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Macrobicyclic d-metal tris-dioximates obtained by cross-linking with p-block elements

Part IV. Crystalline and molecular structure of an iron(II) complex with macrobicyclic fluoroborate-containing tris-diphenylglyoximate ligand and its Mössbauer (^{57}Fe) parameters

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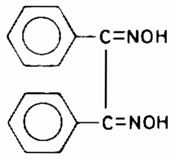
Abstract

Hexagonal $FeBd_3(BF)_2 \cdot 5CHCl_3$ single crystals (space group $P6_3$, $a = 14.975(2)$, $c = 16.301(3)$ Å, $V = 3166(1)$ Å^3, $Z = 2$) have been obtained by recrystallizing a preliminarily synthesized clathrochelate diphenylglyoximate complex. The iron atom is encapsulated by the macrobicyclic ligand and surrounded by a distorted trigonal prismatic coordination consisting of six nitrogen atoms. The distortion angle value found experimentally (*c.* 29.3°) is close to that estimated earlier from Mössbauer parameters (27–30°). The Fe–N bond length (1.91(2) Å) is characteristic of clathrochelate boron-containing iron(II) dioximates and is determined by the superposition of the contributions of metal eletron configuration and ligand geometry.

Introduction

The application of correlations such as 'structure-spectral parameter' permits one to predict in many cases the structure of coordination compounds belonging to one type. To do this, data on the molecular structure of individual representatives of this type or data on the structure of complexes of closely related types in combination with the results of spectroscopic studies are used. The most comprehensive information on the geometry of the coordination polyhedron for iron(II) complexes can be obtained from Mössbauer (^{57}Fe) spectra in which quadrupole splitting (QS) characterizes the electric field gradient on the iron atom nucleus, which was induced by the nearest coordination. It was proposed to use the value of QS (with allowance for its sign) to predict the structure of coordination polyhedron in iron(II) tris-dioximates [1]. More recently, the values of the φ angle characterizing the distortion of the trigonal prismatic coordination consisting of six nitrogen atoms of three dioxime fragments about the Fe^{2+} ion (the value $\varphi = 0°$ corresponds to a trigonal prism of D_{3h} symmetry), which were calculated using a correlation, were rendered more precise using structure data, obtained by an X-ray structural analysis, for one of the clathrochelate alicyclic tris-dioximates [2, 3]. The same studies suggested that the distortion angle value is much higher for macrobicyclic complexes with aromatic dioximes than for aliphatic dioximates, resulting in QS decrease in Mössbauer spectra.

To check whether it is possible to use the QS–φ correlation to determine the geometry of the coordination polyhedron, we carried out an X-ray structural investigation of the clathrochelate $^{57}FeBd_3(BF)_2 \cdot 5CHCl_3$complex formed by an aromatic diphenylglyoxime (α-benzyldioxime, I)



H_2Bd

α-benzyldioxim

I

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Experimental

$^{57}FeBd_3(BF)_2 \cdot 5CHCl_3$ (**A**) single crystals were obtained by boiling down a saturated $^{57}FeBd_3(BF)_2$ complex solution in a chloroform–carbon tetrachloride (1:1) mixture for several weeks. The $^{57}FeBd_3(BF)_2$ complex was synthesized by the method reported in ref. 4 using an iron salt containing ^{57}Fe isotope as the starting material.

The unit cell parameters and the intensities of 3203 unique reflections of **A** were measured at −120 °C with an automatic four-circle Syntex $P2_1$ diffractometer. Crystals of **A** were hexagonal, $a = 14.975(2)$, $c = 16.301(3)$ Å, $V = 3166(1)$ Å^3, space group $P6_3$, $Z = 2(FeC_{42}H_{30}B_2F_2N_6O_6 \cdot 5\ CHCl_3)$. The structure was determined by the heavy atom method and refined in an anisotropic approximation for the atoms molecule **A**. The atomic coordinates are given in Table 1. The chloroform solvate molecules were found in a difference Fourier synthesis and refine anisotropically with the exception of the C(10), Cl(1C), Cl(1D), Cl(1G), Cl(1H) and C(30) atoms, which were refined isotropically. The site occupation factors for the atoms of disordered solvate molecules were selected empirically. The positions of the H atoms in the phenyl groups were calculated geometrically and recalculated after each cycle of least-squares procedure. The H atoms of the chloroform molecules were not included in the calculations. The final discrepancy factors are: $R = 0.133$, $R_w = 0.138$ for 1241 unique reflections with $I > 2\sigma$.

The molecule **A** as well as the solvate molecules $C(20)HCl_3$ and $C(30)HCl_3$ occupy special positions on the three-fold axis. The atoms of the $C(20)HCl_3$ molecule were refined with the occupation factor $G = 0.667$, and the $C(30)HCl_3$ molecule with the Cl atoms disordered over the two positions Cl(31) and Cl(32) was refined with $G = 0.4$ for one and $G = 0.24$ for another orientation. The third chloroform molecule is in a general position and is disordered over four positions, the positions of the Cl(1A) and Cl(1B) atoms ($G = 0.333$) being common for one pair of positions, which differ in the location of the third Cl atom − Cl(1C) or Cl(1D) ($G = 0.167$). Similarly, Cl(1E) and Cl(1F) ($G = 0.333$) are common for another pair of positionsl; the third Cl atom is disordered over the positions Cl(1G) and Cl(1H) ($G = 0.167$). The overall occupation factor for all chloroform molecules is *c*. 2/3, which may be due to a partial desolvation of the crystals investigated.

