4. W. J. Horsley and H. Sternlicht, "Carbon-13 magnetic resonance studies of amino acids and peptides," J. Am. Chem. Soc., 90, No. 14, 3738-3748 (1968).
5. N. A. Kostromina, P. A. Korovaikov, N. V. Beloshitskii, and I. N. Marov, "Investigation of structure of zinc complexes with diethylenetriaminepentaacetate by means of proton magnetic resonance," Zh. Neorg. Khim., 19, No. 5, 1192-1195 (1974).
6. T. N. Polynova and M. A. Porai-Koshits, "Crystal chemistry of metal chelates based on ethylenediaminetetraacetic acid and its analogs," Itogi Nauki Tekh., Ser. Kristallogr. (VINITI, Moscow), 18, 64-274 (1984).

SPECTRA AND KINETICS OF FORMATION OF MACROBICYCLIC BORON-CONTAINING IRON(II) NIOXIMATES

Ya. Z. Voloshin, A. Yu. Nazarenko, É. V. Pol'shin,
S. I. Tyukhtenko, and N. A. Kostromina

UDC 546.722

Macrobicyclic boron-containing iron 4-methylnioximates were synthesized. The compounds obtained were characterized by data from elemental analysis, and electronic and IR spectroscopy. The structure of the immediate coordinational environment and the influence on it of the substituent at the boron atom was studied by the nuclear gamma resonance (NGR) (Mossbauer) method. From the ^{13}C and ^{11}B NMR spectroscopy data, the structure of the peripheral part of molecules of the complexes was determined. The kinetics of the synthesis and decomposition of iron 4-methylnioximate was studied and a mechanism was proposed for the template synthesis of the complex. The influence of the substituent on the structure and properties of macrobicyclic iron dioximates was established.

We have previously synthesized and studied the macrobicyclic complexes of iron(II) with 1,2-cyclohexadione dioxime (nioxime, H_2Nx) [1-3], and obtained data on their composition and structure, determined their spectral characteristics, and studied the formation kinetics. The present work deals with the clarification of the influence of a substituent in the cyclohexanone ring on the properties of the macrobicyclic complexes. We chose 4-methyl-nioxime (4-methyl-1,2-cyclohexadione dioxime H_24MNx) as the object of the investigation, since the methyl group in this compound is located in the β-position with respect to the oxime group, and for this reason should not lead to steric hindrances to the formation of the complex, but may have an inductive effect.

STUDY OF THE COMPLEXES BY THE IR, NMR, NGR AND ELECTRONIC SPECTROSCOPY METHODS

The IR spectra of the synthesized compounds and the initial dioxime were studied in the 400-4000 cm^{-1} region (a UR-20 spectrophotometer, KBr tablets). The NMR spectra on the ^1H, ^{13}C (with uncoupling from protons), and ^{11}B nuclei in DMSO-D_6 solutions were obtained on a Bruker SCR-200 spectrometer. The electronic absorption spectra of the solutions of the complexes in dioxane in the 15,000-25,000 cm^{-1} region were run on an SF-26 spectrophotometer. The X-ray phase analysis of the crystalline, samples, for the confirmation of their individual state, was carried out on a DRON-3 diffractometer (the copper K_α-radiation). The ^{57}Fe NGR spectra were obtained on a YaGRS-4M spectrometer at a natural content of ^{57}Fe in the samples studied at 300°K. The isomeric shifts were determined relative to sodium nitroprusside (±0.01 mm/sec).

The characteristics of the IR spectra of the compounds obtained, and also of the complex with nioxime are given in Table 1. In the IR spectra of the complexes, the bands belonging to the vibrations of free oxime groups at 2660-3100 cm^{-1} [4] are absent and several intense

---

Institute of General and Inorganic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Teoreticheskaya i Éksperimental'naya Khimiya, Vol. 25, No. 3, pp. 322-328, May-June, 1989. Original article submitted April 19, 1986; revision submitted February 14, 1988.

