**Table III.** Summary of the Rate Constants ($k/10^6$ L mol$^{-1}$ s$^{-1}$) for the Reactions of $^{\bullet}C(CH_3)_2OH$ with Imidazolium Ions X,Y-$ImH^+$ and Metal–Imidazole Complexes M(Im-X,Y)$^{3+}$ [a]

| | | | M(Im-X,Y)$^{3+}$ | |
|---|---|---|---|---|
| X | Y | X,Y-$ImH^+$ | M = $Co(NH_3)_5^{3+}$ | M = $Cr(H_2O)_5^{3+}$ |
| 4(5)-$CH_3$ | 5(4)-CN | 4.8 | | |
| 4-Cl | 5-Cl | 3.3 | 18.5 | 1.6 |
| 4(5)-$CH_3$ | 5(4)-$CONH_2$ | 2.05 | | 0.72 |
| 1-$CH_3$ | H | 1.05 | 2.2 | 0.11 |
| 4(5)-$CH_3$ | 5(4)-H | 0.45 | 1.8 | 0.38 |
| H | H | 0.17 | 1.4 | 0.66 |
| 1-$CH_2COOH$ | H | 0.075 | | |
| 2-$CH_3$ | H | 0.013 | 3.0 | 0.21 |

[a] At 25.0 °C and $\mu = 1.0$ M ($HClO_4 + LiClO_4$).

slowly than the other imidazolium ions listed in Table III. Thus, the attack by $^{\bullet}C(CH_3)_2OH$ clearly does not take place at imidazole, which leaves the cobalt center as the only viable alternative.

The reactivity of $(H_2O)_5Cr(Im\text{-}X,Y)^{3+}$ toward $^{\bullet}C(CH_3)_2OH$ is comparable to that of the $(NH_3)_5Co^{III}$ series. This in itself rules out attack at the Cr center owing to the much lower reducibility of Cr(III) ($E^{\circ}_{Cr^{3+/2+}} = -0.41$ V) compared to Co(III) ($E_{Co(NH_3)_6^{3+/2+}} = 0.1$ V). In fact, the reduction of $Co(NH_3)_6^{3+}$ by $^{\bullet}C(CH_3)_2OH$ has a rate constant $4.1 \times 10^5$ L mol$^{-1}$ s$^{-1}$,[8] comparable to that for $(NH_3)_5Co(Im\text{-}X,Y)^{3+}$. Thus, the substitution of one $NH_3$ by Im-X,Y had only a minor effect on the reducibility of the complex. In the Cr(III) case, on the other hand, the effect is dramatic. $Cr(H_2O)_6^{3+}$ reacts with $^{\bullet}C(CH_3)_2OH$ with $k = 560$ L mol$^{-1}$ s$^{-1}$,[21] whereas $(H_2O)_5Cr(Im\text{-}X,Y)^{3+}$ complexes have $k = 10^5$–$10^6$ L mol$^{-1}$ s$^{-1}$, comparable to those for free imidazolium ions. It is highly unlikely that substitution of one $H_2O$ in $Cr(H_2O)_6^{3+}$ by Im-X,Y would have such a dramatic effect on the reduction potential, given that in the cobalt series the response was negligible. Indeed, if there is a change in $E^{\circ}$, one would predict $(H_2O)_5Cr(Im\text{-}X,Y)^{3+}$ to be even *less reducible* than $Cr(H_2O)_6^{3+}$ owing to the fact that imidazoles are good $\sigma$- and $\pi$-electron donors but poor $\pi$-electron acceptors.[22] It thus seems clear that the attack of $^{\bullet}C(CH_3)_2OH$ has to take place on imidazoles of $(H_2O)_5Cr(Im\text{-}X,Y)^{3+}$.

On the basis of the low reactivity of 2-$CH_3$-$ImH^+$, the complex $(H_2O)_5Cr(2\text{-}CH_3\text{-}Im)^{3+}$ was expected to be the least reactive of the chromium complexes. As it turns out, the measured rate constant of $2.1 \times 10^5$ L mol$^{-1}$ s$^{-1}$ is among the lowest in Table III, but it is not exceptionally low. Even more importantly, the range of values of $k_R$ for the chromium complexes is quite narrow relative to those for imidazolium ions. This signals that substituents have a significant, but variable, effect on $\pi$-donation from imidazoles, which alters the reactivity of coordinated imidazoles relative to imidazolium ions.

Unlike in the cobalt series, there is no correlation between the positions of the d–d bands in $(H_2O)_5Cr(Im\text{-}X,Y)^{3+}$ and rate constants for reaction 3. This is again consistent with the attack at imidazole, such that minor changes in the reducibility of the metal center do not result in the corresponding changes in reactivity.

