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# Reaction of Chromium(II) with Iodoacetamide and Properties of $(H_2O)_5CrCH_2CO(NH_2)^{2+}$

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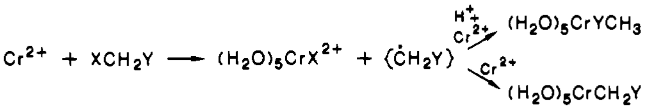
Chromium(II) reacts with iodoacetamide to give $(H_2O)_5CrI^{2+}$ (50%), $(H_2O)_5CrO(NH_2)CCH_3^{3+}$ (18%), and $(H_2O)_5CrCH_2CO(NH_2)^{2+}$ (30%). The rate of the reaction is first order in each reactant and independent of $[H^+]$ with $k = 0.56$ $M^{-1}$ $s^{-1}$ (25 °C), $\Delta H^* = 6.7 \pm 0.8$ kcal $mol^{-1}$, and $\Delta S^* = -37.2 \pm 2.6$ cal $mol^{-1}$ $deg^{-1}$. The organochromium product undergoes a reversible protonation reaction as shown by changes in its ion exchange behavior and electronic spectrum with acidity. The rate law for reaction of the organochromium species with $Hg^{2+}$ indicates that the protonation has a $K_a = (7.1 \pm 1.8) \times 10^{-2}$ and that $Hg^{2+}$ reacts only with the deprotonated form with $k = 2.5 \times 10^3$ $M^{-1}$ $s^{-1}$ (25 °C). Acidolysis of $(H_2O)_5CrCH_2CO(NH_2)^{2+}$ produces the acetato complex $(H_2O)_5CrCH_2CO_2H^{2+}$ and $(H_2O)_5CrO(NH_2)CCH_3^{3+}$ as intermediate products, which ultimately decompose to $Cr(OH_2)_6^{3+}$. The aquation rates of $(H_2O)_5CrO(NH_2)CCH_3^{3+}$ and $(H_2O)_5CrO(NH_2)CCH_2Hg^{4+}$ have been studied between 40 and 63 °C in 2.0 M $NaClO_4$–$HClO_4$. The rates are first-order with $k$ (25 °C), $\Delta H^*$ (kcal $mol^{-1}$), and $\Delta S^*$ (cal $mol^{-1}$ $deg^{-1}$) of $1.56 \times 10^{-6}$ $s^{-1}$, $22.8 \pm 0.8$, and $-8.6 \pm 2.4$, and $1.51 \times 10^{-6}$ $s^{-1}$, $24.2 \pm 0.8$, and $-4.0 \pm 2.5$, respectively.

Chromium(II) reacts by halogen atom abstraction with a wide range of halo-substituted organic compounds.[1] When the organic substrate has another substituent (Y) that can act as a Lewis base toward the chromium, then the reaction mechanism and products are adequately described by eq 1. This scheme is consistent with



(1)

the observed kinetics and products for $ICH_2CO_2H$,[2] $ICH_2CN$,[3] and $Cl_2CHCO_2H$.[4]

The results reported here show that eq 1 is also applicable to $ICH_2CO(NH_2)$. The expected products $(H_2O)_5CrI^{2+}$, $(H_2O)_5CrO(NH_2)CCH_3^{3+}$, and $(H_2O)_5CrCH_2CO(NH_2)^{2+}$ have been identified. The latter species is found to protonate in aqueous acid and to hydrolyze in a complicated way to unexpected products. The organochromium species reacts unusually rapidly with $Hg^{2+}$, and when the ratio $[Hg^{2+}]$:[Cr] = 1:2, a significant amount of the product is the trimetallo species $(H_2O)_5CrO(NH_2)CCH_2HgCH_2C(NH_2)OCr(OH_2)_5^{6+}$.