TABLE 1. Characteristics of Electronic and IR Spectra of Iron(II) 4-Methylnioximates

Compound	$\nu(C=N)$	$\nu(N-O)$	$\nu(B-O)$	$\delta(O-B-O)$	$\delta(\alpha, \alpha'-CH_2)$	$\delta(\beta-CH_2)$	$\nu_{max} \cdot 10^{-3}$, cm^{-1}	$\varepsilon \cdot 10^{-4}$, $dm^3 \cdot mole^{-1} \cdot cm^{-1}$
	cm^{-1}							
H_24MNx	1580 1647, 1658	961, 995 1068, 1227, 1280			1425d	1467		
$Fe(4MNx)_3(BF)_2$	1599	953, 972 1068, 1090 1228, 1260	1190 1044 (B—F)	785, 825	1443	1471	22,2	2,00
$Fe(4MNx)_3(BOH)_2$	1591	935, 955 1067, 1090 1235 d	1195	779, 807	1446	1470	22,2	1,80
$Fe(4MNx)_3 \times$ $\times(BO\ iso-C_3H_7)_2$	1595	940, 965 1070, 1090 1230, 1260	1195	781, 810	1445	1468	22,2	1,68
$Fe(4MNx)_3 \times$ $\times(BO\ n-C_4H_9)_2$	1596	943, 962 1070, 1088 1228, 1243	1193	780, 808	1450	1470	22,3	1,52
$Fe(4MNx)_3 \times$ $\times(BO\ sec-C_4H_9)_2$	1591	945, 968 1059, 1089 1230, 1260	1194	783, 814	1442	1470	22,3	1,54
$Fe(4MNx)_3(BCH_3)_2$	1579	970 d 1062, 1100 1246, 1281	1103	840, 850	1437	1458	22,2	1,88
$FeNx_3(BOH)_2$ [2]	1577	974, 1061 1228, 1270	1199	771, 810	1435	1490	22,3	1,80
H_2Nx [2]	1575 1645	963, 985 1082, 1260			1419	1459		

bands which are characteristic of the boron atom in the tetrahedral environment are observed. The deformational vibrations of the O-B-O fragment in the case of the $Fe(4MNx)_3(BR)_2$ compounds, as in the nioximates are manifested in the form of two lines of equal intensity in the 800 cm^{-1} region. The unusually low frequency value of the stretching vibrations of the B-O bond in the case of the $Fe(4MNx)_3(BCH_3)_2$ complex should be noted; this is due to the strong electron donor effect of the methyl substituent, the characteristic deformational vibrations of which are observed at 1309 cm^{-1} [5].

The stretching vibrations of the C = N bond in the 1650 cm^{-1} region, characteristic of free ligands, do not appear in the complexes, except for the weak bands in the spectra of boromethyl compounds. During coordination, as in the case of the complexes with nioxime, the absorption bands of the stretchig vibrations of the C = N bond in the 1600 cm^{-1} region are shifted as compared with the vibrations of free dioxime, but in the case of 4-methylnioxime the shift (10-20 cm^{-1}) is much greater than in nioxime (2-9 cm^{-1}). The deformational vibrations of the α,α'-methylene groups of 4-methylnioxime are sensitive to coordination: their bands are shifted by 17-25 cm^{-1}, whereas the vibrations of the β-methylene group practically do not change (1-9 cm^{-1}).

The electronic spectra of the compounds obtained in the visible region are similar to the spectra of compounds in the $FeDm_3(BR)_2$ series (Dm^{2-} is the dimethylglyoxime anion) and $FeNx_3 \cdot (BR)_2$. They contain one asymmetric band (which also does not split in the spectrum of the second derivative) with a maximum in the 22,000-22,300 cm^{-1} region, interpreted as a band representing a charge transfer from the d-orbital of iron to the π^*-orbital of the ligand.

