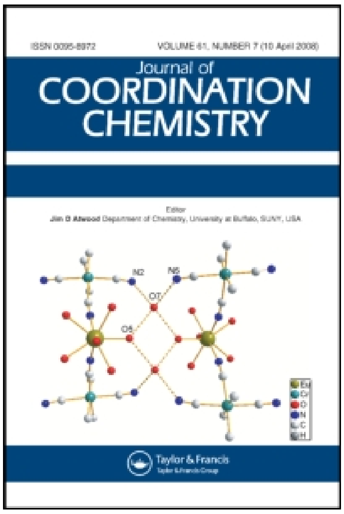

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MACROBICYCLIC D-METAL TRIS-DIOXIMATES OBTAINED BY CROSS-LINKING WITH P-BLOCK ELEMENTS. PART VI. PREPARATION, MOLECULAR STRUCTURE AND MÖSSBAUER (^{57}FE, ^{119}SN) PARAMETERS OF AN IRON(II) COMPLEX WITH A MACROBICYCLIC TIN-CONTAINING TRIS-NIOXIMATE LIGAND

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The tin-containing clathrochelate complex of Fe(II) with cyclohexanedione-1,2-dioxime (nioxime, H_2Nx), $[FeNx_3(SnCl_3)_2]^{2-}\cdot(Et_2NH_2^+)_2\cdot Et_2NH_2^+\cdot Cl^-\cdot 2Pr^iOH$ was prepared by slowly adding diethylamine to a solution containing the macrobicyclic $[FeNx_3(SnCl_3)_2]^{2-}$ anion. The structure of the complex has been determined by X-ray methods. Crystal data: monoclinic, space group $P2_1/c$, $a = 10.565(2)$, $b = 25.413(5)$, $c = 20.198(4)$Å, $\beta = 95.40(3)°$, $Z = 4$. The iron atoms is encapsulated by the clathrochelate ligand and surrounded by a distorted trigonal antiprismatic coordination sphere comprising by six nitrogen atoms of three dioxime residues. The experimental value of the distortion angle (*ca* 37.5°) is close to that predicted by the Mössbauer (^{57}Fe) parameters (*ca* 40°). The average Fe-N bond length of 1.923Å is somewhat greater than that in boron-containing analogues. The Sn atoms have a slightly distorted octahedral coordination, which also correspond to Mössbauer (^{119}Sn) spectroscopic data. The six-membered carbocycles in the dioxime fragments have a half-chair conformation with both β-carbons displaced to the opposite sides of the mid-plane of the remaining atoms. All the active hydrogen atoms of the structure are involved in a hydrogen bond system.

The possibilities of use of Mössbauer parameters and their temperature dependences to determine the geometry of iron(II) tris-dioximates and the sign of Δ in Mössbauer (^{57}Fe) spectra are discussed.

KEY WORDS: Macrobicyclic complexes, X-ray structure, Mössbauer (^{57}Fe, ^{119}Sn) data.

INTRODUCTION

The geometry of the coordination polyhedron in iron(II) tris-complexes with nitrogen-containing ligands is an intermediate one between the trigonal prism (TP) and the trigonal antiprism (TAP), and is described by the distortion angle ϕ (0°

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corresponds to TP, 60° to TAP). A dependence was suggested on the amount of t_{2g} level splitting and Δ in Mössbauer (^{57}Fe) spectra, which characterizes electron density gradient on the iron atom nucleus, with respect to ϕ.[1] This permits one to determine with a high accuracy ϕ values if the signs and values of Δ are known.

When the geometry of the coordination polyhedron is close to TP, Δ has a positive sign and a high value (~1 mm/s). In complexes with TAP geometry Δ has a low value and a negative sign. In terms of this dependence, macrobicyclic boron-containing iron(II) tris-dioximates have a trigonal-prismatic structure ($\phi = 20$–$30°$). The spectroscopic results were confirmed later by an X-ray study of the structure of their complexes.[2,3] The validity of such an approach has been recently confirmed by data obtained concerning the crystal and molecular structure of the $FeBd_3(BF)_2 \cdot 5CHCl_3$ complex (Bd^{2-} is diphenylglyoxime dianion). The value of the distortion angle in this complex is 29.3°,[3] whereas it was estimated[1] to be 27–30°.

