Encapsulation Reactions. Synthesis and Study of Clathro Chelates Derived from Dimethylglyoxime, Cobalt, and Lewis Acids

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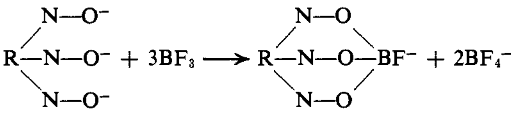
Abstract: The synthesis of four clathro chelates from BF_3, $SnCl_4$, and $SiCl_4$ and a [tris(dimethylglyoximato)cobaltate(III)]$^{3-}$ complex containing all the glyoximato moieties in the anti configuration is reported. The two clathro chelates derived from BF_3, a cobalt(III) and a cobalt(II) species, are both low-spin complexes. Each exhibits high thermal stability as evidenced by sublimation and mass spectrometric experiments. A low-spin cobalt(III) complex is obtained from $SnCl_4$. In this species the tin(IV) is hexacoordinate with three chlorine atoms and three oxygen atoms from the oxime groups bound to the tin. It is proposed that the silicon-containing clathro chelate is formally a derivative of $[OSi(OH)_3]^-$ with the three Si–OH linkages being replaced by three oxime ester groups, Si–O–N=. Such a formulation features the presence of terminal Si–O bonds in the complex.

The concept of clathro chelates was originally put forth by Busch in 1964.[1] However, authentic examples of these compounds have been reported only since 1968.[2-6] In each of the three known classes of clathro chelates, the metal ion is encapsulated by a bicyclic ligand, the donor atoms of which are disposed in a trigonally symmetric array about the metal ion. Two of the classes of clathro chelates have been synthesized from substrate complexes by a ring-closure reaction involving the binding together of three oxime units with a Lewis acid. Such a reaction, leading to the formation of three oxime ester linkages, is schematically represented in eq 1. One class containing the oxime esters, the tris(glyoximato) clathro chelates, can be prepared from hydrated tripotassium tris(dimethylglyoximato)cobaltate(III), $K_3[Co(DMG)_3]$, and Lewis acids such as BF_3.[2] The other class of clathro chelates involving the oxime ester features three instead of six oxime moieties.[3] In this class a phosphorus atom serves as one of the bridgeheads in the bicyclic ligand.[3] In the following discussion we report our studies on the preparation and properties of clathro chelates which have been prepared from hydrated $K_3[Co(DMG)_3]$.



$$\mathrm{R}\begin{matrix}\diagup\mathrm{N{-}O^-}\\ \mathrm{{-}N{-}O^-}\\ \diagdown\mathrm{N{-}O^-}\end{matrix} + 3\mathrm{BF_3} \longrightarrow \mathrm{R}\begin{matrix}\diagup\mathrm{N{-}O}\diagdown\\ \mathrm{{-}N{-}O{-}}\\ \diagdown\mathrm{N{-}O}\diagup\end{matrix}\mathrm{BF^-} + 2\mathrm{BF_4^-} \qquad (1)$$

Results and Discussion

The general preparative route first envisioned for the tris(glyoximato) clathro chelates involves the synthesis of an isomerically pure tris(DMG) complex in which all of the ligands are in the anti configuration, a configuration assuring coordination exclusively between the metal ion and nitrogen atoms.[7] A direct consequence of this all-nitrogen binding is that the oxime oxygen atoms lie in triangular arrays above opposite trigonal faces of the coordination polyhedron, thus placing them in optimum position for a ring-closure reaction involving oxime ester formation with a trifunctional reagent. Well-characterized clathro chelates have been prepared from the all-anti $K_3[Co(DMG)_3]$ using the Lewis acids BF_3 and $SnCl_4$.[8] There is also experimental evidence which indicates that the Lewis acid $SiCl_4$ can be employed to prepare clathro chelates from $K_3[Co(DMG)_3]$. However, the silicon containing species obtained to date is more difficult to definitively characterize than are the cages derived from BF_3 and $SnCl_4$. In all cases the synthesis of the clathro chelate can be accomplished by refluxing $K_3[Co(DMG)_3]$ with an excess of the Lewis acid in an appropriate solvent. The cage derived from BF_3 can also be made by a more direct synthesis modeled after preparations reported in ref 5 and 6.

The products of the reactions involving BF_3, $SnCl_4$, and $SiCl_4$ are represented in Figure 1 and in Table I wherein the formulation and selected physical properties of the clathro chelates are tabulated. Since the formal names of the ligands in this series of complexes are exceedingly cumbersome, the various complexes are referred to in the body of this article by the simplified nomenclature indicated in Table I.

I. Clathro Chelates Derived from BF_3. The clathro chelates which have been most fully explored are the previously reported $[Co(DMG)_3(BF)_2]^+$ and its neutral congener $[Co(DMG)_3(BF)_2]$. The latter complex is prepared from the $[Co(DMG)_3(BF)_2]BF_4$ by reduction with iodide ion in acetonitrile–acetone solution, a process which leaves the ligand cage intact. In this reaction, deep red crystals of the desired product are de-

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(1) D. H. Busch, *Rec. Chem. Progr.*, **25**, 107 (1964).

(2) D. R. Boston and N. J. Rose, *J. Amer. Chem. Soc.*, **90**, 6859 (1968); D. R. Boston and N. J. Rose, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. INOR-96.

(3) J. E. Parks, B. E. Wagner, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 3500 (1970); *Inorg. Chem.*, **10**, 2472 (1971).

(4) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Lett.*, 34, 2889 (1969); B. Metz, D. Moras, and R. Weiss, *Chem. Commun.*, 444 (1971).