In the PMR spectra of the solutions of complexes with nioxime, the cyclohexane ring proton signals are in the form of two broadened singlets with a 1:1 intensity ratio (α- and β-methylene groups). In most of the unsubstituted cycloalkanes with a large size of the ring, this form of the lines indicates their dynamic character: at room temperature, the conformational transition proceeds rapidly and the spin-spin interaction between the protons is not observed

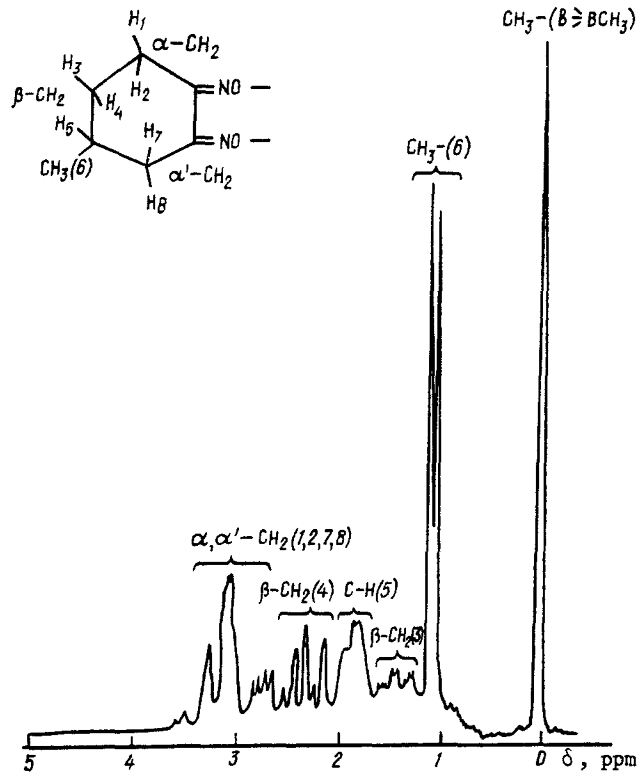

Fig. 1. PMR spectrum of the solution of $Fe(4MNx)_3 \cdot (BCH_3)_2$ in $CDCl_3$.

[6]. In the case of 4-methylinioxime and its complexes, the introduction of a bulky substituent hinders the conformational transitions, and at room temperature, the spin-spin interaction is distinctly manifested in the spectra.

The PMR spectra of 4-methylnioxime and its complexes are very similar to one another, which shows that during the complexation there are only inappreciable changes in the conformation of the oxime. To assign the lines in these spectra, model compounds were examined (cyclohexanone, 4-methylcyclohexanone, and their oximes) and experiments were carried out on double resonance (suppression of the spin-spin interactions), which made it possible to assign the groups of lines (Fig. 1). A more detailed assignment and the values of the spin-spin coupling constants were not obtained because of the complexity of the spin system.

In the ^{11}B NMR spectrum (Table 2) of the $Fe(4MNx)_3(BF)_2$ complex, a doublet is observed due to a ^{11}B-^{19}F interaction, while in the case of $Fe(4MNx)_3(BOH)_2$, there is one broad band ($\Delta\nu_{1/2}$ = 420 Hz), similar to the band of H_3BO_3, but shifted by 14.5 ppm with respect thereto into the strong field. The reason for this is that the boron atom in the complex has a tetrahedral environment.

The signals of the different carbon atoms in the ^{13}C NMR spectra of the complexes are inappreciably shifted in comparison with the initial oxime. As in the case of nioxime, the signal of the α-(CH_2)-group is shifted in the direction of a weak field, while that of the β-(CH_2)-group is shifted in the strong field direction.

