pending upon whether they are associated with the six- or the five-membered rings. Thus, in some cases, it is possible, through infrared studies, to infer directly which rings become uncoordinated as parameters such as pH are changed.

Registry No. $NH_4[Co(S,S\text{-EDDS})]\cdot H_2O$, 38708-81-5; $[Co(NH_3)_5Br]Br_2$, 14283-12-6; $Na[Rh(S,S\text{-EDDS})]$, 38708-60-0; $RhCl_3\cdot 3H_2O$, 13569-65-8; $[(CH_3)_4N]_2[Ni(S,S\text{-EDDS})]$, 38708-61-1; $NiCO_3$, 3333-67-3; $[(CH_3)_4N]_2Ni(EDTA)(H_2O)_x$, 38708-62-2; $[Co(EDTA)]^-$, 15136-66-0; $[Rh(EDTA)]^-$, 38708-82-6.

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Encapsulation Reactions. Synthesis and Characterization of Clathro Chelates Derived from Iron(II), Dimethylglyoxime, and Boron Compounds

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Six low-spin Fe(II) clathro chelates, IV, have been isolated in very high yields from alcoholic or aqueous solutions *via* facile, single-step syntheses using iron salts, dimethylglyoxime, and either BF_3 or boric acid. When BF_3 is used, the two terminal moieties in the clathro chelate molecule (X in Figure 1) are fluorine atoms. When boric acid is employed, the X moieties are hydroxy or alkoxy groups derived from the solvent (H_2O, CH_3OH, C_2H_5OH, $i\text{-}C_3H_7OH$, or $n\text{-}C_4H_9OH$). The cage complexes exhibit high thermal stability as indicated by the fact that under conditions in the mass spectrometer (250°, 70 eV) the parent ion species corresponding to the singly ionized complex is the most predominant peak in the mass spectrum. Mossbauer spectra clearly indicate that there are distinctive differences in the iron–ligand interaction within the clathro chelates compared to low-spin Fe(II) complexes containing three symmetrical α-diimine ligands.

Introduction

A relatively few complexes containing encapsulated metal ions, clathro chelates, have been reported to date.[1-3] Even so, there are already strong reasons to believe that the study of these species will provide especially valuable information pertaining to stereochemistry,[4-6] limited-pathway intramolecular rearrangements,[7] analyses of metal ions, and ion transport phenomena.[2,8]

The synthetic routes to most of the clathro chelates are somewhat involved. Thus, examples of the tris(glyoximato) class of clathro chelates, I, were first prepared by isolating a tris(dimethylglyoximato)cobalt(III) complex and then capping this intermediate with Lewis acids such as BF_3, $SnCl_4$, or $SiCl_4$.[1,7] In another approach a bicyclic ligand flexible enough to encapsulate metal ions is synthesized and then used to prepare complexes, II, of alkali metal ions and other ions.[2] The third approach features the synthesis of a trigonally symmetric hexadentate ligand with a phosphorus bridgehead and three oxime moieties.[3] After coordination to a metal ion, this ligand is converted to a cage, III, *via* treatment with BF_3 or BF_4^-.

Recently we found a simple direct procedure for the preparation of six new clathro chelates of the tris(glyoximato) class.[1b] In this approach a metal ion salt, $DMGH_2$ (dimethylglyoxime), and BF_3 or $B(OH)_3$ are simply mixed together in alcohol. The approach was initially employed to prepare $[Co(DMG)_3(BF)_2]BF_4$, a known compound,[1a] and has subsequently been used to make the first clathro chelates of iron derived from dioximes, $[Fe(DMG)_3(BX)_2]$, IV where X is F, OH, OCH_3, OC_2H_5, $O\text{-}i\text{-}C_3H_7$, or $O\text{-}n\text{-}C_4H_9$. Herein we describe the syntheses and characterization of the six Fe(II) clathro chelates. Mass spectra and Mossbauer spectra of the complexes provide some insight into the thermal stability and the electronic nature of the complexes, respectively.

See Figure 1 for structures I-IV.

Experimental Section

The reagents used as starting materials were obtained commercially as reagent grade chemicals and were employed without further purification. Unless specified the reactions were run in flasks open to the atmosphere. The products were all dried at room temperature for at least 12 hr at ~1 Torr over Drierite.

Preparation of $[Fe(DMG)_3(BF)_2]$. A mixture of $FeCl_2\cdot 4H_2O$ (1.98 g, 0.01 mol), $DMGH_2$ (3.48 g, 0.03 mol), and 1-butanol (25 ml) was stirred for 10 min. Excess $BF_3\cdot O(C_2H_5)_2$ (10 ml) was added to the red-brown mixture; then KOH solution (2.80 g dissolved in 30 ml of 1-butanol, 0.05 mol) was added dropwise. During the addition of KOH, red crystals deposited. After cooling the mixture to room temperature, the red solid was collected and washed with small amounts of 1-butanol and petroleum spirits (yield 2.25 g, 50%). The product may be recrystallized from a hot acetonitrile–water mixture by dissolving the solid in boiling acetonitrile to which a small amount of trifluoroacetic acid (TFAA) is added and slowly adding water to the boiling solution until crystals appear. The solution is filtered and cooled to room temperature whereupon crystals deposit. Note: if the above preparation is followed omitting the

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[1] (a) D. R. Boston and N. J. Rose, *J. Amer. Chem. Soc.*, **90**, 6859 (1968); Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. INOR-96; (b) S. C. Jackels, D. S. Dierdorf, N. J. Rose, and J. Zektzer, *Chem. Commun.*, 1291 (1972).

