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

Part III. Template synthesis, structure and properties of clathrochelate tin-containing iron(II) dioximates formed by tin tetrachloride

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Abstract

The template condensation of a number of aliphatic, aromatic and alicyclic dioximes containing tin(IV) tetrachloride on iron(II) ion results in the formation of anionic clathrochelate complexes, which have been isolated and characterized as salts with organic bases of the general compositions $[FeD_3(SnCl_3)_2](HAm)_2$, where D^{2-} is a dioxime dianion and Am is a aliphatic or aromatic amine. The composition and clathrochelate nature of the complexes obtained are confirmed by the results of elementary analysis, by IR, electronic absorption, ^1H, $^{13}C\{^1H\}$, ^{119}Sn NMR and ^{57}Fe, ^{119}Sn Mössbauer spectra. According to the ^{57}Fe Mössbauer spectroscopic data, the complexes have a trigonal-antiprismatic geometry of coordination polyhedron with a distortion angle of 40–55°. The 'macrocyclic' ligand field force increase effect for clathrochelate tin-containing complexes is less pronounced than for boron-containing macrobicyclic complexes. The parameters of the Mössbauer and ^{119}Sn NMR spectra indicate a highly symmetrical octahedral geometry of the cross-linking tin-containing fragment.

Introduction

A great number of works are known now dealing with the encapsulation of iron(II) tris-dioximates by boron-containing Lewis acids involving the formation of corresponding $FeD_3(BR)_2$ clathrochelate complexes [1]. The formation of macrobicyclic d-metal tris-dioximate complexes by cross-linking with compounds of other p-block elements, which are also Lewis acids, is much less studied. Only clathrochelate tris-dimethylglyoxymates of cobalt(III) were synthesized [2] by the macrocyclization of K_3CoDm_3 with tin(IV) and silicon(IV) tetrachlorides, the complex not having been isolated as an individual compound in the latter case. We have previously reported the possibility of obtaining macrobicyclic iron(II) tris-dioximates by the template cross-linking of three dioxime molecules with inorganic and organic tin(IV), germanium(IV), arsenic(III), bismuth(III) and antimony(III) compounds [1, 3]. The present paper presents the results of studies on the synthesis, structure an d properties of clathrochelate tris-dioximates of iron(II) obtained by encapsulation with tin(IV) tetrachloride.

Experimental

Materials and apparatus

The reagents used, $FeCl_2\cdot 4H_2O$, $SnCl_4$, diethylamine (DEA), pyridine, dimethylglyoxime, α-benzyldioxime, nioxime, as well as organic solvents were obtained commercially. The remaining dioximes listed in Table 1 were synthesized by the methods reported in ref. 4.

The analyses of carbon, hydrogen and nitrogen were carried out with a Carbo Erba model 1106 microanalyser; iron and tin were determined by the atomic-absorption method using an SP2-800 Pye Unicam spectrophotometer. Chlorine analyses were made at the Institute of Organic Chemistry (Kiev).

The IR spectra of solid samples (CsI and KBr tablets) in the range 200–4000 cm^{-1} were recorded on a Specord M-80 spectrophotometer. The assignment of lines was performed using results obtained earlier [1] as well as model compounds. The electron absorption spectra of solutions in acetonitrile in the range 11 000–36 000 cm^{-1} were recorded on a Specord M-40 spectrophotometer. The ^1H, $^{13}C\{^1H\}$ and ^{119}Sn NMR spectra of solutions in DMSO-D_6 and CD_3CN were obtained on a CXP-200 Bruker FT-spectrometer.

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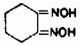
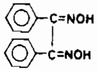
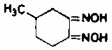
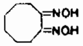
TABLE 1. Characteristics of IR and electron spectra of macrobicyclic tin-containing iron(II) dioximates