Previously[2,4-6] we have studied reactions of $^{\bullet}C(CH_3)_2OH$ with pyridinium ions and pyridine complexes of $(H_2O)_5Cr^{3+}$ and $(NH_3)_5Co^{3+}$. The reactivities of the three series were analyzed quantitatively by use of a Hammett correlation. This analysis showed that the cobalt complexes react by direct reduction of the metal, whereas Cr complexes react by initial reduction of the pyridines. Subsequent rapid intramolecular electron transfer yields $Cr(H_2O)_6^{2+}$ as a final product. Although a Hammett correlation is not applicable to imidazoles and their complexes,[7] the results of this work strongly indicate the same mechanistic pattern. The basis for such an abrupt change in mechanism by changing the metal from cobalt to chromium must lie in the very different reducibilities of the two parent molecules, $Co(NH_3)_6^{3+}$ and $Cr(H_2O)_6^{3+}$, a point mentioned earlier. The low reducibility of Cr(III) channels the reduction toward the coordinated pyridines and imidazoles.

**Acknowledgment.** This work was supported in part by the U.S. Department of Energy through the Joint U.S.-Yugoslav Board for Scientific Cooperation, by the Research Council (SIZZ) of Croatia, and by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82. We are grateful to Dr. Vitomir Sunjić for supplying us with some of the imidazoles and to Prof. C. Frieden for supplying a copy of the program KINSIM.[20]

---

[21] Muralidharan, S.; Espenson, J. H. *Inorg. Chem.* **1984**, *23*, 636.

[22] Jones, C. M.; Johnson, C. R.; Asher, S. A.; Shepherd, R. E. *J. Am. Chem. Soc.* **1085**, *107*, 3772.

---

Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

# Electron Transfer. 101. Reaction of Carboxylato-Bound Chromium(V) with Dimeric Molybdenum(V)[1]

M. C. Ghosh and E. S. Gould*

*Received May 7, 1990*

The bridged dimer of molybdenum(V), $Mo_2O_4^{2+}$(aq), is rapidly oxidized to Mo(VI) by carboxylato-bound chromium(V). With excess $(Mo^V)_2$, a chelated Cr(III) product is obtained, and a pink Cr(IV) intermediate is observed. At high acidities with Cr(V) in excess, the latter is the primary product but undergoes slow reacion with the ligand. No binuclear $Cr^{III}$–$Mo^{VI}$ derivative is found among the reaction products. The intermediacy of Cr(IV) indicates that the oxidation of $(Mo^V)_2$ proceeds in 1e steps, passing through a reactive transient, taken here to be a mixed-valence complex, $Mo^VMo^{VI}$. With $(Mo^V)_2$ in excess at pH 1, the reaction generates a biphasic kinetic pattern corresponding to consecutive bimolecular transformations. The proposed mechanism includes rate-determining reductions of Cr(V) and Cr(IV) by $(Mo^V)_2$, as well as rapid reductions by $Mo^VMo^{VI}$. When the reaction is carried out in buffers of the acid form of the ligating group 2-ethyl-2-hydroxybutanoic acid, autocatalytic profiles are observed. The catalytic sequence features a reversal of selectivity, with $(Mo^V)_2$ reacting more rapidly with Cr(IV) than with Cr(V), but $Mo^VMo^{VI}$ reacting more rapidly with Cr(V).

In a formal sense, chromium(V) and molybdenum(V) are congeners. However, aside from their propensity to form oxo-substituted complexes, little similarity links the aqueous chemistries of these $d^1$ states. Chromium(V) undergoes disproportionation unless incorporated into chelates of hydroxy carboxylic acids[2] or

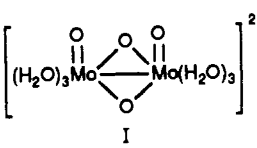
---

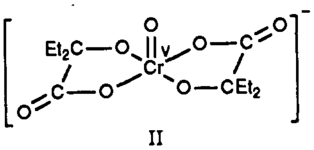
[1] Sponsorship of this work by the National Science Foundation (Grant 8619472) is gratefully acknowledged.

[2] (a) Krumpolc, M.; Roček, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206. (b) Mitewa, M.; Bontchev, P. R. *Coord. Chem. Rev.* **1985**, *61*, 241. (c) Gould, E. S. *Acc. Chem. Res.* **1986**, *19*, 66.