(5) S. C. Jackels, D. S. Dierdorf, N. J. Rose, and J. Zektzer, *J. Chem. Soc., Chem. Commun.*, 1291 (1972).

(6) S. C. Jackels and N. J. Rose, *Inorg. Chem.*, in press.

(7) D. R. Boston, Thesis, University of Washington, 1970.

(8) In conjunction with the search for a preparative scheme for the all-*anti*-DMG product, other tris(DMG) complexes were found which contain a mixture of *anti*- and *amphi*-DMG isomers. One of these complexes, $Na_3[Co(DMG)_3][H_2O]_x$, exhibits six methyl resonances in its pmr spectrum, has multiple bands in the portion of the infrared spectrum associated with N–O stretching motions, and gives a product with BF_3 which is not a clathro chelate: D. R. Boston, N. Howe, and N. J. Rose, unpublished results.

Table I. Clathro Chelates Derived from the $[Co(DMG)_3]^{3-}$ Species[a]

Complex	$[Co(DMG)_3(BF)_2]^+$	$[Co(DMG)_3(BF)_2]$	$[Co(DMG)_3(SnCl_3)_2]^-$	$[Co(DMG)_3(SiO)_2]$[c]
Y	BF	BF	$SnCl_3$	SiO
n	+1	0	−1	0
Counterion	BF_4^-, PF_6^-		$[(n\text{-}C_3H_7)_4N]^+$	*c*
Formal oxidation state of Co	III	II	III	II
Magnetic moment, μ_{eff}, BM	D[b]	2.12	D[b]	2.28
Color	Orange	Red	Yellow	Brown

[a] See Figure 1. [b] D = diamagnetic. [c] Isolated as HPF_6 adduct.

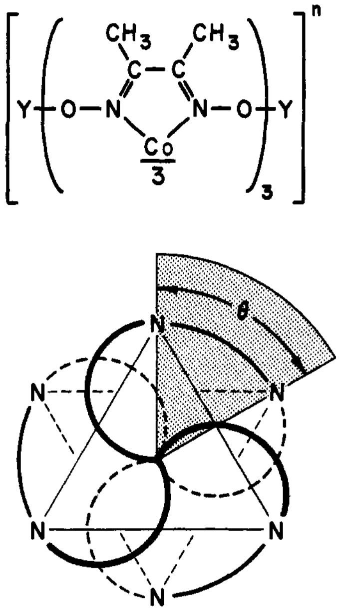

Figure 1. Two representations of the clathro chelates derived from [tris(dimethylglyoximato)cobaltate(III)]$^{3-}$

posited in the reaction vessel within 1–2 min. The parameters associated with this facile process have not been determined, but presumably an outer sphere mechanism must be involved in view of the robust character of the cage ligand and complex (*vide infra*). Although oxidation–reduction studies of the clathro chelates have not been conducted to date, it is appropriate to note that both $[Co(DMG)_3(BF)_2]^+$ and $[Co(DMG)_3(BF)_2]$ are low-spin species, and thus their electron transfer reaction should be rather fast compared to the $[Co(NH_3)_6]^{3+}$–$[Co(NH_3)_6]^{2+}$ system where a spin change accounts for the slowness of electron transfer.[9]

Subsequent to the initial identification of $[Co(DMG)_3(BF)_2]BF_4$ and $[Co(DMG)_3(BF)_2]$ as clathro chelates, structural determinations of both complexes by single-crystal X-ray diffraction studies have been completed by Lingafelter and his coworkers.[10] The crystallographic information pertinent to the gross geometries of $[Co(DMG)_3(BF)_2]^+$ and $[Co(DMG)_3(BF)_2]$ is summarized in Table II. Although it was anticipated by design that the donor atoms in $[Co(DMG)_3(BF)_2]^+$ would be at or near the apices of a trigonal antiprism,[2] the definitive structural data show that there is significant twisting away from the trigonal antiprism toward a trigonal prism for the Co(III) species and even more twisting for the Co(II) complex. The amount of twist is most clearly defined by the angle θ shown in Figure 1. (θ is a projected angle which would have the value 60° for a trigonal antiprism and 0° for a trigonal prism. The angle involves the two nitrogen atoms which are part of the same dimethylglyoximate moiety.) Thus, $[Co(DMG)_3(BF)_2]^+$ is approximately a "half-twist" case, with θ = 31.2°; and $[Co(DMG)_3(BF)_2]$, with θ = 8.6°, is best described as a distorted trigonal prism as is the Co(II) clathro chelate containing the phosphorus bridgehead and three oxime moieties.[11] The difference in the Co–N bond length between $[Co(DMG)_3(BF_2)]$ and $[Co(DMG)_3(BF)_2]^+$ is approximately twice that (0.08 *vs.* 0.04 Å) of other pairs of complexes where only the charge of the two ions is different.[9,12] Still, each of the Co–N distances is very nearly that expected by comparison with other six-coordinate low spin Co(II) and Co(III) species.[10] Both $[Co(DMG)_3(BF)_2]^+$ and $[Co(DMG)_3(BF)_2]$ have essentially D_3 symmetry. The bond angles and distances within the ligand are the same in each species and no major distortions occur within the ligand except for some deviation of the dimethylglyoximate rings from planarity.

Table II. Structural Data from Single-Crystal X-Ray Studies[a]

	$[Co(DMG)_3(BF)_2]^+$	$[Co(DMG)_3(BF)_2]$
θ angle,[b] deg	31.2	8.6
N–Co–N angle,[c] deg	79.8	76.4
N–N distance,[d] Å	2.426	2.441
Co–N distance, Å	1.893	1.973

[a] See ref 10. [b] See Figure 1. [c] Within a five-membered chelate ring. [d] "Bite" of a five-membered chelate ring.