The ^{57}Fe NGR spectra of all the synthesized compounds are in the form of a symmetrical doublet; the parameters of these spectra are characteristic of low spin complexes of Fe(II), and agree well with the results previously obtained for complexes in the $FeD_3(BF)_2$ series [7] (D^{2-} are anions of dioximes of various nature). The isomeric shift decreases inappreciably in the series of substituents at the boron atom: $F \leq OH < O\,(n\text{-}C_4H_9) \leq CH_3$ from 0.35 to 0.31 mm/sec, which formally corresponds to an increase in the strength of the field of the ligand. Increase in the quadrupole splitting in the same series from 0.60 to 0.69 mm/sec indicates that the structure of the fluorine-containing complex is closer to that of a trigonal prism. Replacement of the fluorine atom by the more bulky (and less electronegative) groupings leads to a decrease in the strength of the field of the ligands and the approach

TABLE 2. Characteristics of Magnetic Reasonance Spectra on ^{13}C and ^{11}B Nuclei of Complexes

Compound	δ ^{13}C, ppm (rel. to TMS)						δ ^{11}B, ppm (rel. to NAB(C_6H_5)$_4$	J_{B-F}, Hz.
	α-CH_2	α'-CH_2	β-CH_2	$-\overset{\vert}{\underset{\vert}{C}}-H$	CH_3	$>C{=}NO$		
H_24MNx	35,82	32,97	31,50	26,74	24,37	154,57	—	—
$Fe(4MNx)_3(BF)_2$	36,50	31,70	30,53	28,08	23,69	155,34 155,38	10,36	12,21
$Fe(4MNx)_3(BOH)_2$	36,61	31,05	30,71	28,03	23,88	152,88 153,18	12,0	—
$FeNx_3(BF)_2$ [7]	25,76	—	20,65	—	—	152,47	10,35	13,7

of the coordinational polyhedron to an octahedron form, which is optimal for the d^6-configuration. The angle of distortion of the coordinational polyhedron — the trigonal prism, evaluated from the dependence of the value of quadrupole splitting on this angle, proposed in [7], is equal to 25-29° for 4-methylnioximates.

STUDY OF KINETICS OF SYNTHESIS AND DECOMPOSITION OF THE $Fe(4MNx)_3(BOH)_2$ COMPLEX

The study of the reaction kinetics of the synthesis and decomposition of the $Fe(4MNx)_3\cdot(BOH)_2$ complex was carried out specrophotometrically as described in [3] for the complex with nioxime. For the reaction rate of the synthesis of $Fe(4MNx)_3(BOH)_2$, the following expression is valid over a wide range of concentrations

$$-dc/dt = k_c\,[Fe^{2+}]\,[H_24MNx]^3\,[H_3BO_3]\,[H^+]^{-1}, \tag{1}$$

where $k_c = (2.9 \pm 0.6)\cdot10^2$ $sec^{-1}\cdot dm^9\cdot mole^{-3}$. The energy of activation of the synthesis was determined according to a line plotted in Arrhenius coordinates: $E_a = 21 \pm 4$ kJ/mole.

In acidic solutions in the absence of boric acid, the complex decomposes irreversibly, and the rate of the process is described by the equation

$$-dc/dt = (k_0 + k_1\,[H^+])\,[Fe(4MNx)_3(BOH)_2] \tag{2}$$

($k_0 = 7.4 \pm 1.0)\cdot10^{-4}$ sec^{-1}; $k_1 = (0.32 \pm 0.04)$ $sec^{-1}\cdot dm^3\cdot mole^{-1}$). In the presence of boric acid, the rate of decomposition decreases and the effective rate constant of decomposition has the form

$$k_{eff} = (k_0 + k_1\,[H^+])/(1 + K_2\,[H_3BO_3]\,[H^+]^{-1}), \tag{3}$$

where $K_2 = (40.0 \pm 2.0)$. From the dependence of the rate of decomposition in the absence and presence of boric acid on temperature, the value of the activation energy found for k_1 is $E_a = 81 \pm 8$ kJ/mole, and for K_2 the enthalpy value is $\Delta H = -22 \pm 4$ kJ/mole.

The kinetic equations describing the synthesis and decomposition reactions of the $Fe\cdot(4MNx)_3(BOH)_2$ complex are similar to the equations obtained in [3] for the $FeNx_3(BOH)_2$ complex. The kinetic and thermodynamic parameters of these reactions for 4-methylnioximate and nioximate are also similar to one another. We can thus state that the scheme of the synthesis of the macrobicyclic complexes proposed in [3], also holds for the case of 4-methylnioximate (Fig. 2). It can readily be seen that the equations describing the synthesis and decomposition of the complex by this scheme coincide with the experimentally obtained equations (1)-(3).

