Reviews

✾ Structural chemistry of complexes with an encapsulated metal ion. α-Dioximate, oximehydrazonate, and dihydrazonate clathrochelates*

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The review surveys the main trends in the structural chemistry of clathrochelates: the determination of the crystal and molecular structures of various types of new complexes, their symmetry and functionality; the supramolecular organization and phase transitions of clathrochelate crystals; the structure—spectral parameter relationships and the deduction of the molecular structures; the use of X-ray diffraction data for explanation of the kinetic and thermodynamic parameters of the synthesis and decomposition of clathrochelates.

Key words: macrocycle, clathrochelate, X-ray diffraction analysis, supramolecular chemistry, phase transitions, ^{57}Fe Mössbauer spectra, kinetics of complex formation and decomposition.

1. Introduction

The concept of clathrochelates as a special type of chelate complexes with a metal ion encapsulated in a three-dimensional cavity of a macropolycyclic ligand was proposed[1] in 1964. In 1968, the first clathrochelate, *viz.*, boron-containing cobalt(III) tris-dioximate, was synthesized.[2] It should be noted that the term "clathrochelate" (as well as the term "clathrate") is derived from the Latin word "clathratus," which means "furnished with lattice."

In spite of considerable progress in the synthesis of clathrochelate tris-dioximates in the late 1980s,[3—18] the structural chemistry of these compounds was represented only by fluoroboron-capped cobalt(II) and cobalt(III) tris-dimethylglyoximates.[3,19] The structure of the iron(II) complex with an analogous macrobicyclic ligand was not confirmed later:[20] the atomic coordinates were not reported, and the formation of a solvate with cyclohexane, in which the complex is virtually insoluble, was highly doubtful. Apparently, the authors did not distinguish between the benzene and cyclohexane solvate molecules, which were indicative of a low accuracy of the experimental data.

The paucity of direct X-ray diffraction data on the structures of this type of cage complexes is associated with difficulties of preparation of their single crystals suitable for X-ray diffraction analysis. Most of the clathrochelates synthesized are intramolecular compounds (as a result, strong interparticle Coulomb interactions are absent in the crystals), and the nearly spherical shape of the molecules results in an essential reduction of less strong inter-

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* Hereinafter, the papers marked with an asterisk ✾ are dedicated to Academician Yurii Nikolaevich Bubnov on the occasion of his 70th birthday.

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molecular dipole-dipole and van der Waals interactions. At the same time, difficulties associated with obtaining direct X-ray diffraction data on the structures of clathrochelate complexes gave impetus to the development of approaches, that would allow one to obtain indirect information on the structures of these compounds. These are ^{57}Fe Mössbauer spectroscopy, whose parameters were used for deducing a distortion of coordination polyhedra of the central ions, and EXAFS data on the radial distribution of the atoms surrounding the encapsulated metal ions. X-ray diffraction data were used both in the modern concept of partial quadrupole splitting in Mössbauer spectra[21,22] and as an initial approximation in the fitting procedure between calculated and experimental EXAFS data.[23]

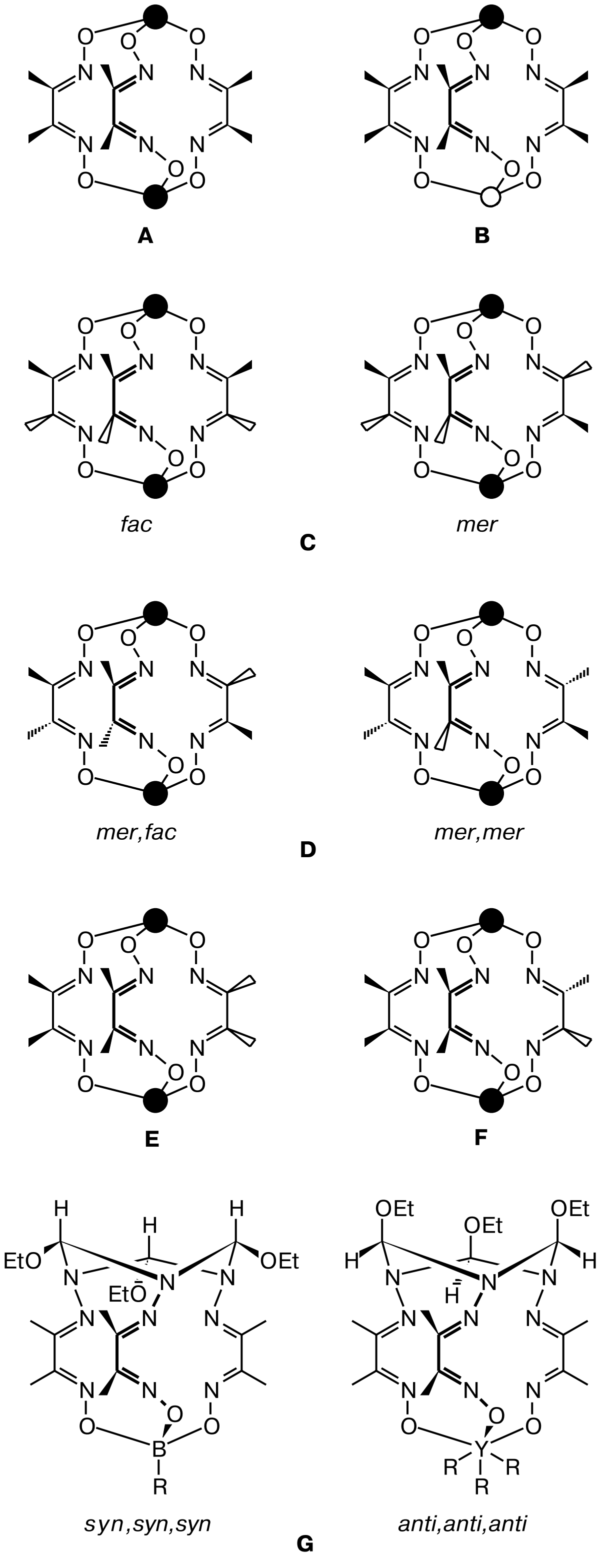
In the last decade, due to an extension of the types of compounds and solvate systems studied (solvate molecules occupy cavities between the macropolycyclic molecules, which is favorable for crystal formation), a considerable amount of crystallographic and structural information was obtained. The structures of more than 80 clathrochelate compounds of various symmetry and functionality have been established. In addition to the above-mentioned topics of research in the structural chemistry of clathrochelate complexes, the supramolecular organization of the clathrochelate crystals, the phase transitions, and the stabilization of the unusual oxidation states of encapsulated metal ions in their crystals are being extensively studied. Finally, X-ray diffraction data made a considerable contribution to the understanding of the kinetics and thermodynamics of the template synthesis and decomposition of macrobicyclic iron(II) tris-dioximates, which made it possible to propose general schemes of these processes.[24]

Hence, it is of interest to review the main results obtained in the field of clathrochelate structural chemistry.