Compound	Starting dioxime	ν(C=N)	ν(N–O) (cm^{-1})	ν(Sn–Cl)	$\nu_{max} \times 10^3$ (cm^{-1})	$\varepsilon \times 10^3$ (mol^{-1} cm^{-1} l)
$[FeNx_3(SnCl_3)_2](HDEA)_2$	 nioxime, H_2Nx	1568	968, 1046	310	17, 92 20, 88 33, 56	6, 16 7, 16 17, 30
$[FeNx_3(SnCl_3)_2](HPy)_2$	H_2Nx	1572	968, 1052	312	18, 00 20, 88 33, 56	5, 85 6, 92 16, 70
$[FeGm_3(SnCl_3)_2](HDEA)_2$	H–C=NOH H–C=NOH glyoxime, H_2Gm	1544	996, 1122	318	18, 48 21, 24 32, 84	4, 53 4, 88 16, 80
$[FeMm_3(SnCl_3)_2](HDEA)_2$	CH_3–C=NOH H–C=NOH methylglyoxime, H_2Mm	1570	918, 1044, 1124	316	18, 36 21, 24 33, 40	5, 15 5, 71 17, 50
$[FeDm_3(SnCl_3)_2](HDEA)_2$	CH_3–C=NOH CH_3–C=NOH dimethylglyoxime, H_2Dm	1580	966, 1074	314	18, 16 21, 32 34, 08	4, 95 5, 66 15, 40
$[FeBd_3(SnCl_3)_2](HDEA)_2$	 α-benzyldioxime, H_2Bd	1578	892, 1094	318	17, 56 20, 56 35, 00- 36, 00sh	9, 41 11, 40 26, 00
$[Fe(4MNx)_3(SnCl_3)_2](HDEA)_2$	 4-methylnioxime, H_24MNx	1572	936, 1006, 1080	306	17, 92 20, 88 33, 52	5, 64 6, 49 15, 50
$[FeOx_3(SnCl_3)_2](HDEA)_2$	 octoxime, H_2Ox	1568	954, 1028	312	18, 04 21, 00 33, 80	5, 85 6, 78 15, 60
$FeNx_3(BF)_2$ [5]	H_2Nx	1584	965, 1070, 1225, 1250		22, 50	18, 40

Mössbauer spectra were obtained on a YGRS-4M spectrometer with a saw-like change of velocity. The spectra were stored in 256 channels of amplitude analyzer. The velocity scale was calibrated relative to the α-Fe foil spectrum. For the ^{57}Fe Mössbauer spectra the origin of the velocity scale was brought into coincidence with the centre of the spectrum of sodium nitroprusside. ^{57}Co in Cr was used as a source. A minimum width of absorption line within the spectrum of a standard sample of sodium nitroprusside is 0.24 mm/s. For the tin Mössbauer measurements the source chosen was $^{119m}SnO_2$ with a minimum line width of 1.17 mm/s. The sources were always kept at room temperature.

Syntheses of complexes

[FeDm$_3$(SnCl$_3$)$_2$](HDEA)$_2$

A total of 2.32 g of dimethylglyoxime (20 mmol) and 1.32 g of $FeCl_2 \cdot 4H_2O$ (6.6 mmol) was dissolved under stirring in 50 ml of isopropanol. After intensive stirring for 20 min a solution of 1.5 ml of tin tetrachloride (13.2 mmol) in 10 ml of n-butanol was added dropwise to the dark-brown solution. The dark-red reaction mixture was stirred for 30 min, heated at 50–60 °C for 10 min and filtered. Then a solution of 3.4 ml of diethylamine (33 mmol) in 10 ml of isopropanol was added dropwise to the filtrate under intensive stirring, a red precipitate being observed. After 30 min stirring the precipitate was filtered off, washed with isopropanol, diethyl ether, hexane and recrystallized from dry acetone. Yield 65%.

Anal. Calc. for $FeC_{20}H_{42}N_8O_6Sn_2Cl_6$: Fe, 5.60; C, 24.07; H, 4.21; N, 11.23; Sn, 23.81; Cl, 21.48. Found: Fe, 5.40; C, 23.93; H, 4.29; N, 11.16; Sn, 23.67; Cl, 21.48%.

[FeGm$_3$(SnCl$_3$)$_2$](HDEA)$_2$

This complex was synthesized by the same procedure as above for [FeDm$_3$(SnCl)$_2$](HDEA)$_2$ except that 1.76 g of glyoxime (20 mmol) were used instead of dimethylglyoxime. The red product obtained was recrystallized from acetonitrile, washed with acetone, diethyl ether, hexane and dried *in vacuo*. Yield 45%.

Anal. Calc. for $FeC_{14}H_{30}N_8O_6Sn_2Cl_6$: Fe, 6.11; C, 18.40; H, 3.29; N, 12.27; Sn, 26.00; Cl, 23.33. Found: Fe, 6.16; C, 18.45; H, 3.31; N, 12.29; Sn, 26.14; Cl, 22.97%.