At the same time, the prediction of the coordination polyhedron geometry in the case of boron-containing clathrochelate complexes was facilitated by knowledge of the fact that Δ had a positive sign. However, for tin-containing Fe(II) tris-dioximates, the sign of Δ is not clear and its determination is difficult. The Δ values in the Mössbauer (^{57}Fe) spectra for tin-containing complexes are low and decrease in the dioxime series in an order which differs greatly from that observed in the case of $FeD_3(BR)_2$ compounds: Δ in the spectrum of the diphenylglyoximate complex $(HDEA)_2[FeBd_3(SnCl_3)_2]$ is, in particular, greater than that in the spectra of most tin-containing complexes with acyclic and alicyclic dioximes.[4]

At the same time, the Δ values observed for the boron-containing dioximate, $FeBd_3(BF)_2$, are much lower than in the spectra of boron-containing complexes with aliphatic dioximes. The higher distortion angle value for compounds with aromatic dioximes is due to steric hindrance arising from the formation of these complexes. In the spectra of boron-containing clathrochelates with a positive sign of Δ, this leads to a decrease in the absolute Δ value. An increase in Δ (absolute value) with increasing distortion angle can only occur if there is an inversion of the e_1 and a_1 levels; as a result, Δ assumes a negative sign.[1]

Along with ther data, this permits one to suppose that Δ in the case of (amine $H^+)_2[FeD_3(SnCl_3)_2]$ complexes (D^{2-} is a dioxime dianion) has a negative sign and corresponds to distortion angles (ϕ) of 40–55°. This indicates the coordination polyhedron to have trigonal-antiprismatic and close to octahedral geometry. In this case, the minimum distortion angle value (~40°) relates to nioximate complexes, whose spectra exhibit the lowest Δ value.[4]

To confirm the suggestions made, an X-ray study of a tin-containing macrobicyclic Fe(II) tris-nioximate complex (I) was carried out.

EXPERIMENTAL

Materials and Apparatus

Preparation

Single crystals of $[FeNx_3(SnCl_3)_2]^{2-}.(Et_2NH_2^+)_2 \cdot Et_2NH_2^+ \cdot Cl^- \cdot 2Pr^iOH$(I) were prepared by slowly precipitating, *via* the vapour phase, for several weeks complex (I) in a dissicator with two inner cells, the first containing an *iso*-propanol (20 cm^3) solution of $FeCl_2 \cdot 4H_2O$, (0.33 g, 1.7 mmol), nioxime (0.71 g, 5.0 mmol) and $SnCl_4$ (0.38 ml, 3.3 mmol) and the second, diethylamine (5 cm^3, 0.53 g, 24%).

Anal. Calc. for $C_{36}H_{67}N_9O_8Cl_7Fe$: C, 33.35; H, 5.2; N, 9.7; Cl, 19.2%. Found: C, 33.5; H, 5.1; N, 9.7; Cl, 19.4%. ν_{max}/cm^{-1} (C=N) 1570s, (N-O) 968s and 1048vs, (Sn-Cl) 312vs, (Md-Lπ^*) 17.94 10^3, 20.88 10^3, (π-π^*) 33.56 10^3; δ_{1H}(CD_3CN) 1.56, 1.82 (12 H, m, β-CH_2) and 2.49, 2.95 (12 H, m, α-CH_2); δ_{13C}(CD_3CN) 21.20 (6 C, s, β-CH_2), 26.15 (6 C, s, α-CH_2) and 155.88 ppm (6 C, s, C=N). The crystals obtained had a size (0.2 × 0.3 × 0.5 mm) and quality suitable for an X-ray diffraction study.

Crystal Data

$C_{36}H_{67}N_9O_8Cl_7Fe$, M = 1295.4, monoclinic, a = 10.565(2), b = 25.413(5), c = 20.198(4)Å, β = 95.40(3)°, U = 5399(2)Å^3 (by least-squares refinement of diffractometer angles for 24 automatically centred reflections, λ = 0.71069Å), space group $P2_1/c$, Z = 4, D_c = 1.594 g cm^{-3}, $F(000)$ = 2620. Dark red, air-unstable tablets; μ(MoK_α) = 15.87 cm^{-1}.

Data Collection and Refinement

The X-ray diffraction data were measured at 183 K (also for decomposition protection) on a four-circle automated Siemens P3/PC diffractometer equipped with a graphite monochromator. The unit cell dimensions were determined from 2θ measurements of 24 carefully centred reflections and refined by least-squares methods. Intensity data were collected in the ω-2θ mode with a scan range of 1.8° to a maximum 2θ value of 60°. The scan rate varied between 3.0–30.0° min^{-1} according to the detected intensity. The intensity of two check reflections showed no decay over the period of data collection. The intensities were corrected for Lorentz and polarization effects but not for absorption or secondary extinction (the linear absorbtion coefficient is relatively small). Some 10087 reflections were recorded, of which 9547 were unique, and 6476 with $I > 2.5\sigma(I)$ were used in the calculation.

The structure was solved by direct methods and refined by least-squares procedures in an anisotropic approximation for nonhydrogen atoms was adopted. The refinement revealed a disorder of both carbon β-atoms in one of the six-membered carbocycles of the complex dianion. We managed to resolve this disorder: the atoms in the C(112) and C(212) positions were refined isotropically with an occupancy (G) of 2/3 and those in the corresponding alternative C(113) and C(213) positions with G = 1/3. A disorder of *iso*-propanol solvate molecules was also found, but only for the α-carbon atoms two positions were resolved: C(1X) with G = 2/3 and C(1XA) with G = 1/3.