The fact that the Co–N bond distance can change 0.08 Å between the two species without causing significant changes in the bond angles and distances within the ligand can be understood by considering the stereochemistry of the cage ligand itself. If it is assumed that the cage is disposed about a central cavity such that the complex possesses D_3 symmetry (the case that pertains to the metal complexes), then the only gross, strain-free, internal motion that the ligand can undertake results in relative twisting of the triangles formed by the nitrogen atoms about the C_3 axis (*i.e.*, a change in the θ angle). An examination of molecular models reveals that such

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(9) H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, **10**, 2304 (1971).

(10) G. A. Zakrzewski, C. Ghilardi, and E. C. Lingafelter, *J. Amer. Chem. Soc.*, 93, 4411 (1971).

(11) E. Larsen, G. N. LaMar, B. E. Wagner, J. E. Parks, and R. H. Holm, *Inorg. Chem.*, **11**, 2652 (1972).

(12) The larger change in bond distance, *i.e.*, 0.08 rather than 0.04 Å, in the clathro chelates is readily understood in terms of the crystal field formalism. Thus, crystal field calculations performed in the manner of Companion and Komarynsky, *J. Chem. Educ.*, **41**, 257 (1964), reveal that, for the Co(III) and Co(II) clathro chelates, the relative ordering of the one-electron orbital energies features a degenerate pair of orbitals in the highest energy (least favorable) position. In the Co(III) complex this degenerate pair is not populated whereas in the Co(II) complex it is. The "addition" of an electron to the highest energy orbitals in the clathro chelate case considered here would be likely to have an effect somewhat similar to adding an electron to e_g rather than to t_{2g} orbitals in octahedral complexes. Notably, the 0.04 Å change is associated with electron population changes in t_{2g} orbitals.[9]

Table III. Selected Infrared Absorption Bands (cm^{-1}) of Clathro Chelates and a Related Complex

Complex	C=N	N—O	B—O	B—F	Unassigned
$K_3[Co(DMG)_3]$	1535 m	1215 s 1080 s			495 s, 740 m, 964 m
$[Co(DMG)_3(BF)_2]BF_4$	1623 m	1250 m 1105 s	1205 s 815 s	1010 s 990 m, sh	500 m, 720 m, 930 s
$[Co(DMG)_3(BF)_2]$	1623 w 1592 w	1220 m 1090 s	1192 s 810 s	1010 sh 990 s	575 m, 625 m, 960 s
$[(n\text{-}C_3H_7)_4N][Co(DMG)_3(SnCl_3)_2]$	1591 s	1220 s 1095 s			512 s, 760 s, 990 s
$[Co(DMG)_3(SiO)_2]HPF_6$	1604 m	1220 s[b] 1083 s			600 s, 750 s,[b] 850,[a] 983 s

[a] PF_6^- absorption. [b] Shoulders are present on these peaks.

a twist from $\theta = 60$ to $\theta = 0°$ is not only accompanied by a change in the coordination polyhedron from a trigonal antiprism to a trigonal prism but also by an increase in the distance from the center of the cavity to the nitrogen atoms.[10] This distance varies smoothly from a minimum value at $\theta = 60°$ to a maximum value at $\theta = 0°$.

Since *both* change in the coordination geometry and change in the Co–N distance are necessarily associated with an unstrained twisting motion of the cage, the observed structural differences between $[Co(DMG)_3(BF)_2]^+$ and $[Co(DMG]_3(BF)_2]$ might simply reflect the fact that θ must be smaller for the latter if the longer Co–N distance expected for a hexacoordinate Co(II) species (relative to a Co(III) complex) is to be found. Thus, it is tempting to conclude that achieving the appropriate Co–N distance is the dominant factor in determining the nature of the coordination polyhedron.

The magnetic moment of $[Co(DMG)_3(BF)_2]$, 2.12 BM at 22°, places it in a class of somewhat limited number, that of hexacoordinate, low-spin Co(II) complexes. Three other cases[13–15] known to us which involve nitrogen donors are $[Co(CN)_6]^{4-}$, $[Co(o\text{-phen})_2(CN)_2]$, and $[Co(NO_2)_6]^{4-}$. Notably the clathro chelate of Parks, Wagner, and Holm, $[Co(PccBF)]^+$ (with its three oxime and three pyridine nitrogen donors), has a moment at room temperature of 4.76 BM,[3] presumably because the pyridine moieties provide a weaker field than do oximes.

Selected bands from the infrared spectra (Nujol mulls) of the clathro chelates are collected in Table III along with tentative assignments based on earlier work.[2,16] These data require no further comment with the possible exception of the 1600-cm^{-1} region of the $[Co(DMG)_3(BF)_2]$ spectrum. There is a distinct doublet centered at 1607 cm^{-1} in this spectrum whereas the other clathro chelates do not have an obvious multiplicity in the band assigned to C=N stretching motions. More than a single infrared absorption is predicted for C=N stretches for either D_3 or D_{3h} symmetry. Thus, *all* the clathro chelates in this series might be expected to exhibit multiple absorptions in the 1600-cm^{-1} region. However, since neither the relative intensity nor the separation of the bands arising from the C=N stretches can be readily estimated, the significance of the clear multiplet character of the 1607-cm^{-1} band cannot be assessed without a much more detailed investigation.