0020-1669/91/1330-0483$02.50/0 © 1991 American Chemical Society

dicarboxylic acids,[3] whereas in the absence of strongly coordinating anions, the reactions of Mo(V) in water are predominantly those of dimeric $\mu$-dioxo complexes such as the orange-yellow $Mo_2O_4(H_2O)_6^{2+}$ ion (I).[4] Cr(V) is an oxidant comparable to Mn(VII), while the reducing characteristics of Mo(V) are not unlike those of $V(III)_{aq}$. An estimated difference[5-9] of 1.0–1.4 V between the formal potentials for $Cr^V \rightarrow Cr^{III}$ and $Mo^{VI} \rightarrow Mo^V$ appearas reasonable.


I


II

The present work deals with reactions of the Cr(V) complex of 2-ethyl-2-hydroxybutanoic acid (II) with the dimeric Mo(V) cation I. The reductions of Cr(V) derivatives may take several mechanistic paths. With 2e metal center reductants such as Sn(II),[10] conversion to Cr(III) follows a straightforward bimolecular course. With 1e reagents, reductions must proceed through Cr(IV). Such an intermediate has been observed in reactions with Fe(II),[11] $VO^{2+}$,[12] and U(IV),[13] but not with the very rapid reductants Ti(III)[14] and Eu(II).[12] With reagents such as sulfite, nitrite, and ascorbate, which may partake in both 1e and 2e transactions, four different acts of 1e transfer are possible, and the interplay of competing steps may lead to slight[15] or severe[16] autocatalysis.

The cation $Mo_2O_4(H_2O)_6^{2+}$ (abbreviated $(Mo^V)_2$) may be considered bifunctional, for oxidation to two Mo(VI) removes one electron per metal center, but two electrons overall. It reacts readily with 1e oxidants,[17] but a recent study[18] suggests that oxidations by oxyhalogen derivatives involve 2e changes. Evidence for its oxidation by both outer- and inner-sphere paths is at hand,[18-20] and in a number of instances, rates of oxidation are controlled by preconversion of $Mo_2O_4^{2+}$ to a more reactive species.[17a,20b] We here observe that the $(Mo^V)_2$–$Cr^V$ system may, depending upon reaction conditions, utilize three distinct mechanistic variations.

## Experimental Section

**Materials.** Sodium bis(2-ethyl-2-hydroxybutanoato)oxochromate(V) (the $Na^+$ salt of anion II) was prepared as described.[2a,12] The "ligand acid", 2-ethyl-2-hydroxybutanoic acid (an Aldrich product) was used as received or after recrystallization from benzene–hexane. Cation-exchange resin (Dowex 50-X8, 400 mesh, $H^+$ form) was pretreated as described.[21] Preparations of $(Mo^V)_2$ solutions were carried out by aquation of $(NH_4)_2MoOCl_5$.[17b,18,22] Separation of $Mo_2O_4(H_2O)_6^{2+}$ from $NH_4^+$ and $Cl^-$ was accomplished on deaerated Dowex 50-X8 resin. For experiments at low pH values, $(Mo^V)_2$ was eluted under $N_2$ from the column with 2 M $HClO_4$. For experiments at higher pHs, elution was with 2 M $NaClO_4$ + 0.1 M $HClO_4$; such solutions were used immediately after elution. Solutions of $(Mo^V)_2$ were standardized at 295 nm ($\epsilon_{295}$ = 3550 $M^{-1}$ $cm^{-1}$).[23]

**Stoichiometric Studies.** The stoichiometry of the $(Mo^V)_2$–$Cr^V$ reaction was determined at pH 1.0 and 3.34. For experiments at the lower pH, the Cr(V) solution was stabilized by addition of 0.1 M ligand acid, whereas at the higher pH, it was stabilized by a buffer of ligand acid and its anion. Experiments with excess $(Mo^V)_2$ were carried out by adding a deficiency of Cr(V) to $(Mo^V)_2$, waiting for completion of the reaction, and then measuring the decrease in absorbance at 295 nm. Changes were compared to those when Mo(V) was treated with excess oxidant. For reactions with excess Cr(V), measurements were made at 510 nm.[24]

**Examination of the Reaction Products.** Reaction mixtures (10 mL) contained 0.090 mmol of Cr(V), 0.14 mmol of $(Mo^V)_2$, and 2.0 mmol of ligand acid (pH 1.12). After 10 min, these were treated with $NaBrO_3$ to consume unreacted Mo(V)[18] and then were subjected to ion-exchange chromatography.[25-28] The Cr(III) products were absorbed on cation-exchange resin. The predominant Cr(III) product, comprising 70% of the Cr(V) taken, was eluted from the resin slowly with water. This fraction exhibited maxima at 585 nm ($\epsilon$ = 44 $M^{-1}$ $cm^{-1}$) and 417 nm ($\epsilon$ = 61 $M^{-1}$ $cm^{-1}$)—a spectrum corresponding to the product earlier obtained by reduction of Cr(V) chelate II with Eu(II) or Fe(II).[12] This fraction also contained Mo(VI) in a quantity nearly equivalent to the $(Mo^V)_2$ taken.