The initial positions of hydrogen atoms were calculated (except for the disordered *iso*-propanol molecule) and refined in an isotropic approximation with fixed U_{iso} = 0.06Å^2 for the complex dianion and 0.08Å^2 for the remaining atoms. We failed to localize the hydroxylic hydrogen atoms in difference Fourier syntheses.

The final values of the discrepancy factors are: R = 0.046, R_w = 0.056 for 6476 reflections (number of parameters refined = 766). The weighting scheme $w^{-1} = \sigma^2(F) + 0.0006F^2$ was used. Largest difference peak 0.91e/Å^3, largest difference minimum −1.16e/Å^3. A summary of crystal and refinement parameters is given in Table 1. All calculations were performed on an IBM-PC/AT computer using SHELXTL PLUS programs.

The structure of complex dianion (I) is shown in Figure 1, the coordinates of the nonhydrogen atoms are given in Table 2, and selected bond lengths and angles are listed in Tables 3 and 4.

Mössbauer data were recorded as described[4] previously.

Table 1 Structure determination summary

Empirical Formula	$C_{36}H_{67}N_9O_8Cl_7FeSn_2$
Space Group	$P2_1/c$
Unit Cell Dimensions	$a = 10.565(2)$Å $b = 25.413(5)$Å $c = 20.198(4)$Å $\beta = 95.40(3)°$
V	5399(2)Å^3
Z	4
Formula weight	1295.4
Density (calc.)	1.594 Mg/m^3
Absorption Coefficient	1.587 mm^{-1}
$F(000)$	2620
2θ Range	4.0 to 60.0°
Scan Type	2θ-θ
Scan Speed	Variable; 3.00 to 30.00°/min. in ω
Scan Range (ω)	1.80° plus Kα-separation
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 16.5% of total scan time
Standard Reflections	2 measured every 98 reflections
Index Ranges	$0 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 30 - 24 \leqslant l \leqslant 23$
Reflections Collected	10087
Independent Reflections	9547 ($R_{int} = 3.22\%$)
Observed Reflections	6476 ($F > 5.0\sigma(F)$)
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0006F^2$
Number of parameters refined	766
Final R indices (obs. data)	$R = 4.60\%$, $R_w = 5.55\%$
R Indices (all data)	$R = 8.82\%$, $R_w = 6.37\%$

Table 2 Atom coordinates ($\times 10^4$) and temperature factors (Å$^2 \times 10^3$)

Atom	x/a	y/b	z/c	U
Fe	−0.4(0.8)	5733.1(0.3)	2917.4(0.4)	19(1)*
Sn(1)	2079.3(0.4)	6449.1(0.2)	4119.6(0.2)	23(1)*
Sn(2)	−2073.5(0.4)	4991.8(0.2)	1735.7(0.2)	26(2)*
Cl(11)	3034.7(1.6)	7272.6(0.7)	3859.2(0.9)	35(1)*
Cl(12)	4030.6(1.6)	6055.7(0.7)	4582.5(0.8)	36(1)*
Cl(13)	1428.8(1.8)	6790.7(0.7)	5136.9(0.8)	40(1)*
Cl(21)	−4028.1(1.7)	5371.1(0.7)	1232.6(0.9)	39(1)*
Cl(22)	−1519.5(2.0)	4639.6(0.8)	709.1(0.9)	44(1)*
Cl(23)	−3078.0(1.8)	4192.9(0.6)	2055.3(0.9)	34(1)*
O(11)	1007(4)	5792(2)	4323(2)	25(1)*
O(12)	478(4)	6767(2)	3552(2)	23(1)*
O(13)	2618(4)	6099(2)	3248(2)	25(1)*
O(21)	−312(4)	4740(2)	2167(2)	29(1)*
O(22)	−2555(4)	5268(2)	2661(2)	26(1)*
O(23)	−1267(4)	5717(2)	1551(2)	27(1)*
N(11)	649(5)	5479(2)	3777(2)	21(2)*
N(12)	−398(5)	6398(2)	3308(2)	21(2)*
N(13)	1652(5)	5993(2)	2766(2)	20(2)*
N(21)	105(5)	4987(2)	2753(3)	24(2)*
N(22)	−1806(5)	5675(2)	2926(2)	20(2)*
N(23)	−212(5)	5848(2)	1969(3)	22(2)*
C(11)	868(6)	4984(2)	3844(3)	22(2)*
C(111)	1456(7)	4719(3)	4470(3)	34(2)*