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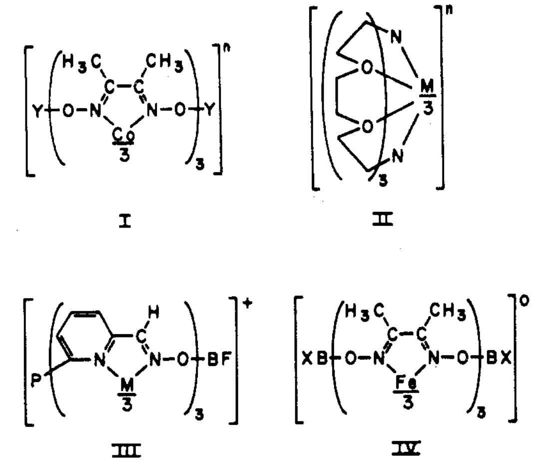

Figure 1. Formulations for various clathro chelates.

addition of KOH and the mixture is stoppered and allowed to stand several days, the product slowly appears as large crystals. Molecular weight: calcd, 458; found, 448 (in dichloroethane).

Preparation of $[Fe(DMG)_3(BOH)_2]$. A mixture of $FeCl_2 \cdot 4H_2O$ (1.98 g, 0.01 mol), $DMGH_2$ (3.48 g, 0.03 mol), $B(OH)_3$ (1.24 g, 0.02 mol), and H_2O (40 ml) was stirred and boiled for about 15 min during which time the solution became deep red and red crystals of product appeared. To the boiling mixture, $Na_2B_4O_7 \cdot 10H_2O$ (0.38 g, 0.001 mol) was added slowly and the resulting deep red solution was boiled 5 min. The crystalline red product was collected immediately (yield 3.5 g, 85%) and washed with H_2O. The product may be recrystallized from hot, slightly acidic acetonitrile–water mixture (50:50 by volume) by heating 1 g of solid in 75 ml of an acetonitrile–water mixture to which 1 drop of TFAA is added, filtering, and then allowing the solution to cool and evaporate whereupon crystals deposit.

Preparation of $[Fe(DMG)_3(BOCH_3)_2]$. A mixture of $FeCl_2 \cdot 4H_2O$ (1.98 g, 0.01 mol), $DMGH_2$ (3.48 g, 0.03 mol), $B(OH)_3$ (1.24 g, 0.02 mol), and anhydrous methanol (75 ml) was stirred and refluxed 10 min in a flask fitted with a reflux condenser. Then $Na_2B_4O_7 \cdot 10H_2O$ (1.90 g, 0.005 mol) was slowly added while continuing to reflux. All solids dissolved and the very dark red-brown solution was refluxed for 10 min. The condenser was removed and the solution volume was reduced to 20 ml by allowing the solvent to evaporate through boiling. Upon cooling, the remaining solution deposited the orange crystalline product which was collected and washed with small amounts of petroleum spirits (yield 4.5 g, 90%). The product may be recrystallized by dissolving 1 g in 25 ml of boiling methanol to which 1 drop of TFAA is added, filtering, and cooling whereupon crystals are deposited. Note: care must be taken in refluxing to prevent the trimethyoxyborane–methanol azeotrope from escaping and thus removing the capping agent from the reaction mixture.

Preparation of $[Fe(DMG)_3(BOC_2H_5)_2]$. A mixture of $FeCl_2 \cdot 4H_2O$ (1.98 g, 0.01 mol), $DMGH_2$ (3.48 g, 0.03 mol), $B(OH)_3$ (1.24 g, 0.02 mol), and 40 ml of absolute ethanol was stirred and refluxed for 15 min whereupon the solution became dark red. Then $Na_2B_4O_7 \cdot 10H_2O$ (1.90 g, 0.005 mol) was slowly added and the dark red solution was boiled open to the atmosphere until the volume reached 20 ml through evaporation of the solvent. Upon cooling, the orange crystalline product was deposited (yield 4.6 g, 90%). The product may be recrystallized from acetonitrile and water mixture by dissolving 1 g of product in 75 ml of acetonitrile and heating to boiling. The solution is filtered and about 40 ml of water is added slowly. Upon cooling red-orange crystals are deposited. Note: care must be taken (see preparation of $[Fe(DMG)_3(BOCH_3)_2]$) to prevent ethanol–triethoxyborane azeotrope from escaping through boiling the reaction mixture. Molecular weight: calcd, 510; found, 518 (in dichloroethane).

Preparation of $[Fe(DMG)_3(BO\text{-}i\text{-}C_3H_7)_2]$. A mixture of $B(OH)_3$ (1.24 g, 0.02 mol), 2-propanol (50 ml), and benzene (15 ml) was boiled (vapor at 72°) so that the vapor escaped into the atmosphere until the temperature of the vapor began to rise, about 10 min. Then $FeCl_2 \cdot 4H_2O$ (1.98 g, 0.01 mol) was added along with 10 ml of benzene and the solution was boiled 5 min. $DMGH_2$ (3.48 g, 0.03 mol) was added followed by 10 min more of boiling during which time the solution became dark red. After adding $Na_2B_4O_7 \cdot 10H_2O$ (1.0 g, 0.00 25 mol), the dark red solution was boiled 5 min and filtered. The volume of the filtrate was reduced to 20 ml by boiling the solvent away and this solution was cooled to yield orange crystals of product (yield 4.45 g, 83%). The product may be recrystallized from slightly acidic, boiling 2-propanol by mixing 1 g of product and about 20 ml of 2-propanol to which 1 drop of TFAA is added, heating to boiling, filtering, and cooling whereupon orange crystals are deposited.

