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Reactions of Bis(dimethylglyoximato)cobalt(II) with $NCCH_2I$ and $(NH_3)_5CoNCCH_2I^{3+}$

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The kinetics and products of the reactions of bis(dimethylglyoximato)cobalt(II) ($Co(DMGH)_2$) with $NCCH_2I$ and $(NH_3)_5CoNCCH_2I^{3+}$ have been studied in aqueous solution at pH 6. With $NCCH_2I$, the products are $(DMGH)_2Co(OH_2)(CH_2CN)$ (25–26%), $(DMGH)_2Co(OH_2)(NCCH_3)^+$ (5.5–6.2%), and $(DMGH)_2Co(OH_2)_2^+$ (66–72%). It is shown that the expected $(DMGH)_2Co(OH_2)(I)$ decomposes to $(DMGH)_2Co(OH_2)_2^+$ under the reaction conditions. With $(NH_3)_5CoNCCH_2I^{3+}$, the products are $(NH_3)_5CoNCCH_2Co(DMGH)_2(OH_2)^{3+}$ (~50%), $((NH_3)_5CoNCCH_2)_2^{6+}$ (~10%), and cobalt(II). The first product listed has been separately prepared and characterized, and it is shown to decompose to $(DMGH)_2Co(OH_2)(CH_2CN)$ in the presence of $Co(DMGH)_2$ in a process competitive with its formation. The kinetics yield k (M^{-1} s^{-1}, 25 °C), ΔH^* (kcal mol^{-1}), and ΔS^* (cal mol^{-1} deg^{-1}) values of 0.38, 15.8, and −7.6, respectively, with $NCCH_2I$, and 2.0, 20.4, and 11.4, respectively, with $(NH_3)_5CoNCCH_2I^{3+}$. The results are compared to previous work using Cr(II) as the reducing agent.

Previous studies[1,2] on the reaction of bis(dimethylglyoximato)cobalt(II) ($Co(DMGH)_2$) with organic halides in benzene have been interpreted in terms of an atom-transfer mechanism as shown by eq 1, where RX is an organic halide.

$$2Co(DMGH)_2 + RX \rightarrow (DMGH)_2Co(X)(OH_2) + (DMGH)_2Co(R)(OH_2) \quad (1)$$

Similar conclusions have been drawn for the reaction of vitamin B_{12r} with organic chlorides and bromides in methanol and water.[3] The proposed mechanism involves rate-controlling halogen atom abstraction by the cobalt(II) complex followed by rapid combination of the organic radical and a second cobalt(II) complex. This mechanism is formally analogous to that proposed for the reaction of organic halides with chromium(II)[4,5] in aqueous solution. More recent work[6-9] is consistent with this general mechanism but indicates that the chromium products can be more complex if the organic halide has a substituent (Y) that can coordinate to the metal. The general scheme for chromium(II) is shown in eq 2.

$$Cr^{2+} + XCH_2Y \rightarrow (H_2O)_5CrX^{2+} + \{YCH_2^{\bullet}\}$$

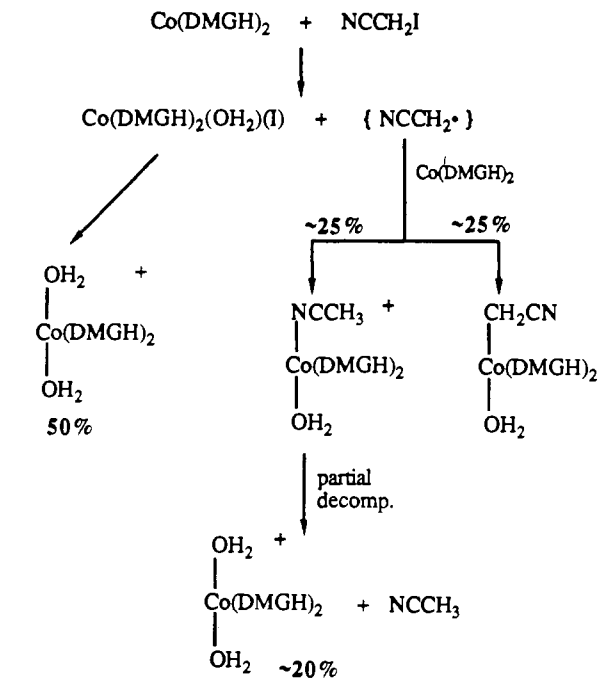
$$Cr^{2+} + \{YCH_2^{\bullet}\} \xrightarrow{H^+} \begin{cases} (H_2O)_5CrYCH_3 \\ (H_2O)_5CrCH_2Y \end{cases} \quad (2)$$

The present work examines the parallel between these reactions with $Co(DMGH)_2$ and chromium(II) for the same substrates in a common solvent, water. The substrates are iodoacetonitrile and $(NH_3)_5CoNCCH_2I^{3+}$. In the latter case, there is the added possibility that the cobalt(II) complex may reduce the cobalt(III) center[10] in competition with the halide abstraction although this does not happen with chromium(II).[5] Therefore, these substrates provide a number of detailed points for comparison in addition to the simple kinetic observations.

