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Synthesis and Characterization of Species Containing Three Metal Atoms

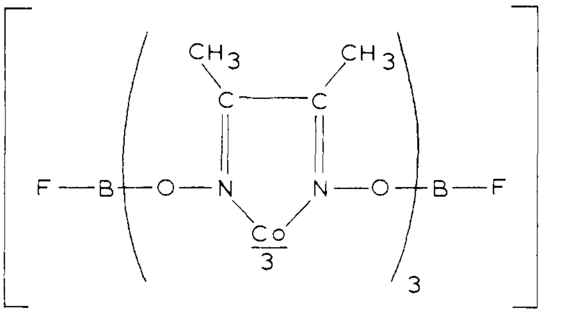
Russell S. Drago* and Joel H. Elias

Contribution from the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801. *Received December 16, 1976*

Abstract: The synthesis of a series of complexes of the general formula CapCo(dmg)$_3$Cap^{n+}, where dmg is dimethylglyoximato and Cap is diethylenetriaminechromium(III); diethylenetriaminecobalt(III); 1,1′,1″-tris(aminomethyl)ethanecobalt(III); triaquonickel(II), diethylenetriaminenickel(II); triaquozinc(II) and diethylenetriaminezinc(II). The proposed structures are supported by elemental analyses, NMR, and conductivity experiments. Magnetic susceptibility studies to 4.2 K indicate little interaction between the unpaired electrons of the paramagnetic capping groups. Electrochemical studies indicate that in contrast to stabilization of the II oxidation state by the BF cap of the clathrochelate FB[Co(dmg)$_3$]BF the metal caps stabilize the III oxidation state. The cobalt center of the metal capped complexes are even more difficult to reduce than the cobalt in K$_3$Co(CN)$_6$. ^{59}Co NMR spectra are reported and discussed.

Current interest in heterogeneous and biological catalytic systems which involve the action of more than one metal center has stimulated the synthesis and study of materials containing more than one metal in the ion or molecule. For ease of discussion, such molecules or ions will be referred to as metallomers and the standard prefixes (di-, tri-, etc.) used to indicate the number of metal ions in the species. Before any generalizations can be established regarding the influences that one metal center in a molecule can have on the chemistry at another metal center, a wide variety of soluble materials will have to be prepared in which the factors influencing metal-metal synergism can be varied in a systematic way. This is a report of the synthesis and characterization of a series of complexes that contain three metal ions in the same molecule. The materials are novel in that soluble species can be synthesized in which two of the metals are different from the third.

The trimetallomers in this system are derived from the salt K$_3$Co(dmg)$_3$ (where dmg represents the dimethylglyoximato anion). The synthesis of this material in the required "anti" configuration,[1] i.e., with all six nitrogen atoms of the three dmg^{2-} ligands coordinated to Co(III), was reported by Boston and Rose.[1a] These authors also reported the reaction of K$_3$[Co(dmg)$_3$] with 2 equiv of the Lewis acid boron trifluoride to produce [Co(dmg)$_3$(BF)$_2$]BF$_4$, in which the tricyclic ligand cage is joined together at both ends by the formation of boron-oxygen bonds to form the *clathrochelate* shown below:



Of particular interest to this work was the fact that this low-spin, diamagnetic Co(III) complex could be readily reduced under mild conditions to the low-spin, paramagnetic Co(II)

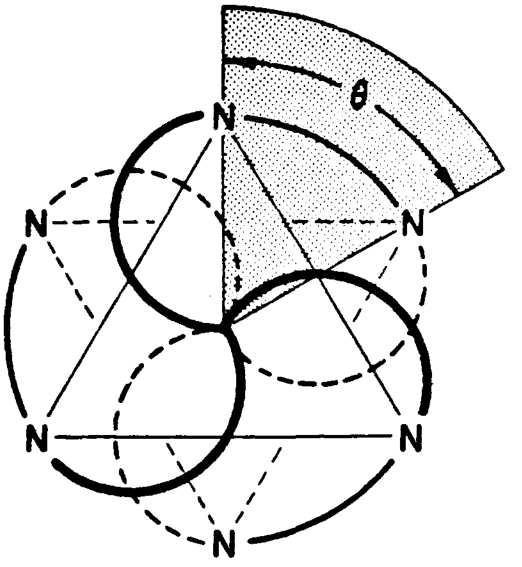


Figure 1. Definition of the twist angle, θ.

clathrochelate. The structures of both of these complexes have been confirmed in an x-ray crystallographic study.[1b] In each case, the coordination sphere of the central ion was found to be distorted from a trigonal prism by a twist θ about the threefold axis of the complex as illustrated in Figure 1. The Co(II) complex was found to be nearly trigonal prismatic while the Co(III) complex was found to be intermediate between trigonal prismatic and trigonal antiprismatic; vide infra.

We noted that the triangular arrays of oxygen atoms on the opposite faces of the $Co(dmg)_3{}^{3-}$ octahedron appeared to have a suitable geometry to serve as tridentate ligands toward transition metal ions. Construction of space-filling models showed that this was indeed sterically possible, making feasible the synthesis of complexes of the type $[Co(dmg)_3(ML_3)_2]^{n+}$ in which M represents a transition metal ion and L_3 is either a tridentate ligand or three unidentate ligands which complete the inner coordination sphere of the capping metal ion. One proposed complex is illustrated in Figure 2 where $Cr(dien)^{3+}$ is the capping ion (dien is diethylenetriamine).

In addition to the preparative challenge and the unique geometry of the proposed complexes, these complexes were of interest because of the possibility of investigating electronic interactions between the capping metal ions mediated by the bridging metal-ligand system $Co(dmg)_3{}^{3-}$. Another interesting manifestation of electronic interactions between the capping ions in the metallomers is the possibility of preparing mixed-valence compounds by selective one- and two-electron reductions or oxidations of the capping ions. Bridged binuclear mixed-valence compounds of iron and ruthenium have been the subject of a number of recent theoretical and experimental studies.[2] The interesting problem with regard to these mixed-valence compounds centers on whether localized or delocalized electronic structures are appropriate for their descriptions.

Experimental Section

Methods. All infrared spectra were obtained as Nujol mulls with a Perkin-Elmer Model 457 infrared spectrometer. Conductivity measurements were made with an Industrial Instruments RC16-B2 conductance bridge. The thermostated cell was calibrated at 25 °C with 0.0100 N KCl solution. Electronic spectra were recorded with a Cary Model 14 spectrophotometer with Infrasil optics.

The magnetic susceptibility of the solid Cr^{3+} capped complex was determined over the temperature range 4.2–290 K with a Princeton Applied Research Model 150A vibrating-sample magnetometer. Room temperature moments on the nickel(II) capped complex were determined using a Faraday balance with a Cahn electrobalance. Diamagnetic corrections were made using Pascal's constants.