Table 2 *Continued*

Atom	*x/a*	*y/b*	*z/c*	*U*
C(112)	1226(13)	4137(5)	4480(7)	44(3)
C(113)	1797(25)	4131(9)	4314(12)	37(6)
C(21)	497(6)	4688(2)	3253(3)	25(2)*
C(211)	546(7)	4104(3)	3229(4)	35(2)*
C(212)	1399(13)	3887(5)	3839(6)	45(3)
C(213)	689(26)	3851(10)	3856(12)	42(6)
C(12)	−1584(6)	6488(3)	3412(3)	24(2)*
C(121)	−2049(6)	6954(3)	3767(4)	31(2)*
C(122)	−3443(7)	6901(3)	3884(4)	39(3)*
C(22)	−2426(6)	6070(2)	3153(3)	22(2)*
C(221)	−3836(6)	6132(3)	3132(4)	32(2)*
C(222)	−4208(7)	6686(3)	3265(4)	39(3)*
C(13)	1861(6)	6120(2)	2163(3)	25(2)*
C(131)	3060(6)	6362(3)	1965(3)	33(2)*
C(132)	2939(8)	6511(4)	1234(4)	48(3)*
C(23)	785(6)	5997(2)	1685(3)	24(2)*
C(231)	901(7)	6028(3)	953(3)	36(2)*
C(232)	2280(8)	6085(4)	811(4)	49(3)*
Cl	2523(2)	1682(1)	6962(2)	83(1)*
O(1)x	4558(6)	1319(2)	8102(3)	61(2)*
C(1)x	4784(17)	1856(6)	8310(8)	71(4)
C(1x)a	5600(28)	1731(11)	8420(14)	52(7)
C(2)x	5074(15)	1882(6)	9009(7)	113(6)*
C(3)x	5786(13)	2085(5)	7890(8)	109(6)*
O(1)y	−2215(6)	6422(2)	559(3)	49(2)*
C(1)y	−2124(11)	6896(3)	951(4)	58(4)*
C(2)y	−2883(16)	6876(5)	1507(7)	93(6)*
C(3)y	−2245(15)	7354(4)	508(6)	83(5)*
C(1)a	5300(30)	3422(10)	562(17)	196(16)*
C(2)a	4978(18)	3895(8)	464(7)	136(8)*
N(3)a	3472(8)	3921(5)	629(5)	89(4)*
C(4)a	3122(13)	4460(6)	674(7)	103(6)*
C(5)a	1800(16)	4507(4)	783(7)	83(5)*
C(1)b	380(17)	7555(6)	2056(6)	93(6)*
C(2)b	971(9)	7915(4)	2593(4)	52(3)*
N(3)b	314(7)	7898(2)	3207(4)	39(2)*
C(4)b	788(8)	8296(3)	3709(5)	44(3)*
C(5)b	243(12)	8182(5)	4354(6)	66(4)*
C(1)c	−2638(9)	4509(4)	3996(5)	52(3)*
C(2)c	−3980(8)	4709(3)	3968(4)	42(3)*
N(3)c	−4588(6)	4705(2)	3271(3)	30(2)*
C(4)c	−5899(7)	4928(3)	3191(4)	36(3)*
C(5)c	−6454(8)	4877(3)	2473(4)	40(3)*

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

RESULTS AND DISCUSSION

The X-ray structural analysis of complex (I) is the first study in this kind for tin-containing clathrochelate complexes. It is also the first example in which the coordination polyhedron geometry of a macrobicyclic iron(II) tris-dioximate is observed to be more close to TAP than to TP. A similar coordination environment

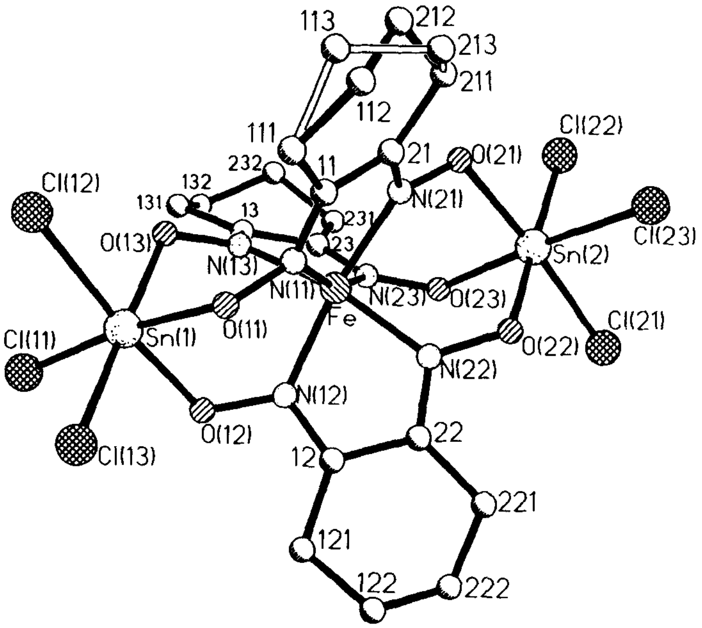

Figure 1 Perspective view of $[FeNx_3(SnCl_3)_2]^{2-}$ anion with the labelling scheme used. H atoms have been omitted for clarity.