Results

Reaction of $Co(DMGH)_2$ and $NCCH_2I$. In a typical experiment, the products of this reaction were determined by the reaction of 2.3×10^{-3} M $Co(ClO_4)_2$, 5.0×10^{-3} M dimethylglyoxime ($DMGH_2$), and 2.3×10^{-2} M iodoacetonitrile at pH 6 (0.01 M MES buffer) under an argon atmosphere at ambient temperature (~23 °C). After 30 min, the reaction mixture was acidified with $HClO_4$ to pH 1 and exposed to air. Dimethylglyoxime was removed by filtration, and the products were separated by ion exchange on Dowex 50 W-X2(H^+) resin.

Scheme I



Three products can be separated: a yellow species passes directly through the cationic resin; a brown species is separated and eluted with 0.1 M $HClO_4$; a brown species is eluted with 0.5 M $NaClO_4$ in 0.1 M $HClO_4$. From the known electronic spectra,[11] the yellow species and the second brown species can be identified as $(DMGH)_2Co(OH_2)(CH_2CN)$ and $(DMGH)_2Co(OH_2)_2^+$, respectively. The first brown species to elute is assigned as $(DMGH)_2Co(OH_2)(NCCH_3)^+$, whose properties are described below.

Cobalt analysis[12] was used to determine the yields of these products as follows: $(DMGH)_2Co(OH_2)(CH_2CN)$, 25–26%; $(DMGH)_2Co(OH_2)(NCCH_3)^+$, 5.5–6.2%; $(DMGH)_2Co(OH_2)_2^+$, 66–72%. The range of product yields represent the results of

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Table I. Electronic Spectral Data[a] for Bis(dimethylglyoximato)cobalt(III) Complexes

$(DMGH)_2Co^{III}(X)(Y)$		λ, nm (ε, M^{-1} cm^{-1})		
X	Y			
OH_2	CH_2CN^-	235.5 (22.6 × 10^3)	370 (1.04 × 10^3)	447.5 (469)
OH_2	OH_2	238(19.5 × 10^3)		
OH_2	I^-	238 (23.0 × 10^3)	270 (sh), 310 (sh)	430 (1.34 × 10^3)
OH_2	$NCCH_3$	238 (19.4 × 10^3)	300 (sh, ~12 × 10^3)	
OH_2	$CH_2CNCo(NH_3)_5^{2+}$	238 (29.4 × 10^3)		452 (400)

[a] Spectra were recorded in 0.10 M perchloric acid.

several experiments under conditions quite similar to the typical ones quoted above. If the concentration of $NCCH_2I$ is increased to ~0.1 M and the reaction time is reduced to ~5 min, then the yield of $(DMGH)_2Co(OH_2)(NCCH_3)^+$ increases to ~10%. This is attributed to the instability of $(DMGH)_2Co(OH_2)(NCCH_3)^+$ noted below. No $(DMGH)_2Co(OH_2)(I)$ was found, but it is shown below that this complex is unstable under the reaction conditions. Free I^- was found in the initial eluate from the cation-exchange column, and analysis[13] revealed this to be 90–97% of the expected amount.

The qualitatively unusual aspect of the product distribution is that the yield of $(DMGH)_2Co(OH_2)_2^+$ is much greater than the 50% predicted from eq 1 if all of the $(DMGH)_2Co(OH_2)(I)$ decomposes to $(DMGH)_2Co(OH_2)_2^+$. The additional 16–22% can be explained if the $(DMGH)_2Co(OH_2)(NCCH_3)^+$ also decomposes partially to $(DMGH)_2Co(OH_2)_2^+$. Then the overall reaction sequence and product distribution can be described by Scheme I. It appears that $Co(DMGH)_2$ reacts with about equal probability at either end of the organic radical to produce initially about equal amounts of $(DMGH)_2Co(OH_2)(NCCH_3)^+$ and $(DMGH)_2Co(OH_2)(CH_2CN)$. Therefore, $Co(DMGH)_2$ is similar to Cr(II), which yields 55% of the corresponding organochromium(III) product.

Kinetics of the Reaction of $Co(DMGH)_2$ and $NCCH_2I$. The reaction was monitored at 470 nm, where the absorbance decreases due to the loss of $Co(DMGH)_2$. The reaction was studied in 0.10 M $NaClO_4$ at pH 6 (0.01 M MES buffer) under an argon atmosphere at 13.6, 25.0, and 34.6 °C. The Co(II) concentration was ~5 × 10^{-5} M, $DMGH_2$ was 1.0 × 10^{-3} M, and $NCCH_2I$ was varied between 4.2 × 10^{-3} and 21.1 × 10^{-3} M. The results are given in the supplementary material (Table S1).