The rate of the reaction represented in Fig. 2 can be written in the form

$$dc/dt = k_{lim}\,[Fe(H_2D)_2(HD)\cdot B(OH)_3^+] = k_{lim}\,K_b\beta_3[Fe^{2+}]\,[H_2D]^3\,[H_3BO_3]\,[H^+]^{-1}$$

which corresponds to equation (1). The decomposition reaction of the complex in an acid medium can be represented as follows:

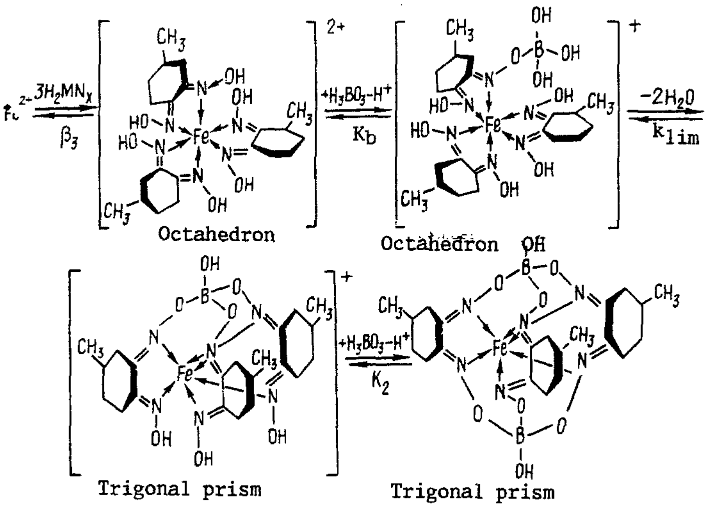

Fig. 2. Mechanism of formation of the macrobicyclic complex $\mathrm{Fe(4MNx)_3(BOH)_2}$.

$$\mathrm{Fe}(4MNx)_3(\mathrm{BOH})_2 \xrightleftharpoons[K_2]{+\mathrm{H_3BO_3}-\mathrm{H^+}} \mathrm{Fe}(\mathrm{H}4MNx)_3(\mathrm{BOH})^+ \xrightarrow[k_0+k_1[\mathrm{H^+}]]{} \mathrm{Fe}^{2+} + \mathrm{H_3BO_3} + \mathrm{H_2}4MNx + \text{decomposition products of } \mathrm{H_2 4MNx}.$$

On the basis of the above scheme, for the concentration of the colored forms, we can write

$$c_{\mathrm{col}} = C_{\mathrm{Fe}(4MNx)_3(\mathrm{BOH})_2} + C_{\mathrm{Fe}(\mathrm{H}4MNx)_3(\mathrm{BOH})^+}, \tag{4}$$

$$K_2 = C_{\mathrm{Fe}(4MNx)_3(\mathrm{BOH})_2}[\mathrm{H^+}]/C_{\mathrm{Fe}(\mathrm{H}4MNx)_3(\mathrm{BOH})^+}[\mathrm{H_3BO_3}]. \tag{5}$$

By substituting (5) into (4), we obtain

$$C_{\mathrm{Fe}(\mathrm{H}4MNx)_3(\mathrm{BOH})^+} = c_{\mathrm{col}}/(1 + K_2(\mathrm{H_3BO_3})[\mathrm{H^+}]^{-1}) \tag{6}$$

and furthermore, taking into account equation (2), we have

$$dc/dt = -c_{\mathrm{col}}(k_0 + k_1[\mathrm{H^+}])/(1 + K_2[\mathrm{H_3BO_3}][\mathrm{H^+}]^{-1}), \tag{7}$$

which conforms with equation (3) obtained experimentally.