Various properties of the $[Co(DMG)_3(BF)_2]^+$ salts in solution have already been reported in some detail,[2] and therefore the following discussion concerning the character of the cobalt clathro chelates in solution will be largely restricted to $[Co(DMG)_3(BF)_2]$. Osmometric molecular weight measurements show that $[Co(DMG)_3(BF)_2]$ is a neutral monomer in $CHCl_3$ (calcd mol wt, 461; found, 447, 479), and, as expected, the chloroform solutions are nonconducting. Although the neutral complex is slightly soluble in a wide variety of nonaqueous solvents, chloroform is one of the best common solvents. A maximum concentration of about 3×10^{-3} *M* can be attained in this solvent.

$[Co(DMG)_3(BF)_2]$ has a very intense red color which arises from two distinct absorption maxima (*e.g.*, in acetonitrile λ_{max} at 28,570 cm^{-1}, ϵ 5770, and λ_{max} at 21,740 cm^{-1}, ϵ 5450). No Laporte-allowed transitions in the visible region of the spectra are found in any other clathro chelates in this series. However, Laporte-allowed transitions corresponding to energies in the visible portion of the spectrum are characteristic of the trigonal prismatic tris(dithiolene) complexes.[17] Presumably, the relationship between the nearly trigonal prismatic coordination of Co(II) in $[Co(DMG)_3(BF)_2]$ and the electronic spectrum of the complex will emerge from extensive calculations of the sort already done on the dithiolene complexes.[17]

Both $[Co(DMG)_3(BF)_2]BF_4$ and $[Co(DMG)_3(BF)_2]$ exhibit sufficient volatility and thermal stability to be sublimed under easily obtainable conditions (215°, 0.2 Torr for $[Co(DMG)_3(BF)_2]BF_4$ and 275°, 0.2 Torr for $[Co(DMG)_3(BF)_2]$). A remarkable observation about the sublimations is the fact that the tetrafluoroborate salt sublimes at a significantly lower temperature than the neutral complex. To our knowledge, no other salt–neutral complex pair in which the compounds are so closely similar exhibits this kind of behavior. This behavior must simply reflect the unlikely fact that the free energy of vaporization of the neutral complex is more negative than that of the salt. Clearly the magnitude of the entropy changes associated with vaporization is significantly influencing the free energy changes since it is reasonable to assume that the lattice energy of the salt is greater than that of the neutral species.

The volatility and high thermal stability of $[Co(DMG)_3(BF)_2]BF_4$ and $[Co(DMG)_3(BF)_2]$ make them well suited for mass spectrometric study, and consequently mass spectra of both complexes were obtained, including some spectra showing the relative intensity of the peaks with respect to the probe temperature. The

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(13) L. Cambi and A. Ferrari, *Gazz. Chim. Ital.*, **65**, 1162 (1935).

(14) L. Cambi and E. Paglia, *J. Inorg. Nucl. Chem.*, **8**, 249 (1958).

(15) J. A. Bertrand and D. A. Carpenter, *Inorg. Chem.*, **5**, 514 (1966).

(16) G. N. Schrauzer, *Chem. Ber.*, **95**, 1438 (1962).

(17) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

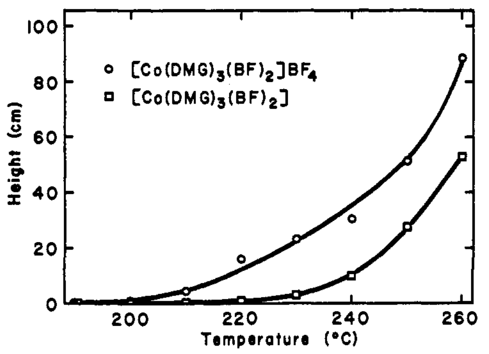

Figure 2. Relative height of mass spectral parent ion peak as a function of probe temperature.

two most striking features of the study are (1) the spectra of $[Co(DMG)_3(BF)_2]BF_4$ and $[Co(DMG)_3(BF)_2]$ are identical in the high mass range (*m/e* >230) and (2) the parent ion peak (parent ion = $[Co(DMG)_3(BF)_2]^+$) is the most intense of those in the high mass range. The measurement of the relative height of the parent ion peak for each of the complexes as a function of temperature is shown in Figure 2. It is to be noted that the first occurrence of a signal with respect to temperature appears at a lower temperature for the salt than for the neutral complex. Thus, the conclusion concerning the relative free energies of vaporization of the neutral complex and the salt (drawn from the sublimation experiments) is also consistent with the data shown in Figure 2.

In Table IV the three major peaks in the 248–461 *m/e* range of the mass spectrum of $[Co(DMG)_3(BF)_2]$ and $[Co(DMG)_3(BF)_2]BF_4$ are listed as well as two of the less intense peaks. Each peak is contained within a cluster of peaks in the actual spectrum, the other peaks in the cluster being due to normal isotopic distributions and to the loss of hydrogen atoms. Examination of the mass spectrum in the stated range reveals a singular point of interest; namely, that the major disintegration mechanism of the clathro chelates must be characterized by a single first step, the loss of most or all of one dioxime unit. Thus, there is a lack of peaks in the 364–461 *m/e* range and the first two peaks which are observed below the parent ion occur at 364 and 347 (Table IV). These two peaks correspond to the formulas $CoC_8H_{13}N_4O_5B_2F_2$ and $CoC_8H_{12}N_4O_4B_2F_2$. They are formed by the removal of $C_4H_5N_2O$ and $C_4H_6N_2O_2$ fragments, respectively. In contrast to the paucity of peaks in the 364–461 *m/e* range, there are, in the 248–364 *m/e* range, at least five peaks having a relative intensity equal to or greater than one-tenth that of the 266 peak. Three of these five are listed in Table IV.