[FeMm$_3$(SnCl$_3$)$_2$](HDEA)$_2$

This complex was synthesized in the same way as the previous one except that 2.04 g of methylglyoxime (20 mmol) were used instead of glyoxime. Yield 42%.

Anal. Calc. for $FeC_{17}H_{36}N_8O_6Sn_2Cl_6$: Fe, 5.84; C, 21.36; H, 3.77; N, 11.73; Sn, 24.86; Cl, 22.30. Found: Fe, 5.72; C, 21.22; H, 3.86; N, 11.77; Sn, 24.48; Cl, 21.93%.

[FeBd$_3$(SnCl$_3$)$_2$](HDEA)$_2$

This complex was synthesized like dimethylglyoximate. A total of 4.80 g of α-benzyldioxime (20 mmol) was taken instead of dimethylglyoxime. The initial volume of isopropanol was 200 ml. Yield 27%.

Anal. Calc. for $FeC_{50}H_{54}N_8O_6Sn_2Cl_6$: Fe, 4.08; C, 36.52; H, 3.94; N, 8.18; Sn, 17.34; Cl, 15.56. Found: Fe, 3.83; C, 36.72; H, 3.96; N, 8.15; Sn, 17.41; Cl, 15.43%.

[Fe(4MNx)$_3$(SnCl$_3$)$_2$](HDEA)$_2$

This complex was synthesized like dimethylglyoximate. A total of 3.12 g of 4-methylnioxime (20 mmol) was taken instead of dimethylgyoxime. Yield 35%.

Anal. Calc. for $FeC_{29}H_{54}N_8O_6Sn_2Cl_6$: Fe, 5.00; C, 31.15; H, 4.83; N, 10.03; Sn, 21.25; Cl, 19.07. Found: Fe, 4.93; C, 31.26; H, 4.81; N, 10.02; Sn, 21.02; Cl, 19.45%.

[FeOx$_3$(SnCl$_3$)$_2$](HDEA)$_2$

This complex was synthesized like the previous one. A total of 3.40 g of octoxime (20 mmol) was used instead of 4-methylnioxime. Yield 38%.

Anal. Calc. for $FeC_{32}H_{60}N_8O_6Sn_2Cl_6$: Fe, 4.81; C, 33.13; H, 5.18; N, 9.66; Sn, 20.48; Cl, 19.07. Found: Fe, 4.80; C, 32.71; H, 5.06; N, 9.53; Sn, 20.27; Cl, 19.45%.

[FeNx$_3$(SnCl$_3$)$_2$](HDEA)$_2$

Two methods were used.

1. The complex was synthesized like dimethylglyoximate. A total of 2.84 g of nioxime (20 mmol) was used instead of dimethylglyoxime. To purify the precipitated red product of impurities it was suspended in 20 ml of acetonitrile at ~30 °C, and after 10 min stirring the solution was filtered off. The filtrate was cooled in a refrigerator to ~0 °C, the white precipitate was isolated, and the complex was again suspended in an acetonitrile solution at ~30 °C. The procedure was repeated several times till there was no white precipitate on cooling. The red purified product was recrystallized from acetonitrile, washed with diethyl ether, hexane and dried *in vacuo*. Yield 73%.

Anal. Calc. for $FeC_{26}H_{48}N_8O_6Sn_2Cl_6$: Fe, 5.19; C, 29.02; H, 4.47; N, 10.42; Sn, 22.08; Cl, 19.81. Found: Fe, 5.17; C, 29.04; H, 4.61; N, 10.52; Sn, 22.25; Cl, 19.82%.

2. A solution of 0.1 ml of tin tetrachloride (0.8 mmol) in 10 ml of benzene was added dropwise

under intensive stirring to a suspension of 0.25 g of $[Fe(H_2Nx)_3SO_4$ (0.4 mmol), synthesized by the method reported in ref. 6, in 20 ml of an acetone–benzene mixture (1:1). While the red solution was stirred for 20 min, a solution of 0.25 ml of diethylamine (2.4 mmol) in 10 ml of benzene was added dropwise. A red precipitate was observed to separate. The suspension was stirred 20 min more, the precipitate was filtered off and recrystallized from dry acetonitrile. Yield 80%.