The absorbance–time curves are well fitted by a simple exponential time dependence, indicating that the reaction is first order in $Co(DMGH)_2$. The variation of the pseudo-first-order rate constant with $[NCCH_2I]$ shows that the reaction is first order in this reagent. At 25 °C, the apparent rate constant is 0.38 M^{-1} s^{-1}. Since the disappearance of $Co(DMGH)_2$ was monitored and 2 mol of it is required, then the specific rate constant is 0.19 M^{-1} s^{-1} and the activation parameters are $\Delta H^* = 15.8 \pm 0.3$ kcal mol^{-1} and $\Delta S^* = 8.95 \pm 1.5$ cal mol^{-1} deg^{-1}.[14]

Stability of $Co(DMGH)_2(OH_2)(I)$. As noted above, the final reaction products contain free iodide ion rather than $Co(DMGH)_2(OH_2)(I)$. The later would be expected according to eq 1. This observation might lead one to conclude that the reaction is not proceeding by halogen atom transfer but possibly by electron transfer followed by halide ion elimination, especially when it is known that $Co(DMGH)_2(OH_2)(I)$ is relatively stable[15] by itself at pH 6. However, experiments have shown that $Co(DMGH)_2(OH_2)(I)$ decomposes rather rapidly in the presence of $Co(DMGH)_2$ under our reaction conditions. For example, a solution initially containing 2.5 × 10^{-5} M $Co(DMGH)_2(OH_2)(I)$ and 5 × 10^{-5} M $Co(DMGH)_2$ at pH 6 under argon was allowed to react for 4 min at 22 °C before exposure to air. Ion-exchange separation reveals only one cobalt product, $Co(DMGH)_2(OH_2)_2^+$, and all of the iodide ion was found in the initial colorless eluate. The reaction is attributed to electron-transfer-catalyzed decomposition as shown in eq 3.

$$Co^{II}(DMGH)_2 + Co^{III}(DMGH)_2(OH_2)(I) \rightarrow Co^{II}(DMGH)_2(OH_2)(I)^- + Co^{III}(DMGH)_2(OH_2)_2^+ \rightarrow Co^{II}(DMGH)_2 + I^- \quad (3)$$

Stability of $Co(DMGH)_2(OH_2)(NCCH_3)^+$. This species was assigned as a minor product (5–6%) on the basis of its ion-exchange properties and the fact that the electronic spectrum differentiates it from other known species in the system. It can be separated from $Co(DMGH)_2(OH_2)_2^+$ on Dowex 50W-X2 by elution with 0.10 M $HClO_4$. As noted above, the amount of this product was somewhat greater if the reaction time was decreased from 20 to ~5 min by using a large excess of $NCCH_2I$. The implied instability of this product was confirmed by observing that it is about 50% decomposed to $Co(DMGH)_2(OH_2)_2^+$ in 60 min at pH 6. It has proven difficult to establish the hydrolysis rate because of the small amounts of material and the fact that the acidic eluates always contain traces of cobalt(II) and dimethylglyoxime. When these eluates are brought to pH 6, the hydrolysis rates proved to be nonreproducible, presumably because of at least some electron-transfer-catalyzed aquation analogous to that observed with $Co(DMGH)_2(OH_2)(I)$. It was observed also that the decomposition rate of this species increases with increasing pH (5.5–6.5). However, it is not clear if this is due to increased formation of the catalyst $Co(DMGH)_2$, to reactivity of the conjugate base of $Co(DMGH)_2(OH_2)(NCCH_3)^+$, or to conversion of the nitrile to the carboxamide.[16]

Reaction of $Co(DMGH)_2$ and $(NH_3)_5CoNCH_2I^{3+}$. The reaction products were determined for solutions initially containing 4.4 × 10^{-3} M $Co(ClO_4)_2$, 2.4 × 10^{-2} M dimethylglyoxime, and 1.1 × 10^{-3} M $(NH_3)_5CoNCCH_2I^{3+}$ at 40 °C and pH 6 (0.01 M MES buffer) under an argon atmosphere. The higher temperature was necessary because of the limited solubility of the Co(III) complex and the dimethylglyoxime. After various reaction times, the reaction was quenched by acidification and exposure to air as before. The products were separated by cation-exchange chromatography on Sephadex SP-C25 resin.

Five reaction products were separated. A yellow species is not retained by the Sephadex, by Dowex 50W-X2(H^+), or Dowex 2-X8(Cl^-) resins, and the electronic spectrum shows that it is $(DMGH)_2Co(OH_2)(CH_2CN)$. A brown species can be eluted from Sephadex with 0.2 M $HClO_4$, and the electronic spectrum identifies it as $(DMGH)_2Co(OH_2)_2^+$. A pink band elutes with 0.3 M $HClO_4$, and tests with ammonium thiocyanate in acetone[12] gave a blue color, expected if the pink product is $Co(OH_2)_6^{2+}$. A yellow-orange band moves on Sephadex with 0.5 M $HClO_4$ and can be efficiently removed with 1 M $HClO_4$. This species has been prepared and characterized separately, as described below, and proves to be $(NH_3)_5CoNCCH_2$–$Co(DMGH)_2(OH_2)^{3+}$. Finally, there is a yellow band that could not be removed from the Sephadex even with 3 M $HClO_4$ or 4 M $NaClO_4$. This product is believed to be $((NH_3)_5CoNCCH_2)_2^{6+}$ on the basis of its color and high charge, but it has not been possible to characterize it further except to show that it does contain cobalt.