2. Crystal and molecular structures of various types of clathrochelate d-metal tris-dioximates and tris-oximehydrazonates of different symmetry and functionality

2.1. d-Metal complexes with symmetric aliphatic and aromatic α-dioximes and equivalent cross-linking fragments

The majority of the clathrochelate structures were solved for this type of complexes (Fig. 1, **A**). Among them are compounds with the encapsulated Fe^{2+}, Ru^{2+}, Co^{2+}, Co^{3+}, Ni^{2+}, Cu^{2+}, or Zn^{2+} ions and boron-, tin-, antimony-, chromium-, iron-, and manganese-containing cross-linking groups (Table 1). The majority of structures known are solved for the complexes of iron(II), which is the most efficient template, and trigonal boron compounds, which are the most active cross-linking agents (electron-pair acceptors, *viz.*, Lewis acids). For boron-containing iron(II) tris-dioximates, the structures of complexes with aliphatic acyclic[25—27] and alicyclic,[24,26,28—32]



Y = Sb, Sn, Ge

Fig. 1. Structural types of clathrochelate ligands.

Table 1. Main structural characteristics (a is the metal—nitrogen distance, h is the height of the coordination polyhedron, α is the bite angle, φ is the distortion angle) of α-dioximate, oximehydrazonate, and dihydrazonate clathrochelates

Complex		a/Å	h/Å	α/deg	φ/deg	Reference
[CoDm$_3$(BF)$_2$](BF$_4$)		1.89	2.29	40.0	31.2	19
CoDm$_3$(BF)$_2$		1.97	2.43	38.3	8.6	19
CoNx$_3$(BBu^n)$_2$		1.94	2.36	37.5	5.7	31
H[CoDm$_3$(SnCl$_3$)$_2$]·2PhH		1.90	2.18	40.2	42.3	36
(Bu$^n_4$N) [CoNx$_3$(SnCl$_3$)$_2$]		1.91	2.24	40.5	41.0	37
(Bu$^n_4$N) [CoNx$_3$(SnBr$_3$)$_2$]		1.89	2.20	40.7	39.9	38
(Bu$^n_4$N)[CoDm$_3$(SnBr$_3$)$_2$]		1.89	2.18	41.0	45.1	37
FePhm$_3$(BPh)$_2$·BF$_3$		1.91	2.34	39.2	21.8	47
FeBd$_3$(BF)$_2$·5CHCl$_3$		1.91	2.29	39.3	29.3	33
FeBd$_3$(BF)(BBu^n)$_2$·0.5*iso*-C$_8$H$_{10}$		1.89	2.31	39.5	17.9	45
FeFd$_3$(BPh)$_2$·0.25CHCl$_3$		1.91	2.31	39.2	26.4	27
FeGx$_3$(BOH)$_2$·3H$_2$O		1.91	2.33	39.1	23.4	28
FeGx$_3$(BPh)$_2$·2CHCl$_3$		1.915	2.35	38.9	20.2	29
FeDm$_3$(BF)$_2$·PhH		1.91	2.40	39.0	21.2	25
FeGm$_3$(BBu^n)$_2$		1.92	2.39	38.6	10.9	27
FeNx$_3$(BFc)$_2$·2CCl$_4$		1.90	2.38	39.3	9.5	30
FeNx$_3$(BBu^n)$_2$		1.91	2.34	39.1	20.3	31
FeGx$_3$(BPr^n)$_2$		1.90	2.31	38.8	21.8	24
FeOx$_3$(BBu^n)$_2$·CCl$_4$		1.90	2.34	39.2	25.2	24
[FeCXO$_3$(BPh)(HCOEt)$_3$](BF$_4$)·0.5PhH		1.90 1.91	2.37	38.7	10.8	59
[FeDXO$_3$(BPh)(HCOEt)$_3$](BF$_4$)		1.90 1.93	2.34	38.8	18.2	59
FeNx$_3$(BCH$_2$—CH=CH$_2$)$_2$	(A type) (B type)	1.90	2.36	38.9	13.8 17.0	26
FeNx$_3$(BC$_{16}$H$_{33}{}^n$)$_2$ at 298 K	(A type) (B type)	1.91	2.37 2.35	38.9	10 18	26
FeDm$_3$(BCH$_2$—CH=CH$_2$)$_2$		1.90	2.35	38.4	8.1	26
FeNx$_3$(BC$_6$H$_3$(OMe)$_2$)$_2$·CHCl$_3$		1.90	2.35	39.1	17.8	32
FeNx$_3$(BC≡C—Ph)$_2$·PhMe	(A type)	1.90	2.36	38.7	11.5	32
	(B type)	1.91	2.35	39.1	20.0	32
Fe(Cl$_2$Gm)$_3$(BPh)$_2$		1.90	2.39	39.0	5.4	51
Fe(Cl$_2$Gm)$_3$(BBu^n)$_2$		1.90	2.38	39.1	16.1	52
Fe(Cl$_2$Gm)$_3$(BF)$_2$·2THF		1.91	2.36	39.0	17.1	52
Fe((PhO)$_2$Gm)$_3$(BBu^n)$_2$		1.91	2.36	39.8	25.2	52
Fe((MeS)$_2$Gm)$_3$(BPh)$_2$·THF		1.91	2.32	39.3	25.3	52
Fe((PhS)$_2$Gm)$_3$(BPh)$_2$		1.91	2.33	39.5	25.6	51
Fe((Bu^{n}NH)$_2$Gm)$_2$(Cl$_2$Gm)(BPh)$_2$	(A type)	1.92	2.33	39.5	27.3	52
	(B type)	1.91	2.30	39.0	29.2	52
Fe((Bu^{n}S)$_2$Gm)$_3$(BPh)$_2$		1.91	2.33	39.4	25.6	55
Fe((AtrS)$_2$Gm)$_3$(BPh)$_2$·3CHCl$_3$		1.94	2.32	32.3	18.0	55
FeBd$_2$(Cl$_2$Gm)(BF)$_2$·2PhH		1.91	2.33	39.3	24.8	56
FeBd$_2$((Et$_2$N)ClGm)(BF)$_2$·PhH		1.91	2.31	39.3	26.6	56
FeBd$_2$((MeS)$_2$Gm)(BF)$_2$		1.90	2.31	39.3	25.8	56
FeNx$_3$(SbEt$_3$)$_2$		1.91	2.26	39.8	35.7	23
[FeNx$_3$(SnCl$_3$)$_2$]$^{2-}$		1.92	2.23	39.5	37.5	34
[Fe(Cl$_2$Gm)$_3$(SnCl$_3$)$_2$]$^{2-}$		1.92	2.24	40.5	40.4	53
FeBd$_2$(QNSGm)(BF)$_2$		1.91	—	39.0	23.6	57
Fe(Cl$_2$Gm)$_3$(Bdbt)$_2$		1.92	2.38	39.8	22.9	32
Fe((C$_6$H$_{11}$NH)$_2$Gm)$_2$(Cl$_2$Gm)(BPh)$_2$		1.90	2.30	39.4	28.7	58
Fe((Bu^{n}NH)ClGm)(Cl$_2$Gm)$_2$(BPh)$_2$		1.91	2.35	—	17.0	58
[FeDXO$_3$(BPy)(CH$_2$)$_3$·Co(HNx)$_2$Br](PF$_6$)·0.5MeOH		1.92	—	—	21.3	60
[FeCx$_3$(CH$_2$)$_3$](PF$_6$)$_2$		1.91	—	39.1	22.1	61