The analytical and spectral characteristics of the complex obtained by this method are identical to those of the complex obtained by method 1.

$[FeNx_3(SnCl_3)_2](HPy)_2$

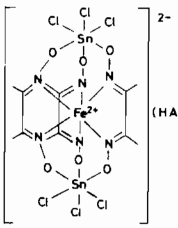
The complex was synthesized like the previous one (method 1). A total of 2.7 ml of pyridine (33 mmol) was used instead of diethylamine. Yield 66%.

Anal. Calc. for $FeC_{28}H_{36}N_8O_6Sn_2Cl_6$: Fe, 5.13; C, 30.91; H, 3.31; N, 10.30; Sn, 21.84; Cl, 19.60. Found: Fe, 4.90; C, 30.79; H, 3.27; N, 10.06; Sn, 21.92; Cl, 19.46%.

Results and discussion

The synthesis of macrobicyclic iron(II) tris-dioximates encapsulated by tin tetrachloride can be performed by two main methods: direct interaction of iron(II), dioxime and $SnCl_4$ or encapsulation of preliminary synthesized non-macrocyclic iron(II) tris-dioximate:

$$Fe^{2+} + 3H_2D + 2SnCl_4 + 6Am \xrightarrow{ROH}$$



$$(HAm)_2 + 2Cl^- + 4HAm \qquad (1)$$

$$[Fe(H_2D_3]^{2+} + 2SnCl_4 + 6Am \xrightarrow[Ac + C_6H_6]{Ac}$$

$$[FeD_3(SnCl_3)_2](HAm)_2 + 2Cl^- + 4HAm \qquad (2)$$

The direct reaction (eqn. (1)) appears to proceed via a protonated tris-complex. For boron-containing clathrochelate dioximates, the formation of such an intermediate complex was confirmed experimentally when studying the kinetics and mechanism of their synthesis and decomposition [7, 8]. Though the product yield in the case of reaction (2) is higher than in the former case, the difficulty of separating non-macrocyclic iron(II) tris-dioximates causes the synthesis of complexes by reaction (1) to be generally preferred. Tin-containing complexes can also be obtained by the interaction of tin(IV) tetrachloride with bis-dioximates of the Tchugaev type, $Fe(HD)_2Am_2$, and by treating labile boron-containing complexes (such as $FeD_3(BOH)_2$) with a considerable excess of $SnCl_4$. The transition from tin-containing complexes to boron-containing ones can be performed only under rigid conditions by treatment with a large excess of boron-containing agent which is a strong Lewis acid (for example, boron trifluoride ethrate). It should be noted that in contrast to boron-containing dioximate complexes, the synthesis of $[FeD_3(SnCl_3)_2](HAm)_2$ compounds involves the separation of a considerable amount of by-products which (according to the data of elementary analysis and IR spectroscopy) are mainly tin(IV) dioximates. This makes it difficult to obtain pure clathrochelate complexes. To purify them one can use the absence of a noticeable temperature dependence of solubility in polar organic solvents, e.g. in acetonitrile. Since such a dependence is rather essential for tin(IV) dioximates, this allows separation of these complexes as was shown for the compound $[FeNx_3(SnCl_3)_2](HDEA)_2$.

The spectral characteristics of tin-containing macrobicyclic iron(II) dioximates are typical of clathrochelate complexes, but at the same time they are considerably different from the characteristics of the corresponding boron-containing compounds which were considered in ref. 1.

This applies especially to the parameters of the electronic and Mössbauer spectra of complexes which are associated with the structure of the coordination polyhedron and with the distribution of electron density on the central metal ion and nitrogen donor atoms.

The parameters of the ^{57}Fe Mössbauer spectra of $[FeD_3(SnCl_3)_2](HAm)_2$ compounds given in Table 2 characterize them as low-spin iron(II) complexes. The 'macrocyclic' effect of ligand field force increases, leading to an increase in s-electron density on the iron atom nucleus, is less pronounced in tin-containing compounds than in their boron-containing analogs: the values of isomeric shift (*IS*), obtained experimentally, which characterizes s-electron density on the iron atom nucleus, are only slightly lower than those calculated in terms of the partial *IS* concept [11].