## Results

**Stoichiometry.** The amount of chromium(II) consumed per mole of iodoacetamide was determined at various initial reagent concentrations. The conditions of [Cr(II)], [iodoacetamide], and $HClO_4$ were as follows: (i) 0.050 M, 0.0219 M, 0.50 M; (ii) 0.100 M, 0.0411 M, 0.20 M; (iii) 0.250 M, 0.115 M, 0.90 M. The remaining chromium(II) was determined by oxidation with $(NH_3)_4Co(OH_2)_2^{3+}$ followed by analysis for cobalt(II) as $Co(NCS)_4^{2-}$.

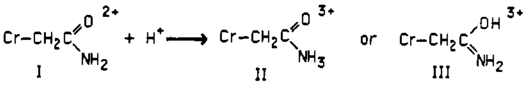
The average result gave 2.02 ± 0.002 mol of chromium(II) consumed/mol of iodoacetamide, where the error limit covers the range of values from 10 determinations. Therefore the observed stoichiometry agrees with that expected from eq 1.

**Reaction Products.** The reaction was initiated by adding a known amount of aqueous chromium(II) perchlorate from a syringe to a deoxygenated solution of iodoacetamide in aqueous perchloric acid under an argon atmosphere. At the completion of the reaction the solution was exposed to air; the products were separated by ion-exchange chromatography at 3–5 °C on Dowex 50W-X2 (100–200 mesh, $H^+$) resin by eluting with concentrations of perchloric acid increasing from 0.5 to 2.0 M. In order of elution the colors of the products were green, blue, greenish blue, and red. A small amount of red materials could not be removed with 2 M $HClO_4$.

The separation of the blue, greenish blue, and red species was not complete so that these fractions were re-ion-exchanged on Dowex 50W-X8 resin, also at 3–5 °C.

The electronic spectra of the products are summarized in Table I. By comparison to previous results, the green species is $(H_2O)_5CrI^{2+}$[5] and the blue species is $Cr(OH_2)_6^{3+}$.[6] The greenish blue species is assigned to $(H_2O)_5Cr(O(NH_2)CCH_3)^{3+}$, probably containing O-bonded acetamide since the absorbance maxima are at longer wavelength than those of $Cr(OH_2)_6^{3+}$.

The red species is clearly an organochromium complex based on its color and spectral features. However the composition of this species seems unusual in that it elutes after $Cr(OH_2)_6^{3+}$ and therefore has a charge of 3+ or greater. A protonation equilibrium seemed to be the most probable cause of the higher than expected charge for the organochromium complex. This was confirmed by carrying out the ion-exchange separation in 0.05 M $HClO_4$ with increasing concentrations of $NaClO_4$. Under these conditions the red species elutes before $Cr(OH_2)_6^{3+}$ as expected for a 2+ charged ion. The electronic spectrum of the red species also varied with $[H^+]$ (Table I) consistent with the following protonation equilibrium.



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There is no firm basis to choose between II and III, but aquation studies reported below indicate that II must be present at least as a reactive intermediate.

The product distributions for various reaction conditions, which are summarized in Table II, show only minor variations with reagent concentration, acidity, and the reagent in excess. The $Cr(OH_2)_6^{3+}$ is thought to result primarily from aquation of $(H_2O)_5CrI^{2+}$ during the separation procedure, and the total of these two products is close to 50% of the total chromium expected. The slightly smaller amounts of the organochromium(III) product when chromium(II) is in excess may be attributed to some chromium(II)-catalyzed decomposition as observed previously with $(H_2O)_5CrCH_2CN^{2+}$.[7]

The red, highly charged, and uncharacterized "polymer" clearly has an organo-chromium bond from its color. It may result from oligomerization as reported for $(H_2O)_5CrCH_2CO_2H^{2+}$ and shown in eq 3.