The most unusual feature of these observations is the formation of $(DMGH)_2Co(OH_2)(CH_2CN)$ in which the $(NH_3)_5Co^{III}$ unit

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(14) Errors are 95% confidence limits, which are about 3 times larger than one standard deviation.
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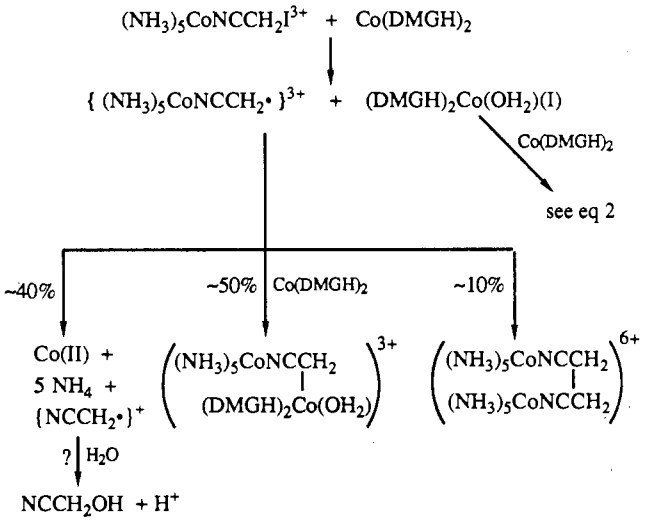
Table II. Variation of the Product Distribution with Reaction Time for the Reaction of $Co(DMGH)_2$ with $(NH_3)_5CoNCCH_2I^{3+}$ [a]

reacn time, min	% $(DMGH)_2$-$Co(OH_2)(CH_2CN)$	% 3+ dimer[b]
2	12	42
18	18	30
30	30	17
40	45	5

[a] The reaction is carried out under an argon atmosphere at pH 6 (0.01 M MES buffer) at 40 °C with initial concentrations of 4.4×10^{-3} M $Co(ClO_4)_2$, 2.4×10^{-2} M $DMGH_2$, and 1.1×10^{-3} M cobalt(III). The product percentages are relative to the deficient reagent, cobalt(III). [b] The dimer species is $(NH_3)_5CoNCCH_2Co(DMGH)_2(OH_2)^{3+}$.

Scheme II



has been lost. This could be due to direct reduction of $(NH_3)_5CoNCCH_2I^{3+}$ by $Co(DMGH)_2$, but further experiments show that the product distribution depends on the reaction time, as shown in Table II. These results indicate that the 3+ dimer is decomposing to $(DMGH)_2Co(OH_2)(CH_2CN)$ during the reaction and that the dimer product is ~50% of the initial Co(III). Experiments described below confirm that the 3+ dimer does decompose in the presence of $Co(DMGH)_2$ and I^-, although it is stable by itself at pH 6.

Total cobalt analysis indicates that the 6+ dimer accounts for about 10% of the original Co(III). This, combined with ~50% of the 3+ dimer, leaves about 40% of the cobalt(III) unaccounted for. This must be present in the Co(II) fraction, although it is not possible to differentiate this from the excess Co(II) present initially. On this basis, the overall reaction can be described by Scheme II.

Properties of $(NH_3)_5CoNCCH_2Co(DMGH)_2(OH_2)^{3+}$. The preparation of the perchlorate salt of this complex is described in the Experimental Section. The electronic spectral properties are given in Table I and have the expected features of the $Co(DMGH)_2$ chromophore at 238 nm and the $(NH_3)_5CoNC$– chromophore at 450 nm. The proton NMR spectrum shows the expected features at 3.36, 3.32, 2.33, and 0.97 ppm, assigned to the cis NH_3 (12), trans NH_3 (3), oxime CH_3 (12) and CH_2 (2) resonances, respectively. The infrared spectrum has a characteristic band due to the C≡N stretch at 2281 cm^{-1}.

The complex appears to undergo a reversible acid–base change, which is manifested by a shift of the peak in the electronic spectrum from 238 to 248 nm. The reversibility indicates that this is not due to carboxamide formation[16] and is therefore assigned to removal of either a DMGH or an OH_2 proton.[11] The distinction between these possibilities[11] on the basis of visible spectral changes cannot be made because of the $(NH_3)_5Co^{III}$ chromophore.

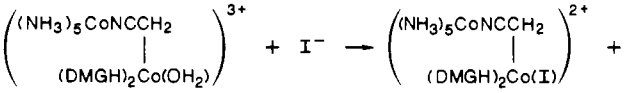
In 0.1 M perchloric acid at 25 °C, the complex is ~50% decomposed in 1 week to a mixture of $(DMGH)_2Co(OH_2)$-(CH_2CN), $(DMGH)_2Co(OH_2)_2^+$, and $(NH_3)_5Co(OH_2)^{3+}$. Solutions of the complex in dilute acid have been stored for several days at 5 °C without significant decomposition.