Preparation of $[Fe(DMG)_3(BO\text{-}n\text{-}C_4H_9)_2]$. A mixture of $FeCl_2 \cdot 4H_2O$ (1.98 g, 0.01 mol), $DMGH_2$ (3.48 g, 0.03 mol), $B(OH)_3$ (1.24 g, 0.02 mol), and 1-butanol (50 ml) was stirred and boiled for 5 min during which time the color of the solution darkened to a deep red. To the boiling mixture, $Na_2B_4O_7 \cdot 10H_2O$ (1.9 g, 0.005 mol) was added slowly and the resulting deep orange-red solution was boiled for 20 min more whereupon the solution volume became about 20 ml due to loss of 1-butanol through evaporation. Some orange crystals of the product deposited during the period when the solution was being concentrated and more appeared when the solution cooled to room temperature. The crystals were collected and washed with small portions of petroleum spirits (yield 4.6 g, 90%). The product may be recrystallized from hot acetonitrile–water mixture (75:35 by volume). One gram of product is dissolved in about 75 ml of acetonitrile by warming the mixture to about 50°. The warm solution is filtered and then 35 ml of H_2O is added while the temperature is maintained at about 50°. The solution is filtered while warm and allowed to cool whereupon crystals of the product deposit.

Physical Measurements. Using KBr plates and Nujol mulls infrared spectra in the range 400–4000 K were obtained with a Beckman IR-10 recording spectrophotometer. A Cary Model 14 R spectrophotometer was used for visible spectra in the range 15.4–33.3 KK. Pmr spectra were run on a Varian A-60 at ambient temperature with internal standard TMS. Elemental analyses were determined by Chemalytics, Inc. Molecular weight measurements were made on a Mechrolab Model 301-A vapor pressure osmometer using benzil as calibrant and $C_2H_4Cl_2$ or CH_3CN as solvent.

High-resolution mass spectra were taken on an Associated Electrical Industries, Ltd., MS-9 mass spectrometer operating at 70-eV ion acceleration voltage with an on-line PDP-12 digital computer. Samples were sublimated into the instrument at 250–300° from solids which had been deposited on the ceramic probe tip from dichloroethane solutions. Masses corresponding to sample peaks were computed *via* a series of computer programs similar to those being used elsewhere,[9] involving on-line recording of data and calculation of masses by interpolation from known masses of an internal standard, perfluorokerosene. Assignment of the peaks involved both mass matching to within 0.01 amu in most cases and matching the relative intensities against those predicted from natural isotopic abundances.

Mossbauer spectra were taken on an apparatus consisting of the following: a 3–5-mCi Pd-^{57}Co source, a Harshaw NaI(Tl) integral line scintillation detector; a Power Designs Pacific, Inc., Model Hv-1544 power supply; a Hamner Electronics Co., Inc., Model N308 pulse height analyzer and linear amplifier; a Nuclear Data ND-10 128 channel analyzer and a Nuclear Data ND-410 display monitor. All spectra were taken at room temperature and at 77°K (liquid nitrogen) and are reported relative to the room-temperature spectrum of a sample of NBS standard ^{57}Fe-enriched $Na_2[Fe(CN)_5(NO)]$. Spectral parameters were computed from the data using the NBS Mossbauer computer program PARLOR.[10]

Results and Discussion

I. Synthesis of the Clathro Chelates. The following equation represents the overall reaction taking place in the synthesis of the clathro chelate derived from BF_3

$$Fe(II) + 3DMGH_2 + 5OH^- \xrightarrow[n\text{-}C_4H_9OH]{\text{excess } BF_3O(C_2H_5)_2} [Fe(DMG)_3(BF)_2] + H^+ + 4BF_4^- \qquad (1)$$

In actually doing the synthesis it has been found that the base must be slowly added after the iron salt, $DMGH_2$, alcohol, and $BF_3O(C_2H_5)_2$ are mixed. If the base is added rapidly an immediate color change to dark brown is observed and a brown, gelatinous solid forms. In order to avoid the brown solid associated with the rapid accumula-

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(9) Programs provided by A. L. Crittenden.

(10) J. T. Spijkerman, D. K. Sneidiker, F. C. Ruegg, and J. R. Devoe, *Nat. Bur. Stand. (U. S.), Spec. Publ.*, No. 260-13 (1967).