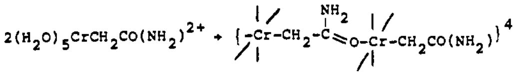

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**Table I.** Electronic Spectra of Products

| species | $[HClO_4]$, M | abs max, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$) | | |
|---|---|---|---|---|
| $(H_2O)_5CrI^{2+}$ | 1.0 | 474 (31.5)[a] | 650 (34.3)[a] | |
| $Cr(OH)_6{}^{3+}$ | 3.0 | 408 (15.4)[b] | 575 (13.2)[b] | |
| $(H_2O)_5Cr(O(NH_2)CCH_3)^{3+}$ | 2.0 | 412 (19.7) | 586 (19.4) | 673 (4.44) |
| $(H_2O)_5Cr(CH_2CO(NH_2))^{2+}$ | 2.0 | 414 (77.9) | 546 (42.8) | 271 ($4.12 \times 10^3$) |
| | 0.04[c] | 413 (90.8) | 541 (37.0) | 272 ($4.05 \times 10^3$) |
| | 0.84[d] | 413 (78.8) | 547 (42.5) | |
| | 0.04[d] | 413 (94.5) | 542 (37.6) | |

[a] Literature values:[5] 474 (32.6), 650 (36.1). [b] Literature values:[6] 408 (15.6), 574 (13.4). [c] Solution contains 0.96 M $NaClO_4$. [d] Solutions contain enough $NaClO_4$ to give a total ionic strength of 1.0 M.

**Table II.** Summary of Product Distributions for the Reaction of Chromium(II) and Iodoacetamide

| | | | % product[a,b] | | | | |
|---|---|---|---|---|---|---|---|
| $[Cr^{2+}]$, M | $[ICH_2C(NH_2)O]$, M | $[HClO_4]$, M | $CrI^{2+}$ | $C(OH_2)_6{}^{3+}$ | $(H_2O)_5Cr$-$(O(NH_2)CCH_3)^{3+}$ | $(H_2O)_5Cr$-$(CH_2CO(NH_2))^{2+}$ | polymer[d] |
| 0.15 | 0.15[c] | 0.30 | 45.0 | 7.0 | 19.3 | 27.5 | 1.0 |
| 0.15 | 0.15[c] | 1.00 | 48.8 | 3.8 | 18.5 | 27.9 | 2.0 |
| 0.15 | 0.15[c] | 1.00 | 47.8 | 5.5 | 18.1 | 26.8 | 2.0 |
| 0.030 | 0.030[c] | 1.00 | 47.0 | 4.0 | 16.5 | 30.0 | 1.0 |
| 0.030 | 0.030[c] | 1.00 | 46.5 | 6.0 | 16.5 | 29.0 | 1.5 |
| 0.050[c] | 0.020 | 1.00 | 48.3 | *e* | *e* | 25.5 | |
| 0.10[c] | 0.030 | 1.00 | 44.0 | *e* | *e* | 24.8 | |

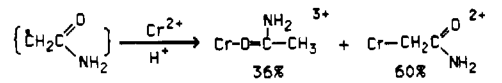
[a] Based on total chromium, analyzed as $CrO_4{}^-$, and a 2:1 reaction stoichiometry. [b] Values are the average of two experiments that agree within <2% in all cases. [c] Reagent in excess. [d] This species was determined by treatment of the resin band with alkaline $H_2O_2$. [e] The $Cr(OH_2)_6{}^{3+}$ formed by oxidation of excess Cr(II) made it impractical to determine these products.

**Table III.** Product Distribution for Acidolysis of $(H_2O)_5Cr(CH_2CO(NH_3))^{3+}$

| conditions[a] | | % of species present[b] | | | | |
|---|---|---|---|---|---|---|
| temp, °C | time, h | reactant | $CrCH_2CO_2H^{2+}$ | $Cr(OH_2)_6{}^{3+}$[b] | $CrO(NH_2)CCH_3{}^{3+}$[c] | polymer |
| 90 | 5 | 30 | 30 | 15 | 20 | 5 |
| 50 | 10 | 10 | 5 | 60 | 15 | 10 |

[a] $[HClO_4]$ = 1.00 M. [b] The products were identified by their ion-exchange characteristics and electronic spectra. [c] These products were separated by a second Dowex 50W-X8 ion-exchange column.