The geometry of the coordination polyhedron in iron(II) tris-dioximates is an intermediate one between trigonal prism (TP) and trigonal antriprism (TAP) and is described by the distortion angle φ (0° corresponds to TP, 60° to TAP). A dependence of the amount of t_{2g} level splitting and quadrupole

TABLE 2. Parameters of the Mössbauer spectra on the ^{57}Fe and ^{119}Sn nuclei of clathrochelate iron(II) dioximates

Compound	^{57}Fe				^{119}Sn
	IS^a (mm/s)	*IS* estimate (mm/s)	*QS*^{a} (mm/s)	*T* (K)	*IS*^{b} (mm/s)
$[FeGm_3(SnCl_3)_2](HDEA)_2$	0.35		0.25	300	0.44
$[FeMm_3(SnCl_3)_2](HDEA)_2$	0.36		0.28	300	0.42
$[FeDm_3(SnCl_3)_2](HDEA)_2$	0.34		0.31	300	0.38
$[FeBd_3(SnCl_3)_2](HDEA)_2$	0.34		0.31	300	0.41
$[FeNx_3(SnCl_3)_2](HDEA)_2$	0.374(4)	0.40	0.185(4)	295	0.43
	0.378(6)	0.40	0.179(6)	295	
	0.389(4)		0.186(4)	253.5	
	0.406(2)		0.188(2)	225.3	
	0.411(2)		0.192(2)	198.3	
	0.426(2)		0.199(2)	159.5	
	0.437(2)		0.202(2)	126.2	
	0.446(2)		0.204(2)	88.5	
$[FeNx_3(SnCl_3)_2](HPy)_2$	0.38	0.40	0.18	300	0.43
$[Fe(4MNx)_3(SnCl_3)_2](HDEA)_2$	0.36		0.24	300	0.46
$[FeOx_3(SnCl_3)_2](HDEA)_2$	0.37		0.36	300	0.42
$FeGm_3(BF)_2$ [1]	0.31		0.56	300	
$FeMm_3(BF)_2$ [1]	0.32		0.70	300	
$FeDm_3(BF)_2$ [1]	0.31		0.90	300	
$FeBd_3(BF)_2$ [1]	0.32		0.25	300	
$FeNx_3(BF)_2$ [1]	0.33	0.40	0.68	300	
$[Fe(H_2Nx)_3]Cl_2$ [9]	0.52	0.52	0.28	300	
$[FePhen_3]C_2O_4$ [10]	0.57	0.58	−0.29	300	

[a] Relative to sodium nitroprusside; ±0.01 mm/s.

[b] Relative to SnO_2; $T = 80$ K; ±0.01 mm/s.

splitting (*QS*) in the ^{57}Fe Mössbauer spectra, which characterizes electron density gradient on the iron atom nucleus, on φ has been suggested [1]. This permits one to determine with high accuracy the φ value if the sign and value of *QS* are known. In terms of this dependence, boron-containing iron(II) dioximates have a trigonal-prismatic structure ($\varphi \sim 20$–$30°$) [1]. The validity of such an approach has been confirmed recently by data obtained on the crystal and molecular structure of the $FeBd_3(BF)_2 \cdot 5CHCl_3$ complex. The distortion angle value in this complex is 29.3° [12], whereas in ref. 1 it was estimated as 27–30°.

When the geometry of the coordination polyhedron is close to TP, *QS* has a positive sign and a high value (~1 mm/s). In complexes with TAP geometry *QS* has a low value and a negative sign.

QS values in the ^{57}Fe Mössbauer spectra (Table 2) for tin-containing complexes are small (Fig. 1) and decrease in the dioxime series in an order which differs greatly from that observed in the case of $FeD_3(BR)_2$ compounds. The *QS* value in the spectrum of the α-benzyldioximate $[FeBd_3(SnCl_3)_2](HDEA)_2$ complex is, in particular, greater than in the spectra of most tin-containing complexes with acyclic and alicyclic dioximes.

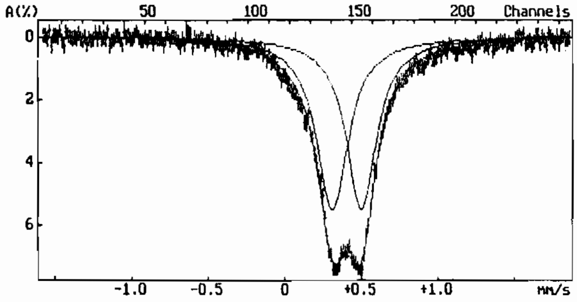


Fig. 1. ^{57}Fe Mössbauer spectra of the $[FeNx_3(SnCl_3)_2](HDEA)_2$ complex with superimposed Lorentzian line-fits at 300 K.

