The synthesis and structure of a macrobicyclic hexahalogenide trisdioximate as a promising precursor of functionalized clathrochelates

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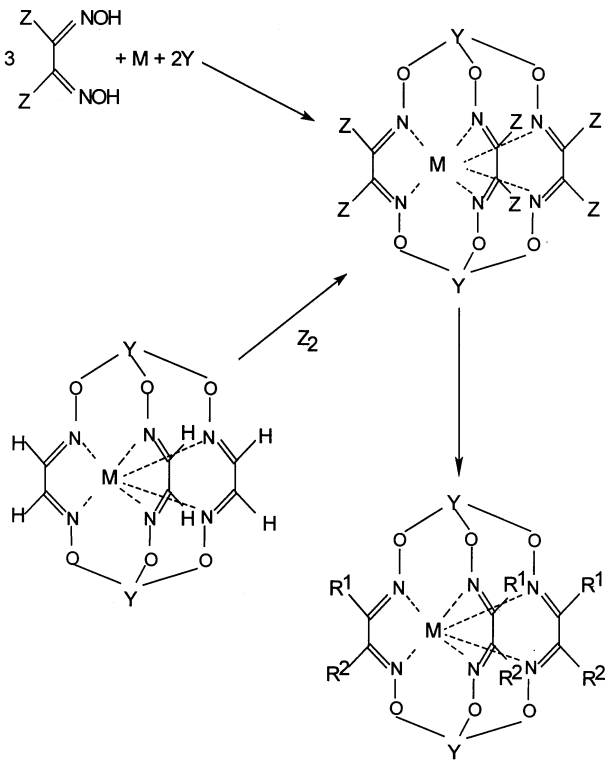
The reactive hexachloride precursor of functionalized α-dioximate clathrochelates and the product of their reaction with thiophenol have been prepared and structurally characterized by single-crystal X-ray diffraction.

Compounds containing an encapsulated metal ion in the three-dimensional cavity of a macropolycyclic ligand have recently become of great interest to scientists working in different fields of chemistry and biochemistry. This is mainly due to the unique properties displayed by ions of a metal that is encapsulated into the "cage" of a macropolycyclic ligand, to a great extent isolated from external factors.[1–5] High selectivity in the formation of such complexes, the screening of an encapsulated metal ion, and the low reactivity exhibited by the majority of the synthesized compounds limit studies of reactions of coordinated metal ions and the reactivity of macrobicyclic ligands. These factors can also explain difficulties in the synthesis of such compounds with a variety of metal ions.

The first stage of the preparation of functionalized macrobicyclic oximates, oximehydrazonates, and their modified complexes has involved the development of synthetic procedures for halide-containing precursors that permit the subsequent modification and functionalization to be carried out by exploring the reactivity of halideoxime fragments. Two strategies for the synthesis of such precursors can be proposed (Scheme). The first one is based on halogenation of presynthesized clathrochelates. High yields and the availability of these clathrochelates are, undoubtedly, the advantages of this approach. However, the proposed reaction pathway cannot commonly be used because of a partial substitution of hydrogen atoms for the halides. In addition, side reactions of the macrobicyclic framework effect by halogenation agents may also take place. Furthermore, with some substituents at the boron atoms, halogenation can also occur under the same conditions.

The second strategy, which is based on the use of preformed dihalodioximes, does not have the disadvantages of the first one. Although conventional synthetic routes were unsuccessful, we have managed to select conditions to give yields of 90%. Stepwise addition of the $Fe(CH_3CN)_4Cl_2$ complex to a boiling solution/suspension of dichloroglyoxime (H_2Cl_2Gm) and phenylboronic acid in nitromethane with a 1 : 3.5 : 2 ratio for 1 h and dehydration of the solvent with 4 Å molecular sieves followed by distillation of a proportion of the solvent led to the formation of a solid $Fe(Cl_2Gm)_3(BC_6H_5)_2$ clathrochelate. After the suspension was cooled, the precipitate was filtered off, washed with nitromethane, a small amount of chloroform, diethyl ether, hexane and recrystallized from hot methylene dichloride. The hexachloride compound **1** readily reacted with active thiol and amino groups to produce functionalized clathrochelates that were capable of coordinating metal ions using peripheral fragments. The intensive stirring of a $Fe(Cl_2Gm)_3(BC_6H_5)_2$ solution/suspension in hot 1,4-dioxane with an excess of thiophenol in the presence of K_2CO_3 led to the formation of a red-brown reaction mixture. The latter was evaporated to a small volume, and the product was precipitated by adding a fivefold volume of ethanol. The resulting crystalline $Fe[(C_6H_5S)_2Gm]_3(BC_6H_5)_2$ precipitate (**2**) was washed with ethanol, diethyl ether and reprecipitated from chloroform with hexame.† Our attempts to remove the Fe^{2+} ion from the cavity and isolate free macrobicyclic ligands were unsuccessful due to decomposition of the latter.