Table 3 Selected bond lengths (Å)

Fe-N(11)	1.918(5)	Fe-N(12)	1.927(5)
Fe-N(12)	1.917(5)	Fe-N(21)	1.929(5)
Fe-N(22)	1.915(5)	Fe-N(23)	1.930(5)
Sn(1)-Cl(11)	2.403(2)	Sn(1)-Cl(12)	2.400(2)
Sn(1)-Cl(13)	2.390(2)	Sn(1)-O(11)	2.081(4)
Sn(1)-O(12)	2.113(4)	Sn(1)-O(13)	2.098(4)
Sn(2)-Cl(21)	2.415(2)	Sn(2)-Cl(22)	2.381(2)
Sn(2)-Cl(23)	2.407(2)	Sn(2)-O(21)	2.081(4)
Sn(2)-O(22)	2.104(4)	Sn(2)-O(23)	2.079(4)
O(11)-N(11)	1.381(6)	O(12)-N(12)	1.376(6)
O(13)-N(13)	1.369(6)	O(21)-N(21)	1.376(7)
O(22)-N(22)	1.378(6)	O(23)-N(23)	1.375(6)
N(11)-C(11)	1.285(8)	N(12)-C(12)	1.310(8)
N(13)-C(13)	1.299(8)	N(21)-C(21)	1.299(8)
N(22)-C(22)	1.305(8)	N(23)-C(23)	1.303(8)
C(11)-C(111)	1.514(9)	C(11)-C(21)	1.434(9)
C(111)-C(112)	1.50(1)	C(111)-C(113)	1.57(3)
C(112)-C(113)	0.72(3)	C(112)-C(212)	1.47(2)
C(112)-C(213)	1.52(3)	C(113)-C(212)	1.19(3)
C(113)-C(213)	1.59(4)	C(21)-C(211)	1.486(9)
C(211)-C(212)	1.56(1)	C(211)-C(213)	1.42(3)
C(212)-C(213)	0.76(3)		

Table 4 Selected bond angles (deg)

