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New hydroxylamine-containing macrobicyclic encapsulating ligand: Unexpected double addition of ethyl radicals to the azomethine fragment of a boron-capped iron(II) clathrochelate dioximate

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ABSTRACT

The reaction of the fluoroboron-capped mixed dimethylglyoximate-α-benzyldioximate iron(II) clathrochelate with $(C_2H_5)_3B–O_2$ system as a "soft" radical source afforded the major macrobicyclic product of the reductive addition of two carbon-centered radicals to the azomethine moiety of the dimethylglyoximate fragment giving the chelate ribbed entity that contains both the oxime and hydroxylamine donor groups. Such an unprecedented cage complex of this new encapsulating ligand was thoroughly characterized both in a solution by one- and two-dimensional NMR and in a solid state using X-ray crystallography.

Recently, we have described, for the first time, the free-radical reactions of a boron-capped iron(II) dichloroclathrochelate, which used its ability to trap the carbon-centered radicals followed by the elimination of ribbed chlorine atom(s) and the formation of a new C – C bond(s) (Scheme 1, [1–4]). Trying to expand the synthetic application of these reactions, we studied the possibilities to generate radical centers on non-halogen-containing ribbed chelate fragments of the clathrochelates. Here, we performed this reaction for the dimethyl-containing clathrochelate $FeBd_2Dm(BF)_2$ (where Bd^{2-} and Dm^{2-} are α-benzyldioxime and dimethylglyoxime dianions, respectively) with $(C_2H_5)_3B–O_2$ system as a "soft" radical source and have described the major macrobicyclic product that contains both the oxime and hydroxylamine donor groups. Such an unprecedented cage complex of this new encapsulating ligand was thoroughly characterized both in a solution by one- and two-dimensional NMR and in a solid state using X-ray crystallography.

Earlier, the synthesis of the clathrochelate precursor $FeBd_2Dm(BF)_2$ by cycloaddition of dimethylglyoxime to the macrocyclic complex $[FeBd_2(CH_3CN)_2(BF_2)_2]$ in acetonitrile as a solvent has been described [5]. However, this synthetic procedure gave this cage complex in a low yield (approximately 25%). Here, we improved the synthetic procedure and this complex was obtained under severe conditions (by a reflux in highly boiling nitromethane as a solvent) in substantially higher yield (67%) [6].

Treatment of a solution of the dimethyl-containing clathrochelate precursor $FeBd_2Dm(BF)_2$ in benzene as an inert solvent with a solution of $(C_2H_5)_3B$ in THF [7] immediately causes the darkening of the reaction mixture: its color changes from red-orange to brownish. After a few hours, the TLC analysis showed the formation of several clathrochelate products, which were then separated, and two main brownish fractions with very close retention factors were isolated by preparative TLC on SiO_2 foils and thoroughly characterized. The major products were studied using the multinuclear 1-D and 2-D NMR spectroscopy (Figs. 1, S1–S6). Both the ^{19}F and ^{11}B NMR (Scheme 2) spectra indicated the substantial non-equivalence of its capping O_3BF fragments, while the 1-D and 2-D ^1H and ^{13}C NMR spectra showed the presence of the functionalizing substituents in one of the chelate ribbed fragments: one of the two methyl groups is attached to the carbon atom of the azomethine donor group, the other methyl substituent and one ethyl group are attached to the quaternary carbon atom (C_q); the second ethyl substituent without an adjacent carbon atom but exhibiting the long-range interactions with C_q was observed. The only non-contradictory and chemically reasonable molecular drawing is shown in Scheme 3.

This molecular drawing suggests an unprecedented reduction of one of the oxime donor groups of the initial clathrochelate to the hydroxylamine. To verify its chemical constitution that was obtained from the

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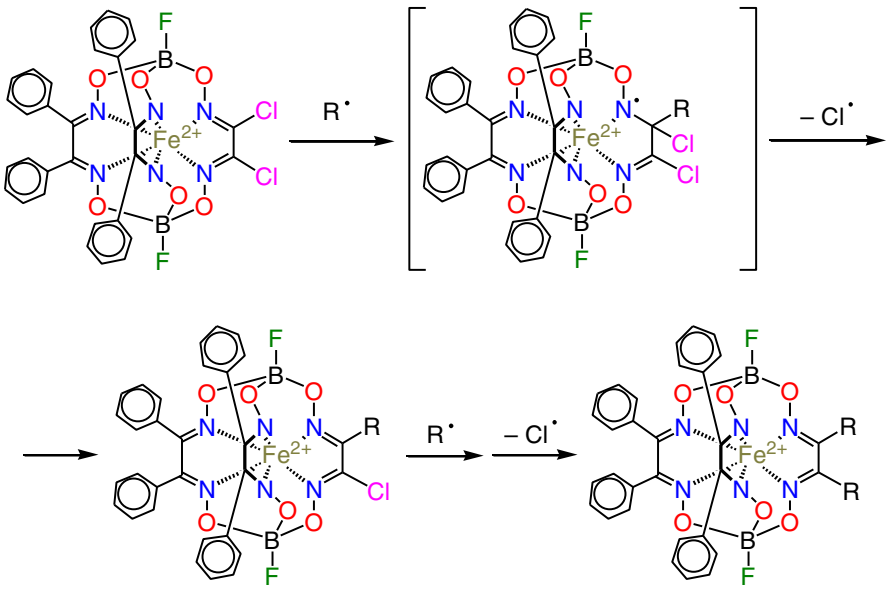

Scheme 1. Reactions of the dichloroclathrochelate precursor $FeBd_2(GmCl_2)(BF)_2$ with carbon-centered radicals.