In a separate experiment, treatment of $Cr(H_2O)_6^{3+}$ with a 5-fold excess of $Na_2MoO_4$ for 50 min at pH 2.0 was found to shift the Cr(III) maximum from 574 nm ($\epsilon$ = 13.4 $M^{-1}$ $cm^{-1}$) to 561 nm ($\epsilon$ = 10 $M^{-1}$ $cm^{-1}$). In addition, the Cr(III) peak at 408 nm became obscured in the tail of a strong absorbance in the near-UV region. The spectrum of this purple solution, taken to be that of a $Mo^{VI}$–$Cr^{III}$ complex, was unaffected by 3-fold dilution (which would approximate the concentrations in our kinetic runs), by treatment with excess 2-ethyl-2-hydroxybutanoate or by acidification with excess $HClO_4$.

**Kinetic Measurements and Estimates of Specific Rates.** Reactions were monitored with a Durrum-Gibson stop-flow spectrophotometer. Aqueous Cr(V) solutions were added to $(Mo^V)_2$ solutions eluted from the cation-exchange column. Total ionic strength was controlled by addition of $NaClO_4$, and buffering was accomplished by using the parent hydroxy acid ($pK_A$ 3.32)[29] and its salt.

Kinetic traces taken with $(Mo^V)_2$ in excess showed the growth and decay of a pink intermediate, but the characteristics of these patterns depended upon the conditions. Curves at pH 1.0 corresponded to the simple superposition of two bimolecular processes. For buffered runs (pH 2.4–3.4) in which the buffer had been premixed with Cr(V), traces exhibited an autocatalytic component.[30]

---

(3) Farrell, R. P.; Judd, R. J.; Lay, P. A.; Bramley, R.; Ji, J.-Y. *Inorg. Chem.* **1989**, *28*, 3401.

(4) See, for example: (a) Sykes, A. G. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1987; Vol. 3, p 1249. (b) Richens, D. T.; Helm, L.; Pittet, P.-A.; Merbach, A. E. *Inorg. Chim. Acta* **1987**, *132*, 85.

(5) The formal potential for $Cr^{VI} \rightarrow Cr^V$ has been estimated [6] as 0.60 V, a value which has been considered by Linck.[7] This potential, in conjunction with the value 1.20 V for $Cr^{VI} \rightarrow Cr^{III}$,[8] leads to a potential of 1.50 V for $Cr^V \rightarrow Cr^{III}$. The value for $Mo^{VI} \rightarrow Mo^V$ has been estimated by Latimer[9a] as 0.4 V and by Anson[9b] as 0.04 V. These estimates apply to 1–2 M $H^+$; each is expected to be pH dependent. Further adjustment of values is necessary to accommodate ligation of Cr(V) and dimerization of Mo(V).

(6) Csanyi, L. J. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1972; Vol. 7, p 510.

(7) Linck, R. G. *Int. Rev. Sci.*: *Inorg. Chem., Ser. Two* **1974**, *9*, 191.

(8) Beattie, J. K.; Haight, G. P., Jr. *Prog. Inorg. Chem.* **1972**, *17*, 97.

(9) (a) Latimer, W. M. *Oxidation Potentials*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1952; p 252. (b) Chalipoyil, P.; Anson, F. C. *Inorg. Chem.* **1978**, *417*, 2418.

(10) Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3357.

(11) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832.

(12) Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 4679.

(13) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 94.

(14) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2645.

(15) Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 2688, 3722.

(16) (a) Bose, R. N.; Rajasekar, N.; Thompson, D. M.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3349. (b) Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 2684.

(17) See, for example: (a) Cayley, G. R.; Taylor, R. S.; Wharton, R. K.; Sykes, A. G. *Inorg. Chem.* 1977, *16*, 1377. (b) Chapelle, G. A.; MacStay, A.; Pittenger, S. T.; Ohashi, K.; Hicks, K. W. *Inorg. Chem.* **1984**, *23*, 2768.

(18) Linn, D. E., Jr.; Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1989**, *28*, 3225.

(19) Millan, C.; Diebler, H. *Inorg. Chem.* **1985**, *24*, 3729.

(20) (a) Wharton, R. K.; Ojo, J. F.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 1526. (b) Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1939.

(21) Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792.