The Mössbauer (^{57}Fe) spectra of the $^{57}FeBd_3(BF)_2 \cdot 5CHCl_3$ single crystal were obtained on a YGRS-4M spectrometer with a ^{57}Co source in a chromium matrix at $T = 300$ K relative to sodium nitroprusside.

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($A^2 \times 10^3$)

	x	*y*	*z*	U_{eq}[a]
Fe	3333	6667	1000	42(2)
F(1)	3333	6667	3673(20)	68(10)
F(2)	3333	6667	−1657(14)	59(9)
B(1)	3333	6667	2817(20)	30(12)
B(2)	3333	6667	−804(55)	79(30)
O(1)	3887(11)	7761(11)	2543(10)	49(8)
O(2)	4369(14)	7493(13)	−540(10)	57(9)
N(1)	4030(12)	7839(10)	1700(10)	31(7)
N(2)	4398(13)	7620(16)	297(12)	44(10)
C(1)	4852(17)	8614(16)	1471(12)	29(11)
C(2)	5029(16)	8564(20)	566(20)	63(12)
C(11)	5598(16)	9511(16)	1913(17)	48(10)
C(12)	5217(22)	10047(22)	2526(19)	83(15)
C(13)	5888(27)	10833(21)	2969(18)	74(17)
C(14)	6964(27)	11251(24)	2916(14)	78(19)
C(15)	7225(26)	10805(24)	2459(23)	96(18)
C(16)	6639(23)	9969(21)	2004(19)	75(16)
C(21)	5730(23)	9399(29)	19(17)	83(19)
C(22)	5803(21)	10437(25)	90(16)	70(17)
C(23)	6441(31)	11263(23)	−413(25)	214(26)
C(24)	6961(33)	10925(55)	−1117(26)	251(51)
C(25)	6909(29)	10090(23)	−1113(24)	74(18)
C(26)	6396(23)	9388(24)	−588(19)	72(17)
C(10)	7330(66)	10204(67)	5799(60)	186(35)
Cl(1A)	7070(17)	8791(11)	5526(16)	78(9)
Cl(1B)	8968(12)	10774(16)	5465(18)	66(9)
Cl(1C)	7057(33)	10688(33)	5044(28)	56(11)
Cl(1D)	7263(31)	10177(34)	6697(28)	60(10)
Cl(1E)	7306(16)	10826(17)	6256(26)	120(18)
Cl(1F)	6951(16)	10152(19)	4617(17)	78(13)
Cl(1G)	6186(50)	8754(50)	5925(52)	131(21)
Cl(1H)	8672(57)	10317(58)	5662(45)	114(26)
C(20)	3333	6667	6439(51)	77(28)
Cl(21)	4522(12)	7589(12)	6187(17)	149(11)
C(30)	0	0	−2013(56)	88(24)
Cl(31)	−997(15)	−1107(21)	−1523(29)	180(21)
Cl(32)	−441(39)	389(54)	−2734(47)	227(51)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Results and discussion

Despite the fact that the results of the X-ray structural analysis are not quite satisfactory (due to a partial desolvation of crystals, see 'Experimental'), the data obtained on the structure of the coordinate polyhedron enable necessary conclusions to be drawn. First of all, it was found that the iron(II) ion is encapsulated by a macrobicyclic ligand (Fig. 1). The Fe–N bond length 1.91 Å, Table 2) agrees with the data on this bond length in the clathrochelate tris-heptoximate $FeGx_3(BOH)_2 \cdot 3H_2O$ [2, 3], where Gx^{2-} = cycloheptandion-1,2-dioxime anione (II).

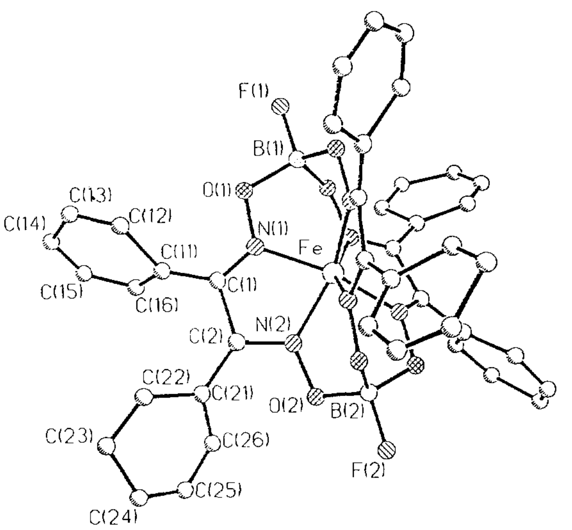
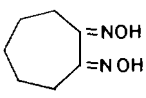


Fig. 1. Perspective view of $FeBd_3(BF)_2$ with the labelling scheme used. H atoms have been omitted.