N(11)-Fe-N(12)	89.8(2)	N(11)-Fe-N(13)	90.4(2)
N(12)-Fe-N(13)	90.0(2)	N(11)-Fe-N(21)	78.7(2)
N(12)-Fe-N(21)	161.7(2)	N(13)-Fe-N(21)	104.1(2)
N(11)-Fe-N(22)	103.8(2)	N(12)-Fe-N(22)	79.0(2)
N(13)-Fe-N(22)	161.9(2)	N(21)-Fe-N(22)	89.9(2)
N(11)-Fe-N(23)	161.4(2)	N(12)-Fe-N(23)	105.4(2)
N(13)-Fe-N(23)	79.2(2)	N(21)-Fe-N(23)	88.9(2)
N(22)-Fe-N(23)	89.9(2)	Cl(11)-Sn(1)-Cl(12)	94.9(1)
Cl(11)-Sn(1)-Cl(13)	91.9(1)	Cl(12)-Sn(1)-Cl(13)	97.0(1)
Cl(11)-Sn(1)-O(11)	171.9(1)	Cl(12)-Sn(1)-O(11)	93.0(1)
Cl(13)-Sn(1)-O(11)	85.2(1)	Cl(11)-Sn(1)-O(12)	83.1(1)
Cl(12)-Sn(1)-O(12)	170.1(1)	Cl(13)-Sn(1)-O(12)	92.7(1)
O(11)-Sn(1)-O(12)	89.5(2)	Cl(11)-Sn(1)-O(13)	91.9(1)
Cl(12)-Sn(1)-O(13)	81.9(1)	Cl(13)-Sn(1)-O(13)	176.2(1)
O(11)-Sn(1)-O(13)	91.2(2)	O(12)-Sn(1)-O(13)	88.5(2)
Cl(21)-Sn(2)-Cl(22)	93.1(1)	Cl(21)-Sn(2)-Cl(23)	93.9(1)
Cl(22)-Sn(2)-Cl(23)	93.8(1)	Cl(21)-Sn(2)-O(21)	174.3(1)
Cl(22)-Sn(2)-O(21)	88.0(1)	Cl(23)-Sn(2)-O(21)	91.6(1)
Cl(21)-Sn(2)-O(22)	88.4(1)	Cl(22)-Sn(2)-O(22)	177.4(1)
Cl(23)-Sn(2)-O(22)	83.9(1)	O(21)-Sn(2)-O(22)	90.7(2)
Cl(21)-Sn(2)-O(23)	85.4(1)	Cl(22)-Sn(2)-O(23)	92.2(1)
Cl(23)-Sn(2)-O(23)	173.9(1)	O(21)-Sn(2)-O(23)	89.0(2)
O(22)-Sn(2)-O(23)	90.1(2)	Sn(1)-O(11)-N(11)	114.7(3)
Sn(1)-O(12)-N(12)	114.3(3)	Sn(1)-O(13)-N(13)	115.9(3)
Sn(2)-O(21)-N(21)	114.9(3)	Sn(2)-O(22)-N(22)	114.6(4)
Sn(2)-O(23)-N(23)	115.2(3)	Fe-N(11)-O(11)	125.2(4)
Fe-N(11)-C(11)	118.1(4)	O(11)-N(11)-C(11)	116.5(5)
Fe-N(12)-O(12)	125.4(4)	Fe-N(12)-C(12)	117.9(4)
O(12)-N(12)-C(12)	116.4(5)	Fe-N(13)-O(13)	125.7(4)
Fe-N(13)-C(13)	118.2(4)	O(13)-N(13)-C(13)	115.9(5)
Fe-N(21)-O(21)	125.3(4)	Fe-N(21)-C(21)	117.4(4)
O(21)-N(21)-C(21)	117.0(5)	Fe-N(22)-O(22)	126.2(4)
Fe-N(22)-C(22)	118.5(4)	O(22)-N(22)-C(22)	115.1(5)
Fe-N(23)-O(23)	125.8(4)	Fe-N(23)-C(23)	117.3(4)
O(23)-N(23)-C(23)	116.2(5)	N(11)-C(11)-C(111)	125.5(6)
N(11)-C(11)-C(21)	113.1(5)	C(111)-C(11)-C(21)	121.4(5)
C(11)-C(111)-C(112)	113.4(7)	C(11)-C(111)-C(113)	109.8(10)
C(112)-C(111)-C(113)	26.9(11)	C(111)-C(112)-C(113)	82.5(22)
C(111)-C(112)-C(212)	112.3(10)	C(113)-C(112)-C(212)	53.0(21)
C(111)-C(112)-C(213)	120.6(13)	C(113)-C(112)-C(213)	82.3(24)
C(212)-C(112)-C(213)	29.4(12)	C(111)-C(113)-C(112)	70.6(21)
C(111)-C(113)-C(212)	125.9(19)	C(112)-C(113)-C(212)	98.0(27)
C(111)-C(113)-C(213)	111.8(18)	C(112)-C(113)-C(213)	71.1(23)
C(212)-C(113)-C(213)	27.1(13)	N(21)-C(21)-C(11)	112.5(5)
N(21)-C(21)-C(211)	124.7(6)	C(11)-C(21)-C(211)	122.8(6)
C(21)-C(211)-C(212)	110.3(7)	C(21)-C(211)-C(213)	115.3(11)
C(212)-C(211)-C(213)	29.2(12)	C(112)-C(212)-C(113)	28.9(14)
C(112)-C(212)-C(211)	115.7(10)	C(113)-C(212)-C(211)	126.2(15)
C(112)-C(212)-C(213)	78.9(22)	C(113)-C(212)-C(213)	107.6(26)
C(211)-C(212)-C(213)	65.1(21)	C(112)-C(213)-C(113)	26.6(12)
C(112)-C(213)-C(211)	121.6(18)	C(113)-C(213)-C(211)	109.1(19)
C(112)-C(213)-C(212)	71.7(21)	C(113)-C(213)-C(212)	45.3(19)
C(211)-C(213)-C(212)	85.7(24)		

is expected for other tin- and germanium-containing clathrochelates. Therefore the comparison of Mössbauer spectra and X-ray data is of principal importance. The data obtained could be used as a bench-mark for the determination of the structure of other macrobicyclic complexes with TAP geometry. The Mössbauer structure data for complex (**I**) obtained are consistent with the results of the X-ray study.

The central iron atom of the complex dianion has a coordination intermediate between octahedral (trigonal-antiprismatic) and trigonal-prismatic: the relative twist of the N(11), N(12), N(13) and N(21), N(22), N(23) bases is $\phi = 37.5°$. The distortion angle ϕ of the coordination polyhedron determined by the present X-ray study is somewhat lower than the value (*ca* 40°) predicted[4] from the Δ value of Mössbauer (^{57}Fe) spectra. The observed discrepancy between the calculated (Mössbauer data) and the experimental (X-ray data) Δ values may be due to an increase in the size of the macrobicyclic ligand cavity: the average Fe-N bond length in the tin-containing clathrochelate is 1.923(5)Å. For boron-containing analogues this bond length is 1.91Å.[2,3]

An obvious likeness between the proposed[1] and the experimentally observed Δ-ϕ relation is revealed (Figure 2), though the agreement is imperfect. This is primarily due to the fact that the former was based on one-electron d-orbital energy calculations, as made earlier, and on Mössbauer and X-ray structure data for similar complexes. However, the lack of sufficient structural information made it impossible to take into account[1] all the spatial and electronic features of the macrobicyclic tris-dioximates, and this leads to slight discrepancies between the calculated and experimentally