(22) (a) Sasaki, Y.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1974**, 1468. (b) Sasaki, Y.; Taylor, R. S.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 396.

(23) (a) Richens, D. T.; Sykes, A. G. *Inorg. Synth.* **1985**, *23*, 137. (b) Ardon, M.; Pernick, A. *Inorg. Chem.* **1973**, *12*, 2484.

(24) Detailed stoichiometric data (Table IV) are included as supplementary material.

(25) Separations were carried out by using 5-cm columns, capacity 2 mequiv. For estimations of extinction coefficients of Cr(III) species, aliquots were oxidized with basic $H_2O_2$, and the total chromium content was determined as chromate.[26] Molybdenum was estimated by the method of Allen and Hamilton,[27] using solutions of 4-methyl-1,2-benzenedithiol stabilized by sodium mercaptoacetate.[28]

(26) Haupt, G. W. *J. Res. Natl. Bur. Stand. Sect. A* **1952**, *48*, 414.

(27) Allen, S. H.; Hamilton, M. B. *Anal. Chim Acta* **1952**, *7*, 483.

(28) Clark, L. J.; Axley, J. H. *Anal. Chem.* **1955**, *27*, 2000.

(29) Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 3176.

Kinetic profiles were fitted to a four-step reaction sequence (see the Discussion Section) by using the program INTEGRAL to generate curves that were compared to those observed.[16a,31,32] Individual rate constants were subjected to further refinement using a nonlinear least-squares procedure.[33,34] Parameters resulting from the final refinements reproduced the observed curves closely.

Reactions carried out in the presence of $(NH_4)_2MoO_4$ showed no indication of inhibition by added Mo(VI).[35]

## Results and Discussion

The reactions of $(Mo^V)_2$ with Cr(V) chelate II in solutions buffered by the parent hydroxy acid and its anion are found[24] to involve nearly equimolar quantities of the two redox partners, and 1:1 stoichiometry is observed near pH 1 with the reductant in excess.

$$(Mo^V)_2 + Cr(V) \rightarrow 2Mo(VI) + Cr(III) \qquad (1)$$

However, kinetic profiles indicate the intervention of an intermediate that strongly absorbs in the region characteristic of Cr(IV).[11,12,16] This state is the predominant primary product at high acidity with Cr(V) in excess, for here each unit of $(Mo^V)_2$ is found to reduce nearly two Cr(V) centers. Under these conditions, Cr(V) reacts more rapidly with $(Mo^V)_2$ than does Cr(IV) (see below); moreover, Cr(IV) is partially consumed via the known[36] reduction by the ligand acid.[37]

The characteristics of the Cr(III) product formed with $(Mo^V)_2$ in excess correspond to those observed when Cr(V) is reduced by Fe(II)[11] or Eu(II).[12] The extinction coefficients ($\epsilon_{585} = 44$ $M^{-1}$ $cm^{-1}$, $\epsilon_{417} = 61$ $M^{-1}$ $cm^{-1}$) are charcteristic of bis-chelation by the hydroxy acid,[12] and the ease with which this product is eluted with water alone (zero net charge) points to the inclusion of an additional negative ligand, i.e., a third unidentate carboxylato group. Partial loss of the latter on polysulfonate resin is in accord with behavior reported for (carboxylato)chromium(III) complexes.[38,39] Although molybdenum is eluted with this Cr(III) product, it is not Cr(III)-bound. Attachment of Mo(VI) to a Cr(III) center is found to shift the low-energy Cr(III) peak and to result in strong absorbance in the near-UV region, but our reduction product exhibits neither of these features.

**Table I.** Kinetic Data for Reduction of (Carboxylato)chromium(V) with Dimeric Molybdenum(V) at pH 1 (21 °C, $\mu = 1.0$ M)

| $10^3[Cr^V]$, M[a] | $10^3[(Mo^V)_2]$, M | λ, nm | $k_1$, $M^{-1}$ $s^{-1}$ [b] | $k_3$, $M^{-1}$ $s^{-1}$ [b] | $\epsilon_{inter}$, $M^{-1}$ $cm^{-1}$ [c] |
|---|---|---|---|---|---|
| 0.50 | 1.50 | 600 | 53 ± 3 | 38 ± 2 | 206 |
| 0.50 | 3.0 | 600 | 55 ± 2 | 44 ± 1 | 219 |
| 0.50 | 4.5 | 600 | 56 ± 3 | 37 ± 2 | 201 |
| 1.00 | 3.0 | 600 | 54 ± 2 | 37 ± 1 | 196 |
| 1.00 | 3.0 | 570 | 54 ± 1 | 30 ± 1 | 284 |
| 1.00 | 3.0 | 540 | 54 ± 2 | 33 ± 1 | 360 |
| 1.00 | 3.0 | 530 | 54 ± 2 | 32 ± 1 | 393 |
| 1.00 | 3.0 | 520 | 59 ± 3 | 30 ± 1 | 376 |
| 1.00 | 3.0 | 510 | 54 ± 5 | 32 ± 1 | 407 |
| 1.00 | 3.0 | 500 | 53 ± 5 | 32 ± 1 | 452 |
| 0.15 | 0.75 | 380 | 55 ± 3 | *d* | |
| 0.15 | 1.50 | 380 | 50 ± 4 | *d* | |