R^1, R^2 = $P(C_6H_5)_2$, $NAlk_2(Ar_2)$, crown ether or another macrocycle, ferrocenyl, SAlk(Ar), C_5H_5, CN, $PO(OH)_2$

(R^1, R^2) = crown ether or another macrocycle fragment
Z = halogen
Y = Lewis acid
M = metal ion

Scheme

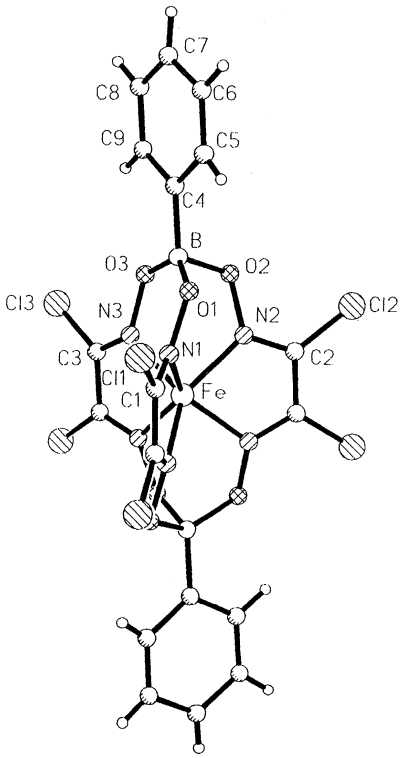


Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and bond angles (°) are as follows: Fe—N1, 1.894(8); Fe—N2, 1.905(8); Fe—N3, 1.913(8); O1—B, 1.51(3); N1—C1, 1.27(1); Cl1—C1, 1.712(9); C1—C1$^{\#1}$, 1.42(2); N1$^{\#1}$—Fe—N1, 78.7(6); N1—Fe—N2, 85.4(4); O1—N1—Fe, 121(1); C1—N1—Fe, 117.8(8); N1—O1—B, 110(2); N1—C1—C1$^{\#1}$, 112.8(6); O2—B—O1, 106(1). Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+1, y, -z+1/2$.

The ^{1}H NMR spectrum of precursor **1** contained two multiplets at approximately 7.4 and 7.85 ppm, whereas that of complex **2** revealed only one multiplet at approximately 7.1 ppm. The ^{13}C NMR spectra (with and without ^{13}C–^{1}H interaction decoupling) permitted the identification of a signal of

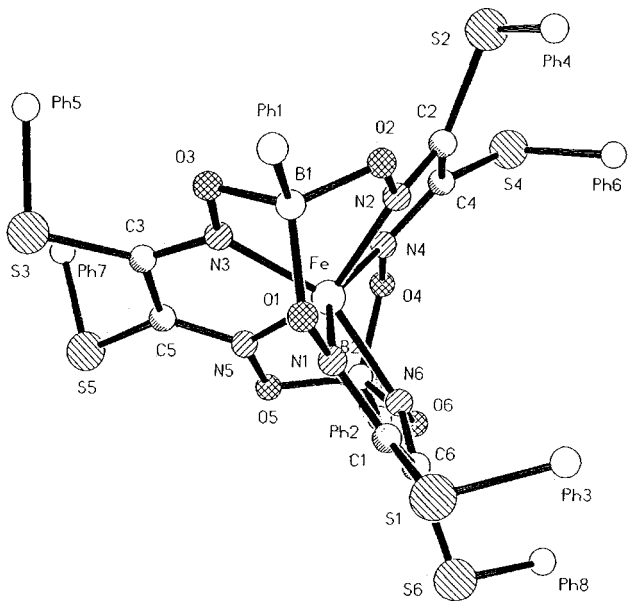


Fig. 2 Molecular structure of **2**. H atoms are omitted and phenyl substituents are denoted as Ph for clarity. Selected bond lengths (Å) and bond angles (°) are as follows: Fe—N1, 1.920(4); Fe—N2, 1.901(4); Fe—N3, 1.922(4); O1—N1, 1.361(4); O1—B1, 1.495(7); N1—C1, 1.297(6); C1—C6, 1.447(6), N6—Fe—N1, 78.6(2); C1—N1—Fe, 117.7(3); O2—B1—O1, 109.5(4); C1—S1—C19, 96.1(2); N1—O1—B1, 113.2(4).