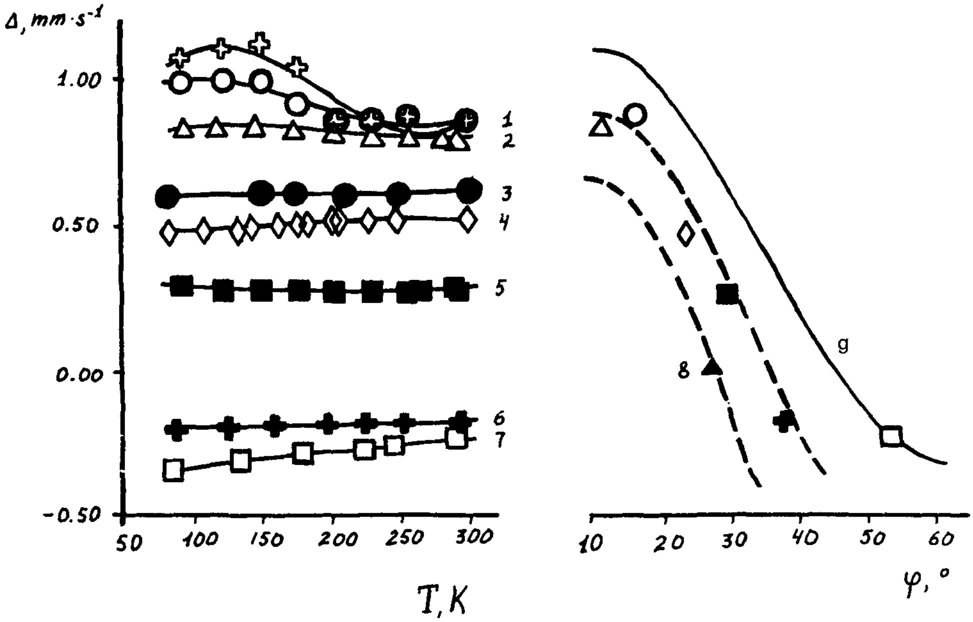

Figure 2 Quadrupole splitting, Δ, in the Mössbauer (^{57}Fe) spectra of $FeDm_3(BF)_2$ (1), $FeGm_3(Bn\text{-}C_4H_9)_2$ (2), $FeNx_3(BOH)_2$ (3),[1] $FeGx_3(BOH)_2{\cdot}3H_2O$ (4),[1] $FeBd_3(BF)_2{\cdot}5CHCl_3$ (5), $(HDEA)_2[FeNx_3(SnCl_3)_2]$ (6),[4] $[Fe(H_2Nx)_3]SO_4$ (7),[1] $FeFd_3(BC_6H_5)_2{\cdot}1/4CHCl_3$[8] complexes *versus* temperature and corresponding ϕ value. The theoretical dependence[1] also presented, as curve (9).

observed ϕ values. It is obvious that for each type of cross-linking group the Δ versus ϕ plot will shift along the Δ axis while retaining its general form. The amount of shift can be determined by using a new version of the partial quadrupole splitting concept in Mössbauer (^{57}Fe) spectra of Fe(II) coordination compounds.[9] According to this approach, Δ is expressed as $\Delta = f{\cdot}PQS$, where f is a function of iron atom arrangement geometry. Simple calculations give a dependence of the f value on ϕ and α (α is a half the N′-Fe-N″ angle in the chelate ring): $f = 12\text{–}18\ \cos^2\alpha/\cos^2(\phi/2)$.

The α angle values are practically constant for all compounds of this type and lie in the range 38.6–39.5° (in molecule (**I**) $\alpha = 39.5°$). Therefore Δ is a function of the geometrical parameter ϕ, and PQS, which is connected to the electron density distribution.

For compounds of the same type, the PQS values almost coincide and Δ is a function only of the ϕ value. Compounds of other types lead to changes of PQS and therefore to shifts of the curve. In the case of complexes with the $SnCl_3^+$ cross-linking group, this shift is equal to $-0.2\,\mathrm{mm\,s^{-1}}$ (as compared with the value obtained using the PQS value $= \pm 0.5\,\mathrm{mm\,s^{-1}}$) for uncharged macrobicyclic iron dioximates (calculated for $\alpha = 39.5°$; $\phi = 37.5°$; $PQS = +0.5\,\mathrm{mm\,s^{-1}}$: $0.02\,\mathrm{mm\,s^{-1}}$, found experimentally: $-0.18\,\mathrm{mm\,s^{-1}}$).

Data for the complex structure and the ligand can be used for determining the sign of Δ, which is of great importance when the splitting value is small and experimental sign determinations becomes very difficult.

Figure 2 shows temperature dependences of Δ in Mössbauer (^{57}Fe) spectra of iron(II) tris-dioximates as well as Δ-ϕ correlation curves.