Table I. Yield Data and Analyses for $[Fe(DMG)_3(BX)_2]$

		Analyses, %					
		C		H		N	
Complex	Yield,[a] %	Calcd	Found	Calcd	Found	Calcd	Found
$[Fe(DMG)_3(BF)_2]$	~50	31.49	31.72	3.96	3.98	18.36	18.46[b]
$[Fe(DMG)_3(BOH)_2]$	~85	31.76	32.01	4.44	4.58	18.52	18.35[b]
$[Fe(DMG)_3(BOCH_3)_2]$	>90	34.90	34.78	5.02	5.05	17.44	17.65[b]
$[Fe(DMG)_3(BOC_2H_5)_2]$	>90	37.69	37.59	5.53	5.43	16.48	16.04,[b] 16.58[c]
$[Fe(DMG)_3(BO\text{-}i\text{-}C_3H_7)_2]$	~83	40.33	40.47	6.00	5.83	15.62	16.08,[c] 15.83[b]
$[Fe(DMG)_3(BO\text{-}n\text{-}C_4H_9)_2]$	>90	42.44	42.54	6.41	6.13	14.85	14.88[b]

[a] See Experimental Section for details. [b] C–H–N analyzer. [c] Coleman nitrogen analyzer.

Table II. Transesterification Reactions

$$[Fe(DMG)_3(BOR)_2] + 2R'OH \overset{H^+}{\rightleftarrows} 2ROH + [Fe(DMG)_3(BOR')_2]$$

R		R′
H	$\rightarrow$	CH_3, C_2H_5, n-C_4H_9
CH_3	$\rightarrow$	H, C_2H_5, i-C_3H_7, n-C_4H_9
C_2H_5	$\rightarrow$	H, CH_3, n-C_4H_9
i-C_3H_7	$\rightarrow$	H, C_2H_5, n-C_4H_9
n-C_4H_9	$\not\rightarrow$	H, CH_3, C_2H_5, i-C_3H_7

tion of base, the reaction mixture is kept slightly acidic not only by adding the base slowly but also by using only 5 of the 6 mol of base theoretically required (eq 1). When the reaction is run as described in the Experimental Section, it requires about 30 min, but the product is also observed to form over a period of days if no base is added. Significant yields of the product are also obtained if Fe(III) salts are substituted for the ferrous chloride normally used (see Experimental Section). Limited attempts to prepare an Fe(III) clathro chelate *via* oxidation of $[Fe(DMG)_2(BF)_2]$ were not successful. Thus far our efforts using Br_2, I_2, O_2, H_2O_2, Ce(IV), and Cu(II) as oxidants have led either to obvious decomposition of the complex or to no reaction. The qualitative observations made to date concerning reactions of $DMGH_2$, BF_3, and either Fe(II) or Fe(III) suggest that under acidic conditions $[Fe(DMG)_3(BF)_2]$ is clearly the thermodynamically favored product.

The reactions involving boric acid are best represented by

$$Fe(II) + 3DMGH_2 + 2B(OH)_3 \xrightarrow[\Delta]{ROH} [Fe(DMG)_3(BOR)_2] + 2H^+ + 6H_2O \qquad (2)$$

where R = H, CH_3, C_2H_5, i-C_3H_7, or n-C_4H_9. In the synthesis of the borate ester species the appropriate reagents are simply mixed and boiled in alcohol (ROH). As noted in the Experimental Section $FeCl_2 \cdot 4H_2O$ is routinely employed to prepare the $[Fe(DMG)_3(BOR)_2]$ species. However, successful preparations also may be done using Fe(III) salts or elemental iron in place of the ferrous salt. For example, from 1-butanol (10 hr, 118°), $[Fe(DMG)_3(BO\text{-}n\text{-}C_4H_9)_2]$ can be prepared in 60% yield starting with iron powder, $DMGH_2$, and boric acid.

As seen in eq 2, both hydrogen ion and water are formed in the reaction. The acidic character of the reaction mixtures is most readily confirmed for the aqueous solutions where it is found that the pH of the reaction mixture is ~1 at the time when the product is collected. When the reaction mixtures are partially neutralized by addition of small amounts of borax, sodium acetate, or ammonium acetate (0.25-0.5 equiv/equiv of boric acid used), yields increase relative to reactions employing only boric acid. However, when either borax or an acetate salt is used, care must be taken to add it slowly such that the reaction mixture always retains an acidic character. Otherwise, a brown insoluble solid forms reminiscent of that discussed above with respect to the reaction employing BF_3. There is further experimental evidence that the neutralization of some of the H^+ formed in the reaction is desirable. In the absence of the added base the same yield of product is obtained when the reaction mixture is boiled for several hours or for only 1 hr. However, when the base is used, the yield is improved and the reaction is complete within minutes (see Table I for yields). In spite of the fact that borax itself, through reaction with ROH (eq 3), provides all of the

$$B_4O_7^{2-} + 14ROH \rightleftarrows 2B(OR)_3 + 2B(OR)_4^- + 7HOH \qquad (3)$$

appropriate boron-containing species necessary for the encapsulation reaction (eq 2), it has been found to be an unsuitable reagent to substitute for boric acid. Thus, when borax alone is used, the clathro chelates which form are contaminated with a brown insoluble product similar to that mentioned twice previously. As before, it is presumed that the formation of the brown product is associated with the reaction mixture being basic at some point.

In some of the syntheses it is desirable to remove water, the other by-product noted in eq 2. For instance, in the case of 2-propanol the product $[Fe(DMG)_3(BO\text{-}i\text{-}C_3H_7)_2]$ is recovered free from contamination with $[Fe(DMG)_3(BOH)_2]$ only when steps are taken to reduce the concentration of water in the reaction mixture (*e.g.*, *via* the benzene-2-propanol-water azeotrope). Since the borate esters of most of these complexes have been found to transesterify easily in boiling acidic alcohol (*vide infra*), it seems likely that $[Fe(DMG)_3(BOH)_2]$ may form initially and then transesterify to the product appropriate for the alcohol in question. Thus, reducing the concentration of H_2O in the reaction medium clearly favors the product derived from the alcohol.

