# An Encapsulation Reaction. Synthesis of the Clathro Chelate 1,8-Bis(fluoroboro)-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-4,5,11,12,17,18-hexamethylbicyclo[6.6.6]eicosa-3,5,10,12,16,18-hexaenecobalt(III) Ion

*Sir:*

Molecular cages have recently been of interest to scientists of several disciplines as is evidenced by work with materials of the Zeolite type, by the synthesis of organic encapsulation compounds,[1] and by reports of clathrate salts.[2,3] For coordination compounds in which the metal ion is both coordinately saturated and surrounded by a cage of ligand atoms, the term clathro chelate has been coined.[4] Depending upon the coordination polyhedron being considered, the design of such a chelate may be envisioned in several ways. One approach to the preparation of an octahedral clathro chelate involves a template reaction between a complex containing three bidentate donors and a reagent meant to join or cap the trio of bidentate ligands at each "end" of the $C_3$ axis of the complex (Figure 1B). We report here the application of this approach to encapsulate a cobalt(III) ion in the first example of a clathro chelate known to us. For this work dimethylglyoxime ($dmgH_2$) was selected as the bidentate ligand because of the proclivity with which N-bonded oximes react at the oxygen atoms,[5-8] and boron trifluoride was selected as the capping agent because it is known to link coordinated oximes.[5,6,8]

Although two tris-dmg complexes have been reported, neither has been completely characterized.[9-17] In spite of the availability of these reports, some difficulty was experienced in preparing a tris-dmg complex of cobalt(III) in which coordination occurred exclusively through nitrogen atoms. A satisfactory complex can be synthesized by bubbling air through an aqueous solution of $dmgH_2$, KOH, and $CoSO_4 \cdot 7H_2O$ present in mole ratios of 3:5:1, respectively. Reduction of the solution volume followed by extraction and recrystallization from absolute ethanol yields an extremely hygroscopic potassium tris(dimethylglyoximato)cobaltate(III) complex. Analytical data give C/Co and N/Co ratios of 12.6 and 5.9, respectively (calcd, 12.0 and 6.0). Further support for the proposed formulation arises from the similarity in the infrared spectrum of this complex with those of $[Ni(dmgH)_2]$[18] and the cobaloximes[19] (1080, 1215 $cm^{-1}$, N–O stretch; 1375, 1440 $cm^{-1}$, $-CH_3$ deformation; 1535 $cm^{-1}$, C=N stretch). Unlike products prepared by methods similar to those reported in the literature,[9] the pmr spectrum of this complex in $D_2O$ exhibits only one peak (1.0-cps half-width) at 152.3 cps downfield from external TMS. This datum is consistent with that expected from a complex with oxime units bonded only through nitrogen, and thus the oxygen atoms are thought to be in the optimum position for reaction with the capping reagent.[5,8]

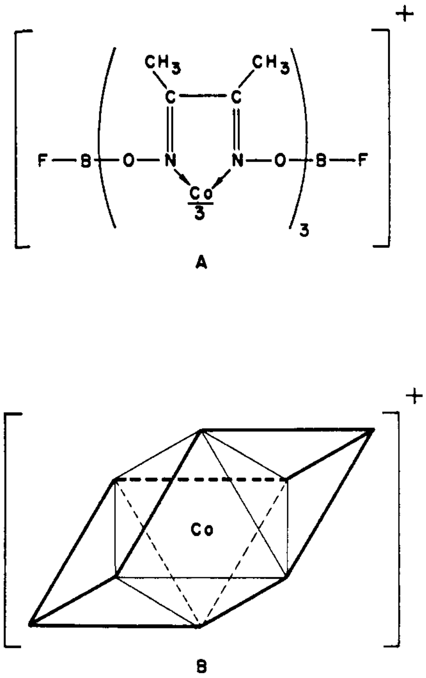

Figure 1. Clathro chelate derived from dimethylglyoxime, boron trifluoride, and cobalt(III). The dark lines of B represent the chelate rings of the complex.

The $BF_4^-$ salt of the desired clathro chelate, $[CoL]^+$, is prepared from the tris complex just described and boron trifluoride etherate by refluxing in ether (Figure 1A,B). A predominant by-product of the reaction, $KBF_4$, is precipitated by the addition of $CH_2Cl_2$ and is removed by filtration. The orange-red $[CoL]BF_4$ is obtained from the resulting solution by addition of more ether and is readily recrystallized from an acetonitrile–ether mixture. Characterization was done with this $BF_4^-$ salt and with a $PF_6^-$ salt made by metathesis. (*Anal.* Calcd for $CoC_{12}H_{18}N_6O_6B_3F_8$: 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. 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). The infrared spectra of the two salts in Nujol, Fluorolube, and KBr disks are extremely similar except for the absorptions

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characteristic of their respective anions. The following assignments are made by comparison with those reported by Schrauzer for his macrocycle[5] (990, 1010 cm$^{-1}$, B–F stretch; 1105, 1250 cm$^{-1}$, N–O stretch; 815, 1205 cm$^{-1}$, B–O stretch; 1375, 1430 cm$^{-1}$, $-\mathrm{CH}_3$ deformations; 1623 cm$^{-1}$, C=N stretch).