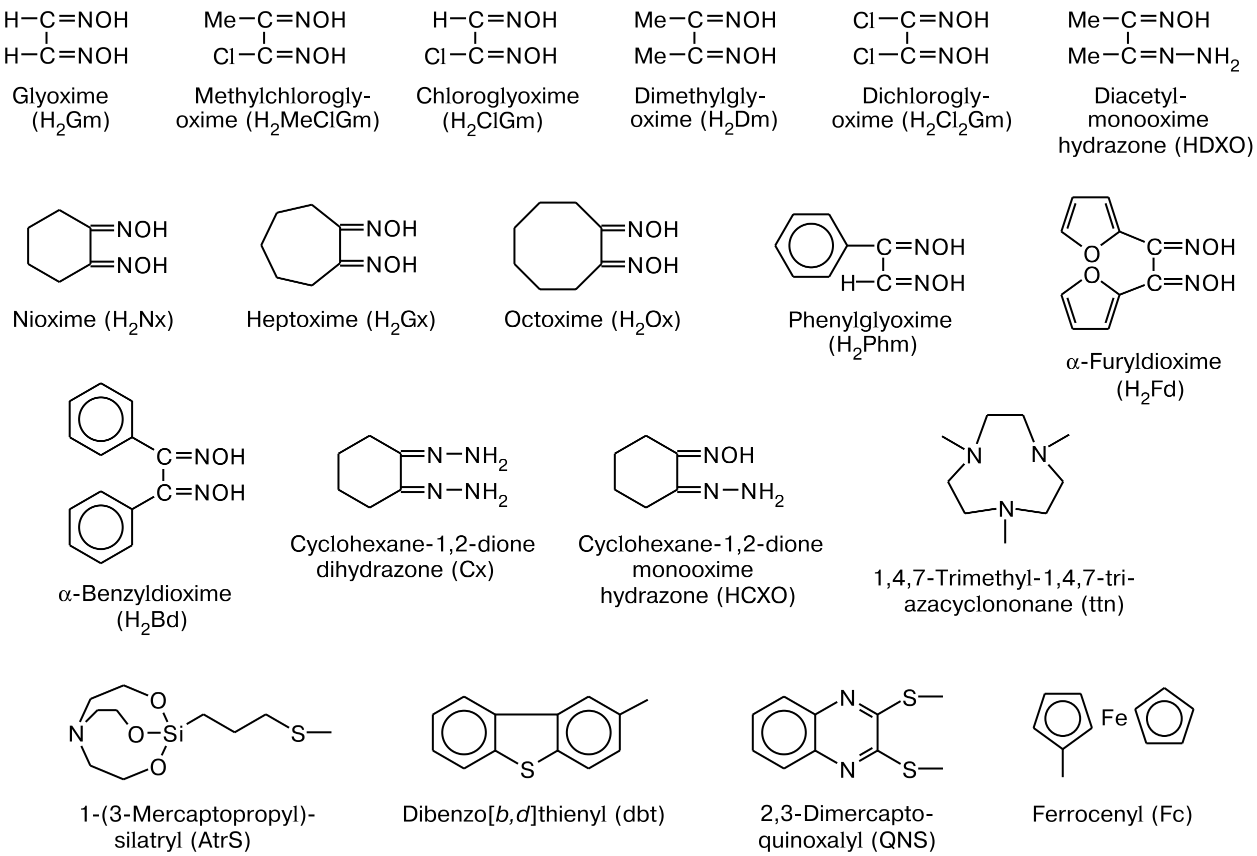
(*to be continued*)

Table 1 (*continued*)

Complex	*a*/Å	*h*/Å	α/deg	φ/deg	Reference
$Ru(Cl_2Gm)_3(BBu^n)_2$	1.98	2.47	38.8	2.6	54
$Ru((MeS)_2Gm)_3(BF)_2$	1.99	2.42	38.6	20.2	54
$Ru((PhO)_2Gm)_3(BBu^n)_2$	1.99	2.45	39.0	19.5	54
$RuNx_3(BBu^n)_2$	1.97	—	38.6	12.0	31
$[H_2Dm_3(ttnCr)_2](ClO_4)_2 \cdot MeOH$	—	2.67	—	5.7	44
$[ZnDm_3(ttnMn)_2](ClO_4)_2$	2.163	2.58	36.8	8.4	39
$[ZnNx_3(ttnMn)_2](ClO_4)_4 \cdot MeCN$	2.091	2.52	37.7	5.1	40
$[ZnDm_3(ttnCr)_2](ClO_4)_2 \cdot MeOH$	2.149	—	37.0	7.0	41
$[FeDm_3(ttnCr)_2](ClO_4)_2 \cdot H_2O$	1.936	2.27	39.3	34.7	35
$[CuNx_3(ttnMn)_2](ClO_4)_4 \cdot MeCN$	2.09	—	—	7.6	40
$[CuDm_3(ttnFe)_2](ClO_4)_2 \cdot 0.5MeOH$	2.16	2.53	40.4	11.5	42
$[CuDm_3(ttnCr)_2](ClO_4)_2 \cdot MeOH$	2.125	2.55	37.3	8.3	35
$[NiDm_3(ttnCr)_2](ClO_4)_2$	2.066	2.46	38.1	23.8	35
$[NiDm_3(ttnFe)_2](PF_6)_2 \cdot 0.5MeOH$	2.035	2.37	37.9	27.5	43

as well as with aromatic dioximes[27,33] (see Scheme 1) and with various apical substituents at the cross-linking boron atom (allyl, hexadecyl, fluoride, phenyl, *n*-butyl, *n*-propyl, hydroxy, ferrocenyl, *o*-methoxyphenyl, and phenylethynyl substituents) were determined. For other types of cross-linking atoms (antimony, tin, and chromium), very few structures with an encapsulated iron(II) ion were described.[23,34,35] Only one structure of an alicyclic ruthenium(II) clathrochelate with butylboronic cross-linking group was established.[31] For boron-containing cobalt clathrochelates, the structures of two complexes with the same fluoroboronic tris-dimethylglyoximate ligand and the encapsulated metal ion in two oxidation states (II and III)[3,19] as well as the structure of cobalt(II)