The temperature dependence of Δ for the $(HDEA)_2[FeNx_3(SnCl_3)_2]$ complex demonstrates an increase in splitting with decreasing temperature. Δ decreases with decreasing temperature for trigonal-prismatic boron-containing alicyclic iron(II) dioximates and increases for non-macrocyclic complexes, $[Fe(H_2Nx)_3]SO_4$, having a TAP structure.[1] Comparison of these facts with the shape of the Δ *versus* temperature plot for a tin-containing complex and the value found for the distortion angle ϕ confirms indirectly that Δ in the Mössbauer (^{57}Fe) spectra of tin-containing iron(II) tris-dioximates has a negative sign: a much lower ϕ angle (*ca* 30°) corresponds to a positive value of Δ with the same magnitude (0.18 mm/s).[1]

It should be mentioned that for a cyclic dioximies (in contrast to alicyclic ones), a temperature decrease causes an increase in Δ (Figure 2). The peculiarities of temperature dependences for alicyclic diomixes seem to be connected with geometrical changes associated with cycloalkane ring.

The dihedral angle between the planes of the coordination polyhedron bases is 0.9°, and the base spacing is 2.23Å, which is much smaller than in cycloheptanedione-1,2-dioximate, $FeGx_3(BOH)_2{\cdot}3H_2O$ (2.33Å at $\phi = 23.4°$) and diphenylglyoximate $FeBd_3(BF)_2{\cdot}5CHCl_3$ (2.29Å at $\phi = 29.3°$).[2,3] Thus, when ϕ increases, the base plane spacing decreases. This decrease may be represented as a rotational-translational motion along the triad axis. During such motion five-membered chelate rings remain practically planar (the atomic displacements from their mid-plane do not exceed 0.04Å).

The coordination polyhedron of Sn atoms is a slightly distorted octahedron, in agreement with data on the structure of cross-linking fragments: Mössbauer (^{119}Sn) spectra also indicate a slightly distorted octahedral geometry.[4] Distortions manifest themselves mainly by an increase in Cl-Sn-Cl angles (91.9–97.0(1)°), whereas O-Sn-O angles vary between 88.5 and 91.2(2)°. The average Sn-Cl and Sn-O bond lengths are 2.399(2) and 2.093(4)Å. The Fe^{2+} ion does not deviate much from the Sn...Sn axis (the Sn...Fe...Sn angle is 178.8°). Nonbonded Fe...Sn distances are 3.612(1)Å.

The six-membered carbocycles in dianion (I) have a half-chair conformation with both carbon β-atoms displaced from the mid-plane of the remaining atoms in opposite directions (−0.332 and +0.313Å for C(112) and C(212), +0.374 and −0.419Å for C(113) and C(213), +0.351 and −0.492Å for C(122) and C(222), +0.345 and −0.494Å fpr C(132) and C(232).

Diethylammonium cations have an alongated transoid conformation (the C-C-NC torsion angles are 167.3–177.0°). Dianion (I) is associated with two ammonium counter-ions by weak hydrogen bonds (O(12)...H(3BB)-N(38); O...N = 2.959(7)Å and O(22)...H(3CA)-N(3C); O...N = 2.945(7)Å). The third ammonium cation is also associated with the Cl anion by a weak hydrogen bond N(3A)-H(3AB)...Cl (N...Cl = 3.331(5)Å).

Both ionic associates are joined into cyclic centrosymmetrical "dimers" $[I^{2-}\cdot 2Et_2NH_2^+\cdot 2Pr^iOH\cdot Cl^-\cdot Et_2NH_2^+]_2$ *via* solvate *iso*-propanol molcules which form hydrogen bonds (O(1X)...H(3CB)-N(3C); O...N = 2.764(6)Å; O1X-(H)...Cl^-; O...Cl = 3.138(5)Å; O(1Y)...H(3AA)-N(3A); O...N = 2.771(6)Å; O(1Y)-(H)...O(23'); O...O = 2.801(6)Å). In addition, the "dimers" form a two-dimensional network through Cl^-...H(3BA)-N(3B) hydrogen bonds (Cl...N = 3.170(5)Å). Thus, all the active hydrogen atoms in structure (I) are involved in the formation of hydrogen bonds.

Correlations between Δ in Mössbauer (^{57}Fe) spectra and the geometry of the coordination polyhedron in iron(II) TAP-TP complexes permit structural features to be determined with high accuracy. In tin-containing iron(II) tris-dioximates, the coordination polyhedron has a distorted TAP structure. The sign of Δ was determined from the temperature dependences of Mössbauer parameters. In boron-containing clathrochelates, Δ is positive, and in tin-containing complexes, negative. Structural differences are due to an increase of cross-linking group size; this makes it possible to cross-link the dioximate fragments at large angles of rotation, optimal for low-spin d^6 configurations.

Supplementary Material

A summary of data collection and refinement parameters, tables of bond lengths and angles, hydrogen atom parameters, anisotropic temperature factors and lists of observed and calculated structure factors are available from Dr Y.Z. Voloshin on request.

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