At the same time *QS* observed for boron-containing dioximate, $FeBd_3(BF)_2$, is much smaller than in the spectra of boron-containing complexes with aliphatic dioximes (Table 2).

The higher distortion angle value for compounds with aromatic dioximes is due to steric hindrances arising from the formation of these complexes.

In the case of boron-containing clathrochelates with a positive sign for *QS*, this leads to a decrease in the *QS* absolute value. An increase in *QS* (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, *QS* assumes a negative sign [1].

Along with other spectral data this permits one to suppose that *QS* in the case of the $[FeD_3(SnCl_3)_2(HAm)_2$ complexes has a negative sign and corresponds to distortion angles φ of 40–55°. This indicates the geometry of the coordination polyhedron to be 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 *QS* value.

The temperature dependence of *QS* for the $[FeNx_3(SnCl_3)_2](HDEA)_2$ complex shown in Fig. 2 demonstrates an increase in splitting with decreasing temperature. As shown in ref. 1, *QS* decreases with decreasing temperature for trigonal-prismatic boron-containing iron(II) dioximates and increases for the non-macrocyclic complex $[Fe(H_2Nx)_3]SO_4$ having a TAP structure. A comparison of these facts with the shape of the *QS*–temperature plot for the tin-containing complex also confirms the TAP nature of the coordination polyhedron of this complex.

The temperature dependence of *IS* for the $[FeNx_3(SnCl_3)_2](HDEA)_2$ complex (Fig. 2) is an intermediate one between the similar temperature dependence for the boron-containing $FeNx_3(BOH)_2$ dioximate and the non-macrocyclic $[Fe(H_2Nx)_3]SO_4$ complex. This also indicates that the field force of a tin-containing macrobicyclic ligand is lower than that of its boron-containing analog but higher than in a non-macrocyclic tris-dioximate.

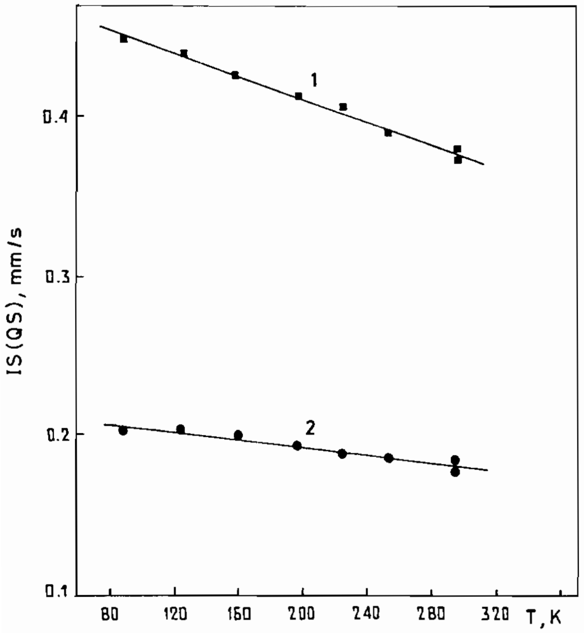


Fig. 2. Temperature dependences of isomeric shift (1) and quadrupole splitting (2) in the Mössbauer ^{57}Fe spectra for the complex $[FeNx_3(SnCl_3)_2](HDEA)_2$.

The Mössbauer spectra (^{119}Sn) of complexes of this type contain a broadened singlet band with practically the same *IS* value as with K_2SnCl_6 ($\delta_{SnO_2}=0.52$ mm/s). This indicates an octahedral environment of the cross-linking tin atoms.