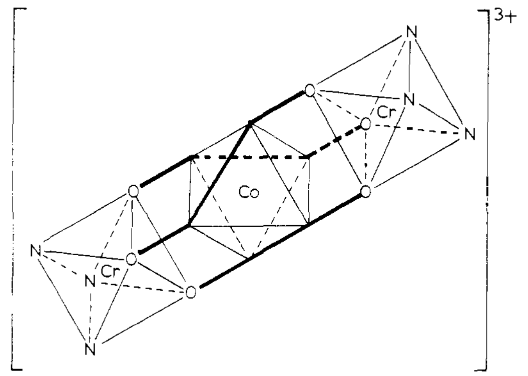


Figure 2. Proposed structure of the $Cr(dien)^{3+}$ capped metallomer.

Polarographic, voltammetric, and cyclic voltammetric measurements were carried out with a Princeton Applied Research Model 174 polarograph. All solutions were degassed with a stream of dry nitrogen and a nitrogen flow was maintained at all times during measurements. Polarograms on $\sim 10^{-4}$ M solutions of the metallomers were obtained in acetone solvent with 10^{-2} M $Et_4N^+ClO_4^-$ as the supporting electrolyte. Voltammograms were obtained on 10^{-3} to 10^{-4} M solutions in acetonitrile with 10^{-2} M $Et_4N^+ClO_4^-$.

^1H NMR spectra were obtained on a Jeolco C 60-H high-resolution spectrometer. ^{59}Co NMR spectra were measured at room temperature on a field-swept Varian WL-115 wide-line spectrometer. The cobalt spectra were run as saturated solutions in acetonitrite and referenced to saturated aqueous $[Co(NH_3)_6]Cl_3$ (external).

Preparation of the Complexes. All chemicals used in this work were reagent grade with the exception of toluenesulfonyl chloride (Eastman), sodium azide (Fisher Scientific Co.), silver trifluoroacetate (Aldrich), trifluoroacetic acid and triethyl orthoformate (Matheson Coleman and Bell), potassium and ammonium hexafluorophosphate (Ozark Mahoning), and diethylenetriamine (Eastman). $K_3[Co(dmg)_3]$, 1,2,3-Cr(dien)Cl_3, 1,1′,1″-tris(azidomethyl)ethane, Co(tame)$(NO_2)_3$, and Co(tame)$(NO_3)_3$ were prepared by adaptations of published procedures.[1,3,4] Solutions of $Li_3[Co(dmg)_3]$ were prepared by metathesis from the potassium salt using lithium nitrate. Cr(dien)$(CF_3CO_2)_3$ was prepared by metathesis from the chloride salt using silver trifluoroacetate and trifluoroacetic acid. Tame·3HCl was prepared from the triazide by reduction with hydrogen sulfide. Explicit preparations of these eight starting materials, along with their chemical analyses, appear in the microfilm edition.

Preparation of 1,8-Bis(1,2,3-diethylenetriaminechromium(III))-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) Hexafluorophosphate Ethanolate, $[Co(dmg)_3\{Cr(dien)\}_2](PF_6)_3 \cdot EtOH$. A solution of $K_3[Co(dmg)_3]$ (3.30 g, 0.00535 mol) in 25 mL of MeOH was added slowly to a solution of Cr(dien)$(CF_3CO_2)_3$ (6.00 g, 0.0121 mol) in 50 mL of methanol and stirred for 6 h at 50 °C. The solvent was then removed in vacuo on a rotary evaporator, and the residue was then dissolved in 30 mL of ethanol to which solid lithium nitrate (1.32 g, 0.0192 mol) was added. After stirring for 15 min, the precipitate of potassium nitrate was removed by filtration. Ammonium hexafluorophosphate (5.00 g, 0.0307 mol) was added to the filtrate and the solution allowed to stand overnight. The orange-red solid which formed was collected by filtration and dissolved in a mixture of acetone (30 mL) and ethanol (100 mL). The red-orange microcrystalline solid obtained when the solvent volume was reduced to approximately 30 mL was washed with ethanol. After this procedure was repeated three times, the product was dried overnight in vacuo over P_2O_5. The product is soluble in acetone, acetonitrile, and MeOH and insoluble in EtOH, yield 1.1 g, 17%.

Anal. Calcd for $[Co(dmg)_3\{Cr(dien)\}_2](PF_6)_3 \cdot EtOH$, $CoCr_2C_{22}H_{50}N_{12}O_7P_3F_{18}$: C, 22.16; H, 4.23; N, 14.09; Co, 4.94; Cr, 8.72. Found: C, 22.20; H, 4.08; N, 13.94; Co, 4.83; Cr, 8.86.

Preparation of 1,8-Bis(1,2,3-diethylenetriaminecobalt(III))-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) Hexafluorophosphate Methanolate, $[Co(dmg)_3\{Co(dien)\}_2](PF_6)_3 \cdot MeOH$. Potassium hexafluorophosphate (1.58 g, 0.0858 mol) and

$Co(dien)(NO_3)_3$ (1.00 g, 0.0287 mol) were stirred together with mild heating in 100 mL of acetonitrile. After removal of potassium nitrate, solid $K_3[Co(dmg)_3]$ (0.75 g, 0.0121 mol) was added to the stirred solution. A deep green solution formed immediately. After stirring for 4 h, the solvent was evaporated off and the solid was extracted with 25 mL of acetone and filtered. Methanol (200 mL) was added to the filtrate and when the volume was reduced to approximately 5 mL, a black, microcrystalline solid formed which was washed with methanol and ether.

The product was recrystallized from boiling methanol, after filtering and evaporating the solvent to a volume of 15 mL. The solid was washed with small portions of methanol and ether and dried in vacuo over phosphorus pentoxide. The solubilities of this product were similar to those of the $Cr(dien)^{3+}$ capped complex. The yield was 0.93 g, 64%.

Anal. Calcd for $[Co(dmg)_3\{Co(dien)\}_2](PF_6)_3 \cdot MeOH$, $Co_3C_{21}H_{48}N_{12}O_7P_3F_{18}$: C, 21.15; H, 4.06; N, 14.10; Co, 14.38. Found: C, 21.29; H, 4.06; N, 14.32; Co, 14.99.

Preparation of 1,8-Bis(1,1′,1″-tris(aminomethyl)ethanecobalt(III))-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) Hexafluorophosphate, $[Co(dmg)_3\{Co(tame)\}_2](PF_6)_3$. A mixture of $Co(tame)(NO_3)_3$ (1.00 g, 0.00276 mol) and excess potassium hexafluorophosphate (2.00 g, 0.0109 mol) was heated to near boiling in 100 mL of acetonitrile for 4 h with stirring. Potassium nitrate was filtered off and $K_3[Co(dmg)_3]$ (0.72 g, 0.00139 mol) was added to the pink solution which turned a dark greenish brown color. After stirring overnight, the solvent was distilled off and the remaining solid dissolved in 15 mL of acetone. After filtration, 60 mL of ethanol was added and the solvent volume reduced to approximately 20 mL. The resulting solid was filtered, then dissolved in 15 mL of methanol and filtered. A brown precipitate formed on addition of ethanol. The product was washed with hot ethanol, recrystallized twice from acetone and ethanol, and dried overnight in vacuo. The solubilities of this product were similar to those of the $Cr(dien)^{3+}$ capped complex. The yield was 0.60 g, 35%.