SYNTHESIS OF COMPLEXES

"Analytically pure" grade $\mathrm{H_3BO_3}$, $\mathrm{FeCl_2 \cdot 4H_2O}$, $\mathrm{FeSO_4 \cdot 7H_2O}$ were used in the investigation. 4-Methylglyoxime was obtained according to [8] and was purified by recrystallization from water. Compounds of the $\mathrm{Fe(4MNx)_3(BR)_2}$ series (R = F, $\mathrm{CH_3}$, OH, $\mathrm{O(iso\text{-}C_3H_7)}$, $\mathrm{O(sec\text{-}C_4H_9)}$, $\mathrm{O(n\text{-}C_4H_9)}$) were obtained similarly to the compounds of the $\mathrm{FeNx_3(BR)_2}$ series.

The $\mathrm{Fe(4MNx)_3(BF)_2}$ Complex. Iron(II) chloride tetrahydrate $\mathrm{FeCl_2 \cdot 4H_2O}$ (0.34 g, 0.0017 mole) and 4-methylnioxime (0.78 g, 0.005 mole) were dissolved in 10 ml of butanol, the mixture was heated for 5 min, and 10 ml of $\mathrm{BF_3 \cdot (C_2H_5)_2O}$ was added. Orange crystals thus precipitated. The product was filtered and recrystalized from hol acetonitrile. The crystals that separated were washed with ether, and dried at 60°C. For $\mathrm{Fe(4MNx)_3(BF)_2}$: found, %: Fe 9.92; B 3.55; N 14.7; calculated, %: Fe 9.69; B 3.77; N 14.5.

The $\mathrm{Fe(4MNx)_3(BCH_3)_2}$ Complex. Iron(II) chloride tetrahydrate $\mathrm{FeCl_2 \cdot 4H_2O}$ (0.34 g, 0.0017 mole) and 4-methylnioxime (0.78 g, 0.005 mole) were dissolved in 10 ml of methanol, the mixture was stirred for 5 min, and 2 g of $\mathrm{B(CH_3)_3 \cdot NH_3}$ was added. A red-grey precipitate separated, which was filtered and recrystallized from methylene chloride. The crystals that separated were washed with ether and dried at 60°C. For $\mathrm{Fe(4MNx)_3\ (BCH_3)_2}$: found, %: Fe 9.80; B 3.74; N 14.5; calculated, %: Fe 9.82; B 3.79; N 14.6. N 14.7.

The $Fe(4MNx)_3(BOH)_2$ Complex. Iron(II) sulfate heptahydrate $FeSO_4 \cdot 7H_2O$ (0.48 g, 0.0017 mole), 4-methylnioxime (0.78 g, 0.005 mole, and H_3BO_3 (0.42 g, 0.0068 mole) were dissolved in 20 ml of water, a solution of $Na_2B_4O_7 \cdot 10H_2O$ (0.30 g, 0.00085 mole) in 5 ml of water was added dropwise, and the mixture was heated for 5 min. A red-orange precipitate separated, which crystallized poorly from water, and was dissolved in hot acetonitrile. After cooling, light-orange crystals precipitated, which were washed with ether, and dried at 60°C. For $Fe(4MNx)_3$ $(BOH)_2$: found, %: Fe 9.96; B 3.86; N 14.4; calculated %: Fe 9.76; B 3.80; N 14.6.

The $Fe(4MNx)_3$ $(BO\ iso\text{-}C_3H_7)_2$ Complex. Iron(II) chloride tetrahydrate $FeCl_2.4H_2O$ (0.34 g, 0.0017 mole), 4 methylnioxime oxime (0.78 g 0.005 mole, and H_3BO_3 (0.42 g, 0.0068 mole) were dissolved in 10 ml of isopropanol, and the mixture was heated under reflux for 5 min. A solution of $Na_2B_4O_7 \cdot 10H_2O$ (0.30 g, 0.00085 mole) was added, and the mixture was heated for another 10 min. The solution was filtered, evaporated to dryness on a rotary evaporator at room temperature. The dry residue was treated with 10 ml of acetonitrile, filtered and left to stand for several hours. When practically all the acetonitrile evaporated, 20 ml of benzene were added to the oily residue, the mixture was filtered, and fine yellow crystals of the complex were precipitated by adding 60 ml of hexane. The compound obtained was filtered and dried at 60°C. For $Fe(4MNx)_3(BOiso\text{-}C_3H_7)_2$: found, %: Fe 8.83; B 3.36; N 12.8; calculated %: Fe 8.52; B 3.31; N 12.8.