[a] Chromium(V) was added as sodium bis(2-ethyl-2-hydroxybutanoato)oxochromium(V) (II). [b] Second-order specific rates for the initial $(Mo^V)_2$–$Cr^V$ reaction (eq 2 in the text) and the $(Mo^V)_2$–$Cr^{IV}$ reaction (eq 4), obtained from least-squares refinements in which the observed absorbances were compared to those obtained by integration of differential equations based on sequence 2–5. (See text and refs 16a and 33.) [c] Estimated extinction coefficient of the Cr(IV) intermediate at the wavelength indicated. [d] Value cannot be determined at this wavelength.

**Table II.** Absorbance Data for Ligation of Dimeric Molybdenum(V), $(Mo^V)_2$, in 2-Hydroxy-2-ethylbutanoate Buffers[a]

| $10^3[Lig^-]$, M | pH | $abs_{obsd}$ | $abs_{calcd}$[b] |
|---|---|---|---|
| 0.0 | 3.30 | 1.028 | 1.023 |
| 0.50 | 3.33 | 1.065 | 1.071 |
| 0.75 | 3.29 | 1.083 | 1.088 |
| 1.00 | 3.34 | 1.097 | 1.102 |
| 1.50 | 3.31 | 1.125 | 1.124 |
| 2.0 | 3.35 | 1.150 | 1.140 |
| 4.0 | 3.35 | 1.180 | 1.176 |
| 8.0 | 3.32 | 1.205 | 1.205 |
| 16.0 | 3.29 | 1.224 | 1.223 |
| 32 | 3.29 | 1.229 | 1.234 |

[a] Data were taken in a 1.00-cm cell at 25 °C. Equimolar concentrations of 2-hydroxy-2-ethylbutanoate ($Lig^-$) and its parent acid (HLig) were maintained in each case; $[(Mo^V)_2] = 2.1 \times 10^{-4}$ M throughout. Absorbances were taken 7 s after mixing, i.e., before further stages of ligation were significant (see text). [b] Values were calculated by using eq 6 in the text, taking $\epsilon_0$ as $4.87 \times 10^3$ $M^{-1}$ $cm^{-1}$, $\epsilon_1$ as $5.92 \times 10^3$ $M^{-1}$ $cm^{-1}$, and $K$ as $5.5 \times 10^2$ $M^{-1}$.

The biphasic reaction curves obtained at pH 1 with the reductant in excess reflect the formation and attrition of a pink intermediate. The approach to 2:1 stoichiometry seen with $(Mo^V)_2$ in deficiency, the autocataysis at high pHs, and the absorbance of this intermediate in the region 570–600 nm point to a reaction via a Cr(IV) complex, as has been shown for Cr(V) reductions with Fe(II)[11] and V(IV).[12] We are thus dealing with 1e oxidations of $(Mo^V)_2$, and these must generate a short-lived transient, which is best considered to be a mixed-valence species, $Mo^VMo^{VI}$, rather than monomeric Mo(V) (since our reactions are not inhibited by Mo(VI)).

The overall redox reaction may then be represented as sequence 2–5. Expression of eqs 2–5 as differential kinetic equations, application of the steady state approximation to $Mo^VMo^{VI}$, and employment of a stepwise integration procedure were as described for the $Cr^V$–$S^{IV}$ system.[16a]

$$Cr(V) + (Mo^V)_2 \xrightarrow{k_1} Cr(IV) + Mo^VMo^{VI} \qquad (2)$$

$$Cr(V) + Mo^VMo^{VI} \xrightarrow{k_2} Cr(IV) + 2Mo(VI) \qquad (3)$$

$$Cr(IV) + (Mo^V)_2 \xrightarrow{k_3} Cr(III) + Mo^VMo^{VI} \qquad (4)$$

$$Cr(IV) + Mo^VMo^{VI} \xrightarrow{k_4} Cr(III) + 2Mo(VI) \qquad (5)$$

Profiles at pH 1 with $(Mo^V)_2$ in excess correspond to the superposition of two straightforward bimolecular processes and, at the higher concentrations of reductant, become a combination of two succesive pseudo-first-order changes. Such simplification is

---

(30) When both Cr(V) and $(Mo^V)_2$ were prebuffered and allowed to equilibrate for at least 1 h, the growth of the Cr(IV) intermediate was accelerated whereas its decay was much slower and very nearly linear, indicating that the rate of conversion of Cr(IV) to Cr(III) was determined by a process not involving chromium. Uncertainty as to the nature of the ligated Mo(V) species present under these conditions prevented our further defining this reaction.