Anal. Calcd for $[Co(dmg)_3\{Co(tame)\}_2](PF_6)_3$, $Co_3C_{22}H_{48}N_{12}O_6P_3F_{18}$: C, 22.24; H, 4.07; N, 14.14; Co, 14.88. Found: C, 22.47; H, 4.16; N, 14.38; Co, 14.71.

Preparation of 1,8-Bis(1,2,3-triaquonickel(II))-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) Hexafluorophosphate Tetrahydrate, $[Co(dmg)_3\{Ni(H_2O)_3\}_2]PF_6 \cdot 4H_2O$. Nickel nitrate hexahydrate (20.0 g, 0.105 mol) was dehydrated in triethyl orthoformate.[5] On cooling, a solution of $Li_3[Co(dmg)_3]$ in ethanol was added dropwise to the nickel solution and refluxed overnight. The light yellow precipitate was washed with ether, dissolved in 50 mL of methanol, filtered, and precipitated with ether. The solid was washed with ether and dissolved in 50 mL of methanol. Addition of a solution of ammonium hexafluorophosphate (1.6 g, 0.010 mol) yielded a yellow solid. The solid was recrystallized from 100 mL of hot methanol and dried in vacuo overnight.[24] This complex, as well as the $Ni(dien)^{2+}$ capped complex and the Zn(II) capped complexes, was found to be soluble in water and acetonitrile and insoluble in ether. The yield was 4.05 g, 50%.

Anal. Calcd for $[Co(dmg)_3\{Ni(H_2O)_3\}_2]PF_6 \cdot 4H_2O$, $CoNi_2C_{12}H_{38}N_6O_{16}PF_6$: C, 17.08; H, 4.54; N, 9.96; Co, 6.98; Ni, 13.92. Found: C, 16.90; H, 4.38; N, 9.71; Co, 6.98; Ni, 13.87.

Preparation of 1,8-Bis(1,2,3-diethylenetriaminenickel(II))-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) Hexafluorophosphate Tetrahydrate, $[Co(dmg)_3\{Ni(dien)\}_2]PF_6 \cdot 4H_2O$. $[Co(dmg)_3\{NiH_2O)_3\}_2]PF_6 \cdot 4H_2O$ (1.0 g, 0.00106 mol) was dissolved in 20 mL of acetonitrile. A solution of diethylenetriamine (0.26 g, 0.0025 mol) in 20 mL of acetonitrile was added dropwise with stirring. The resulting solution was filtered and 75 mL of ether was added. The precipitate was washed with ether and recrystallized from acetonitrile and ether. The sample was dried in vacuo overnight and was found to be hygroscopic. It was then allowed to equilibrate to a constant weight in a stream of filtered air for 24 h. The yield was 0.95 g, 85%.

Anal. Calcd for $[Co(dmg)_3\{Ni(dien)\}_2]PF_6 \cdot 4H_2O$, $CoNi_2C_{20}H_{52}N_{12}O_{10}PF_6$: C, 25.50; H, 5.56; N, 17.84; Co, 6.26; Ni, 12.46. Found: C, 25.44; H, 5.32; N, 18.14; Co, 6.44; Ni, 12.41.

Preparation of 1,8-Bis(1,2,3-triaquozinc(I)-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) Hexafluorophosphate Trihydrate, $[Co(dmg)_3\{Zn(H_2O)_3\}_2]PF_6 \cdot 3H_2O$. Zinc nitrate hexahydrate (10.0 g, 0.051 mol) was dehydrated in triethyl orthoformate.[5] On cooling, a solution of $Li_3[Co(dmg)_3]$ was added to the zinc solution with rapid stirring. A bright yellow precipitate formed immediately and was washed with ether and dissolved in hot methanol. The resulting solution was filtered and a methanol solution of ammonium hexafluorophosphate (1.0 g, 0.0062 mol) was added. Evaporation of solvent to approximately 50 mL produced a yellow precipitate which was recrystallized once more from hot methanol. The product was allowed to equilibrate in a stream of filtered air for 24 h. The yield was 1.80 g, 53%.

Anal. Calcd for $[Co(dmg)_3\{Zn(H_2O)_3\}_2]PF_6 \cdot 3H_2O$, $CoZn_2C_{12}H_{36}N_6O_{15}PF_6$: C, 17.18; H, 4.32; N, 10.02; Co, 7.02; Zn, 15.58. Found: C, 17.26; H, 4.26; N, 10.15; Co, 6.81; Zn, 15.75.

Preparation of 1,8-Bis(1,2,3-diethylenetriaminezinc(II))-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) Hexafluorophosphate Dihydrate, $[Co(dmg)_3\{Zn(dien)\}_2]PF_6 \cdot 2H_2O$. Diethylenetriamine (0.26 g, 0.0025 mol) in acetonitrile was added to a slurry of $[Co(dmg)_3\{Zn(H_2O)_3\}_2]PF_6 \cdot 3H_2O$ (1.0 g, 0.00119 mol) in acetonitrile forming a yellow-orange solution. The volume was reduced to approximately 30 mL and the solution was filtered. Addition of ether yielded an orange-yellow precipitate which was washed with ether and dried in vacuo overnight. The sample was dried at 100 °C in vacuo for 12 h, and then equilibrated in a stream of filtered air for 12 h. The yield was 0.95 g, 87%.

Anal. Calcd for $[Co(dmg)_3\{Zn(dien)\}_2]PF_6 \cdot 2H_2O$, $CoZn_2C_{20}H_{18}N_{12}O_8PF_6$: C, 26.13; H, 5.26; N, 18.28; Co, 6.41; Zn, 14.22. Found: C, 26.18; H, 5.13; N, 18.28; Co, 6.35; Zn, 14.13.

Results and Discussion

A. Preparation of the Complexes. The synthetic strategy applied to the preparation of trimetallomers involved using $K_3[Co(dmg)_3]$ as the "coordination template" for reaction with suitable capping agents. The use of transition metal ion complexes as capping groups imposes stringent restrictions on the stereochemistry and chemical reactivity of the complexes chosen. The capping group must have three sites available for coordination to $Co(dmg)_3{}^{3-}$ and the ligands occupying those sites must be sufficiently labile so that their replacement by $Co(dmg)_3{}^{3-}$ is both kinetically and thermodynamically feasible. Furthermore, if capping complexes capable of octahedral coordination are used, precautions must be taken to prevent the possible formation of aggregates in which two $Co(dmg)_3{}^{3-}$ moieties are bonded to a single metal ion, M^{n+}, producing, for example, $[Co(dmg)_3MCo(dmg)_3]^{n-}$ and higher polymers of this type. In view of the above restrictions, two synthetic approaches were tried and found to be successful in the preparation of metallomers.