Table IV. Selected Peaks in the Mass Spectrum of $[Co(DMG)_3(BF)_2]$ and $[Co(DMG)_3(BF)_2]BF_4$

Obsd mass	Calcd mass	Rel intensity	Formula
461.08	461.08	4.34	$^{59}Co^{12}C_{12}{}^{1}H_{18}{}^{14}N_6{}^{16}O_6{}^{11}B_2{}^{19}F_2$
364.04	364.04	1.00	$^{59}Co^{12}C_8{}^{1}H_{13}{}^{14}N_4{}^{16}O_5{}^{11}B_2{}^{19}F_2$
347.04	347.03	0.34	$^{59}Co^{12}C_8{}^{1}H_{12}{}^{14}N_4{}^{16}O_4{}^{11}B_2{}^{19}F_2$
265.99	265.95	1.22	$^{59}Co^{12}C_4{}^{1}H_1{}^{14}N_4{}^{16}O_5{}^{11}B_2$
248.99	248.94	0.12	$^{59}Co^{12}C_4{}^{14}N_4{}^{16}O_4{}^{11}B_2$

II. Clathro Chelates Derived from $SnCl_4$. The second type of clathro chelate prepared in the current series is formed by the reaction of $K_3[Co(DMG)_3]$ with $SnCl_4$ and is an anionic complex which contains octahedrally bound Sn(IV) as the bridgehead atoms (Figure 1). The $[Co(DMG)_3(SnCl_3)_2]^-$ ion was isolated first as a species presumed to be the potassium salt as inferred by a flame test and by a knowledge of the cations present in the reaction mixture. This crude product was purified by metathesis to the tetra-*n*-propylammonium salt which then was used for all of the characterization studies reported herein. The infrared spectrum of $[Co(DMG)_3(SnCl_3)_2]^-$ (Table III) clearly shows an absorption pattern which is characteristic of the two clathro chelates previously discussed. This pattern, which consists of a set of four bands in the vicinities of 1600, 1220, 1100, and 960 cm^{-1}, is found in the substrate complex $K_3[Co(DMG)_3]$ as well. The first three of these bands are assigned to the C=N stretch, the N—O asymmetric, and the N—O symmetric stretches, respectively. The pattern is taken to be characteristic of the DMG portions of the clathro chelates and not to be reflective of the bridgehead units. It is further inferred that the presence of this pattern, without multiplicities in the bands, is a consequence of the fact that the three ligand arms are symmetrically disposed about the metal ion in each of the complexes. In this context then the infrared spectrum provides evidence for the proposed bicyclic cage structure of $[Co(DMG)_3(SnCl_3)_2]^-$.

The ^1H nmr spectrum of $[n\text{-}C_3H_7)_4N][Co(DMG)_3(SnCl_3)_2]$ lends strong support to the proposed cage-like disposition of the DMG units. The spectrum in nitrobenzene contains four sets of peaks. Three sets of peaks, centered respectively at 3.45, 1.98, and 1.16 ppm downfield from internal TMS, are characteristic of the tetra-*n*-propylammonium ion as is indicated by a direct comparison of the spectrum in question with that of $[n\text{-}C_3H_7)_4N]PF_6$. The single peak at 2.61 ppm downfield from TMS, along with its two satellites at 2.69 and 2.53 ppm, is assigned to the six equivalent methyl groups of the clathro chelate anion. Integration of peak areas yields the correct ratio of 14:9 for the resonances assigned to $[(n\text{-}C_3H_7)_4N]^+$ *vs.* those assigned to $[Co(DMG)_3(SnCl_3)_2]^-$. The two small satellite peaks on either side of the methyl singlet are thought to arise from coupling between the methyl hydrogens and the ^{119}Sn isotope. The observed splitting is confidently attributed to a coupling constant because the separation, 9.6 Hz, is the same, measured on both 60 and 100 MHz instruments. It is likely that the satellites which should be present due to coupling with the ^{117}Sn isotope are "hidden" in the singlet peak, a notion consistent with the fact that ^{117}Sn–H coupling constants are typically less than for ^{119}Sn–H coupling constants, and with the fact that the singlet peak is relatively broad (2 Hz at half-height).[18,19] The magnitude of J is surprisingly large considering that the ^{119}Sn–H coupling occurs through five bonds. The corresponding coupling constants in a 2,4-pentanediono complex of tin are reported as 5.8 and 6.6 Hz.[20] In the latter complex four bonds separate the tin and hydrogen nuclei.

The conducting properties of $[(n\text{-}C_3H_7)_4N][Co\text{-}$

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(18) N. A. Matwiyoff and R. S. Drago, *Inorg. Chem.*, 3, 337 (1964).

(19) M. M. McGrady and R. S. Tobias, *Inorg. Chem.*, 3, 1157 (1964).

(20) J. W. Faller and A. Davison, *Inorg. Chem.*, 6, 182 (1967).

$(DMG)_3(SnCl_3)_2]$ in acetone at 25° were measured in the concentration range 1×10^{-3} to 1×10^{-4} M, and the data were analyzed according to the Onsager limiting law[21] with a view to confirming the postulated molecularity of the complex. From the Onsager plot, Λ_0 is found to be 121.4 cm^2 ohm^{-1} $equiv^{-1}$ and the slope is found to be 575, a value in good agreement with that calculated (526), assuming the salt to be a uni-univalent electrolyte.