The pmr spectrum of $[\mathrm{CoL}]\mathrm{BF}_4$ in acetonitrile consists of a singlet (0.5-cps half-width) at 34.3 cps downfield from the methyl resonance of the solvent. The equivalency predicted for the methyl groups (see Figure 1) is thereby demonstrated subject to the limit of resolution of the nmr spectrometer. The fluorine ($^{19}$F) magnetic resonance spectra also tend to confirm the structure in that (1) the splitting attributed to the boron of the terminal B–F units is observed,[20] and (2) corroborative evidence of the proposed formulation is obtained from relative intensity data. The spectrum for each salt in acetonitrile consists of a quartet ($J_{\mathrm{B-F}}$ = 17.3 ± 0.5 cps) upfield 957 and 5418 cps, respectively, from the characteristic fluorine resonances of $\mathrm{BF}_4^-$ and $\mathrm{PF}_6^-$. Integration by use of a time-averaging computer gives a 1:2.1 ratio for the areas of the BF and $\mathrm{BF}_4^-$ resonances of $[\mathrm{CoL}]\mathrm{BF}_4$ (calcd, 1:2).

Further support for the proposed structure is found in the results from molecular weight determinations and from conductivity measurements. In acetonitrile the apparent molecular weights of the $\mathrm{BF}_4^-$ and $\mathrm{PF}_6^-$ salts are 278 ± 15 and 303 ± 15 (calcd: $[\mathrm{CoL}]\mathrm{BF}_4/2$, 273.6; $[\mathrm{CoL}]\mathrm{PF}_6/2$, 302.7). Conductivity measurements were made at 25° for acetonitrile and acetone solutions, and the equivalent conductances were calculated from these data using the molecular weight values which had been authenticated by the determinations mentioned above (found in acetonitrile: $[\mathrm{CoL}]\mathrm{BF}_4$ at $2.49 \times 10^{-3}$ *M*, $\Lambda_{\mathrm{e}}$ = 140.6 ohm$^{-1}$ equiv$^{-1}$ cm$^2$; $[\mathrm{CoL}]\mathrm{PF}_6$ at $9.30 \times 10^{-4}$ *M*, $\Lambda_{\mathrm{e}}$ = 146.6 ohm$^{-1}$ equiv$^{-1}$ cm$^2$). For $10^{-3}$ *M* solutions typical values of $\Lambda_{\mathrm{e}}$ range from 130 to 160 ohm$^{-1}$ equiv$^{-1}$ cm$^2$.[21] In acetone, a plot of conductivity as a function of dilution ($\Lambda$ *vs.* $\sqrt{C}$) resulted in a straight line typical of the classical Onsager limiting law for strong electrolytes. The slope of the line is 982 which is to be compared with 1000 observed for the uniunivalent electrolyte KI.[22] The equivalent conductance at infinite dilution ($\Lambda_{\mathrm{o}}$) is 173 ohm$^{-1}$ equiv$^{-1}$ cm$^2$, well within the range expected for such an electrolyte (157–190 ohm$^{-1}$ equiv$^{-1}$ cm$^2$).[23]

The visible region of the electronic spectrum of $[\mathrm{CoL}]\mathrm{BF}_4$ in acetonitrile is dominated by the low-energy portion of an intense absorption whose maximum is in the ultraviolet. There is also a small shoulder (~21,370 cm$^{-1}$ ($\epsilon$ ~500)) on this portion of the ultraviolet peak. Clearly no simple ligand field arguments can be applied to these data in order to extract bonding or symmetry information about the complex.

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## Evidence for a "Proton Chelate" in Aqueous Salts of *dl*-Propylenediaminetetraacetic Acid

*Sir:*

There has been considerable discussion in regard to the conformations of salts of ethylenediaminetetraacetic acid (EDTA) and analogous polyaminocarboxylate compounds in aqueous solution at various pH values.[1–8] A knowledge of the conformations of these ligands is an important aid to understanding the thermodynamics and kinetics of their reactions. Various authors[1,3,7,8] have presented evidence in support of the suggestion that in monoprotonated salts of EDTA ($\mathrm{HY}^{3-}$) and its homologs, the acidic proton is shared among several donor atoms in what might be termed a "proton chelate."

Recently we reported nmr studies of the conformations of aqueous salts of *dl*-propylenediaminetetraacetic acid (PDTA) which illustrate the power of this technique in detecting the presence of chelates—even the weakest of the alkali metal chelates.[9] Now we present conclusive evidence that monoprotonated PDTA ($\mathrm{HL}^{3-}$) exists virtually completely in the *gauche* conformation with respect to the central carbon–carbon bond (as shown in I), and is thus a "proton chelate." Although complete information on the bonding and the conformations of carboxylate groups is lacking, the *gauche* conformation would not be favored in the absence of chelation involving both ends of the molecule.[9,9a] It is known that the acidic proton in $\mathrm{HL}^{3-}$ undergoes rapid exchange (mean lifetime is maximum ~$10^{-3}$ sec), spending approximately 50% of its time on each of the nitrogen atoms.[10] In structure I the acidic proton is, therefore, bonded to one nitrogen atom and connected with dotted lines to the opposite nitrogen atom and its two

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[9a] NOTE ADDED IN PROOF. As a result of the increased sum of $J_{\mathrm{ab}}$ and $J_{\mathrm{ac}}$ due to electronegativity effects in the present work, the values of $J_{trans}$ (dihedral angle = 180°) and $J_{gauche}$ (dihedral angle = 60°) employed in calculating formation constants ($K_{\mathrm{f}}$) of chelates of monovalent cations have been reduced by an appropriate factor. This removes the undesirable result of having equal populations of rotamers IIa and IIIa in the absence of chelation as in the previous report.[9] Values of $J_{trans}$ = 10.2 Hz and $J_{gauche}$ = 3.0 Hz lead to ~0% rotamer IIa at probe temperature (35°) in $\mathrm{Cs}_4\mathrm{PDTA}$. The new values of $K_{\mathrm{f}}$ based on these assumptions are as follows: for KPDTA, 1.5 at 100° and 5.7 at 35°· for $[(\mathrm{CH}_3)_4\mathrm{N}]\mathrm{PDTA}$, 0.10 at 100°; and for RbPDTA, 0.16 at 100°.

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