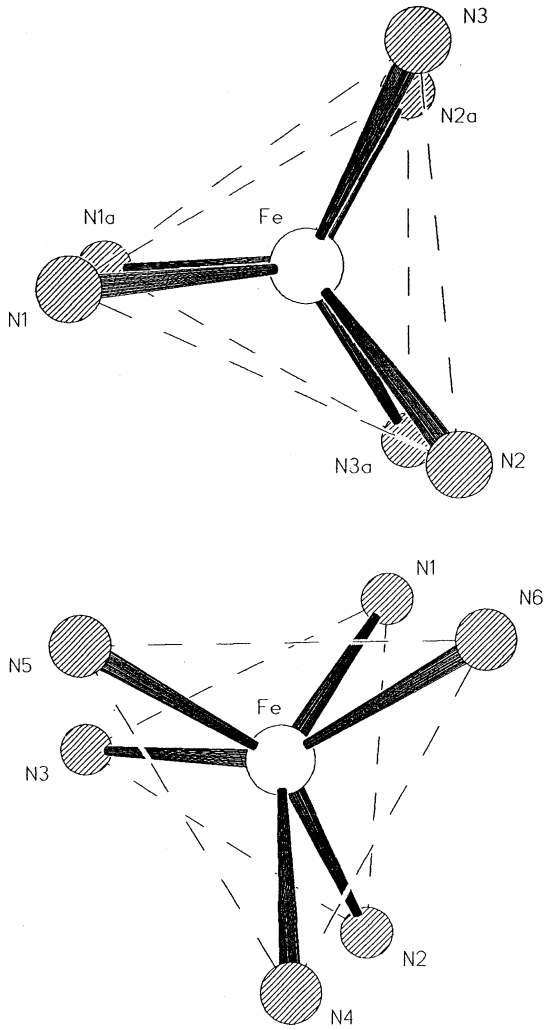


Fig. 3 The iron(II) coordination polyhedra in precursor **1** (top) and in the resulting clathrochelate **2** (bottom).

the azomethine fragment in the precursor (131.6 ppm) practically coinciding with one of the signals of a phenyl substituent at the boron atom (127.7, 128.9 and 131.7 ppm). The signal of the carbon atom bound to the boron atom was not detected because of quadrupole broadening. The ^{13}C NMR spectrum of the starting dichloroglyoxime contained a signal due to the azomethine groups at 130.9 ppm, which is lower than those of alicyclic and acyclic dioximes. The spectrum of clathrochelate **2** indicated that four more intense signals of thiophenyl groups appeared in the same spectral range (128–132 ppm), and the signal of azomethine groups was observed in the range characteristic of the majority of alicyclic, acyclic and aromatic clathrochelate trisdioximates (148.5 ppm). The parameters of the Mössbauer ^{57}Fe spectra of the complexes obtained characterize the s-electron density on the iron nucleus and the ligand field force (isomer shift, IS) as well as the electric field gradient on it (quadrupole splitting, QS). The QS magnitude is determined by the geometry of a coordination polyhedron and can be used for its prediction.[6] A comparison of the parameters of complexes **1** (IS = 0.39 mm s^{-1}, QS = 0.68 mm s^{-1}) and **2** (IS = 0.34 mm s^{-1},QS = 0.25 mm s^{-1}) revealed that the clathrochelate ligands have close ligand field force values and appreciably different geometries. All compounds of this type have a geometry intermediate between that of a trigonal prism (TP, twist angle $\varphi = 0°$) and that of a trigonal antiprism (TAP, $\varphi = 60°$). Judging from the correlation relationships[6] and equations,[7] the observed discrepancy in the QS values corresponds to an increase in the twist angle value by about 15 to 20° in passing from precursor **1** to func-

tionalized complex **2**.

The X-ray analyses of complexes **1** and **2** from crystals obtained by slow evaporation of their solutions in $CHCl_3$–CCl_4 (1 : 1) and benzene, respectively, has confirmed this conclusion (Fig. 1–3).‡ The mean Fe–N distances (1.90 and 1.91 Å) and the bite angles (half of the chelate angles) are practically identical (39.0 and 39.5°) and typical for clathrochelate trisdioximate iron(II) complexes, whereas the twist angles (5.4 and 25.6°) and the distances between the trigonal-prismatic coordination polyhedron bases are significantly different (2.39 and 2.33 Å, respectively), which is in agreement with the Mössbauer ^{57}Fe data. Hexachloride complex **1** has the lowest value among the known compounds of this type.[9] The relatively short (approximately 3.5 Å) S···S contacts between the adjacent molecules in the crystals of complex **2** should also be noted.