These results indicate that the salt is "well behaved" in acetone in the classical sense, and they provide an interesting behavioral contrast to that normally observed for electrolytes in acetone. Thus, many 1:1 salts deviate considerably from expected behavior, showing Onsager slopes of up to twice the predicted values.[21,22] Since acetone is a poor ionizing solvent, these deviations might well be due to extensive association. The more nearly classic behavior of $[(n\text{-}C_3H_7)_4N][Co(DMG)_3(SnCl_3)_2]$ suggests that a minimum of association takes place, a postulate consistent with the very large size of both the cation and anion and with the concomitant large separation of the centers of positive and negative charge.

III. Clathro Chelates Derived from $SiCl_4$. To date the product derived from $SiCl_4$ which is most definitively characterized as a clathro chelate is formed by a two-step process. In the first step, the reaction of $K_3(Co(DMG)_3]$ with $SiCl_4$ in tetrahydrofuran, a light green solid forms. In the second step, the addition of an aqueous $NaPF_6$ solution to a methanol solution of the green solid, a dark brown solid volunteers from a dark brown solution which is acidic. This solid is formulated as a hydrohexafluorophosphate adduct of the silicon containing clathro chelate, $[Co(DMG)_3(SiO)_2]HPF_6$. Our formulation rests primarily on the results of elemental analyses and on the comparison of the infrared spectrum with that of other clathro chelates. Analyses for C, H, N, Si, P, F, and Co are satisfactory and the expected Co:DMG:Si ratio is found, *i.e.*, 1:3:2. The pattern of bands in the 600–2000-cm^{-1} region of the Nujol mull spectrum is the same as that found in the tin clathro chelate, *vide infra* (Table I).

Part of the problem of characterizing the product in question (or others we have obtained from the $SiCl_4$ reaction) relates to difficulty in readily manipulating the samples. For instance, normal precipitation and crystallization techniques applied to $[Co(DMG)_3(SiO)_2]HPF_6$ result in the formation of gels. The hydrohexafluorophosphate adduct can be dried quantitatively, but the anhydrous species readily picks up two to three water molecules of hydration from the atmosphere. Conductivity and molecular weight measurements of the adduct in dilute acetonitrile solutions ($\sim 10^{-3}$ M) show that the complex is highly aggregated; that is, "clusters" of up to six complex molecules must be postulated in order to rationalize the solution data. The proposed formulation for the clathro chelate is consistent with the foregoing observations since terminal SiO moieties could readily foster the formation of aggregates or gels *via* the formation of hydrogen bonds with water present in the solvents and/or the formation of $\geqslant$Si–O–Si$\leqslant$ linkages.

The cobalt ion in $[Co(DMG)_3(SiO)_2]HPF_6$ is confidently assigned a formal oxidation state of II due to the fact that the magnetic moment for the complex is 2.28 ± 0.05 BM (at 23°). Even though there is a 0.05 BM uncertainty in the moment,[23] it seems most appropriate to assume that the species does contain low spin Co(II) (as does $[Co(DMG)_3(BF)_2]$) rather than Co(III) ions in either an unusual spin state or a mixture of two spin states.

Conclusions

The successful synthesis of clathro chelates of the tris(glyoximato) class from a tris(DMG) complex and three Lewis acids (BF_3, $SnCl_4$, and $SiCl_4$) suggests that a wide variety of new cages of this class can be made by incorporating various other atoms into the bridgehead position, Y, in Figure 1. For instance, synthesis of phosphorus, carbon, and antimony containing cages can probably be done using PCl_5 or $(EtO)_3CH$ or $SbCl_5$. The incorporation of metal ions into the bridgeheads is also readily envisioned. Thus, the placing of a metal ion with a coordination number of six in the Y position might well lead to a linear polymeric species if the only donor atoms in the system were the nitrogen and oxygen atoms of DMG. In fact, it is quite probable that such a polymer was synthesized by Weeldenburg in 1924. He reports the preparation of an insoluble iron–cobalt–DMG species with a Fe:Co:DMG ratio of 1:1:3.[24]

Experimental Section

All solvents and chemicals used in experiments were obtained commercially and were of reagent grade; they were used without further purification except for nitrobenzene, which was distilled over P_4O_{10}. No laboratory hardware of special design was used.

All infrared spectra were recorded on a Beckman IR 10 infrared spectrophotometer in the range 4000–380 cm^{-1}. Samples were prepared as Nujol (mineral oil) mulls. The mulls were suspended between crystalline KBr plates. All spectra were standardized at 1601 cm^{-1} with polystyrene film. A Beckman RC 18-A conductivity bridge was utilized for all conductivity measurements. Generally, a cell with electrodes separated by about 1 cm ($k = 0.3247$ cm^{-1}) was used. All measurements were made at 25.0°. Ultraviolet and visible spectra were obtained using a Cary Model 14 recording spectrophotometer within the range 10,000–2000 Å. Sample cells were of 1 or 2.5 cm in length depending on the concentration and intensity of absorption of the sample. A solvent baseline was recorded for each spectrum. All elemental analyses except nitrogen were performed by Alfred Bernhardt Microanalytical Laboratories, 5251 Elbach über Engelskirchen, West Germany. Nitrogen analyses were done by the authors using a Coleman Model 29 nitrogen analyzer. Typically, acetanilide was used as a standard and cobalt oxide was employed as the combustion agent. Molecular weight measurements were made on a Mechrolab Model 301-A vapor pressure osmometer. Sample concentrations were determined graphically, by comparison to standard solutions of benzil which had been recrystallized from ethanol. ^1H nmr spectra were obtained using variously the Varian Associates, Inc., A-60, T-60, HR/HA 60-IL, or HA-100 nmr spectrometers.

Magnetic susceptibilities of paramagnetic complexes were measured on a Faraday balance consisting of a Varian Associates V-4005 4-in. electromagnet, a Cahn RG automatic electrobalance, and a L&N Speedomax H recorder. All measurements were taken in a helium atmosphere at 195 Torr.