The IR spectra of $[FeD_3(SnCl_3)_2](HAm)_2$ complexes contain, in addition to the bands relating to vibrations in the dioxime fragments, the characteristic Sn–Cl bond stretching vibration bands for the cross-linking fragment at 306–318 cm^{-1} (Table 1) and a system of bands relating to the stretching and bonding vibrations of different protonated-amine groups. In particular, a number of intensive bands at 2800–3200 cm^{-1} for complexes with the $HDEA^+$ cation are due to the stretching vibrations of its N–H and C–H bonds. At the same time there are no vibrations of free oxime groups in the spectra. This supports a clathrochelate nature of the complexes. The C=N bond stretching vibration bands for fragments are much stronger, as in the case of boron-containing complexes, but shifted towards low frequencies and

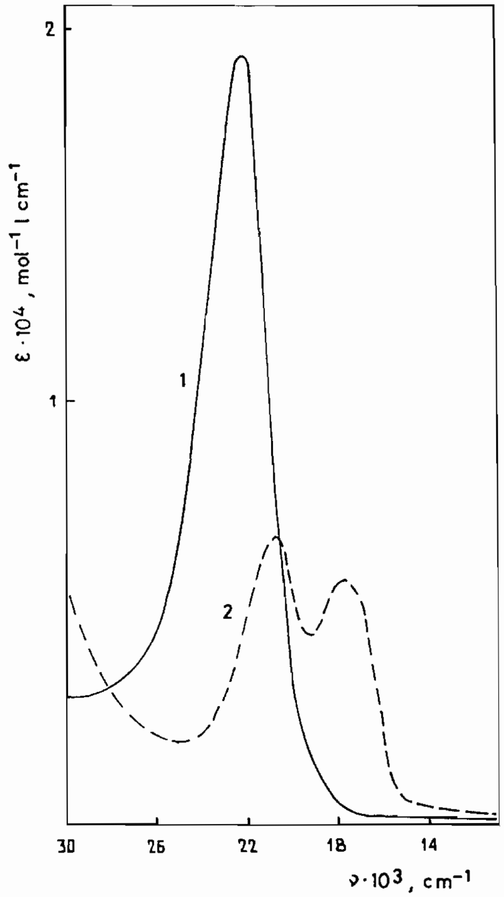


Fig. 3. Fragments of the electronic absorption spectra of the $FeNx_3(BF)_2$ (1) and $[FeNx_3(SnCl_3)_2](HDEA)_2$ (2) clathrochelate complexes.

TABLE 3. Parameters of the ^{1}H, $^{13}C\{^{1}H\}$ and ^{119}Sn NMR spectra of clathrochelate iron(II) complexes

Compound	^{1}H relative to TMS (ppm)			^{13}C relative to TMS (ppm)			^{119}Sn relative to $Sn(CH_3)_4$ (ppm)	
	$\delta\left(\begin{smallmatrix}H\\ \ \end{smallmatrix}\!\!>\!C{=}NO\right)$		$\delta(R)$	$\delta\left(\begin{smallmatrix}H\\ \ \end{smallmatrix}\!\!>\!C{=}NO\right)$	$\delta\left(\begin{smallmatrix}R\\ \ \end{smallmatrix}\!\!>\!C{=}NO\right)$	$\delta(R\text{–})$		
$FeGm_3(SnCl_3)_2](HDEA)_2$	7.74			144.72				−625.4
$[FeMm_3(SnCl_3)_2](HDEA)_2$	7.74m[a]	2.25m		146.59	154.84	12.98		−632.4
								−629.9
$[FeDm_3(SnCl_3)_2](HDEA)_2$		2.29			156.05	12.68		−637.1
		7.23m						
$[FeBd_3(SnCl_3)_2](HDEA)_2$		7.42m			157.62	127.21		−633.9
						128.35		
						130.57		
						131.60		
$[FeNx_3(SnCl_3)_2](HDEA)_2$		1.52m	1.78m		156.14	21.31		
		2.47m	2.92m			26.09		−637.3
$[FeNx_3(SnCl_3)_2](HPy)_2$		1.45m	1.70m		154.96	21.09		
		2.66m	2.87m			25.79		−639.9
$[Fe(4MNx)_3(SnCl_3)_2](HDEA)_2$		1.02			155.40	19.81	20.22	
		1.77m			155.69	24.41	25.14	
		2.08				27.47		
		2.54m				27.86		
		3.13m				28.74	29.04	−636.7
						33.17	33.59	
$[FeOx_3(SnCl_3)_2](HDEA)_2$		1.22			161.48	22.23		
		2.15–2.30m				25.66		−634.4
						30.08		

[a] m = multiplet.

are found in the range 1568–1580 cm^{-1} for all clathrochelate tin-containing compounds, except glyoximate (the ν(C=N) band is observed in its IR spectrum at 1554 cm^{-1}). This is associated with its greater C=N bond length [13]. It should be noted that the ν(N–O) bands are absent from the spectra of [FeD$_3$(SnCl$_3$)$_2$](HAm)$_2$ complexes at 1250 cm^{-1} when the band intensity of these vibrations increases sharply near 1100 cm^{-1}.