Essential differences in the geometry of coordination polyhedra and in the behavior of the substituents in dioxime fragments are responsible for appreciable differences in the UV-vis spectra: in the spectrum of complex **2** the intense $Md \rightarrow L\pi^*$ charge transfer band in the visible region is shifted to the long-wavelength region by approximately 40 nm and has twice the intensity compared to the spectrum of complex **1**.

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Notes and references

† Analytical, MS(FAB, PD), IR(CsI) and UV-vis (solvent: $CHCl_3$) spectral data: **1.** Anal. calcd. for $C_{18}H_{10}N_6O_6B_2Cl_6Fe$: C, 31.02; H, 1.44; N, 12.06; Cl, 30.59; Fe, 8.01. Found: C, 30.95; H, 1.44; N, 11.99; Cl, 30.78; Fe, 7.95%. MS(PD): *m/z* (%) 696 (20) $[M]^{+\cdot}$, 573 (100) $[M - Cl_2C_2N_2]^{+\cdot}$, 541 (35) $[M - Cl_2C_2N_2O_2]^{+\cdot}$. IR: 1533 (C=N); 905, 980 (N—O); 1225 (B—O) cm^{-1}; $\lambda_{max}(10^{-3}\ \varepsilon/mol\ L^{-1}\ cm^{-1}) = 266$ (12), 290 (7.9), 308 (4.9), 346 (2.8), 425 (5.9), 454 (14) nm. **2**. Anal. calcd. for $C_{54}H_{40}N_6O_6B_2FeS_6$: C, 56.90; H, 3.51; N, 7.38; Fe, 4.90. Found, C, 56.76; H, 3.56; N, 7.30; Fe, 4.86%. MS(FAB): *m/z* (%) 1139 (100) $[M + H]^+$, 1062 (40) $[M + H - C_6H_5]^+$. IR: 1582 (C=N); 893, 972 (N—O); 1233 (B—O) cm^{-1}; λ_{max} $(10^{-3}\ \varepsilon/mol\ L^{-1}\ cm^{-1}) = 276$ (23), 320 (18.5), 388 (4.5), 495 (25) nm.

‡ Crystal data for **1**: $C_{18}H_{10}B_2Cl_6FeN_6O_6$, crystal size 0.60 × 0.20 × 0.02 mm, $M = 696.49$, monoclinic, space group $C2/c$, $a = 24.290(5)$, $b = 8.169(2)$, $c = 15.807(3)$ Å, $\beta = 127.42(3)°$, $U = 2491.0(9)$ Å^3, $Z = 4$, $D_c = 1.857$ g cm^{-3}, $\mu = 1.300$ mm^{-1}, $F(000) = 1384$. 864 independent reflections were collected at 293 K on a Syntex P$\bar{1}$ diffractometer using Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) with $\theta/2\theta$ scans ($2.11 < \theta < 22.49°$). The structure was solved by the heavy-atom method, refinement was done by a full-matrix least squares on F^2 for all data with anisotropic thermal parameters for non-hydrogen atoms; phenyl substituents were constrained in accordance with a riding model {goodness-of-fit = 1.108, final R indices $[I > 2\sigma(I)R_1 = 0.0480$, $wR_2 = 0.1098$, $w^{-1} = \sigma^2(F_o^2) + (0.046P)^2 + 20.19P$, $P = (F_o^2 + 2F_c^2)/3]$}. All oxygen atoms are statistically disordered in two equivalent positions each.

Crystal data for **2**: $C_{54}H_{40}B_2FeN_6O_6S_6$, crystal size 0.70 × 0.35 × 0.35 mm, $M = 1138.75$, monoclinic, space group $C2/c$, $a = 16.874(2)$, $b = 20.477(3)$, $c = 31.705(3)$ Å, $\beta = 104.62(3)°$, $U = 10600(7)$ Å^3, $Z = 8$, $D_c = 1.427$ g cm^{-3}, $\mu = 0.578$ mm^{-1}, $F(000) = 4688$. 7437 independent reflections were collected at 293 K on a CAD4 diffractometer using Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) with $\theta/2\theta$ scans ($1.60 < \theta < 22.47°$). The structure was solved by the heavy-atom method, refinement was by a full-matrix least squares on F^2 for all data with anisotropic displacement parameters for non-hydrogen atoms; phenyl substituents were constrained in accordance with a riding model {goodness-of-fit = 1.034, final R indices $[I > 2\sigma(I)]R_1 = 0.0342$, $wR_2 = 0.0947$, $w^{-1} = \sigma^2(F_o^2) + (0.063P)^2 + 26.56P$, $P = (F_o^2 + 2F_c^2)/3]$}.

All calculations were made using the SHELXTL-93 program package.[8]

CCDC reference number 440/098. See http://www.rsc.org/suppdata/nj/1999/355/ for crystallographic files in .cif format.

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