Table III. Kinetic Results for the Reaction of $Co(DMGH)_2$ and $(NH_3)_5CoNCCH_2I^{3+}$ [a]

temp, °C	10^3[Co(III)], M	$10^3 k_{obsd}$, s^{-1}	k_{obsd}/[Co(III)], M^{-1} s^{-1}
25.0	0.840	2.10	2.56
25.0	0.880	2.56	2.91
25.0	1.04	2.50	2.40
25.0	1.06	2.48	2.34
25.0	1.255	2.91	2.32
25.0	1.46	3.03	2.07
25.0	1.67	3.37	2.02
25.0	1.77	3.66	2.07
25.0	2.13	4.24	1.99
17.1	0.910	0.910	1.00
17.1	1.04	0.950	0.913
17.1	1.385	1.11	0.801
17.1	1.52	1.35	0.888
17.1	1.78	1.47	0.826
17.1	1.96	1.57	0.801
17.1	2.08	1.53	0.736
9.6	0.970	0.431	0.444
9.6	1.13	0.457	0.404
9.6	1.52	0.613	0.403
9.6	1.63	0.571	0.350
9.6	1.97	0.589	0.299
9.6	2.175	0.715	0.329
9.6	2.53	0.770	0.304
9.6	2.925	0.935	0.320
9.6	3.17	0.914	0.288
9.6	3.55	1.02	0.287
9.6	4.35	1.16	0.267

[a] In 0.10 M $NaClO_4$ at pH 6 (0.01 M MES buffer) under an argon atmosphere with [Co(II)] = $\sim 5 \times 10^{-5}$ M and [DMGH] = 1.25×10^{-3} M.

The results in Table II imply that the dimer does decompose under the conditions of the reaction with $Co(DMGH)_2$. When the dimer is reacted with $Co(DMGH)_2$ at pH 6 and 40 °C for 40 min, some reaction occurs. But only 20% of the maximum amount of $(DMGH)_2Co(OH_2)(CH_2CN)$ is produced, while the data in Table II would predict >90% decomposition. However, if iodide ion is added at the same concentration as the Co(III), then there is 100% formation of $(DMGH)_2Co(OH_2)(CH_2CN)$ in the same time period. If the reaction time is shortened to ~5 min with I^- present, then 20% of the $(DMGH)_2Co(OH_2)$-(CH_2CN) has formed. It is clear from these observations that the 3+ dimer does decompose under the conditions of the product analysis study summarized in Scheme II and Table II. It appears that $Co(DMGH)_2$ can react with the 3+ dimer to reduce the $(NH_3)_5Co^{III}$ center and that iodide ion somehow catalyses the process. Iodide could complex either with the 3+ dimer (eq 4) or with $Co(DMGH)_2$ (eq 5) to produce a species that would be susceptible to bridged electron transfer in the former case and/or a better reducing agent in the latter case. The product in eq 4



H_2O (4)

$$(DMGH)_2Co^{II}(OH_2)_2 + I^- \rightarrow (DMGH)_2Co^{II}(OH_2)(I)^- + H_2O \quad (5)$$

could use the I^- ligand to form an inner-sphere precursor complex with $Co(DMGH)_2$. The product in eq 5 could just be a stronger and therefore more reactive outer-sphere reducing agent.

Kinetics of the Reaction of $Co(DMGH)_2$ and $(NH_3)_5CoNCCH_2I^{3+}$. The reaction was monitored at 470 nm under pseudo-first-order conditions with cobalt(III) in excess. The Co(II) concentration was $\sim 5 \times 10^{-5}$ M, and the $DMGH_2$ was 1.25×10^{-3} M. The reaction was studied in 0.10 M $NaClO_4$ at pH 6 (1×10^{-2} M MES buffer) under an argon atmosphere.

These results are summarized in Table III.

The absorbance–time curves are satisfactorily fitted by a single-exponential time dependence, indicating that the reaction is first order in $Co(DMGH)_2$. The results in Table III can be represented by the rate law given by eq 6. It is difficult to account

$$\text{rate} = (k_0 + k_1[Co(III)])[Co(II)] = k_{obsd}[Co(II)] \quad (6)$$

for a term in the rate law that is independent of the oxidant, since there are no obvious reasons that the rather labile reducing agent should have to undergo any rate-controlling changes before being oxidized. Previous work[10] with $Co(DMGH)_2$ and various cobalt(III) oxidants has shown a simple first-order dependence on the oxidant, as have the results in this study on ICH_2CN. A probable source of the k_0 term is discussed in the next paragraph, but the following results are reported for completeness. The activation parameters have been determined by simultaneously fitting the temperature and Co(III) dependence to obtain $\Delta H_0^* = 15.1 \pm 4.3$ kcal mol^{-1}, $\Delta S_0^* = -21.9 \pm 19$ cal mol^{-1} deg^{-1} and $\Delta H_1 = 20.3 \pm 1.3$ kcal mol^{-1}, $\Delta S_1^* = 10.4 \pm 7.5$ cal mol^{-1} deg^{-1}.[14] At 25 °C, the values of the rate constants calculated from the activation parameters are $k_0 = 8.8 \times 10^{-4}$ s^{-1}, $k_1 = 1.5$ M^{-1} s^{-1}. From a simple fit of the experimental rate constants at 25 °C, the values are $k_0 = (9.8 \pm 5.2) \times 10^{-4}$ s^{-1}, $k_1 = 1.48 \pm 0.34$ M^{-1} s^{-1}.[14]