The results of the transesterification reactions supporting the above conclusion are summarized in Table II. In each transesterification reaction, $[Fe(DMG)_3(BOR)_2]$ was boiled in R′OH to which a small amount of trifluoroacetic acid was added. The solution was allowed to cool whereupon the solid present was collected and its infrared spectrum taken. In all cases except $[Fe(DMG)_3(BO\text{-}n\text{-}C_4H_9)_2]$ the product is $[Fe(DMG)_3(BOR')_2]$. For $[Fe(DMG)_3(BO\text{-}n\text{-}C_4H_9)_2]$ no reaction takes place in ~1 hr. The results of the experiments indicate that the transesterifications are generally facile reactions requiring only a few minutes. That most of the clathro chelates would undergo facile hydrolysis (transesterification with H_2O) is not surprising since it is known that tetraalkoxyborates hydrolyze readily.[11] In fact, $B(OR)_4^-$ salts derived from low molecular weight alcohols appear to hydrolyze with half-lives too fast to be measured by conventional techniques.[11] Although all but the $[Fe(DMG)_3(BO\text{-}n\text{-}C_4H_9)_2]$ species hydrolyze readily, some qualitative differences in the tendency of the other clathro chelates to hydrolyze were observed. Thus, $[Fe(DMG)_3(BOCH_3)_2]$ and $[Fe(DMG)_3(BO\text{-}i\text{-}C_3H_7)_2]$ both are hydrolyzed under mild conditions (*e.g.*, in warm acetonitrile-water solutions) whereas $[Fe(DMG)_3(BOC_2H_5)_2]$ does not hydrolyze under similar conditions. When hydrolyses

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[11] H. Steinberg, "Organoboron Chemistry," Wiley, New York, N. Y., 1964, p 618.

Table III. Infrared Spectral Data for [Fe(DMG)$_3$(BX)$_2$] (cm^{-1})

Complex	C=N str	N–O str	B–O str	Unassigned	DMG band
[Fe(DMG)$_3$(BF)$_2$]	1582 m	1238 s, 1094 s	1193 s, 1000 s (B–F?), 815 s	1492 m, 1384 m, 1275 m, 1072 m, 853 w, 720 m, 640 m, 592 s, 495 m	947 s
[Fe(DMG)$_3$(BOH)$_2$]	1578 m	1239 s, 1088 s	1176 s, 991 s, 797 s	1490 s, 1363 s, 1278 m, 1050 m, 846 w, 706 w, 646 m, 589 m, 498 m	918 s
[Fe(DMG)$_3$(BOCH$_3$)$_2$]	1573 m	1250 br, 1088 s	1200 s, 1000 s, 806 s	1491 s, 1396 s, 1354 s, 1152 s, 1072 s, 1040 s, 842 m, 718 m, 635 m, 591 m, 495 m	932 s
[Fe(DMG)$_3$(BOC$_2$H$_5$)$_2$]	1578 m	1236 s, 1088 s	1188 s, 998 s, 801 s	1483 m, 1367 s, 1253 s, 897 m, 840 m, 716 m, 656 m, 590 m, 496 m	936 s
[Fe(DMG)$_3$(BO-*i*-C$_3$H$_7$)$_2$]	1576 m	1242 s, 1088 s	1182 s, 1000 s, 794 m	1482 m, 1362 s, 1256 s, 1130 s, 844 m, 834 w, 812 w, 714 w, 662 w, 592 m, 499 m	929 s
[Fe(DMG)$_3$(BO-*n*-C$_4$H$_9$)$_2$]	1576 m	1235 s 1092 s	1187 s, 1004 s, 796 s	1485 m, 1367 s, 1249 s, 1125 m, 1078 s, 940 m, 843 m, 816 m, 721 m, 661 w, 590 w, 497 m	917 s

are attempted in hot concentrated acid (>1 *M* HCl) instead of the weakly acidic conditions mentioned earlier, a pale yellow solution results for *all* the clathro chelates thereby indicating that decomposition has occurred. The experimental observations concerning decomposition, reaction yields, and conditions employed in the syntheses lead us to conclude that the formation of [Fe(DMG)$_3$(BOR)$_2$] is very strongly favored kinetically and/or thermodynamically in weakly acidic media.

The formation of the clathro chelates, [Fe(DMG)$_3$(BX)$_2$], also represents a large degree of molecular organization. Thus, in order for [Fe(DMG)$_3$(BOR)$_2$] molecules to form, eight separate ions or molecules must eventually come together. We presume that the iron ions are playing a critical role in the reactions by binding the DMG moieties in an anti configuration thereby (1) blocking further reaction at the nitrogen atoms (with BF$_3$ or B(OR)$_3$) and (2) placing the oxygen atoms of the oxime group in appropriate position for reaction with the boron-containing molecules.[1] The extent of molecular organization in the clathro chelate reactions is reminiscent of that found in the formation of a macrocyclic complex from [Ni(en)$_3$]$^{2+}$ and acetone in that six new bonds contained within chelate rings are formed in each reaction (not counting any metal-nitrogen bonds).[12]