If the polymeric material is counted as organochromium product, then the products are 30% organochromium species and 18% acetamido complex. Therefore the acetamido radical reacts with $Cr^{2+}$ as follows.



$$\{\cdot CH_2C(O)NH_2\} \xrightarrow[H^+]{Cr^{2+}} \underset{36\%}{Cr{-}O{=}C(NH_2){-}CH_3{}^{3+}} + \underset{60\%}{Cr{-}CH_2C(O)NH_2{}^{2+}} \quad (4)$$

**Acidolysis of the Organochromium Product.** From studies on other systems,[1] this process is expected to proceed by

$$(H_2O)_5CrR^{2+} + H_3O^+ \rightarrow Cr(OH_2)_6{}^{3+} + RH \quad (5)$$

The acidolysis of $(H_2O)_5CrCH_2CO(NH_2)^{2+}$ did not conform to these simple expectations. Spectrophotometric observations indicated at least two, and probably three reaction steps with half-times within a factor of 10 of each other. This behavior was not qualitatively affected by doing the reaction in an argon atmosphere or by changing the acidity.

To determine the reason for this complexity, the reaction products were determined at various extents of reaction. It was crucial to these studies that the organoacetamido complex can be protonated and separated from 2+-charged products. The results of this study are summarized in Table III. The most surprising observation is the formation of the organoacetato complex $(H_2O)_5CrCH_2CO_2H^{2+}$, and equally unexpected is the formation of $(H_2O)_5CrO(NH_2)CCH_3{}^{3+}$.

On the basis of the reaction products, the reaction can be described by Scheme I, where the reaction half-times have been estimated at 50 °C from independent observations on $CrCH_2CO_2H^{2+}$ and $CrO(NH_2)CCH_3{}^{3+}$, and from the amount of reactant left after 5 and 10 h (Table III).

**Scheme I**

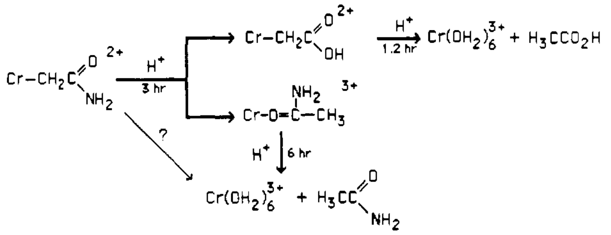


**Table IV.** Kinetic Results for the Reaction of Hg(II) and $(H_2O)_5CrCH_2C(NH_2)O^{2+}$[a]

| | | $k_{obsd}$, $s^{-1}$ | |
|---|---|---|---|
| $10^2[Hg^{2+}]$, M | $[H^+]$, M | obsd | calcd[b] |
| 1.334 | 0.48 | 4.32 | 4.37 |
| 2.670 | 0.48 | 9.27 | 8.74 |
| 5.340 | 0.48 | 16.7 | 17.5 |
| 8.000 | 0.48 | 24.0 | 26.2 |
| 10.67 | 0.48 | 34.8 | 34.9 |
| 13.34 | 0.48 | 44.5 | 43.6 |
| 2.67 | 0.88 | 5.54 | 5.07 |
| 2.67 | 0.68 | 6.54 | 6.42 |
| 2.67 | 0.280 | 13.4 | 13.7 |
| 2.67 | 0.160 | 20.4 | 20.9 |
| 2.67 | 0.120 | 26.3 | 25.2 |
| 2.67 | 0.080 | 32.2 | 31.4 |
| 2.67 | 0.060 | 36.6 | 36.7 |

[a] Results at 25.0 °C in 1.00 M $HClO_4$-$NaClO_4$, with $1.2 \times 10^{-3}$ M organochromium(III) reactant, monitored at 414 nm.

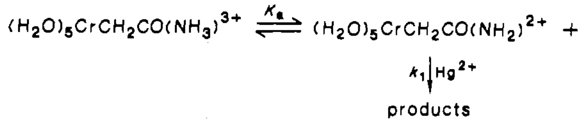
**Reactions with Mercury(II).** The Cr–C bond is subject to electrophilic attack by Hg(II). When $Hg(ClO_4)_2$ is added to a solution of $(H_2O)_5CrCH_2CO(NH_2)^{2+}$ there is an immediate change of color from red to blue.