The electronic absorption spectra of clathrochelate tin-containing complex solutions differ greatly from the spectra of clathrochelate FeD$_3$(BR)$_2$ complexes and are close to the absorption spectra of iron(II) tris-phenanthrolinates and dipyridinates [14]: two metal–ligand charge transfer bands (CTB) are observed in the visible region at 17 570–18 480 and 20 560–21 320 cm^{-1} with an intensity of (5–10)$\times 10^3$ mol^{-1} l cm^{-1} as compared with one intensive ($\varepsilon \sim (2\text{–}3)\times 10^4$ mol^{-1} l cm^{-1}) asymmetric CTB at 19 000–23 000 cm^{-1} for boron containing complexes, Fig. 3. The bands in the UV regions of the spectra of tin-containing clathrochelate complexes may be assigned either to intraligand transitions or to charge transfer from the iron(II) d-orbitals to the second acceptor π^* level of the ligand [14].

The peculiarities of the electronic spectra of [FeD$_3$(SnCl$_3$)$_2$(HAm)$_2$ complexes also permit one to suppose that their coordination polyhedra have a trigonal-antiprismatic geometry which is close to an octahedral one and similar to the geometry of the coordination polyhedron in iron(II) tris-orthophenanthrolinates and dipyridinates.

The ^{1}H and ^{13}C{^{1}H} NMR parameters of tin-containing iron(II) dioximate solutions (Table 3) also differ greatly from the spectra of boron-containing complexes. First of all, signals of carbon atoms and organic cation protons appear in the spectra of the above dioximates. Their integral intensity corresponds to the stoichiometric composition [FeD$_3$(SnCl$_3$)$_2$-(HAm)$_2$. The singlet character in the PMR spectra for dioxime fragment protons is retained only for dimethylgyoximate and glyoximate. The chemical shift value is much lower for the latter than for the analogous boron-containing complex and practically coincides with the values obtained for the starting dioxime and those presented in ref. 1. For the rest of the complexes one can observe a multiplet character of these fragments' proton signals. In the case of nioximate and α-benzyldioximate the PMR spectra show a distinct doubling of these signals. An analogous phenomenon was also found in the ^{13}C{^{1}H} NMR spectrum of a complex with 4-methylnioxime. The appearance of such a magnetic non-equivalence in the case of tin-containing complexes may be due, first of all, to the considerable change in the symmetry of complex molecules in solution as compared with their boron-containing analogs.

The ^{111}Sn NMR spectra of [FeD$_3$(SnCl$_3$)$_2$](HAm)$_2$ complex solutions contain a narrow singlet line in the range -620 to -640 ppm relative to the Sn(CH$_3$)$_4$ signal. The chemical shift value and the line shape, along with the Mössbauer ^{119}Sn spectroscopy data, indicate a highly symmetrical octahedral SnO$_3$Cl$_3$ environment of the tin atom; δ(Sn(CH$_3$)$_4$) for (NH$_4$)$_2$SnCl$_6$ is -670.4 ppm. The non-equivalence of the cross-linking tin atoms is observed and the line doubles only for a complex with non-symmetrical methylglyoxime, the chemical shift value of both ^{119}Sn atom types being an intermediate one between the chemical shift values for glyoximate and dimethylglyoximate. Analogous effects were observed in the case of the FeMm$_3$(BF)$_2$ complex [1].

The considerable change in the structure of tin-containing complexes in comparison with the corresponding boron-containing iron(II) dioximates is primarily associated with a change in the geometric and electronic parameters of the cross-linking group, which permits cross-linking dioximate fragments at large distortion angles optimal for the d^6 configuration of the central iron(II) ion. Under these conditions, the geometry of the coordination polyhedron becomes close to TAP. Besides, tin(IV) tetrachloride is a less strong Lewis acid than boron-containing analogs, which causes considerably smaller differences of electron density distribution in clathrochelate complexes formed by it from that in non-macrocyclic iron(II) tris-dioximates.

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