Scheme 1



clathrochelate, which is analogous to the above-mentioned ruthenium complex,[31] were determined. Macrobicyclic cobalt(III) tris-dimethylglyoximates and tris-nioximates formed by tin(IV) tetrachloride and tetrabromide were structurally characterized in most detail.[36—38]

Lewis acidity of iron, manganese, and chromium(III) complexes with the triazacyclononane macrocyclic ttn ligand (see Scheme 1) was used[35,39—43] for the synthesis of macrobicyclic tris-dimethylglyoximates and tris-nioximates, which can be considered as a special structural type, due to the cavity size in these compounds (unlike the macrobicyclic tris-dioximates cross-linked by p-block elements), which is suitable for encapsulation of transition metal ions with substantially larger ion radii (Zn^{2+}, Ni^{2+}, Cu^{2+}). The protonated form of one of these clathrochelate tris-dioximate ligands was isolated and structurally characterized in the study[44] for the first time.

2.2. Iron(II) clathrochelates with symmetric α-dioximes and nonequivalent cross-linking fragments

So far, only two structures of this type have been described (see Fig. 1, **B**), *viz.*, macrobicyclic iron(II) tris-α-benzyldioximate with different boron-containing cross-linking fragments[45] and hybrid iron(II) phthalocyaninoclathrochelate with cross-linking boron(III) and hafnium(IV) ions. The Hf^{4+} ion coordinates four nitrogen atoms of the phthalocyanine macrocycle, but it deviates substantially from the N_4 mean plane, which allows one to realize its Lewis acidity.[46]

2.3. Macrobicyclic iron(II) tris-complexes with unsymmetric α-dioximes

The template synthesis of this type of complexes results in a mixture of the *fac-* and *mer-*isomers of clathrochelates (see Fig. 1, **C**) that could not be separated by chromatography. However, crystallization of a mixture of isomers of iron(II) phenylglyoximate clathrochelate gave single crystals of the *mer* isomer, whose structure was established.[47] In contrast, the crystals of statistically minor *fac-*isomer of iron(II) tris-chloroglyoximate clathrochelate, suitable for X-ray diffraction analysis, were obtained in the study[48] and its structure was solved. Unusual results have been obtained for tris-methylchloroglyoximates, in which the crystallographic volumes of the methyl and chloride substituents are virtually equal.[49] As a result, the clathrochelate molecules in the crystals of these complexes are disordered in two positions and their *fac-* and *mer-*isomers are indistinguishable.[49] The nucleophilic substitution of phenylboronic iron(II) tris-methylchloroglyoximates with *n*-butylamine afforded the diamine complexes, with substitution of two of the three chlorine atoms. Crystallization of a mixture of these diamine clathrochelates[49] gave single crystals containing 90% of the *mer,mer-*isomer (see Fig. 1, **D**) and 10% of the chloroform solvate of the *fac,fac-*isomer. This unusual result was attributed to the fact that only the *fac,fac-*isomer crystals contain cavities, able to include the chloroform solvate molecules.

2.4. Iron and ruthenium(II) complexes with hexachloride clathrochelate ligands and their hexasubstituted derivatives

The structures of four hexachloride iron(II) precursors with fluoride, phenyl, *n*-butyl, and dibenzothienyl substituents at the cross-linking boron atoms[32,50—52] and the structure of one trichlorotin-capped complex of this type (see Fig. 1, **A**)[53] were established. For ruthenium(II) ion, only *n*-butylboronic hexachloride complex was structurally characterized.[54] Hexafunctionalized derivatives of these clathrochelate compounds were characterized by X-ray diffraction data in detail. Triribbed-functionalized iron and ruthenium(II) clathrochelates with pendant alkylthio,[52,54,55] phenylthio,[51,54] phenoxy,[52,54] and silatryl[55] substituents were structurally characterized.

2.5. Iron(II) clathrochelates with nonequivalent dioximate fragments

Some clathrochelates of this type (see Fig. 1, **D**) were prepared by the straightforward synthesis of monoribbed-functionalized complexes, whereas other structurally characterized clathrochelates were synthesized by the partial nucleophilic substitution in iron(II) hexachloride clathrochelates. Among the former clathrochelates, the structure of a dichloride α-benzyldioximate precursor of monoribbed-functionalized clathrochelates[56] is of particular interest. The structures of its monodiethylamino derivative and dimethyl sulfide clathrochelate were established.[56] Besides, the structure of the complex with the ribbed quinoxaline fragment proposed for the efficient intercalation into DNA structure, was determined.[57]

In the most solvents, the nucleophilic substitution of chlorine atoms of hexachloride iron and ruthenium(II) clathrochelates with primary spatially unhindered amines gives tetraamine clathrochelates with substituents in two of the three dioximate fragments.[58] This conclusion was confirmed by the X-ray diffraction data for *n*-butylamine and cyclohexylamine iron(II) complexes.[52,58] Selection of solvents and reaction conditions with *n*-butylamine allowed the monoamine clathrochelate to be isolated and structurally characterized.[58]

2.6. Oximehydrazonate and dihydrazonate clathrochelates

The structures of only three boron-capped oximehydrazonate[59,60] and one dihydrazonate[61] clathrochelates were established by X-ray diffraction. In all the cases they contain the incansulated Fe^{2+} ion, and in the case of oximehydrazonates the cross-linking group is the boron atom. Two oximehydrazonate iron(II) clathrochelates were obtained by macrocyclization of the hydrazonate fragments of the initial semiclathrochelate precursor with triethyl orthoformate.[59] According to the X-ray diffraction data, three ethoxy groups in the cross-linking 1,3,5-triazacyclohexane fragment of these compounds have *syn,syn,syn* orientation relative to the trigonal-prismatic semiclathrochelate fragment, and these substituents are located between the "petals" of three chelate π-conjugated rings (see Fig. 1, **G**). The substituents in these rings determine the geometry of the resulting trisubstituted 1,3,5-triazacyclohexane fragment, because the ethoxy substituents in trigonal-antiprismatic germanium-, tin-, and antimony-capped clathrochelates of this type have *anti,anti,anti* orientation (see Fig. 1, **G**).[59,62,63] Therefore, one of the cross-linking groups determines the geometry of another cross-linking fragment at a distance more than 5 Å through the substituents in the rigid macrobicyclic ligand, which is unusual for steric control.