(31) Kinetic fits, which utilized a fourth-order Runge–Kutta integration technique,[32] were accomplished by a FORTRAN-77 program on an IBM 3081D system. The FORTRAN-IV version, for which we thank Professor Gilbert Gordon (Miami University, Oxford, OH), was modified to incorporate the appropriate differential equations and stoichiometric relationships.

(32) (a) Margenau, H.; Murphy, G. M. *The Mathematics of Physics and Chemistry*; Van Nostrand: New York, 1943; p 469. (b) Wiberg, K. In *Techniques of Chemistry*, 3rd ed.; Lewis, E. S., Ed.; Wiley: New York, 1974; Vol. VI, Part I, p 764.

(33) This program, developed by R. Moore and T. W. Newton, was obtained from Professor Gilbert Gordon. The FORTRAN-IV version was changed, with the help of Dr. J. W. Reed, to FORTRAN-77 in order to adapt to the IBM 3100 system. The program, which minimizes the function $(abs_{calcd} - abs_{obsd})^2$, uses the Gaussain method described by McWilliams and co-workers.[34] Trial values of the rate constants were obtained from the INTEGRAL procedure.

(34) McWilliams, P.; Hall, W. S.; Wegner, H. E. *Rev. Sci. Instrum.* **1965**, *33*, 76.

(35) The reaction between $(Mo^V)_2$ and the buffering anion in the absence of Cr(V) was examined briefly at 295 nm. Two exponential processes were evident: the first an absorbance increase ($k > 3 \times 10^3$ $M^{-1}$ $s^{-1}$ at 19 °C), the second a decrease ($k = 0.14$ $M^{-1}$ $s^{-1}$ at pH 3.08).

(36) Bose, R. N.; Neff, V. D.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 165.

(37) Slight but reproducible departures from 2:1 stoichiometry with Cr(V) in excess at pH 1 indicate that 5–10% of the added $(Mo^V)_2$ is consumed by Cr(IV) under these conditions.

(38) Hollaway, W. F.; Srinivansan, V. S.; Gould, E. S. *Inorg. Chem.* **1984**, *23*, 2181.

(39) Gould, E. S. *J. Am. Chem. Soc.* **1968**, *90*, 1740 (ref 10).

**Table III.** Kinetic Data for the Autocatalytic $(Mo^V)_2$–$Cr^V$ Reaction in Buffered Solution (pH 2.5–3.3, $\mu$ = 0.60 M ($NaClO_4$), 19 °C, 600 nm)[a]

| $10^3[(Mo^V)_2]$, M | $[Lig^-]$,[b] M | [HLig],[c] M | pH | $k_1$,[d] $M^{-1}\ s^{-1}$ | $k_3$,[d] $M^{-1}\ s^{-1}$ | $k_2/k_4$[d,e] | $\epsilon_{Cr(IV)}$,[d,f] $M^{-1}\ cm^{-1}$ |
|---|---|---|---|---|---|---|---|
| 1.50 | 0.10 | 0.10 | 3.31 | 20 ± 1 | 106 ± 3 | 4.1 ± 0.5 | 148 |
| 3.0 | 0.10 | 0.10 | 3.32 | 23 ± 1 | 94 ± 3 | 3.5 ± 0.3 | 140 |
| 4.5 | 0.10 | 0.10 | 3.29 | 25 ± 1 | 92 ± 2 | 2.8 ± 0.3 | 155 |
| 6.0 | 0.10 | 0.10 | 3.28 | 26 ± 1 | 92 ± 3 | 3.0 ± 0.4 | 152 |
| 3.0[g] | 0.10 | 0.10 | 3.30 | 21 ± 1 | 109 ± 2 | 4.8 ± 0.4 | 171 |
| 3.0 | 0.05 | 0.35 | 2.49 | 36 ± 2 | 107 ± 4 | 3.9 ± 0.7 | 171 |
| 3.0 | 0.05 | 0.25 | 2.61 | 32 ± 2 | 107 ± 4 | 4.3 ± 0.7 | 153 |
| 3.0 | 0.05 | 0.15 | 2.84 | 24 ± 1 | 108 ± 3 | 3.9 ± 0.4 | 135 |
| 3.0 | 0.05 | 0.05 | 3.30 | 25 ± 2 | 88 ± 4 | 2.3 ± 0.5 | 150 |
| 3.0 | 0.15 | 0.15 | 3.32 | 26 ± 2 | 104 ± 4 | 4.2 ± 0.7 | 158 |