The source of the k_0 term in eq 6 requires special consideration. The effect of hydrolysis of the nitrile complex to the carboxamide[16] has been examined, but the rate is too slow ($k \sim 2.5 \times 10^{-4}$ s^{-1}, pH 6)[17] for this to be a significant complication. In addition, the carboxamide complex is much less reactive[17] with $Co(DMGH)_2$ and the effect of this hydrolysis would be to make the rates too small rather than too large at low [Co(III)]. The instability of the immediate reaction products, which has been discussed in the preceding section, seems to be the most probable source of the k_0 term. These products are minor chromophores at 470 nm (see Table I), and their decomposition is kinetically competitive with the initial reaction as shown in Table II. Therefore, one might expect the absorbance–time curves to show some deviation from a simple exponential decay. A reanalysis of these curves for the lower range of [Co(III)] shows that the standard error of the least-squares fit is improved by ~20% by using a two-exponential model with one rate constant fixed at $\sim 1.5 \times 10^{-3}$ s^{-1}, and the other rate constant falls into the range expected from the data at higher [Co(III)] and a first-order dependence on [Co(III)]. However, since the one-exponential fits are already quite reasonable, it is not possible to define a true least-squares best fit value for a second rate constant. In any event this analysis cannot be entirely appropriate because the product decomposition is a second-order process, catalyzed by $Co(DMGH)_2$, which is disappearing by the first reaction. At higher [Co(III)], the $Co(DMGH)_2$ disappears more quickly and the larger rate difference makes the product decomposition a less competitive process. This can explain why $k_{obsd}/[Co(III)]$ achieves a reasonably constant value at the higher [Co(III)] levels, as shown in the last column of Table III.

For the above reasons, we feel that the k_0 term in eq 5 is essentially an artifact and that the best available values for the second-order rate constant are those obtained at the higher range of [Co(III)] in Table III. Analysis of this data gives $\Delta H_1^* = 20.4 \pm 0.4$ kcal mol^{-1}, $\Delta S_1^* = 11.5 \pm 2.1$ cal mol^{-1} deg^{-1}.[14] The calculated rate constants are 2.07, 0.789, and 0.300 M^{-1} s^{-1} at 25, 17.1, and 9.6 °C, respectively.

Discussion

The results of this study allow one to compare the reactions of $Co(DMGH)_2$ and aqueous Cr(II)[5] with $NCCH_2I$ and $(NH_3)_5CoNCCH_2I^{3+}$. The kinetic results for these systems are summarized in Table IV. The rate constants for both iodides are 20–30 times smaller with $Co(DMGH)_2$, but the general reactivity pattern seems similar to that of Cr(II) in that the cobalt(III) complex is about 5 times more reactive. However, an examination of the activation parameters indicates major differences between the two reactants. Both the ΔH^* and ΔS^* are substantially more positive for $Co(DMGH)_2$ compared to Cr(II). It is also noteworthy that $(NH_3)_5CoNCCH_2I^{3+}$ has the larger ΔH^* with $Co(DMGH)_2$ but smaller with Cr(II). The latter effect was attributed[5] to a weaker C–I bond in $(NH_3)_5CoNCCH_2I^{3+}$.

Table IV. Comparison of Kinetic Results for Reactions of Cr(II) and $Co(DMGH)_2$[a]

	Cr(II)			$Co(DMGH)_2$		
reacn	k(25 °C)	ΔH^*	ΔS^*	k(25 °C)[b]	ΔH^*	ΔS^*[b]
$NCCH_2I$	9.2	5.4	−35.8	0.38	15.8	−7.6
$(NH_3)_5CoNCCH_2I^{3+}$	45	3.8	−38.2	2.0	20.4	11.4

[a] The units of k, ΔH^*, and ΔS^* are M^{-1} s^{-1}, kcal mol^{-1}, and cal mol^{-1} deg^{-1}, respectively. [b] These values refer to the observed second-order rate constant. If the stoichiometry corresponds to that in eq 1, then the specific rate constant is 2 times smaller and ΔS^* is 1.4 units more negative.