In the first approach, complexes of the type MLX_3 were chosen as capping groups and stoichiometric amounts of the capping complex and $K_3[Co(dmg)_3]$ were allowed to react in solution. The ligand L was chosen to be diethylenetriamine, a tridentate nitrogen donor capable of facial coordination in octahedral complexes. The ligands X were chosen to be ligands of reasonably poor coordinating ability, capable of being replaced by $Co(dmg)_3{}^{3-}$. Metallomers with Cr(III) and Co(III) as capping ions were prepared from $Cr(dien)(CF_3CO_2)_3$, $Co(dien)(NO_3)_3$, and $Co(tame)(NO_3)_3$ by this method.

In the second approach, solutions of $Co(dmg)_3{}^{3-}$ were added dropwise to stirred solutions containing a large excess of the solvated capping ion so that the probability of undesirable side reactions was minimized. Complexes with Ni(II) and Zn(II) capping ions were prepared in this manner. Solutions of the ethanol solvates of the above ions were prepared by refluxing the nitrates in triethyl orthoformate. The nitrate salts of the metallomers were obtained from solution on addition of $Co(dmg)_3{}^{3-}$ and converted to the hexafluorophosphate salts by metathesis in methanol. The salts obtained in this manner were found to have the proper M:Co:N ratios. The assignments of the coordination spheres of Ni(II) and Zn(II) were made

Table I. Conductivities of $[Co(dmg)_3(Cap)_2]^{n+}$

Cap	Λm^a	Cap	Λm^a
$Ni(dien)^{2+}$	90	$Co(dien)^{3+}$	305
$Ni(H_2O)_3{}^{2+}$	82	$Co(tame)^{3+}$	297
$Zn(dien)^{2+}$	94	$Cr(dien)^{3+}$	288
$Zn(H_2O)_3{}^{2+}$	93		

^{a} At 25.0 °C in H_2O. Concentrations 10^{-3}–10^{-4} M.

Table II. μ_{eff} of $[Co(dmg)_3\{Cr(dien)\}_2](PF_6)_3$

μ_{eff}, μ_B	Temp, K	μ_{eff}, μ_B	Temp, K
5.63	283.0	5.61	31.5
5.75	247.7	5.48	26.0
5.68	218.3	5.34	20.5
5.62	188.4	5.23	15.7
5.59	156.7	5.02	11.7
5.55	117.2	4.91	9.3
5.54	73.6	4.74	7.3
5.58	59.5	4.53	5.6
5.53	47.8	4.33	4.7
		4.23	4.2

on the basis of the commonly observed coordination number of these metals with water as a ligand. Both complexes reacted further with 2 equiv of diethylenetriamine to yield $[Co(dmg)_3\{Ni(dien)\}_2]PF_6\cdot4H_2O$ and $[Co(dmg)_3\{Zn(dien)\}_2]PF_6\cdot2H_2O$. With the exception of $[Co(dmg)_3\{Zn(H_2O)_3\}_2]PF_6\cdot3H_2O$, which was found to form an insoluble product on standing in air over a period of several weeks, these compounds were observed to be stable in the atmosphere over a period of months.

Numerous attempts were made to prepare metallomers with $Co(dmg)_3{}^{3-}$ and several other first-row capping agents by the general methods described above. No pure compounds have been isolated using Fe(II) and Fe(III) salts, Co(II) salts in an oxygen-free atmosphere, $Cu(NO_3)_2\cdot3H_2O$, or $Cu(dien)(NO_3)_2$ as sources of the metal in the capping group.

B. Physical Measurements. The evidence assembled from a variety of physical measurements supports the model that the trimetallomers remain intact in solution and that the gross structural characteristics of the boron-capped clathrochelates[1] are also found in the metal-capped complexes. However, there are striking differences in the electrochemical behavior of the metal ion contained within the clathrate. In addition, it is likely that the larger size of the metal ion capping groups afford coordination polyhedra of the central metal ions in which the twist angle θ approaches 60°.

Conductivity. The molar conductances of aqueous solutions of the metallomers were measured in aqueous solution at 25.0 °C. The results of these measurements are presented in Table I. The values of the molar conductances indicate that the Ni(II) and Zn(II) capped species are 1:1 electrolytes. The tabulated values are on the low side of the conductance range normally observed for 1:1 electrolytes. This result, however, is expected owing to the decreased mobility of these large ions. The cobalt(III)- and chromium(III)-capped complexes are 3:1 electrolytes.

Magnetic Susceptibility. Room- and low-temperature magnetic susceptibility measurements for these complexes are indicative of magnetic behavior in which the metal centers of the trimetallomers are not interacting to a large extent. Table II shows the results of a temperature-dependent study of the complex $[Co(dmg)_3\{Cr(dien)\}_2](PF_6)_3$. The effective moment remains above the calculated spin-only moment of 5.48 μ_B for two d^3 ions down to 20 K and drops to 4.23 μ_B at 4.2 K. The decreased moment at low temperatures could arise from small intra- or intermolecular exchange interactions or from the effects of zero field splittings. The calculated moment at 10 °C of 5.64 μ_B corresponds to a value of 3.99 μ_B per Cr(III) ion, a value within the range observed for other Cr(III) complexes. The room temperature magnetic moments for the Ni(II) capped complexes were 4.31 and 4.15 μ_B for the $Ni(H_2O)_3{}^{2+}$ and $Ni(dien)^{2+}$ capped complexes, respectively. These figures correspond to values of 3.05 and 2.93 μ_B per Ni(II) ion, also within the range commonly observed for complexes containing a single Ni(II).

Table III. ^1H NMR Spectra of $[Co(dmg)_3(Cap)_2]^{n+}$ at 60 MHz

Cap	$\Delta\nu$, Hz	Area obsd (theor)	Assignment
$Co(dien)^{3+}$ ^{a}	138.2		
	141.3		$dmg\text{-}CH_3$
	143.0		
	185		$dien\text{-}CH_2$
	303		$dien\text{-}NH_2$
	364		dien-NH
$Co(tame)^{3+}$ ^{a}	52.9	1 (1)	$tame\text{-}CH_3$
	140.9	2.7 (3)	$dmg\text{-}CH_3$
	156.7	2.0 (2)	$tame\text{-}CH_2$
	292.0	1.9 (2)	$tame\text{-}NH_2$
$Zn(dien)^{2+}$ ^{b}	121.5	8.9 (9)	$dmg\text{-}CH_3$
	164.5	8 (8)	$dien\text{-}CH_2$
$Zn(H_2O)_3{}^{2+}$ ^{b}	134.9		$dmg\text{-}CH_3$

^{a} In acetone-d_6 vs. internal Me_4Si. ^{b} In D_2O vs. internal DSS.