The kinetics of the reaction have been studied by stopped-flow methods. The results are summarized in Table IV. The pseudo-first-order rate constant ($[Hg^{2+}] >> [Cr]$) is given by eq 6,

$$k_{obsd} = \frac{a[Hg^{2+}]}{b + [H^+]} \qquad (6)$$

with $a = (1.80 \pm 0.12) \times 10^2$ s$^{-1}$[8] and $b = (7.1 \pm 1.8) \times 10^{-2}$ M.[8] The experimental and calculated values of $k_{obsd}$ are compared in Table IV.

The form of the rate law and the previous observation that the organo carboxamide complex can be protonated at modest acidities, are consistent with the following mechanism.

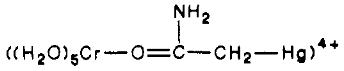


$$\begin{array}{ccc}(H_2O)_5CrCH_2CO(NH_3)^{3+} & \overset{K_a}{\rightleftharpoons} & (H_2O)_5CrCH_2CO(NH_2)^{2+} + H^+ \\ & & \downarrow k_1,\ Hg^{2+} \\ & & \text{products}\end{array} \qquad (7)$$

The predicted first-order rate constant is given by eq 8. Comparison of eq 6 and 8 shows that $k_1 = 2.5 \times 10^3$ M$^{-1}$ s$^{-1}$ and $K_a = 7.1 \times 10^{-2}$ M. The latter value is consistent with the spectrophotometric observations (Table I) and the changes in ion-exchange properties with acidity.

$$k_{obsd} = \frac{k_1 K_a [Hg^{2+}]}{K_a + [H^+]} \qquad (8)$$

The reaction products were determined at 2 °C in solutions with various initial concentrations of $Hg(ClO_4)_2$ ((2–30) × $10^{-3}$ M), in excess over chromium(II) ((5–100) × $10^{-4}$ M) and in 0.015–2.0 M $HClO_4$. The products were separated at 5 °C on Dowex 50W-X2 by eluting with 1.5–3.0 M $HClO_4$. There are two products; the first to elute is $Cr(OH_2)_6^{3+}$, and the second is eluted with 3.0 M $HClO_4$ and contains mercury. The electronic spectrum of the second product has the following absorption maxima (nm) and extinction coefficients (in parentheses, M$^{-1}$ cm$^{-1}$): 415 (23.3), 588 (23.3), 674 (5.6). The spectrum is similar to that of $CrO(NH_2)CCH_3^{3+}$, but the ion-exchange properties and mercury content indicate that this product is IV.



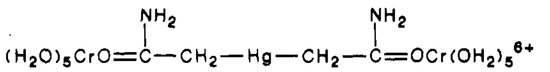
$$((H_2O)_5Cr{-}O{=}\overset{NH_2}{C}{-}CH_2{-}Hg)^{4+}$$

IV

The ratio of the two products has been determined at nine acidities in the range from 0.015 to 2.0 M. The products are formed in nearly equal amounts, but the ratio of $Cr(OH_2)_6^{3+}$:IV changes slightly from 1:1.10 to 1:0.99 as the acidity is increased. In 1 M $HClO_4$ the product distribution is the same at 2 and 22 °C.

The formation of IV when $[Hg^{2+}] >> [Cr]$ suggests that a dichromium–organomercury species should form in reasonable amounts if the initial ratio $[Cr]:[Hg^{2+}] = 2:1$. The reaction was done at 22 °C by the dropwise addition of 5.5 mL of 0.10 M $Hg(ClO_4)_2$ to a vigorously stirred solution of 40 mL of 2.56 × $10^{-2}$ M $CrCH_2CO(NH_3)^{3+}$ in 2 M $HClO_4$. Two minutes after the mercury(II) was added, the products were separated on Dowex 50W-X2 ($H^+$) by elution with increasing concentrations of aqueous $HClO_4$. With 1–2 M $HClO_4$, $Cr(OH_2)_6^{3+}$ was eluted, identified by the electronic spectrum, and found to constitute 48% of the initial chromium. With 2–3 M $HClO_4$, a product eluted with absorption maxima of 415 (23.8) and 584 nm (23.7), and contained 24% of the initial chromium. The final product was eluted with 4 M $HClO_4$ and has absorption maxima at 414 (23.8) and 589 nm (25.2) and contained 24% of the initial chromium.