NMR data, we performed the single-crystal X-ray diffraction study of the complex **3**. Although its best-available crystals were of a rather poor quality, it appeared sufficient for resolving the molecular structure of this clathrochelate (Fig. 2). Note that the NMR and X-ray data perfectly match each other: the X-rayed complex also contains two ethyl groups attached to both the nitrogen and carbon atoms of the azomethine

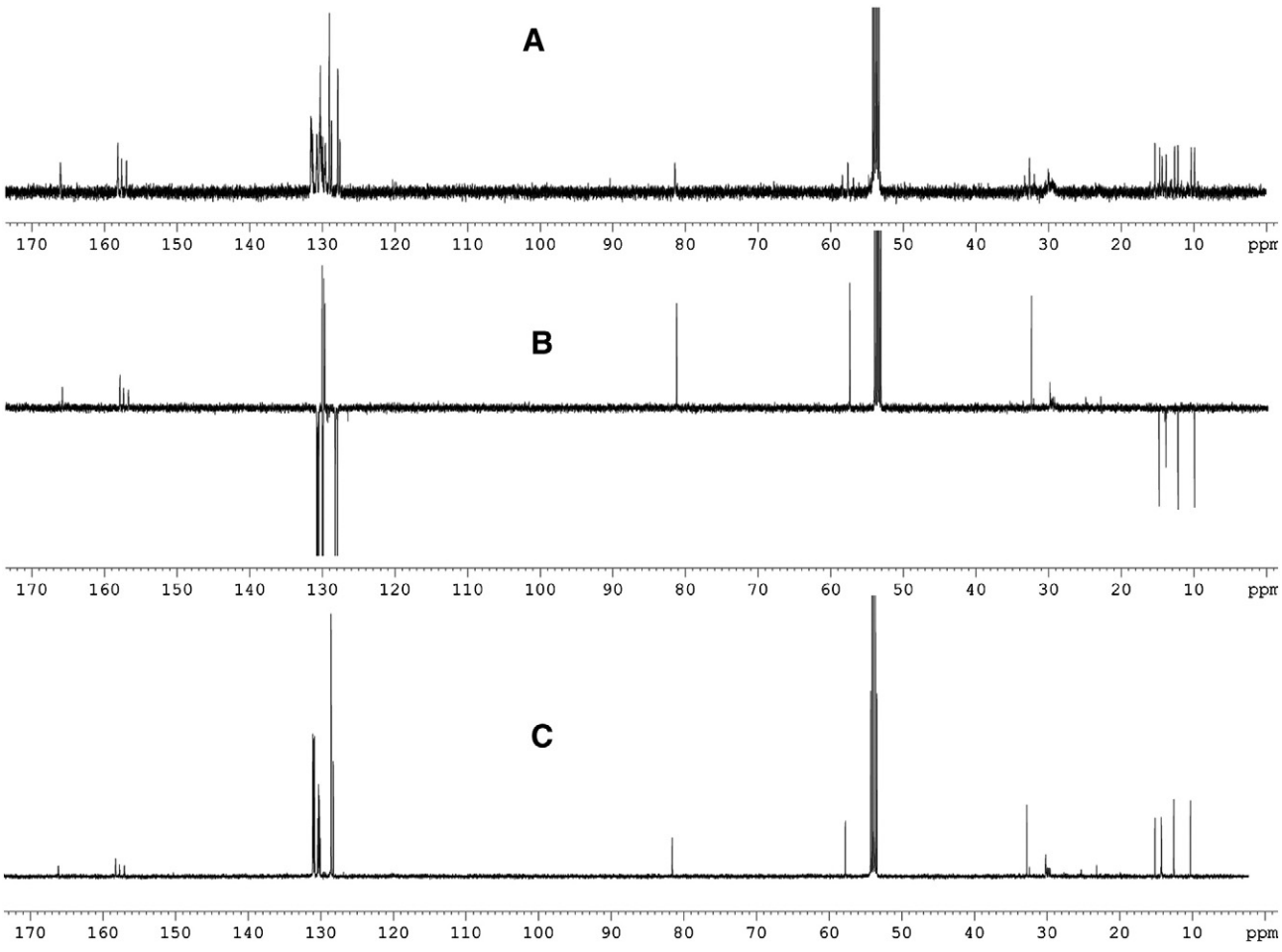

Fig. 1. $^{13}C\{^1H\}$ (A), JMOD (B) and ^{13}C (C) NMR spectra of the clathrochelate **3**.