NMR. The results of a ^1H NMR investigation of the diamagnetic complexes (reported in Table III) support an assignment of the expected structures for the metallomers. If the asymmetry introduced by the diethylenetriamine ligand is neglected, these molecules have local D_3 symmetry if the θ twist angle, θ around the C_3 axis, vide supra, is in the range $0° < \theta \leqslant 60°$ and they have D_{3h} symmetry if $\theta = 0°$. In any case regardless of the twist angle, all six methyl groups of the three dmg ligands are equivalent and are expected to give rise to one resonance in the NMR.[1] The spectrum of the $Co(dien)^{3+}$ capped metallomer exhibits a multiplet in the region 140 Hz downfield from Me_4Si assigned as the $dmg\text{-}CH_3$ resonance along with broad resonances arising from the CH_2, NH_2, and NH resonances of the diethylenetriamine. The diethylenetriamine moiety reduces the symmetry of this molecule to C_1 and gives rise to the possibility of observing six separate methyl resonances. Other geometrical isomers are possible depending on the relative orientations of the diethylenetriamine ligands at each end of the molecule with respect to each other. These factors could account for the three peaks in the observed spectrum.

The possibility exists that methyl nonequivalence could arise from dmg ligands in which one arm is coordinated to the central cobalt ion via oxygen. The NMR of the complexes $Na_3[Co(dmg)_3]$ and $[Co(en)_3]$ $[Co(dmg)_3]$ which contain dmg ligands coordinated in this fashion have $dmg\text{-}CH_3$ resonances that are shifted well out of the range of the nitrogen coordinated ligands. The assignment of the broad peak under the CH_2 resonances as that of water was confirmed by enrichment.

Further support for our interpretation of the methyl resonance nonequivalence was obtained by preparing a metallomer in which the symmetrical ligand tame is used instead of diethylenetriamine. The observed spectrum of this complex consists of a single $dmg\text{-}CH_3$ resonance along with a single $tame\text{-}CH_3$ resonance and broad CH_2 and NH_2 resonances for the tame. The spectra of the $Zn(dien)^{2+}$ capped metallomer in D_2O consists of only two resonances from the $dmg\text{-}CH_3$ protons and the $dien\text{-}CH_2$ protons. The fact that only a single methyl resonance is observed in this complex is likely due to rapid exchange of the diethylenetriamine or the $Zn(dien)^{2+}$ group or both. Only a single CH_3 resonance is observed in the

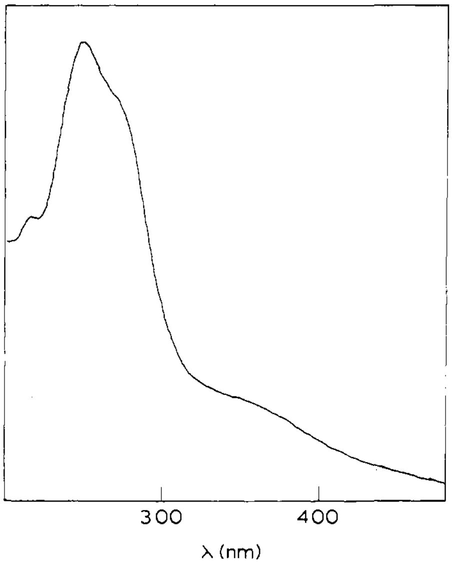


Figure 3. UV spectrum of the Co(dien)$^{2+}$ capped *clathrochelate*.

NMR spectrum of the Zn$(H_2O)_3^{2+}$ capped metallomer, 13.4 Hz downfield from the CH_3 resonance in the Zn(dien) capped complex. The water resonances are omitted from Table III. No spectra were observed for the paramagnetic metallomers in the range from 300 ppm downfield to 25 ppm upfield from DSS.

Electronic Spectra. The ultraviolet and visible spectra of the metallomers are dominated by an extremely strong absorbance in the ultraviolet region. In each case, the band is asymmetric with either a second maximum, a shoulder, or a broadening of a high-energy absorbance in the neighborhood of 270 nm along with a shoulder which tails into the visible region. The spectrum of [Co(dmg)$_3${Co(dien)}$_2$]$^{3+}$ is illustrated in Figure 3 and absorption maxima and extinction coefficients for the complexes are tabulated in Table IV. Bands in this region have been assigned as π-π^* transitions of dimethylglyoxime[7] and also for a series of transition metal ion complexes of dimethylglyoxime.[8,9,10] Maxima attributed to the capping ions were observed in the visible spectra of the Co(III), Cr(III), and Ni(II) capped species. The band at 525 nm in the spectrum of [Co(dmg)$_3${Cr(dien)}$_2$]$^{3+}$ is very close in energy to the visible band at 510 nm in 1,2,3-Cr(dien)$(H_2O)_3^{3+}$ observed by Caldwell and House[3] and is assigned as a d-d transition of Cr(III). This similarity indicates that the CrN_3O_3 donor environment is similar in both molecules. Likewise, the bands at 575 nm in the visible spectrum of the Co(III) capped complexes are assigned as Co(III) d-d transitions by comparison with the visible spectrum of 1,2,3-Co(dien)$(H_2O)_3$.[11] The relatively high apparent extinction coefficients are due to the fact that these peaks appear on the base of the strong ultraviolet absorption. The absorbance at 1160 nm in the Ni$(H_2O)_3^{2+}$ capped complex has an extinction coefficient per Ni(II) of 4.5 cm^{-1} mol^{-1}. The energy and intensity of this band closely resemble those of the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition in Ni$(H_2O)_6^{2+}$ with λ_{max} 1150 nm and ϵ 1.6 cm^{-1} mol^{-1}. In the latter complex, the energy of this transition is equal to 10 *Dq*. These results indicate that the O_3O_3' donor environment in the capped complex is quite similar to that in Ni$(H_2O)_6^{2+}$. The absorbance in the Ni(dien)$^{2+}$ capped complex is more intense and is observed at higher energy (λ 980 nm) than that in the Ni$(H_2O)_3^{2+}$ capped complex. These observations are consistent with the higher average ligand field strength and lower symmetry of the N_3O_3 donor environment relative to the O_3O_3' ligand system. However, no attempt was made to derive crystal field parameters from the spectral data owing to the distorted nature of the environment of the capping ions in these complexes.

Infrared Spectra. Infrared frequencies and intensities for the bands observed in the spectra of the metallomers are reported in the microfilm edition. The C=N stretch is seen to be some 40-60 cm^{-1} lower in energy in these compounds than the C=N stretch in [Co(dmg)$_3$(BF)$_2$]$^+$. These are not pure C=N stretches;[12] the results in Table VII of the microfilm edition show that the frequencies of these bands are dependent on the nature of the capping group, making interpretation of spectral differences impossible.