Among dihydrazonate clathrochelates, only a complex, which was prepared by condensation of three cyclohexane-1,2-dione dihydrazone molecules (see Scheme 1) with formaldehyde on a Fe^{2+} ion matrix, was characterized by X-ray diffraction.[61]

3. Supramolecular organization and phase transitions in the crystals of clathrochelates

The crystal packing is influenced[46,52] by π,π interactions between the adjacent clathrochelate molecules. For example, in the crystal of hexaphenoxy iron(II) clathrochelate,[52] the molecules form columns due to the π,π interactions between the phenoxy substituents in one of the three dioximate fragments (Fig. 2). In the crystals of hybrid phthalocyaninoclathrochelates, the adjacent molecules form "base-to-base" oriented dimers due to the π,π-overlapping of two pyrrole fragments of the phthalocyanine macrocycles at a distance of 3.3 Å.[46]

The study of influence of the solvate molecules nature on the supramolecular organization of the crystals of allylsulfide α-benzyldioximate iron(II) clathrochelate showed[64] no solvent effect on the molecular structure of the clathrochelate. However, the packings of the clathrochelate molecules are similar only in the structures with the polar and low donor chloroform and with polar and high donor acetonitrile solvate molecules, but differ substantially from the packing for the solvate with nonpolar *n*-hexane. The main differences are the shift and different orientation of these molecules in crystal. The solvate chloroform and acetonitrile molecules occupy the centrosymmetric cavities formed by four clathrochelate molecules. In the crystal of *n*-hexane solvate, these cavities are formed by the phenyl and allyl substituents of six clathrochelate molecules. Thus, crystal packings of these solvates are determinated by polarity of the solvent molecules rather than their size. The weak intermolecular interactions between the clathrochelate "host" molecules allow one to use the "guest" solvate molecules for straightforwarded changes of their supramolecular organization in crystals.[64]

Fig. 2. Supramolecular organization of the crystal of iron(II) hexaphenoxy clathrochelate.[52]

X-ray diffraction study[26,65] revealed two different types of reversible phase transitions in the single crystals of iron(II) hexadecylboronate nioximate (Fig. 3) with retention of the number of formula units in unit cell (Fig. 4). One phase transition (between the phases I and II) is associated with an unusual change in the translational symmetry (one primitive translation disappears, while another translation appears). Another phase transition (between the phases II and III) is associated only with a stepwise change in the unit cell parameters. Both transitions are accompanied by distortions of the molecular geometry, in particular, by a distortion of the planar transoid conformation of particular hexadecyl substituents. In addition, these transitions are accompanied by changes in the geometry of the coordination polyhedron in two types of clathrochelate molecules (**A** and **B**) present in the crystals. As a result, these changes were observed in the distortion angle φ (17 and 10° for molecules **A** and **B** in the phase I, 19 and 14° in the phase II, and 20° for

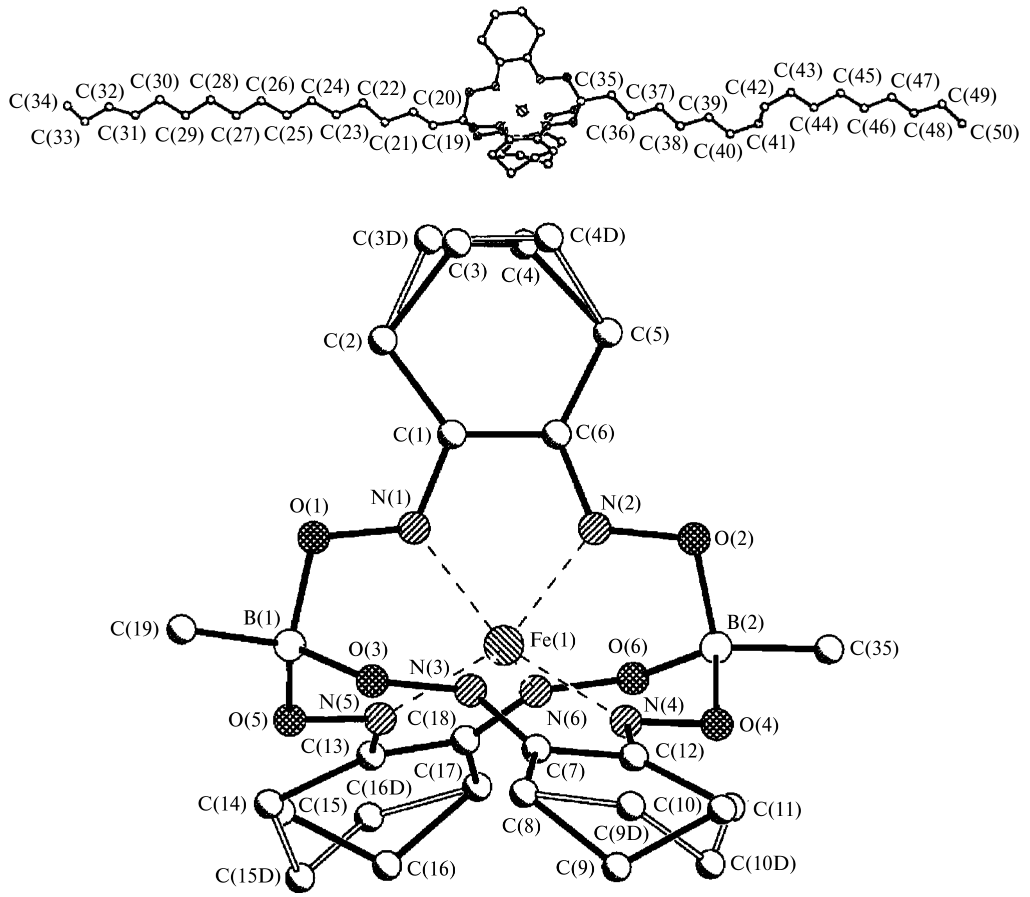


Fig. 3. Molecular structure of iron(II) nioximate hexadecylboronate.[25]