The magnetic susceptibility of the $HgCo(SCN)_4$ standard is 16.44×10^{-6} cgs unit at 20°.[25] A temperature correction factor

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[21] S. Glasstone, "An Introduction to Electrochemistry," Van Nostrand, New York, N. Y., 1942, p 93.

[22] J. Nusz, Ph.D. Thesis, University of Washington, Seattle, Wash., 1970.

[23] The uncertainty, ±0.05 BM, in the magnetic moment arises from uncertainty as to the extent of hydration of the complex under the conditions used to make the magnetic measurements, ~195 Torr of helium (see Experimental Section).

[24] J. G. Weeldenburg, *Recl. Trav. Chim. Pays-Bas*, 43, 465 (1924).

[25] B. N. Figgis and J. Lewis, *Tech. Inorg. Chem.*, 4, 137 (1968).

$$\chi_{\text{corr}} = \chi + (0.0033)(\chi)(20 - T)$$

where T is in °C, was applied to this value as necessary.[26] Molar susceptibilities were corrected for diamagnetism of the ligands with Pascal's constants and converted to values expressed in Bohr magnetons by use of the standard equation[25]

$$\mu_{\text{eff}} = 2.84(\chi_{\text{M}}T)^{1/2}\text{BM}$$

where T is in °K.

All mass spectra were taken on an Associated Electrical Industries, Ltd. (AEI), MS-9 mass spectrometer. Masses corresponding to sample peaks were found by a mass matching procedure using perfluorotributylamine as the standard. Samples were introduced into the instrument as solids which had been deposited on the ceramic probe tip from saturated solutions in volatile solvents such as dichloromethane or acetone.

Preparations. 1. Preparation of Tripotassium Tris(dimethylglyoximato)cobaltate(III), $K_3[Co(DMG)_3]$. Potassium hydroxide (10.00 g, 0.179 mol), dimethylglyoxime (12.41 g, 0.107 mol), and $CoSO_4 \cdot 7H_2O$ (10.00 g, 0.036 mol) were added to 100 ml of water with rapid stirring. After mixing for 15 min the solution was filtered into a suction flask and air was drawn through it for 16 hr. The resulting dark red solution was transferred to a round-bottom flask and taken to complete dryness at 60°, using a rotatory evaporator.

Next, 125 ml of absolute ethanol was added to the dry solid. The mixture was stirred vigorously until the solid mass had been broken up, after which the remaining undissolved solid, K_2SO_4, was removed by suction filtration. The filtrate was placed in a dry 1000-ml flask, and about 1 l. of acetone was added to cause precipitation of the desired product. Then the supernatant liquid was removed from the precipitate by decantation. (Normally, the precipitate settles to the bottom of the flask in about 0.5 hr and consequently the decantation is readily accomplished. However, if the precipitate does not settle, the *bulk* of the liquid must be removed by suction filtration. Filtration should be suspended as soon as the precipitate and accompanying liquid form a total volume of about 100 ml. The rest of the normal procedure may then be followed.) The precipitate was dissolved in 100 ml of absolute ethanol, transferred to a round-bottom flask, and reduced in volume to about 30 ml, during which time yellow crystals of solvated $K_3[Co(DMG)_3]$ appeared. (If the solutions or precipitate have been exposed to excessive moisture, no solid product will appear.) The solid product was filtered under dry air, washed with 30 ml of a 4:1 acetone–absolute ethanol by volume mixture, then with 30 ml of acetone, and immediately dried at 0.2 Torr over Drierite for about 12 hr before the solid was removed from the filter.

The product is quite hygroscopic but can be handled in air for a short period of time once it has been dried. If desired, the product may be recrystallized by volume reduction of an absolute ethanol solution. However, the unrecrystallized product is pure enough for further use. After drying to constant weight at 50° and 2 Torr, the unrecrystallized complex is best formulated as $K_3[Co(DMG)_3] \cdot EtOH \cdot 3H_2O$ (hereafter this compound will be referred to simply as $K_3[Co(DMG)_3]$). The yield was 2.83 g, 13%. *Anal.* Calcd for $C_{14}H_{30}N_6O_{10}CoK_3$: C, 27.15; H, 4.85; N, 13.58; Co, 9.52; K, 24.00. Found: C, 27.28; H, 4.26; N, 13.53; Co, 9.44; K, 25.37. Note, the presence of EtOH is confirmed in the pmr spectrum.

2. Preparation of 4,5,11,12,17,18-Hexamethyl-1,8-difluoro-1,8-dibora-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaazabicyclo[6.6.6]-eicosa-3,5,10,12,16,18-hexaenediylcobalt(III) Tetrafluoroborate, $[Co(DMG)_3(BF)_2]BF_4$. A 500-ml, three-neck 24/40 flask equipped with a Friedrichs condenser, dropping funnel, gas inlet tube, heating mantle, and magnetic stirrer was flushed with dry nitrogen and charged with $K_3[Co(DMG)_3]$ (1.83 g) and 75 ml of dry ether. After stirring for 10 min, $BF_3{:}O(C_2H_5)_2$ (65 ml) was added dropwise over a 10-min period.