H_2Gx
heptoxime

II

TABLE 2. Selected bond lengths and angles

Bond lengths (A)	
Fe–N(1)	1.908 (14)
Fe–N(2)	1.902(16)
Fe–N(1A)	1.908 (15)
Fe–N(1B)	1.908(10)
Fe–N(2A)	1.902 (24)
Fe–N(2B)	1.902(14)
B(1)–O(1)	1.487 (18)
B(1)–O(1A)	1.487(18)
B(1)–O(1B)	1.488 (11)
B(2)–O(2)	1.484(32)
B(2)–O(2A)	1.484 (36)
B(2)–O(2B)	1.484(32)
O(1)–N(1)	1.385 (24)
O(2)–N(2)	1.376(25)
N(1)–C(1)	1.254 (22)
N(2)–C(2)	1.322(31)
C(1)–C(2)	1.508 (38)
C(1)–C(11)	1.439(27)
C(2)–C(21)	1.466 (39)
Bond angles (°)	
N(1)–Fe–N(2)	78.6(8)
N(1)–Fe–N(1A)	87.9(6)
N(2)–Fe–N(1A)	155.6(10)
N(1)–Fe–N(1B)	87.9(7)
N(2)–Fe–N(1B)	111.6(9)
N(1A)–Fe–N(1B)	87.9(7)
N(1)–Fe–N(2A)	111.6(8)
N(2)–Fe–N(2A)	87.4(7)
N(1A)–Fe–N(2A)	78.6(8)
N(1B)–Fe–N(2A)	155.6(7)
N(2A)–Fe–N(2B)	87.4(8)
Fe–N(1)–O(1)	121.6(10)
Fe–N(1)–C(1)	120.3(15)
O(1)–N(1)–C(1)	114.3(15)
Fe–N(2)–O(2)	122.5(12)
Fe–N(2)–C(2)	119.0(18)
O(2)–N(2)–C(2)	115.6(20)
N(1)–C(1)–C(2)	111.1(17)
N(2)–C(2)–C(1)	109.2(20)

Such a Fe–N distance appears to be optimal for macrobicylic boron-containing iron(II) tris-dioximates and independent of the nature of dioxime. This is also confirmed by EXAFS data, which were obtained for a number of complexes of this type [5]. The size of the macrobicyclic ligand cavity is 'matched' to the iron(II) ion size by the rotational-translational change of the geometry of the coordination polyhedron-trigonal prism about the axis of three-fold symmetry.

The distortion angle φ of the trigonal prismatic coordination consisting of six atoms of three dioxime groups about the central ion is 29.3° for the $FeBd_3(BF)_2 \cdot 5CHCl_3$ complex. It is substantially higher than with the alicyclic $FeGx_3$ $(BOH)_2 \cdot 3H_2O$ heptoximate ($\varphi = 23{,}5°$), as was predicted for aromatic dioximates [2].

The distance between the prism bases decreases from 2.33 to 2.29 Å with increasing distortion angle on passing from heptoximate to α-benzyldioximate. As a result, the Fe–N distance does not change and remains optimal. The φ angle value determined objectively in the crystal is in the range 27–30° which was predicted earlier from the dependence of *QS* in Mössbauer (^{57}Fe) spectra on φ [2]. The Mössbauer parameters of the $^{57}FeBd_3(BF)_2 \cdot 5CHCl_3$ single crystal (isomeric shift (*IS*): 0.31 mm/s; *QS*: 0.26 mm/s) practically coincide with the values obtained for the non-solvated $FeBd_3(BF)_2$ complex (*IS*:0.32mm/s; *QS*: 0.25 mm/s). Thus, the quadrupole splitting–distortion angle correlation proposed in ref. 2 allowed the geometry of the coordination polyhedron to be predicted with sufficient accuracy and may be used to predict the structure of compounds of this type.

The presence of bulky phenyl substituents gives rise to significant steric hindrances in a dioxime fragment: the dihedral angles between the planes of these substituents and the chelate ring plane are 47.7 and 45.2°. The dihedral angle between the planes of the phenyl groups is 62.9°. The consequence of steric hindrances is a substantially greater deviation of the dioxime fragment from planarity in an α-benzyldioximate complex as compared with a macrobicyclic heptoximate. In the former case, the chelate ring distortion is *c.* 0.07 Å and in the latter *c.* 0.05–0.06 Å.

The oxygen atoms of the dioxime groups in the $FeBd_3(BF)_2 \cdot 5CHCl_3$ molecule are displaced from the chelate ring plane by 0.241 (O(1)) and 0.258 (O(2)) Å to the opposite side. The oxygen atoms in the $FeGx_3(BOH)_2 \cdot 3H_2O$ molecule are displaced from the planes of the chelate rings by 0.080–0.186 Å [3]. The significant displacement of the oxygen atoms, as is reported in ref. 2, makes it possible to 'cross-link' three aromatic dioxime molecules at large angles of rotation and results in a more trigonal-antiprismatic structure.

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