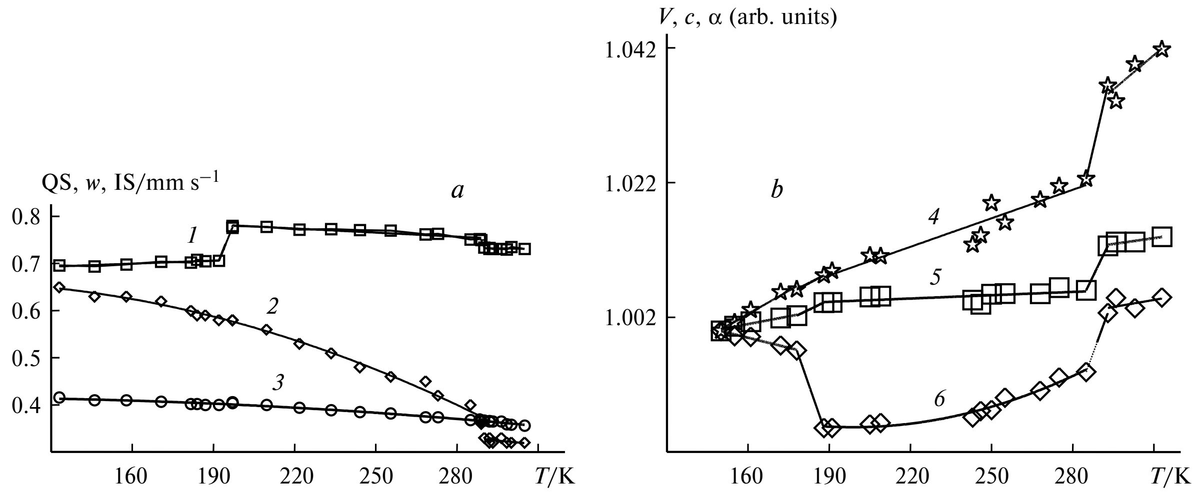
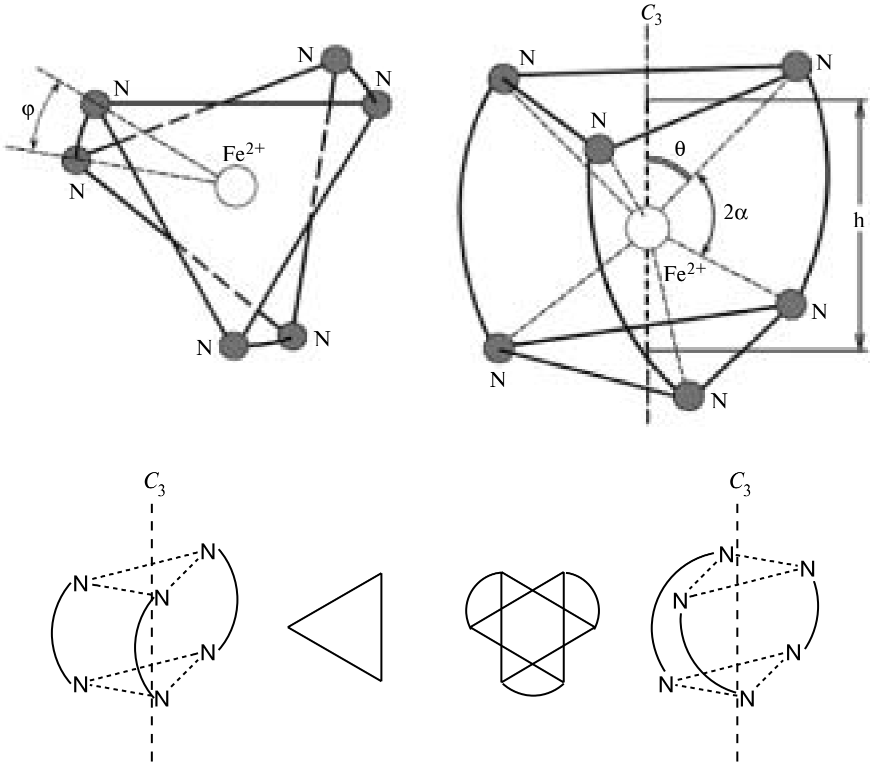


Fig. 4. Phase transitions in the crystal of iron(II) nioximate hexadecylboronate:[65] (*a*) ^{57}Fe Mössbauer parameters: quadrupole splitting (QS, *1*), half-width of a spectral line (*w*, *2*), isomer shift (IS, *3*); (*b*) unit cell parameters: *V* (*4*), *c* (*5*), α (*6*).

molecules of both types in the phase III). Both these transitions were also detected by ^{57}Fe Mössbauer spectroscopy (primarily, from the temperature dependence of quadrupole splitting, see Fig. 4). The mechanisms of both phase transitions are complicated and can be considered as superpositions of the processes, such as displacements and intramolecular distortions.[65]

The structure of hexachloride *n*-butylboronate iron(II) clathrochelate was established by X-ray diffraction at four temperatures from 180 to 300 K. Based on the results of



D_{3h}, $\varphi = 0°$ D_3, $\varphi = 60°$

Fig. 5. TAP—TP geometry of the coordination polyhedron of iron(II).[22]

this study combined with ^{57}Fe Mössbauer spectroscopic and calorimetric data, the model of temperature-dependent dynamic disorder of the macrobicyclic ligand was proposed.[66]

4. Structure—spectral parameter correlations and deducing of molecular structures

4.1. Modern version of the concept of the partial quadrupole splitting in ^{57}Fe Mössbauer spectra

4.1.1. Concept of partial quadrupole splitting (PQS). Quadrupole splitting (QS) in Mössbauer spectra is determined by the electric field gradient on the nucleus of the X-ray absorbing atom. A simple concept of PQS was developed[67—69] in order to explain QS values in iron and tin compounds and in all cases QS value has been determined as the difference in the partial electric field gradients. Therefore, the absolute value of PQS could not be calculated from the experimental QS value.

The trigonal-prismatic (TP) and trigonal-antiprismatic (TAP) geometries of iron(II) tris-diiminates provide a unique opportunity to obtain the QS values in the complexes with equivalent donor groups, and the resulting PQS values are "absolute".[21,22] The degree of distortion of the iron(II) coordination polyhedron can be characterized by the distortion angle φ (φ = 0° for TP and φ = 60° for TAP) and is influenced by the ligand nature. The sign of QS varies in the series of complexes with different φ (Fig. 5). In low-spin iron(II) complexes, the three lowest d-orbitals are occupied (for octahedral complexes these are t_{2g}-orbitals). In the case of a trigonal distortion, the t_{2g}-level splits into a_1 and e_1. At φ = 60°, tris-diimine complexes have the D_3 symmetry instead of O_h, which results in the non-zero value of splitting. With decrease of φ the splitting goes down to zero (φ = 40—50°), after which an inversion of the levels takes place, and the splitting increases again (Fig. 6). The splitting of the t_{2g}-levels and the absolute value of QS change parallel.