II. Characterization of the Clathro Chelates. The formulation of the clathro chelates has been established by inferences derived from several physical techniques, by comparison of the properties of the species reported here with known clathro chelates of the tris(glyoximato) class, and by a single-crystal X-ray diffraction study[13] of [Fe(DMG)$_3$(BF)$_2$]. The structure of [Fe(DMG)$_3$(BF)$_2$] is best described as intermediate between those of [Co(DMG)$_3$(BF)$_2$]$^+$ and [Co(DMG)$_3$(BF)$_2$] in that the Fe complex has a twist angle of 16.5° (based on the nitrogen atoms of the same chelate ring) and an M-N distance of 1.92 Å.[6] A consideration of the structures of these three complexes taken with the theoretical calculations of Lingafelter, *et al.*,[6] suggests that the boron-capped tris(glyoximato) class of clathro chelates can only be prepared with metals that can have M-N distances of 2.00 Å or less. In this context it is interesting to note that we have not succeeded in our efforts to prepare the boron-capped clathro chelates of Ni(II). These failures may be due to the fact that the typical Ni-N distances in hexacoordinate complexes are greater than 2.00 Å. In contrast to the nickel case we note that [Co(DMG)$_3$(BF)$_2$]BF$_4$ is prepared by the original route of Boston[1a] or by simply mixing Co(II) salts, DMGH$_2$, NaOH, and BF$_3\cdot$OC$_2$H$_5$ in a flask open to the atmosphere (see eq 4 where oxygen from the atmosphere is assumed to be the oxidizing agent). Thus, it may well be that the

$$2\text{Co(II)} + 6\text{DMGH}_2 + 10\text{OH}^- + {}^1/_2\text{O}_2 + 10\text{BF}_3 \xrightarrow[\text{xs BF}_3\cdot\text{O(C}_2\text{H}_5)_2]{n\text{-C}_4\text{H}_9\text{OH}} 2[\text{Co(DMG)}_3(\text{BF})_2]\text{BF}_4 + 6\text{BF}_4^- + 11\text{HOH} \quad (4)$$

reactions represented by eq 1, 2, and 4 are limited to certain metal ions depending only on their "sizes."

Elemental analyses, molecular weight determinations (where applicable), and infrared spectral data are all consistent with the proposed formulations for the five Fe(II) clathro chelates derived from boric acid. Elemental analyses are collected in Table I and the molecular weight data are reported in the Experimental Section. Characteristic bands in the infrared spectra of the complexes are given in Table III. Band assignments included in the table are made following those given for the Co(II) and Co(III) clathro chelates and for DMG complexes.[1a,7b] The most striking feature of the spectra is their overall similarity to

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(13) M. Dunaj-Jurco and E. C. Lingafelter, private communication.

each other as well as to $[Co(DMG)_3(BF)_2]^{0,+}$. The differences which are seen occur mainly in the region from 1000 to 3000 cm^{-1} and relate to the number of strongly intense bands in this region. However, the absorption bands assigned specifically to the N-O and B-O stretches are seen to be relatively insensitive to changes in X (see IV in Figure 1). This insensitivity implies that there are no gross changes in the cage upon substitution at the boron atom.[7] The band attributed to the C=N stretching motion (the only band between 1500 and 2700 cm^{-1}) appears not to be influenced by changes in the alkoxyborate group. However the position of this band, 1582 cm^{-1}, for $[Fe(DMG)_3(BF)_2]$ is significantly lower than for the C=N bands observed for $[Co(DMG)_3(BF)_2]$ (1623 and 1592 cm^{-1}) and for $[Co(DMG)_3(BF)_2]BF_4$ (1623 cm^{-1}).[7] This decrease in energy is probably due to a lowering of the C=N bond order due to extensive d-p π bonding between Fe and the imines, a postulate consistent with that made for various other iron(II) complexes of α-diimines.[14,15] It is also notable that the intensity of the band attributed to the C=N stretch is strong in the iron complex relative to the cobalt complexes. This band in the tris(α-diimine) complexes is absent or very weak for low-spin Fe(II) but relatively intense for Co(II), Ni(II), Cu(II), etc.[14,15]

Recently infrared absorptions due to metal-nitrogen vibrations have been identified for several Fe(II) tris(α-diimine) complexes through metal isotopic substitution.[16] Since these absorptions are observed at frequencies less than 400 cm^{-1}, the M-N bands for the clathro chelates also are probably located at frequencies less than 400 cm^{-1}. Thus, the bands observed between 600 and 400 cm^{-1} for the clathro chelates are most likely ligand bands (Table III).

Electronic spectral data are given in Table IV. The electronic spectrum of each complex in dichloromethane solution consists of a single, extremely intense band in the region of 22.6 kK (half-width about 3.35 kK) and a less intense shoulder in the region of 27-30 kK. Spectra of iron(II)-tris(α-diimine) complexes are also characterized by one or more intense bands in the visible region.[17,18] In comparison with the α-diimine complexes ν_{max} for the clathro chelates occurs at higher frequency, for example, for $[Fe(bipy)_3]^{2+}$, ν_{max} = 19.1 kK, for $[Fe(phen)_3]^{2+}$, ν_{max} = 19.6 kK, and for $[Fe(BMI)_3]^{2+}$, ν_{max} = 17.6 kK (where BMI = biacetylmethylimine).[17] Since it has been concluded[18] that the intense bands in the electronic spectrum of $[Fe(bipy)_3]^{2+}$ may be assigned to $M \rightarrow \pi^*$ transitions we assume that the two bands reported for the clathro chelate spectra are also charge-transfer bands. No bands attributable to d-d transitions were observed for any of the clathro chelates. Generally speaking the extinction coefficients of ν_{max} for the clathro chelates are somewhat greater than those for the tris(α-diimine) complexes.[17]