The final species to elute is assigned to the predicted species V, based on its elution characteristics and the fact that its electronic spectrum is similar to that of IV.



$$(H_2O)_5CrO{=}\overset{NH_2}{C}{-}CH_2{-}Hg{-}CH_2{-}\overset{NH_2}{C}{=}OCr(OH_2)_5^{6+}$$

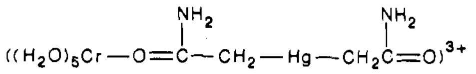
V

**Table V.** Kinetic Results for the Reaction of $Cr^{2+}$ with $ICH_2CO(NH_2)$ (1.0 M $NaClO_4$–$HClO_4$)[a]

| temp, °C | $10^2[ICH_2CO(NH_2)]$, M | $[HClO_4]$, M | $10^2k$, s$^{-1}$ obsd | $10^2k$, s$^{-1}$ calcd |
|---|---|---|---|---|
| 18.9 | 0.930 | 0.40 | 0.455 | 0.405 |
| | 1.89 | 0.40 | 0.844 | 0.823 |
| | 2.85 | 0.40 | 1.22 | 1.24 |
| | 3.82 | 0.20 | 1.66 | 1.66 |
| | 3.82 | 0.40 | 1.62 | 1.66 |
| | 3.82 | 0.60 | 1.63 | 1.66 |
| | 3.82 | 0.80 | 1.58 | 1.66 |
| | 4.78 | 0.40 | 2.09 | 2.08 |
| | 5.74 | 0.40 | 2.45 | 2.50 |
| | 6.70 | 0.40 | 2.86 | 2.92 |
| 27.0 | 1.89 | 0.40 | 1.17 | 1.16 |
| | 2.85 | 0.40 | 1.64 | 1.74 |
| | 3.82 | 0.40 | 2.21 | 2.33 |
| 35.8 | 0.93 | 0.40 | 0.845 | 0.806 |
| | 1.89 | 0.40 | 1.67 | 1.64 |
| | 2.85 | 0.40 | 2.44 | 2.47 |

[a] $[Cr^{2+}] \leqslant 1 \times 10^{-3}$ M in all runs.

The second product to elute has ion-exchange properties and an electronic spectrum quite similar to those of IV. However, it cannot be IV because each Hg(II) in the products must be coordinated to two alkyl groups because there are two alkyl groups per mercury in the reactants and the reaction goes to completion. Therefore this product is assigned to VI.



$$((H_2O)_5Cr{-}O{=}\overset{NH_2}{C}{-}CH_2{-}Hg{-}CH_2\overset{NH_2}{C}{=}O)^{3+}$$

VI

The observed product distribution can be rationalized with the simplest assumption that $Hg^{2+}$, $HgCH_2CO(NH_2)^+$, and $CrO(NH_2)CH_2Hg^{4+}$ all react with $CrCH_2CO(NH_3)^{3+}$ to give close to equal amounts of $Cr(OH_2)_6^{3+}$ and carboxamide-bound chromium–organomercury species. This predicts that $Cr(OH_2)_6^{3+}$, VI, and V should contain 50%, 25%, and 25% respectively of the total chromium, compared to the observed 48%, 24%, and 24%.

**Aquation Kinetics of $(H_2O)_5CrO(NH_2)CCH_3^{3+}$ and $(H_2O)_5CrO(NH_2)CCH_2Hg^{4+}$.** The kinetics were followed spectrophotometrically at 590 nm in 2.0 M $NaClO_4$–$HClO_4$. For $(H_2O)_5CrO(NH_2)CCH_3^{3+}$ the acidity was varied from 0.18 to 1.94 M and the reaction was studied at 39.6, 48.8, and 59.5 °C, while for $(H_2O)_5CrO(NH_2)CCH_2Hg^{4+}$ the acidity range was 0.26–1.80 M and the temperatures were 45.5, 55.2, and 63.2 °C. The reaction rate is independent of acidity for both complexes.