If it is presupposed that both $Co(DMGH)_2$ and Cr(II) are reacting by a halogen-abstraction mechanism, then it is clear that there is some major difference in the energetics of the process. A possible detailed reaction sequence is given by the following equations.

$$LM^{II}(OH_2) \rightleftarrows \{LM^{II}\} + OH_2 \quad (7)$$

$$\{LM^{II}\} + R\text{–}I \rightleftarrows \{LM^{II}\text{---}I\text{–}R\} \quad (8)$$

$$\{LM^{II}\text{---}I\text{–}R\} \rightarrow LM^{III}\text{–}I + \{R^{\bullet}\} \quad (9)$$

The formation of the unsaturated metal complex (eq 7) or formation of the M---I bond (eq 8) could be the source of differences between the two metal complexes studied here. It should be noted that aqueous Cr(II) is a much stronger reducing agent ($E^\circ = -0.38$ V) than aqueous $Co(DMGH)_2$ ($E^\circ = 0.36$ V).[18] Other studies[2,19] of $Co(DMGH)_2(L)$ complexes with organic halides in benzene and acetone have found activation energies and entropies in the range of 10 kcal mol^{-1} and −25 cal mol^{-1} deg^{-1}, respectively, with substantial kinetic effects of the axial ligand L.[2] It is difficult to make meaningful comparisons because of the differences in the cobalt(II) reactant and the solvent. The activation parameters for Cr(II) are similar to those for the reduction of $(NH_3)_5Co^{III}(X)$ complexes, but these values are not available for $Co(DMGH)_2$.[10]

The reaction product with $NCCH_2I$ is about 25% of the organometal(III) complex in both systems. Since there are only two points of comparison, this constancy of product amount could be fortuitous, but it may also reflect a constant unpaired electron density on the methylene carbon of ~25% in the $NCCH_2^{\bullet}$ radical intermediate. Another product has been shown to be the $LM^{III}NCCH_3$ complex both in the system studied here and with Cr(II).[5,20] Unfortunately, this species is unstable under the reaction conditions in both systems and it has not been possible to prove whether free acetonitrile is a direct reaction product.

The products with $(NH_3)_5CoNCCH_2I^{3+}$ are significantly different. In the case of Cr(II), 100% of the cobalt(III) ends up as $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$, but $Co(DMGH)_2$ forms ~50% $(NH_3)_5CoNCCH_2Co(DMGH)_2(OH_2)^{3+}$ and about 10% of the dimer $((NH_3)_5CoNCCH_2)_2^{6+}$, while none of the latter was detected with Cr(II). The simplest explanation for these differences would seem to be that $Co(DMGH)_2$ is significantly less reactive than Cr(II) with the radical intermediate $(NH_3)_5CoNCCH_2^{\bullet}$. Then the radical has more opportunity to dimerize or undergo intramolecular electron transfer in competition with combination with $Co(DMGH)_2$. These observations indicate that earlier suggestions[5] concerning the lack of intramolecular electron transfer with Cr(II) based on the energetics of the reduction are not valid. It now seems more probable that $(NH_3)_5CoNCCH_2^{\bullet}$ is just trapped too efficiently by Cr(II)[4] to allow any intramolecular transfer in the radical intermediate. If Cr(II) reacts with the

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$(NH_3)_5CoNCCH_2^{\bullet}$ radical at about the same rate as with other organic radicals ($\sim 10^7$ M^{-1} s^{-1})[4], then the Cr(II) concentration of $\sim 10^{-2}$ M in the earlier study allows one to estimate an upper limit for the intramolecular electron transfer of $\sim 10^5$ s^{-1}. The suggestion that $Co(DMGH)_2$ reacts more slowly than Cr(II) with the radical is consistent with the observations of Elroi and Meyerstein[21] from a pulse radiolysis study. Their results with a cobalt(II) macrocycle imply that the rate constant for a radical with an electron-withdrawing substituent, such as $NCCH_2^{\bullet}$ would be $<10^7$ M^{-1} s^{-1}. Flash photolysis studies of Endicott and coworkers[22] give much larger rates near the diffusion-controlled limit. These differences can be rationalized if the flash photolysis is measuring a cage recombination process.

Experimental Section

Materials. Iodoacetonitrile and $((NH_3)_5CoNCCH_2I)(ClO_4)_3$ were prepared as described previously.[5] Dimethylglyoxime (Aldrich) and 4-morpholineethanesulfonic acid (MES) (Aldrich) were used as supplied.

Solutions of bis(dimethylglyoximato)cobalt were prepared by adding an appropriate volume of aqueous cobalt(II) perchlorate from a syringe to a solution of dimethylglyoxime in MES buffer. The pH was adjusted by addition of NaOH or $HClO_4$ before the addition of cobalt(II). All solutions were deoxygenated by bubbling argon that was passed through a chromium(II) scrubber, and they were protected from air by standard serum caps. Deoxygenated solutions of the substrates, iodoacetonitrile or $((NH_3)_5CoNCCH_2I)(ClO_4)_3$, were added by syringe to the $Co(DMGH)_2$ as soon as possible after preparation of the latter.

$(NH_3)_5CoNCCH_2Co(DMGH)_2(OH_2)(ClO_4)_3$. This solid was prepared from an aqueous solution initially containing 4.4×10^{-3} M cobalt(II) perchlorate, 2.4×10^{-2} M dimethylglyoxime, and 2.0×10^{-3} M $((NH_3)_5CoNCCH_2I)(ClO_4)_3$ at pH 6.0 in 0.01 M MES at 40 °C. Reagents were mixed as described in the preceding paragraph, and the reaction was quenched after 3-4 min by exposure to air. The products were separated on Sephadex SP-C25 resin by elution with increasing concentrations of $HClO_4$ from 0.1 to 1.0 M. The desired product is contained in 1.0 M $HClO_4$ eluant, and cooling of this solution at 5 °C yielded the desired solid. The properties of this species are described elsewhere in the text.

