial QS (PQS) value, which is 0.5 mm/s for compounds of this type[8]: $QS = f \cdot PQS = 18 - 12\cos^2 \alpha/(\cos^2(\varphi/2))$ where α is the bite angle, which is a half angle in the chelate ring. The calculated value $QS_{calc} = 0.40$ mm/s is slightly lower than that found experimentally.

The Fe–N distance and the bite angle α in the compound are typical for clathrochelate tris-dioximates (1.91 Å and 39.2°) and determine the distance between the trigonal prismatic polyhedron bases (2.34 Å), which corresponds to the given φ value.[6]

As in the case of the $FeBd_3(BF)_2 \cdot 5CHCl_3$ complex,[3] the presence of bulky phenyl substituents gives rise to significant steric hindrance in a dioxime fragment; the dihedral angles between the planes of these substituents and the chelate ring plane are in the range 31.1–42.1°.

The five-membered chelate rings are practically planar; the maximum displacements from the chelate ring plane are in the range 0.03–0.05 Å.

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SUPPLEMENTARY MATERIAL

Summary of data collection and reginement, tables of bond and angles, hydrogen atom parameters, anisotropic temperature factors and listings of observed and calculated structure factors are available from Dr Y.Z. Voloshin on request.

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