The activation enthalpy and entropy for aquation of $(H_2O)_5CrO(NH_2)CCH_3^{3+}$ are 22.83 ± 0.80 kcal mol$^{-1}$ and −8.55 ± 2.4 cal mol$^{-1}$ deg, respectively.[8] The calculated rate constant at 25 °C is 1.56 × $10^{-6}$ s$^{-1}$. For $(H_2O)_5CrO(NH_2)CCH_2Hg^{4+}$ the analogous parameters are 24.2 ± 0.83 kcal mol$^{-1}$, −4.0 ± 2.5 cal mol$^{-1}$ deg and 1.51 × $10^{-6}$ s$^{-1}$.

**Kinetics of the Reaction of $Cr^{2+}$ and $ICH_2CO(NH_2)$.** This study was complicated somewhat by the subsequent reactions of the initial products. These problems were minimized by monitoring the reaction at 570 nm, an isosbestic point for $(H_2O)_5CrI^{2+}$ and $Cr(OH_2)_6^{3+}$, and by using excess $ICH_2CO(NH_2)$ to reduce the $Cr^{2+}$-catalyzed processes. Good pseudo-first-order plots were obtained for over 80% reaction, and the results are summarized in Table V.

The rate is independent of $[H^+]$ and first order in $[Cr^{2+}]$ and $[ICH_2CO(NH_2)]$. From a least-squares analysis of the data, $k$(25 °C) = 0.56 M$^{-1}$ s$^{-1}$, $\Delta H^* = 6.71 \pm 0.84$ kcal mol$^{-1}$ and $\Delta S^* = -37.2 \pm 2.6$ cal mol$^{-1}$ deg$^{-1}$.[8]

## Conclusions

The results for the reactions of chromium(II) with several $ICH_2Y$ species are summarized in Table VI. In general, a more electron-withdrawing Y substituent increases the reaction rate constant. A similar trend has been noted by Blaser and Halpern[9]

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[8] Errors are 95% confidence limits.

**Table VI.** Summary of Results for Reaction of $Cr^{2+}$ and $ICH_2Y$

| Y | $k$(25 °C), $s^{-1}$ | $\Delta H^*$, kcal $mol^{-1}$ | $\Delta S^*$, cal $mol^{-1}$ $deg^{-1}$ | % $CrYCH_3$ product |
|---|---|---|---|---|
| $-CO(NH_2)^a$ | 0.56 | 6.7 | −37.2 | 38 |
| $-CO_2H^b$ | 1.1 | 5.4 | −40.4 | 81 |
| $-CN^c$ | 9.2 | 5.4 | −35.8 | 75 |
| $-CNCo(NH_3)_5{}^c$ | 45.2 | 3.8 | −38.2 | 0 |

[a] This work. [b] Reference 2. [c] Reference 7.

**Table VII.** Summary of Results for Reaction of $Hg^{2+}$ and $CrCH_2Y$

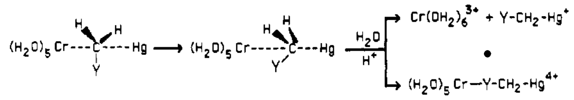
| Y | $k$(25 °C), $M^{-1}$ $s^{-1}$ | % $CrYCH_2Hg$ product | $\sigma_I$ for $Y^a$ |
|---|---|---|---|
| $-CO(NH_2)^b$ | $2.5 \times 10^3$ | 50 | 0.28 |
| $-CO_2H^c$ | | 100 | 0.30 |
| $-CN^d$ | 8.7 | 50 | 0.57 |
| $-OCH_3{}^e$ | 91 | | 0.30 |
| $-CH_2CN^e$ | 81 | | 0.20 |

[a] Reference 12. [b] This work. [c] Reference 2. [d] References 3 and 7. [e] Reference 1.