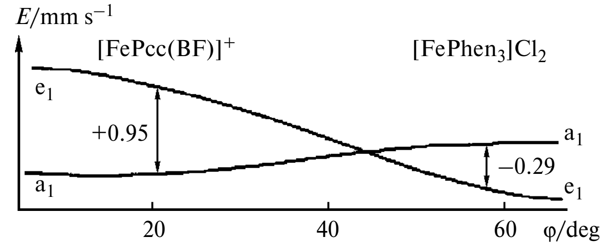


Fig. 6. Dependence of splitting of the t_{2g} level on the distortion angle φ for the coordination polyhedron of iron(II).[22]

It is known that the QS for ^{57}Fe nucleus can be expressed as

$$0.5e^2qQ(1 + \eta^2/3)^{1/2},$$

where $q = V_{zz}/e$, $\eta = (V_{xx} - V_{yy})/V_{zz}$, and V are the components of the electric field gradient tensor. From symmetry reasons, in TP-TAP complexes $V_{xx} = V_{yy}$, $\eta = 0$, and QS can be expressed as $6(3\cos^2\theta - 1)$PQS, or QS = f(PQS), where f is a function of iron atom arrangment geometry and θ is the angle between the symmetry C_3 axis and the Fe—N bond. For a given bidentate ligand, θ is a function of both bite angle α and distortion angle φ, and $f = 12 - 18\cos^2\alpha/\cos^2(\varphi/2)$.

Using the structural data for Mössbauer-characterized iron complexes, we calculated[21,22] the absolute values of PQS for a great number of ligands. For iron tris-dioximates the range of α angle usually observed is narrow and the QS value is the function of only φ angle and the effect of cross-linking groups. This allows one to predict the geometry of iron(II) complexes with high accuracy.

The modern version of PQS concept was applied successfully for the prediction of geometry of the hexadecyl- and allylboronate tris-dioximates,[26] ferrocenylboronic clathrochelates,[30] and macrobicyclic tris-oximehydrazonates.[59] A good coincidence between the experimental and calculated QS values has been observed even in the case of monoribbed-functionalized iron(II) clathrochelates with nonequivalent dioximate fragments.[56]

4.1.2. Limitations in the use of PQS concept. The applicability of the major concepts of the PQS model to iron(II) complexes is associated with axial C_3 symmetry of the electron density distribution (EDD) about the iron atom. Such a symmetry is most important to establish the correlation between QS and the geometry of the coordination environment.

It was found[25] that the experimental QS value (~0.7 mm s^{-1}) for fluoroboron iron(II) tris-dimethylglyoximate is much higher than the value calculated from the PQS model (0.38 mm s^{-1}). The molecular (Fig. 7) and crystal structure of this complex has been studied by X-ray diffraction analysis at 138, 208, and 291 K and compared with the ^{57}Fe Mössbauer parameters for this complex in the temperature range from 135 to 290 K.

It appeared[25] that the iron(II) coordination polyhedron is intermediate between a TP and a TAP (distortion angle φ is 21.2°). At 138 K, the iron(II) ion is displaced from the center of the N_6 polyhedron by 0.034 Å along the threefold pseudoaxis. At 208 and 291 K, this displacement is 0.026 and 0.023 Å, respectively. This feature distinguishes this complex from the known clathrochelates with equivalent α-dioximate fragments and cross-linking groups, for which this displacement has not been observed.

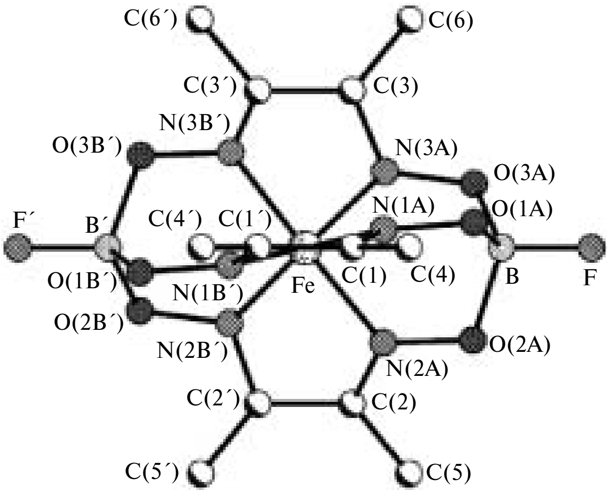


Fig. 7. Molecular structure of iron(II) dimethylglyoximate clathrochelate (hydrogen atoms are omitted).[25]

The deformation electron density (DED) in the vicinity of the iron atom has been examined by X-ray diffraction. The DED maxima were found in the vicinity of the metal ion (Fig. 8). The accumulation of the DED along the threefold pseudoaxis corresponds to the the a$_1$-MO, and the accumulation of the DED in the equatorial plane corresponds to the e$_1$-MO. However, unlike the expected axial symmetry of the DED distribution, the corresponding e$_1$-MO is characterized (as is seen from the section *b*) only by the symmetry plane passing though the threefold axis of the molecule. Therefore, in spite of the chemical equivalence of the bidentate chelating fragments, the interaction of the iron(II) ion with these fragments (according to the DED map) is anisotropic.[25]

The observed discrepancy between the experimental and calculated (from the PQS model) QS values is attributable to the fact that two major concepts of the PQS model are unapplicable for this complex: (1) the iron(II) ion is displaced from the center of the coordination polyhedron along the threefold axis of the molecule, resulting in the nonequivalence of the nitrogen atom contributions to QS, and (2) the axial symmetry of the electron density distribution about the encapsulated metal ion is distorted.