Electrochemical Studies. In line with the goal of preparing reduced species of the metallomers, a series of electrochemical studies was initiated to determine which species could be produced and what potentials are required for chemical syntheses. Polarographic, voltammetric, cyclic voltammetric, and controlled potential coulometric studies were performed. The results of these studies are summarized in Table V and discussed below.

Polarographic studies of the Cr(dien)$^{3+}$ and the Co(dien)$^{3+}$ capped complexes yielded some puzzling results. The complex [Co(II)(dmg)$_3$(BF)$_2$] was prepared[1] from [Co(III)(dmg)$_3$(BF)$_2$]$^+$ by chemical reduction under very mild conditions. This reduction occurred[13] at a potential of +0.3 to +0.4 V vs. the saturated calomel electrode, and one-electron reduction was confirmed by controlled potential coulometry. Thus, the metallomers were expected to undergo a similar one-electron reduction of the central Co(III) ion in approximately the same potential range along with either a simultaneous two-electron reduction or sequential one-electron reductions of the capping metal ions. Two reduction waves of equal height were observed

Table IV. UV and Visible Spectra

Cap	λ, nm	ϵ	λ, nm	ϵ	λ, nm	ϵ	λ, nm	ϵ
Co(dien)$^{3+}$	575	776	249	54 600	270	(48 000)[c]	365	10 800
Co(tame)$^{3+}$	575	812	249	49 600	272	48 300	365	11 600
Cr(dien)$^{3+}$	525	327	237	65 800 (asym)			335	8 820
Ni(dien)$^{2+}$	980	45	241	70 300 (asym)			575	106
Ni$(H_2O)_3^{2+}$	1160	9	237	40 400	270	(22 100)		
Zn(dien)$^{2+}$			238	44 300	265	29 300	445	2 730
Zn$(H_2O)_3^{2+}$			238	43 700	265	29 900	450	2 470
Compd								
Co(dmgH)$_3$[a]			218	41 100	265	45 900		
dmgH$^-$ [a]			218	16 300	265	18 800		
[1,2,3-Cr(dien)$(H_2O)_3$]$^{3+}$ [b]	510	67						
	375	32						
[1,2,3-Co(dien)$(H_2O_3$]$^{3+}$ [b]	520	99						
	365	52						
[Ni$(H_2O)_6$]$^{2+}$	1150	1.6						

[a] Reference 8. [b] Reference 3. [c] Parentheses denote shoulder.

Table V. Electrochemical Results for $[Co(dmg)_3(Cap)_2]^{n+}$

Cap	$E_{1/2}$, V[a]	$E_{3/4} - E_{1/4}$, mV
$Cr(dien)^{3+}$ [b]	−0.98	63
	−1.58	63
$Co(dien)^{3+}$ [b]	−0.15	55
	−0.46	55
$Ni(dien)^{2+}$ [c]	+0.48 (+0.46)[d]	77 (100)
	+0.87 (+0.85) estd	77
$Ni(H_2O)_3^{2+}$ [c]	+0.73 (+0.70)	97 (125)
	+1.24 (+1.16) estd	120

[a] V vs. SCE. [b] Polarography with DME. [c] Voltammetry with RPE. [d] Values in parentheses are the results of cyclic voltammetric studies. Cathodic waves for the second oxidation in the Ni(II) complexes were poorly defined.

in the polarograms for each complex, and no activity was observed in the region +0.3 to +0.4 V where $[Co(dmg)_3(BF)_2]^+$ is reduced. The observed reduction potentials for the Co(III) capped complex fall in the range observed for a number of Co(III) to Co(II) reductions and those in the Cr(III) capped complex are much more negative and fall in a range expected for Cr(III) to Cr(II) reduction. These results imply that the observed reductions in both metallomers may be due to redox activity of the capping metal ions and not the central Co(III) ion. Results on the Zn(II) and Ni(II) complexes support this possibility, vide infra.

In view of the above results, an attempt was made to determine the number of electrons involved in the above reductions. Since $E_{3/4} - E_{1/4}$ is equal to 56 mV/n for a reversible polarographic wave, where n is the number of equivalents involved in a redox process, the above results indicate that the four reductions observed are either reversible or nearly reversible one-electron waves or irreversible multielectron waves. In order to determine the n values for the reductions observed in these two complexes, a controlled potential coulometric experiment was carried out on the $Co(dien)^{3+}$ capped complex. A 10^{-3} M sample of the $Co(dien)^{3+}$ capped complex in acetonitrile with 10^{-1} M Et_4NClO_4 as supporting electrolyte was reduced at a potential of −0.600 V vs. the SCE at a stirred mercury pool electrode. The operating potential was chosen to be more negative than the potentials of *both* reduction waves observed in the polarographic study of this complex. Graphical integration of the current vs. time plot for this experiment yielded a value of 1.95 equiv of charge transferred in the course of the electrolysis, i.e., 0.98 equiv per reduction. This result, coupled with the observation that the diffusion currents (i_d/c of the Ilkovic equation) for the Co(III) and Cr(III) complexes are equivalent, indicate that the four observed reductions are one-electron reductions.

Since both Ni(II) and Zn(II) are both relatively stable toward reduction, it was expected that any reductions observed in these complexes could be attributed to activity of the Co(III) centers. No reductions or oxidations were observed in the Zn(II) capped complexes over the potential range +2.4-2.1 V. This result is consistent with the observation, vide supra, that the reductions observed in the Co(III) and Cr(III) metallomers might be attributed to activity of the capping ions. Two irreversible oxidations were observed in the Ni(II) capped complexes. Comparison of the limiting currents in these compounds with those obtained for the Co(III) → Co(II) reduction of a sample of $[Co(dmg)_3(BF)_2]BF_4$ identifies these waves as corresponding to one-electron reductions. Figure 4 shows the cyclic voltammogram of the $Ni(dien)^{2+}$ metallomer. The asymmetry of the second wave is indicative of an oxidation followed by a relatively slow chemical reaction.

In conclusion, these electrochemical results indicate no activity of the Co(III) center in the potential region studied but show the expected activity of the capping metal ions.