Table IV. Electronic and Pmr Spectral Data for $[Fe(DMG)_3(BX)_2]^a$

Complex	$\nu_{max}{}^b$ (ϵ)	Shoulder^b (ϵ_{approx})	δ^c
$[Fe(DMG)_3(BF)_2]$	22.68 (17,500)	27.7–29.4 (2200)	2.40
$[Fe(DMG)_3(BOH)_2]$	22.68 (17,600)	27.7–29.4 (1700)	2.38
$[Fe(DMG)_3(BOCH_3)_2]$	22.65 (16,600)	27.7–29.4 (2300)	2.36
$[Fe(DMG)_3(BOC_2H_5)_2]$	22.62 (18,500)	27.7–29.8 (2300)	2.20
$[Fe(DMG)_3(BO\text{-}i\text{-}C_3H_7)_2]$	22.52 (15,400)	29.4–30.3 (3000)	2.35
$[Fe(DMG)_3(BO\text{-}n\text{-}C_4H_9)_2]$	22.52 (16,100)	28.2–29.8 (2700)	2.37

^{a} Dichloromethane solution. ^{b} In kK. ^{c} Methyl resonance in ppm downfield from internal TMS.

Table V. Masses (amu) of Parent Ion Peaks with Isotopic Composition $^{11}B^{56}Fe^{12}C^{1}H^{14}N^{16}O$

Complex	Calcd	Found
$[Fe(DMG)_3(BF)_2]$	458.079	458.080 (±0.006)
$[Fe(DMG)_3(BOH)_2]$	454.087	454.081 (±0.010)
$[Fe(DMG)_3(BOCH_3)_2]$	482.119	482.121 (±0.016)
$[Fe(DMG)_3(BOC_2H_5)_2]$	510.150	510.139 (±0.013)
$[Fe(DMG)_3(BO\text{-}n\text{-}C_4H_9)_2]$	566.212	566.155 (>±0.025)

All the pmr spectra of the clathro chelates in dichloromethane solution feature a singlet at ~2.40 ppm and other peaks which are characteristic of the alkoxy group present in the molecule. The singlet is unambiguously assigned to the methyl protons of the DMG group in that its area relative to that of the alkoxy peaks is that expected for the presence of two alkoxy groups per three DMG units (Table IV). The resonances of the alkoxy groups bound in the clathro chelate are 2-4 Hz downfield from the position of "free" alcohol added to the dichloromethane. We conclude that the cage complex is more electron withdrawing than hydrogen and that, at least, for R = C_2H_5, *i*-C_3H_7, and *n*-C_4H_9, exchange of free and bound alkoxy groups is slow relative to the nmr time scale because the peaks of both the bound and free moieties are very sharp.

The mass spectra of the clathro chelates definitely indicate their thermal stability. That is, under the conditions in the mass spectrometer, ~250° and 70 eV, the parent ion species is the most prominent peak present for all the complexes done to date (Table V). The character of the parent ion region of the mass spectra is indicated in Table VI where the data for that region of the spectrum of $[Fe(DMG)_3(BOC_2H_5)_2]$ are compiled. The multiplicity of the peaks arises mainly from the presence of ^{10}B, ^{11}B, ^{54}Fe, ^{56}Fe, and ^{57}Fe. Nine combinations are possible considering only these isotopes. Due to the relative isotopic abundance of the five isotopes listed, seven of the nine possible B_2Fe combinations are accounted for in the five peaks which are observed. The influence of ^{13}C-containing species is mainly on the relative peak intensities because peaks due to these species are not resolved from those of the various $^{12}CB_2Fe$ species. In Table VI only the major contributors to each peak are listed and the ^{13}C contribution is omitted from all but the highest mass peak, E.

In Table V the theoretical and experimental masses of the most intense peak corresponding to the parent ion ($^{11}B_2{}^{56}Fe$) are given for each complex. The only major fragments observed in the high-mass region (above mass 200) other than the parent ion of each clathro chelate are due to the complex with one dioxime unit, methyl groups, and parts of the alkoxyborate groups missing. These results parallel very closely those observed for $[Co(DMG)_3(BF)_2]$ and $[Co(DMG)_3(BF)_2]^+$.[7] A suitability for mass spectrometric studies is clearly indicated by the foregoing data. This indication coupled with the high yields of the clathro chelate syntheses (*vide supra*) suggests the feasibility of several

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Table VI. Parent Ion Cluster in the Mass Spectrum of $[Fe(DMG)_3(BOC_2H_5)_2]$