for analogous reactions of vitamin $B_{12r}$. The products of the chromium(II) reaction are also given in Table VI. The amount of $CrYCH_3$ clearly depends on the Y substituent. The basicity of the Y group appears to have a minor influence on the amount of $CrYCH_3$ product since a nitrile function generally is a much poorer base toward metal ions than a carboxamide group, yet the latter gives much less $CrYCH_3$ product. The unpaired electron distribution in the $^{\bullet}CH_2Y$ radical intermediate might affect the product distribution. Unfortunately, the theoretical predictions for the electron distribution are only available for $^{\bullet}CH_2CN$.[10,11] It is noteworthy that the reactions with vitamin $B_{12r}$ do not appear to yield the analogous $CoYCH_3$ products.[9]

The results for some reactions of $Hg^{2+}$ with $CrCH_2Y$ are summarized in Table VII. The reactivity trends of these reactions are consistent with electrophilic attack of $Hg^{2+}$ at the α-carbon.[1] The rate decreases with increasing electron-withdrawing power and steric bulk of the Y group.[1] On the basis of th $\sigma_I$ values for the substituents (Table VII)[12] the rate constant for Y ≡ $-CO(NH_2)$ should be similar to that for Y ≡ $-OCH_3$. In fact, $CrCH_2CO(NH_2)^{2+}$ is about 25 times more reactive than expected on this basis. This may be due to neighboring-group participation of the carboxamide group in the reaction with $Hg^{2+}$.

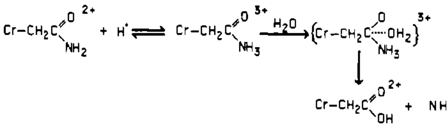
The formation of the $CrYCH_2Hg$ product was originally explained for Y ≡ $-CO_2H$ on the basis of chelation in the reactant.[2] However, the more recent work with Y ≡ $-CN$[3] indicates that competition between solvent water and −Y for the coordination site on chromium is a more probable explanation, as shown in eq 9.



(9)

The protonation equilibrium of $CrCH_2CO(NH_2)^{2+}$ was unexpected in view of the normally low basicity of the carboxamide group. The simplest rationalization is that the $-CH_2CO(NH_2)^-$ ligand retains a substantial amount of anion character in the complex, with the result that it is far more basic than a normal carboxamide substituent.

The acidolysis of $CrCH_2CO(NH_2)^{2+}$ is unusual in that substantial amounts of the carboxylate analogue are produced. This reaction can be understood in conjunction with the protonation reaction by the reaction sequence shown in eq 10.



(10)

The parallel formation of the O-bonded carboxamide complex in the acidolysis reaction can be explained if the attack of $H_2O$ or $H_3O^+$ is analogous to that of $Hg^{2+}$, shown in eq 9, to generate some $Cr(OH_2)_6{}^{3+}$ and some $(H_2O)_5CrO(NH_2)CCH_3$ in this reaction pathway.

## Experimental Section

The preparation and handling of standard reagents and general experimental procedures and equipment have been described previously.[2,7] The iodoacetamide (Aldrich Chemical Co.) was used as supplied.

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# Notes

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## A Proton Magnetic Resonance Study of the Conformational Characterization of Nickel(II)–Tetraaza Macrocyclic Complexes

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The coordination chemistry of metal-ion complexes of macrocyclic tetraamine ligands has attracted great interest because they provide stimulating examples for studying the conformational properties of the molecules, owing to the possible stable arrangements that the ligand can adopt around the metal ion.[1] Proton magnetic resonance spectroscopy is perhaps the most powerful tool available to inorganic chemists for obtaining conformational information about metal complexes in solution.[2] Previously, Ito and Busch reported the detailed stereochemistry of [1*SR*,2*SR*,4*RS*,7*RS*,8*SR*,9*SR*,11*RS*,14*RS*)-2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II) chloride.[3]

In order to investigate the effects of methyl substituents on the conformational characterization of nickel(II)–tetraaza macrocyclic complexes, the detailed stereochemistry in solution of three closely related complexes that have the same trans-I or 1*SR*,4*RS*,8*SR*,11*RS* configuration arising from the four chiral nitrogen centers,[4,5] as shown in Figure 1, has been accomplished

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