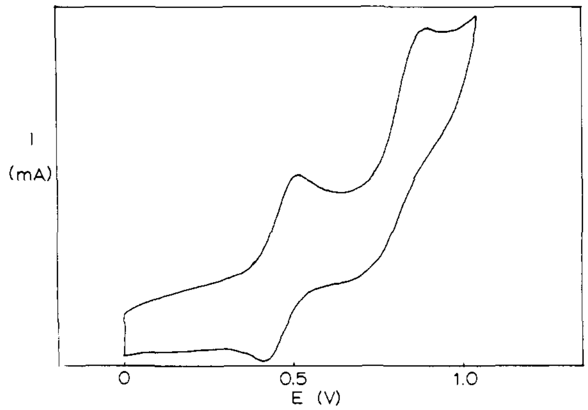


Figure 4. Cyclic voltammogram of the $Ni(dien)^{2+}$ capped *clathrochelate.*

The electrochemical results on these complexes and results[13] on the boron fluoride capped complexes point up anomalous behavior in both types of complexes. The reduction potential of +0.3 to +0.4 V vs. the SCE for the boron fluoride capped complex indicates an unusually high stability for the +2 oxidation state when this value is compared with reduction potentials for other Co(III) complexes with strong field ligands. Values for $Co(NH_3)_6^{3+}$ and $Co(CN)_6^{3-}$ are reported to be −0.24 and −1.08 V (vs. SCE), respectively. In a more closely related series of Co(III) complexes $[Co(dmg)_2XY]^{n+}$, half-wave reduction potentials[14] are in the range of −0.15 V for X = NO_2^-, Y = H_2O to −0.65 V for X = Y = NH_3. For the complex with X = Y = CN^-, only one two-electron reduction with $E_{1/2}$ = −1.10 V was observed. A trend toward more negative values of $E_{1/2}$ with increasing strength of the ligand field is noted. The apparent inert behavior of the central Co(III) ion toward reduction is indicative of an unusually high stability of the Co(III) state relative to the Co(II) state in these complexes.

On the basis of the information available on these metallomers, it is impossible to assess quantitatively the factors influencing the stability of one oxidation state relative to another. The possibility of gross structural differences between the metal ion capped complexes and the boron fluoride capped clathrochelates giving rise to differing amounts of strain in the ligand systems and different amounts of ligand field stabilization energies (LFSE) exists.[15,16] It should be noted that these differences would have to be very large to account for the observed electrochemical behavior; i.e., if reduction were possible in the metal capped *clathrochelates* at potentials more negative than those in the observed range, these potentials would have to be at least 2.5 V more negative than the half-wave potential for the reduction of $[Co(dmg)_3(BF)_2]^+$.

In order to probe further the electronic nature of the cobalt in these complexes, the ^{59}Co NMR spectra were investigated. A theoretical relationship between the chemical shifts and the ligand field strengths has been derived.[17-19] There has been experimental confirmation of the relation for a wide range of nitrogen and oxygen donors. Deviations from this relation have also been reported.[20-22] However, in a series of closely related complexes, the ^{59}Co chemical shift should provide a reliable indication of the similarity or lack thereof of the cobalt center. The line widths of this quadrupolar nucleus are also of interest, for they are related to the electric field gradient and correlation time for rotational motion. The results of our studies are summarized in Table VI. The Δ' values span a range of less than 700 cm^{-1}. The tris-dmg ligand set produces a strong ligand field that is intermediate between that of $Co(NH_3)_6^{3+}$ and $Co(CN)_6^{3-}$ with $\Delta' \sim 25\,000\ cm^{-1}$. This value of Δ should

Table VI. ^{59}Co NMR Results

Complex	δ ppm[a]	ΔH (G)[b]	Δ', cm^{-1} (calcd)
$K_3[Co(dmg)_3]$	2940	12	25 100
$[Co(dmg)_3(BF)_2]BF_4$	3130	19	25 400
$[Co(dmg)_3\{Zn(dien)\}_2]^+$	3300	0.7	25 600
$[Co(dmg)_3\{Co(dien)\}_2]^{3+}$	3480	4	25 800
	−1810	5	18 600
$K_3[Co(CN)_6]$	8100	0.05	32 100
$[Co(NH_3)_6]Cl_3$	0	0.22	21 100

[a] Shifts ±50 ppm vs. aqueous $[Co(NH_3)_6]Cl_3$. [b] Width, peak to peak, of the derivative of the absorption line.

give rise to an absorption band in the neighborhood of 400 nm which could easily be hidden under the intense charge transfer bands in the ultraviolet region of these complexes.

The line widths observed in these complexes indicate[23] a θ value much closer to 60° in the metal capped *clathrochelates* (particularly the Zn(II) capped complex), compared to $K_3[Co(dmg)_3]$ and the boron fluoride capped complex. This observation correlates well with the prediction of a θ value near 60° for these complexes. In this respect, the narrow line width for the Zn(II) capped complex could be due to the larger ionic radius of the Zn(II) cap and its flexibility due to the lack of ligand field stabilization energy in the d^{10} ion.

These ^{59}Co results make our observations of the electrochemistry of these systems all the more surprising.

C. Stereochemical Considerations. A qualitative evaluation of strain and LFSE is useful in that it leads to a prediction of the most likely structure for the metal ion capped complexes. The most stable geometry for a six-coordinate complex would result from "(a) maximizing bonding interactions between the atoms of the ligand itself; (b) minimizing all nonbonded contacts; and (c) maximizing the metal-ligand bonding interaction".[15] Using a crystal field model to calculate the effect of a smooth distortion toward trigonal prismatic symmetry on the energies of the t_{2g} and e_g orbital sets in octahedral symmetry, the octahedral structures are predicted to be more stable by 40/3 *Dq* than a trigonal prismatic one.[15] All other factors being equal, a near-octahedral structure is expected for the Co(III) and Co(II) *clathrochelates* on the basis of crystal field effects. Structures of the boron fluoride capped *clathrochelates* have been reported by Lingafelter et al.[1b] They calculated that the metal to ligand bond distances in the "natural" (trigonal prismatic) conformation of the "empty" ligand cage would be 1.99–2.00 Å based on the bond angles and distances in the Co(II) and Co(III) complexes. Boston and Rose[16] have pointed out that the size of the cage in these complexes will be a smooth function of the twist angle θ with a maximum value at $\theta = 0$. The geometry of the complexes which have been studied reflects the tendency of the cage to distort toward octahedral symmetry in order to maximize bonded interactions and CFSE, but limited by the amount of strain this distortion imposes on the rigid ligand structure.

Although no structural data are available, application of the above considerations to the metallomers leads to some interesting predictions. The maximum size of the ligand cage in the metallomers is estimated as follows. If a rigid structure is assumed for the three dmg ligands, the maximum size of the trigonal prismatic cage will be determined by the size of the triangular face of the capping group which joins the three arms of the cage. The size of this triangular face in the metallomers is easily estimated using a metal-oxygen bond distance of 2.00 Å and an octahedral O-M-O bond angle of 90°. The O-O distance (the length of one side of the triangular octahedral face) calculated in this manner is 2.83 Å, much larger than the size of the triangular tetrahedral face of 2.46 Å in the boron fluoride capped complexes calculated in a similar manner from Lingafelter's data. An estimate of the Co-N distance expected for the metal capped cage in the trigonal prismatic configuration is then easily made using Lingafelter's structural data for the dmg ligands along with the O-O distance calculated above. The value of the Co-N bond distance of 2.13 Å calculated in this manner, Figure 5, is much larger than the observed bond length of 1.89 Å in $[Co(dmg)_3(BF)_2]^+$ and larger than the value of 1.99–2.00 Å calculated for the "empty" cage.[1b] A greater deviation from trigonal prismatic symmetry toward a geometry in which θ approaches 60° is expected in the metal ion capped complexes, in order to maximize metal-ligand bonding interactions, than is observed in the boron fluoride capped complexes.