The $Fe(4MNx)_3(BOsec\text{-}C_4H_9)_2$ Complex was synthesized in a similar way, but using 2-butanol instead of isopropanol. For $Fe(4MNx)_3(BOsec\text{-}C_4H_9)_2$: found, %: Fe 8.35; B 3.12; N 12.7; calculated %: Fe 8.16; B 3.18; N 12.3.

The $Fe(4MNx)_3(BOn\text{-}C_4H_9)_2$ Complex was synthesized in a similar way, but using 1-butanol instead of 2-butanol. For $Fe(4MNx)_3(BO\ n\text{-}C_3H_7)_2$: found, %: Fe 8.29; B 3.02; N 12.7; calculated %: Fe 8.16; B 3.18; N. 12.3.

The compounds obtained are orange or yellow crystals, which are readily soluble in chloroform, acetonitrile, dimethyl sulfoxide, and dioxane and stable on heating up to 200°C. The $Fe(4MNx)_3(BF)$ and $Fe(4MNx)_3(BCH_3)_2$ complexes are chemically stable, and are decomposed only by concentrated acids. The remaining complexes decompose readily in an acid medium. Only $Fe(4MNx)_3(BF)_2$ and $Fe(4MNx)_3(BCH_3)_2$ crystallize well from organic solvents, while the $Fe \cdot (4MNx)_3(BOR)_2$ compounds crystallize much more poorly.

Analysis of the data obtained shows that the introduction of a substituent into the cyclohexane ring has virtually no influence on the structure of the immediate coordination sphere and the mechanism of formation of the macrobicyclic complexes, while the peripheral part of the molecule substantially changes, which leads to a sharp change in the physical properties, such as, for example, the solubility. Thus, the directed introduction of a substituent, while virtually not changing the chemical properties of a compound, makes it possible to change its physical properties in the desired direction.

LITERATURE CITED

1. A. Yu. Nazarenko and Ya. Z. Voloshin, "Determination of iron as macrocyclic complex with nioxime and boric acid," Zh. Anal. Khim., 37, No. 8, 1469-1472 (1982).
2. A. Yu. Nazarenko and Ya. Z. Voloshin, "Boron-containing complexes of iron with 1,2-cyclohexanedione dioxime," Zh. Neorg. Khim., 29, 1776-1780 (1984).
3. Ya. Z. Voloshin and A. Yu. Nazarenko, "Kinetics of tempate synthesis and decomposition of macrobicyclic iron(II) complex," Dokl. Akad. Nauk USSR, Ser. B., No. 10, 34-38 (1985).
4. D. G. Batyr, I. I. Bulgak, and L. D. Ozol, "Molecular complexes of iron(II) cyclohexanedione dioxime," Koord. Khim., 4, No. 1, 84-87 (1978).
5. A. Smith. Applied IR Spectroscopy, [Russian translation], Mir, Moscow (1982).
6. C. Hunter, Introduction to a Course of NMR Spectroscopy [Russian translation], Mir, Moscow (1984).
7. E. V. Pol'shin, V. V. Trachevskii, S. I. Tyukhtenko, et al., "Effect of the ligand nature on structure and spectra of boron-containing iron(II) dioximates," Koord. Khim., 13, No. 1, 96-99 (1987).
8. C. V. Banks D. T. Hooker, and I. I. Richard, "Preparation and properties of some alkyl-1,2-cyclohexanedione dioximes," J. Org. Chem., 21, No. 5, 547-550 (1956).