Therefore, the PQS values obtained in the studies[21,22] have a real physical meaning and reflect the electron density distribution in the molecule allowing one to explain QS values for a great number of iron coordination compounds with different geometry. These values make also it possible to deduce the structures of new compounds from the "structure *vs.* quadrupole splitting"-type correlations and taking into account the peculiarities of ligands (*e.g.*, cross-linking groups, substituents, protonation-deprotonation processes, *etc.*). The main reason for deviation from the proposed PQS model is an asymmetry of the electron density distribution caused by nonequivalence of donor atoms.[25]

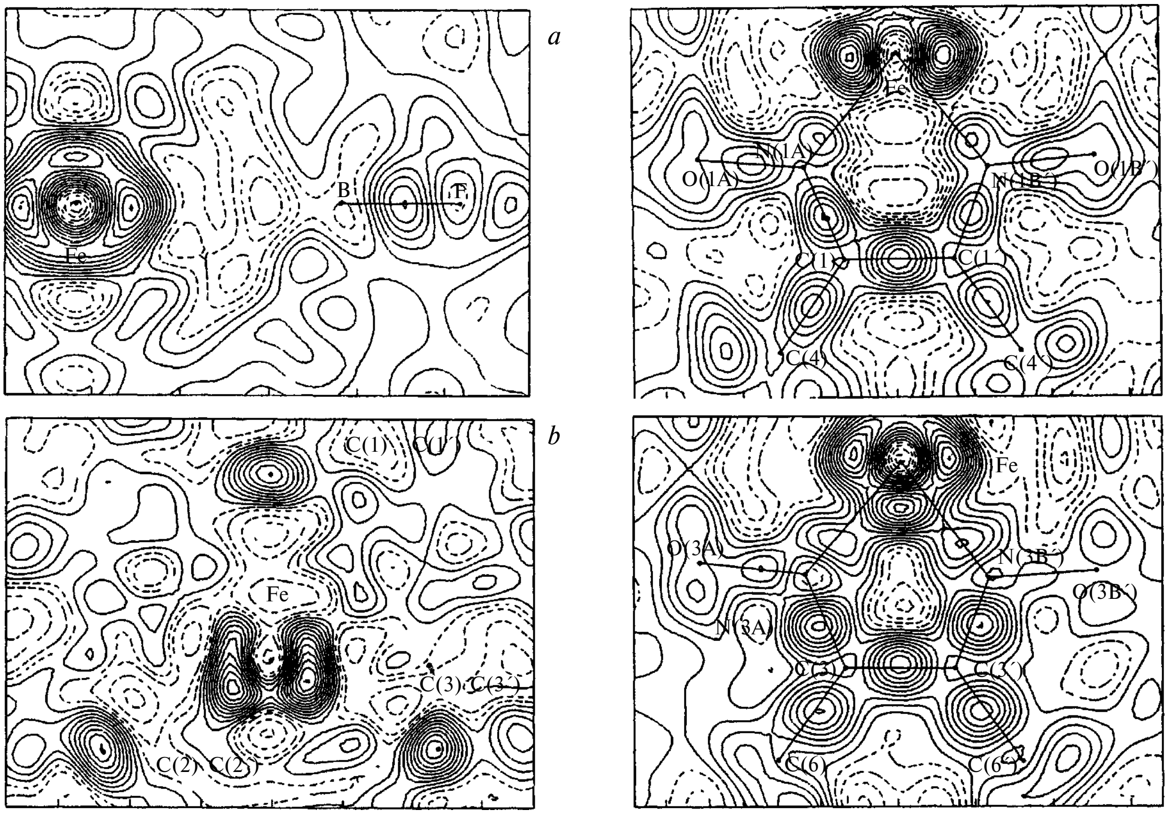


Fig. 8. Electron density distribution maps for the iron(II) dimethylglyoximate clathrochelate molecule.[25]

4.2. X-ray diffraction analysis and EXAFS data processing

If attempts to obtain single crystals suitable for X-ray diffraction study failed, the structures of compounds can be deduced using both the structure—spectral parameter correlations (see Section 4.1), which allow one to deduce the angular characteristics of the coordination polyhedron, and EXAFS data on the radial distribution of atoms (RDA) about the scattering nucleus.[70] Both the encapsulated metal ion nucleus and the cross-linking atom nucleus are generally used as the scattering nuclei. The RDA functions for these two types of scattering nuclei partially overlap, and the use of a superposition of their RDA functions improves the reliability of results. However, it is important to perform the iteration fitting procedure for EXAFS data using an initial theoretical approximation, which is most consistent with the real distances in the molecule. It was suggested[23] that this model may use X-ray diffraction data for structurally similar complexes. On the first step of molecular mechanics calculations, certain distances in the coordination polyhedra were fixed rigidly, and the calculated atomic coordinates were used as the initial approximation in the fitting procedure.

On the second step of molecular mechanics calculations, the RDA functions obtained were used to calculate other distances in the molecule. For a number of structurally characterized complexes, the results of molecular mechanics calculations were in good agreement with the X-ray diffraction data that confirms the validity of the approach proposed.[23]

5. X-ray diffraction analysis and the kinetics of the formation and decomposition of clathrochelates

X-ray diffraction data provided an explanation for the changes in the kinetic and thermodynamic parameters of the formation and decomposition of clathrochelates in the series from six- to eight-membered alicyclic dioximes (see Scheme 1).

It was found that the torsion angle between the oxime fragments in the seven-membered heptoxime molecule is twice as large as the corresponding angles in the six- and eight-membered dioximes due to the steric strain in the alicyclic fragment of the former compound.[71] An analogous effect was observed in clathrochelate complexes of the corresponding dioximes. The experimentally determined stability constant of the intermediate nonmacrocyclic tris-heptoximate (and, as a result, the formation rate constant for the corresponding macrobicyclic complex) is 500 times lower than the constants obtained for complexes with the six- and eight-membered dioximes.

Moreover, based on X-ray diffraction data for the formed on the first stage nonmacrocyclic iron(II) tris-dioximates (TAP geometry) and for the resulting boron-containing iron(II) tris-dioximates (TP geometry), the intramolecular condensation accompanied by a change of the complex geometry (TAP → TP) was suggested[24] as the rate-determining stage of the clathrochelate synthesis.

At the same time, a decrease in the complex formation rate constant in the case of heptoximate clathrochelates was used[28] for the kinetically controlled template synthesis of the corresponding hydroxyboronate iron(II) clathrochelate in a dilute aqueous solution, which made it possible to obtain its single crystals suitable for X-ray diffraction analysis.

6. Conclusions

The available X-ray diffraction data enable one

1) to perform the straightforwarded synthesis of new types of clathrochelate complexes with a desired encapsulated metal ion and to propose a new types of macrobicyclic ligands for the efficient encapsulation of this ion;

2) to change the supramolecular organization of the clathrochelate crystals in a desired way by choosing an appropriate solvent and to perform the structural phase transitions in these crystals;

3) to use the "structure—property" correlations for deducing of a structures and a properties of new compounds;

4) to explain changes in the kinetic and thermodynamic parameters of the clathrochelate synthesis and decomposition.

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