Analytical Methods. Cobalt was determined in $(NH_3)_5CoNCCH_2Co(DMGH)_2(OH_2)^{3+}$ by heating the complex in alkaline solution for ~2 h at ~70 °C to remove the ammonia. Then the solution was acidified, hydrogen peroxide was added, and the solution was heated as before to remove the DMGH. The resultant solution was analyzed for cobalt(II), as described previously.[5,12]

Iodide was determined spectrophotometrically by the method of Nikolelis et al.[13] When the analyte solution was yellow, then iodide was oxidized to iodine and the iodine extracted into chloroform and determined spectrophotometrically (ϵ 917 M^{-1} cm^{-1} at 470 nm).

Kinetic Methods. Solutions for kinetic analysis were prepared by adding a solution of the substrate to a solution of $Co(DMGH)_2$, MES, and $NaClO_4$ in a 5-cm path length cell. The latter solution was preequilibrated at the appropriate temperature in a thermostated cell holder. All solutions were deoxygenated with argon. The measurements were done on a Hewlett-Packard 8451 diode array spectrophotometer and analyzed by nonlinear least squares to obtain the rate constant.

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Registry No. $Co(DMGH)_2$, 3252-99-1; $NCCH_2I$, 624-75-9; $(NH_3)_5CoNCCH_2I^{3+}$, 88157-85-1; $(NH_3)_5CoNCCH_2ICo(DMGH)_2(OH_2)(ClO_4)_3$, 119480-27-2.

Supplementary Material Available: Table SI, containing kinetic results for the reaction of $Co(DMGH)_2$ with $NCCH_2I$ (1 page). Ordering information is given on any current masthead page.

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Synthesis, Kinetics, and Stereochemistry of the Aquation of *cis*-[Chlorosulfitobis(ethylenediamine)cobalt(III)]

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The synthesis of *cis*-$[Co(en)_2(SO_3)Cl]$ by SO_3^{2-} substitution on aqueous *cis*- or *trans*-$[Co(en)_2Cl_2]^+$, *cis*- or *trans*-$[Co(en)_2(NCS)Cl]^+$, or *cis*-$[Co(en)_2ACl]^+$ ($A^- = N_3^-, NO_2^-$) is described. This unusual observation, preferential loss of A^- rather than Cl^-, is discussed and a redox mechanism proposed. The stereochemistries for the unusually rapid (and clean) SO_3^{2-} substitution on the dichloro complexes have been determined by ^{13}C NMR spectroscopy; remarkably, the same initial distribution of $[Co(en)_2(SO_3)Cl]$ isomers (>75% cis) is observed, but principally trans isomer results on standing. A high-yield synthesis of either isomer can be obtained by control of the reaction conditions; mechanisms are discussed. The kinetics (k_1) and steric course of spontaneous aquation of *cis*-$[Co(en)_2(SO_3)Cl]$ have been investigated, as well as the steric course of its Hg^{2+}-induced hydrolysis and the temperature dependence of the kinetics (k_2) of the subsequent *cis*- to *trans*-$[Co(en)_2(SO_3)OH_2]^+$ isomerization. The *cis*-$[Co(en)_2(SO_3)Cl]$ isomer gives 53 ± 3% *cis*- and 46 ± 3% *trans*-$[Co(en)_2(SO_3)OH_2]^+$ in spontaneous aquation but 62 ± 2% *cis*-$[Co(en)_2(SO_3)OH_2]^+$ in the induced reaction. These results are discussed with respect to recent related work. The following specific rates and activation parameters were determined: $k_1 = 5.0 \times 10^{-4}$ s^{-1} at 25 °C, $\Delta H^{\ddagger} = 86 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = -20 \pm 9$ J mol^{-1} K^{-1}; $k_2 = 1.5 \times 10^{-3}$ s^{-1} at 25 °C, $\Delta H^{\ddagger} = 107 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = 60 \pm 13$ J mol^{-1} K^{-1}. Trans activation by S-bonded sulfite is well documented, but we show that a cis SO_3^{2-} is quite unremarkable, kinetically and stereochemically.

Introduction

The sulfite ion can bond to cobalt(III) through either the sulfur or the oxygen center.[1,2] The oxygen-bonded isomers, for example, *cis*-$[Co(en)_2(OH_2)OSO_2]^+$ [3] or $(NH_3)_5CoOSO_2^+$,[4] are unstable and undergo an internal redox reaction ultimately yielding Co(II) quantitatively. However the oxygen-bonded isomers of polydentate aminecobalt(III) complexes are more resistant to reduction; for example, the $\alpha,\beta(R)$- and $\alpha,\beta(S)$-Co(tetren)OSO_2^+ species can be observed to isomerize slowly but completely to the more stable[2] S-bonded forms.[5]

The area of inorganic reaction mechanisms has been well served by the S-bonded sulfitotetraaminecobalt(III) complexes.[6-8]

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