The reaction mixture was heated to about 40° and a gentle stream of nitrogen passed over it for 30 min in order to reduce the volume to about 65 ml. The remaining solution was refluxed gently for 40 min and then cooled to room temperature; 80 ml of dichloromethane was added, the precipitate, KBF_4, was removed by fitration, and 200 ml of dry ether was added to the solution, which was cooled in ice for 15 min. Another 150 ml of ether was added and the solution was cooled for 2 hr, whereupon red-orange crystals of the desired product were formed, yield 1.17 g (60%). The product was recrystallized from acetonitrile and ether. *Anal.* Calcd for $CoC_{12}H_{18}N_6O_6B_3F_6$: C, 26.33; H, 3.34; N, 15.34; B, 5.92; F, 20.83; Co, 10.76. Found: C, 26.50; H, 3.45; N, 15.34; B, 6.00; F, 21.07; Co, 10.66.

3. Preparation of $[Co(DMG)_3(BF)_2]PF_6$. $[Co(DMG)_3(BF)_2]BF_4$ (1.00 g, 1.83 mmol) was dissolved in a minimum of acetonitrile (about 50 ml). A solution of $NaPF_6$ (3.00 g, 18.0 mmol) in 50 ml of water was added to the acetonitrile solution; the resulting orange precipitate was filtered, washed with water, and dried in air. The product was recrystallized from acetone and ether, yield of recrystallized product 0.5 g (45%). *Anal.* Calcd for $CoC_{12}H_{18}N_6O_6PB_2F_8$: C, 23.78; H, 3.00; N, 13.88; F, 25.10; Co, 9.72. Found: C, 23.69; H, 2.75; N, 13.83; F, 24.67; Co, 9.45.

4. Preparation of $[Co(DMG)_3(BF)_2]$. $[Co(DMG)_3(BF)_2]BF_4$ (2.00 g, 3.66 mmol) was dissolved in 100 ml of acetonitrile, and 30 ml of a saturated solution of NaI in acetone was added. The color of the solution darkened immediately and deep red (black to the eye) cystals were deposited within 2 min. The crystals were filtered from the solution, and then 50 ml of water was added, causing the remainder of the product to be formed as a tan precipitate. The product was recrystallized from hot dichloromethane solution, yield 1.6 g (90%). *Anal.* Calcd for $CoC_{12}H_{18}N_6O_6B_2F_2$: C, 31.25; H, 3.97; N, 18.23; Co, 12.79; F, 8.25. Found: C, 31.34; H, 4.09; N, 18.03; Co, 12.46; F, 7.93.

5. Preparation of $[(n\text{-}C_3H_7)_4N][Co(DMG)_3(SnCl_3)_2]$. A 500-ml, three-neck 24/40 flask was equipped with reflux condenser, heating mantle, and magnetic stirrer and flushed with dry nitrogen. Then $K_3[Co(DMG)_3]$ (3.37 g) and 200 ml of dry dichloromethane were added. This mixture was stirred for 5 min and anhydrous $SnCl_4$ (5.00 ml) was added. The reactants were heated to slow reflux for 3 hr, and the resulting light yellow solid was filtered from the reaction mixture and washed with ether.

The yellow solid was then taken up in 100 ml of acetone and the KCl solid was filtered off. $[(n\text{-}C_3H_7)_4N]PF_6$ (10.0 g) was dissolved in 100 ml of acetone and added to the reaction product solution. Subsequent addition of about 150 ml of H_2O caused a flocculent yellow precipitate of the desired product to form. (If too much H_2O is added, $[(n\text{-}C_3H_7)_4N]PF_6$ will coprecipitate.) This precipitate was filtered, washed with H_2O, and dried in air. The product was recrystallized from acetone–ether solution, yield 1.22 g (18%). *Anal.* Calcd for $CoC_{24}H_{46}N_7O_6Sn_2Cl_6$: C, 27.76; H, 4.49; N, 9.45; Co, 5.67; Sn, 22.88; Cl, 20.50. Found: C, 27.85; H, 3.90; N, 9.28; Co, 5.55; Sn, 23.01; Cl, 20.64.

6. Preparation of $[Co(DMG)_3(SiO)_2]HPF_6$. A 500-ml, three-neck 24/40 flask was equipped with a reflux condenser and flushed with dry nitrogen. The flask was then charged with $K_3[Co(DMG)_3]$ (2.00 g) and 200 ml of tetrahydrofuran (THF) which had been previously dried by shaking over Na_2SO_4. This mixture was stirred rapidly for 5 min and $SiCl_4$ (4.0 ml) was added. The mixture turned brown immediately and upon heating to reflux turned to a yellow color in about 1 hr. Continued reflux for 24 hr produced a light green solid in the reaction vessel. This was filtered from the supernatant liquid with suction, washed with THF and ether, and dried in air. The crude solid was dissolved in 400 ml of methanol and filtered; then $NaPF_6$ (10.00 g) in 50 ml of H_2O was filtered into the solution. The ensuing brown precipitate was filtered and washed with H_2O, alcohol, and ether. The dry solid was extracted with 140 ml of acetonitrile; the resulting solution was filtered, and then the filtrate was taken to dryness in a rotatory evaporator, thereby yielding the desired solid, yield 0.5 g (20%). (Alternatively, the product may be precipitated by addition of ether to the acetonitrile solution. However, this precipitate had a gel-like consistency and was hard to dry uniformly.) The undried product was found to be a hydrate (probably a trihydrate) by nitrogen analysis. After drying to constant weight at 0.2 Torr at room temperature over P_4O_{10}, the hygroscopic product was analyzed. *Anal.* Calcd for $CoC_{12}H_{19}N_6O_8Si_2PF_6$: C, 22.66; H, 2.99; N, 13.22; Si, 8.84; P, 4.88; F, 17.94; Co, 9.27. Found: C, 22.82; H, 3.03; N, 13.38; Si, 8.65; P, 4.75; F, 17.70; Co, 9.46.

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[26] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).