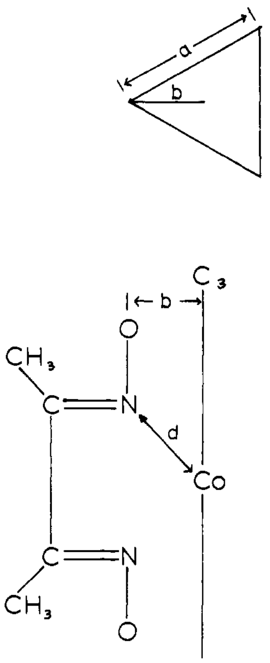


Figure 5. Geometry used for the calculation of the cage size in the metal ion capped *clathrochelates*.

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Supplementary Material Available: Table of IR spectra of $[Co(dmg)_3(Cap)_2]^{n+}$ and preparations of the eight starting materials and their chemical analyses (3 pages). Ordering information is given on any current masthead page.

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(24) Microanalysis showed high carbon to metal ratios and it was found that the sample lost weight on standing indicating a loss of solvent of crystallization and/or replacement of solvent by atmospheric water. To provide a sample of suitable stability for the measurement of its magnetic susceptibility by the Faraday method, the solid was allowed to equilibrate to constant weight in a stream of filtered air for 24 h; analyses of this sample are best fit by the formula $[Co(dmg)_3\{Ni(H_2O)_2\}_2]PF_6\cdot 4H_2O$. A similar procedure was used in the preparations to follow.

Quenching and Quenching Reversal of Tris(2,2′-bipyridine)ruthenium(II) Emission in Polyelectrolyte Solutions[1]

Dan Meisel* and Max S. Matheson

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439.

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Abstract: The emission from the lowest charge transfer excited state of $Ru(bpy)_3^{2+}$ is very efficiently quenched by low concentrations of Cu^{2+} ions when polyvinylsulfate (PVS) is present in the solution. Stern–Volmer constants 2×10^3 higher than in the absence of PVS can be easily obtained. This efficient quenching completely vanishes and the emission is nearly totally restored when higher concentrations of the same quencher, or of inert cations, are added. The efficient quenching results from Cu^{2+} and $Ru(bpy)_3^{2+}$ residing in the potential field of the same polymer. However, as soon as the quencher (or the inert cation) displaces $Ru(bpy)_3^{2+}$ from the polyelectrolyte, quenching reversal is observed. Quantitative results regarding the number of available sites and the relative binding constants of Cu^{2+} and $Ru(bpy)_3^{2+}$ can be deduced from the minima and the quenching reversal portions of the quenching curves. Possible utilization of this or similar systems in solar energy conversion and storage is indicated.

The physical properties of polyelectrolytes have long attracted the attention of various interdisciplinary interests. The resemblance of polyelectrolyte solutions to many biological fluids as well as their obvious practical and theoretical importance has yielded a large volume of studies. Although in many of these studies the emphasis is on the thermodynamics of such systems,[2,3] their inevitable influence on reaction kinetics has been recognized.[4] The work of Morawetz and co-workers and of Ise and co-workers has shown, for example, that the rate of the Hg^{2+} sensitized aquation of Co(III) pentaamine halide complexes, as well as the rate of reduction of these complexes by various cations, is accelerated by several orders of magnitude when small amounts of polyelectrolytes are added to these solutions.[5,6]

The photoredox properties of tris(2,2′-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$) have drawn much attention recently.[7-10] The ability of the lowest charge transfer excited state (CT)-$Ru(bpy)_3^{2+*}$ to participate as an electron donor in redox reactions as well as the ability of the oxidized $Ru(bpy)_3^{3+}$ to oxidize water or hydroxide ions[11] has been utilized in several proposed solar energy conversion systems.[12,13] In a recent communication from this laboratory it was shown that the $Ru(bpy)_3^{2+}$ complex can be solubilized in negative micellar solutions, thereby greatly affecting the specific reaction rates of this complex, both in the ground and excited states, with charged entities such as e_{aq}^-, Zn^+, Co^+, Cd^+, Cu^{2+}, or $Fe(CN)_6^{3-}$.[14] These results and the current interest in both $Ru(bpy)_3^{2+}$ and polyelectrolytes led us to study the effect of polyelectrolytes on the rate of quenching of emission from $(CT)Ru(bpy)_3^{2+*}$. Effects essentially similar to those described here were observed for the quenching of uranyl fluorescence by Fe^{2+} ions in polyelectrolyte solutions.[15]

Experimental Section

All nonpolymeric chemicals used in this study were of reagent grade and, except where otherwise indicated, were once recrystallized. The potassium salt of polyvinylsulfate (PVS) was purified as described by Breslow and Kutner.[16] The specific viscosity of a 1% solution of the polymer was determined with a Cannon viscometer and from the correlation between this and the intrinsic viscosity in 0.1 M Na_2SO_4, the average molecular weight[16] was determined to be ~250 000. Solutions for irradiation were prepared from the stock 1% polymer solution in water and were irradiated a few hours after preparation. Emission spectra were recorded on a Hitachi fluorescence spectrometer (Model MPF-2A). Excitation was carried out at 450 nm and emission was usually recorded at 605 nm (emission slit ±5 nm). $Ru(bpy)_3Cl_2$ was twice recrystallized and its concentration in solution was determined spectrophotometrically assuming an ϵ_{453} of 14 000. Triply distilled water was used in this study. For measurement of the oxygen effect on the emission intensity, solutions were saturated with the desired gas (prepurified argon, dry air, or prepurified oxygen) by bubbling for 15 min in the rubber capped irradiation cells. For all other experiments air saturated solutions were used. Several comparison experiments were run with excitation at 480 nm where the extinction is 50% that at 450 nm. Since in these experiments the only noticeable effect was to cut the intensity of emission by about 50%, we conclude that no complications due to the amount of absorbed light affect our results.

Results and Discussion

The Effect of PVS on Absorption and Emission Spectra. Up to 0.9% PVS was found to be without any noticeable effect on the absorption spectrum of 2×10^{-5} M $Ru(bpy)_3^{2+}$ in the visible region where $Ru(bpy)_3^{2+}$ has its CTTL band (λ_{max} 453 nm). In the UV region the spectrum matched exactly the sum of the $Ru(bpy)_3^{2+}$ absorption and the residual absorption of the polymer (or impurities therein). Similarly, the effect of