Peak	Obsd mass,[a] amu	Rel intens	Assignment
A	507.15	11	$^{12}C_{16}{}^{1}H_{28}{}^{14}N_6{}^{16}O_8{}^{10}B^{11}B^{54}Fe$
B	508.15	40	$^{12}C_6{}^{1}H_{28}{}^{14}N_6{}^{16}O_8{}^{11}B_2{}^{54}Fe$, $^{12}C_6{}^{1}H_{28}{}^{14}N_6{}^{16}O_8{}^{10}B_2{}^{56}Fe$
C	509.14	114	$^{12}C_6{}^{1}H_{28}{}^{14}N_6{}^{16}O_8{}^{10}B^{11}B^{56}Fe$, $^{12}C_6{}^{1}H_{28}{}^{14}N_6{}^{16}O_8{}^{10}B_2{}^{57}Fe$
D	510.14	288	$^{12}C_6{}^{1}H_{28}{}^{14}N_6{}^{16}O_8{}^{11}B_2{}^{56}Fe$
E	511.14	67	$^{12}C_6{}^{1}H_{28}{}^{14}N_6{}^{16}O_8{}^{11}B_2{}^{57}Fe$, $^{12}C_5{}^{13}C^{1}H_{28}{}^{14}N_6{}^{16}O_8{}^{11}B_2{}^{56}Fe$

[a] Approximate error ±0.01 amu.

Table VII. Parameters of Mossbauer Spectra at 77°K

Complex	δ,[a] mm/sec	ΔEq, mm/sec
$[Fe(DMG)_3(BF)_2]$	0.42	1.05
$[Fe(DMG)_3(BOH)_2]$	0.38	0.76
$[Fe(DMG)_3(BOCH_3)_2]$	0.35	0.71
$[Fe(DMG)_3(BOC_2H_5)_2]$	0.33	0.80
$[Fe(DMG)_3(BO\text{-}n\text{-}C_4H_9)_2]$	0.35	0.70
$[Fe(DMG)_3(BO\text{-}i\text{-}C_3H_7)_2]$	0.32	0.64
$[Fe(bipy)_3](PF_6)_2$[b]	0.64	0.42
$[Fe(phen)_3](PF_6)_2$[b]	0.65	0.26
$[Fe(BMI)_3](PF_6)_2$[b]	0.57	0.47
$[Fe(GMI)_3](PF_6)_2$[b]	0.50	0.53

[a] Relative to sodium nitroprusside at room temperature. [b] See ref 20.

analytical applications (*i.e.*, ultra trace analyses and isotopic distribution studies).

Isomer shifts (δ) and quadrupole splittings (ΔEq) taken from the Mossbauer spectra of the clathro chelates at 77°K are given in Table VII. All of the complexes have δ values in the range expected for low-spin Fe(II) species (0.00–0.67 mm/sec).[19] However, the clathro chelates are readily distinguished in both δ and ΔEq from low-spin tris(α-diimine)iron(II) complexes containing the following symmetrical α-diimine ligands: biacetylmethylimine (BMI), glyoxalmethylimine (GMI), *o*-phenanthroline (phen), and bipyridine (bipy).[20] As can be seen in the table the clathro chelates as a class exhibit lower δ and higher ΔEq values. Since δ for the clathro chelates is lower than that for the α-diimine species the s-electron density at the iron nucleus for the former class is larger than for the latter. Presumably this difference can be attributed to the fact that the cage ligands are better σ donors and/or $d\pi$ electron acceptors than are the α-diimine species although crystal packing effects[21] and the differences in charge (neutral *vs.* 2+) for the two types of complexes may well be important factors. The larger ΔEq for the clathro chelates is most likely a reflection of the fact that the donor atoms in the cage complexes do not approach an octahedral array as nearly as do those of the α-diimine complexes. That is, the twist angle for $[Fe(phen)_3]^{2+}$ is 54°,[22] only 6° away from that expected for a trigonal antiprism, whereas $[Fe(DMG)_3(BF)_2]$ has a twist angle of approximately 17°[13] a value nearer to that of a trigonal prism (0°) than a trigonal antiprism. Since ΔEq is determined by the electric field gradient at the iron nucleus and since the magnitude of that gradient depends in part on the degree to which the donor atoms do not possess cubic symmetry, the foregoing conclusion concerning the relative ΔEq values seems justified.[23]

The accuracy with which the isomer shift values in Table VII were determined (±0.02 mm/sec) makes it impossible to distinguish between adjacent entries in the table (*i.e.*, 0.35 and 0.33 mm/sec); however, an overall trend is recognizable. Thus, as the group attached to the boron atom changes from F to alkoxy the isomer shift value decreases. This fact is probably a direct reflection of the greater "electron-releasing" character of the alkoxy groups (relative to the F^- group). In any case some indication of the importance of the σ-bonding network in the peripheral portions of the cage ligand is indicated. The group bound to the boron must be "perturbing" the iron largely through σ bonds since the π character of the B–X bond must be very small.

Registry No. $DMGH_2$, 95-45-4; $BF_3 \cdot O(C_2H_5)_2$, 109-63-7; $B(OH)_3$, 10043-35-3; CH_3OH, 67-56-1; C_2H_5OH, 64-17-5; $i\text{-}C_3H_7OH$, 67-63-0; C_4H_9OH, 71-36-3; $[Fe(DMG)_3(BF)_2]$, 39060-38-3; $[Fe(DMG)_3(BOH)_2]$, 39060-43-0; $[Fe(DMG)_3(BOCH_3)_2]$, 39060-42-9; $[Fe(DMG)_3(BOC_2H_5)_2]$, 39060-41-8; $[Fe(DMG)_3(BO\text{-}i\text{-}C_3H_7)_2]$, 39060-40-7; $[Fe(DMG)_3(BOC_4H_9)_2]$, 39060-39-4.

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