[a] Chromium(V), added as sodium bis(2-ethyl-2-hydroxybutanoato)oxochromate(V), was 7.5 × $10^{-4}$ M unless otherwise indicated. [b] 2-Ethyl-2-hydroxybutanoate. [c] 2-Ethyl-2-hydroxybutanoic acid. [d] Parameters obtained from nonlinear least-squares refinements in which observed absorbances were compared to those obtained by integration of differential equations based on sequence 2–5. (See text and refs 16a and 33.) [e] $k_2/k_4$ is dimensionless. [f] 600 nm. [g] $[Cr(V)] = 3.8 \times 10^{-4}$ M.

compatible with sequence 2–5 only if the ratio $k_2/k_4$ approaches $k_1/k_3$. In this framework, values of $k_1$ and $k_3$ were allowed to vary, and integration then yielded the concentrations of $(Mo^V)_2$ and Cr(III), -(IV), and -(V) at 0.2-s intervals, as well as total absorbance. Specific rates approximating the observed curve were used as trial values for an iterative least-squares refinement.[33]

Values of $k_1$, $k_3$, and $\epsilon_{Cr(IV)}$ at pH 1 are summarized in Table I. Variation of wavelength points to a broad maximum near 530 nm ($\epsilon$ = 393 $M^{-1}\ cm^{-1}$) for the Cr(IV) transient, in addition to strong absorbance in the near-UV region.

In solutions buffered by the ligating acid and its anion, the Cr(V) chelate is partially converted to an extraligated species,[12] and there are at least two stages of ligation of $(Mo^V)_2$.[35] Only one of these is more rapid than the redox reaction. Absorbance changes for the $(Mo^V)_2$–$Lig^-$ system, observed at 295 nm immediately after mixing (in the absence of Cr(V)) (Table II), conform to (6), which is in accord with replacement of one unit

$$\text{abs} = [(Mo^V)_2]\frac{\epsilon_0 + \epsilon_1 K[Lig^-]}{1 + K[Lig^-]} \qquad (6)$$

of bound $H_2O$ in $[Mo_2O_4(H_2O)_6]^{2+}$ by a carboxylate anion,[40,41] related by an anation constant $K$. Treatment of data in terms of (6) yields extinction coefficients $\epsilon_0 = (4.87 \pm 0.02) \times 10^3\ M^{-1}\ cm^{-1}$ for the aquo cation and $\epsilon_1 = (5.93 \pm 0.03) \times 10^3\ M^{-1}\ cm^{-1}$ for the carboxylato complex (pH 3.3) and $K = (5.5 \pm 0.6) \times 10^2\ M^{-1}$. Subsequent stages of ligation are too slow to affect the picture under our conditions of mixing.

Kinetic traces in these buffers again feature the growth and loss of the pink intermediate, but the decay is more sudden than that for an uncatalyzed system, indicating autocatalysis (see Figure 1). Sequence 2–5 is again applicable, but here the ratio $k_2/k_4$ greatly exceeds $k_1/k_3$. In utilization of the stepwise integration procedure for this autocatalytic system,[16a] the ratio $k_2/k_4$ (as well as $k_1$ and $k_3$) was allowed to vary independently.

Refined[33] values of $k_1$, $k_3$, and $k_2/k_4$, and $\epsilon_{Cr(IV)}$ for the buffered systems are assembled in Table III. Absorbances calculated from a representative set of parameters are compared to an observed trace in Figure 1.

The ratio $k_3/k_1$ (4–5) lies close to the corresponding $k_{Cr(IV)}/k_{Cr(V)}$ ratio for reactions with U(IV) (10–29). Since the latter reductant is thought to utilize an outer-sphere route,[13] a similar mechanistic assignment for oxidations of $(Mo^V)_2$ is admissible although not required. The $Mo^VMo^{VI}$ intermediate is seen to react with Cr(V) more rapidly than with Cr(IV) ($k_2/k_4 > 1$), whereas $(Mo^V)_2$ reacts more rapidly with Cr(IV). This inversion of selectivity, which is the source of autocatalysis,[42] suggests that the $Cr^V$–$Mo^VMo^{VI}$ reaction ($k_2$) has an important inner-sphere component.[43]

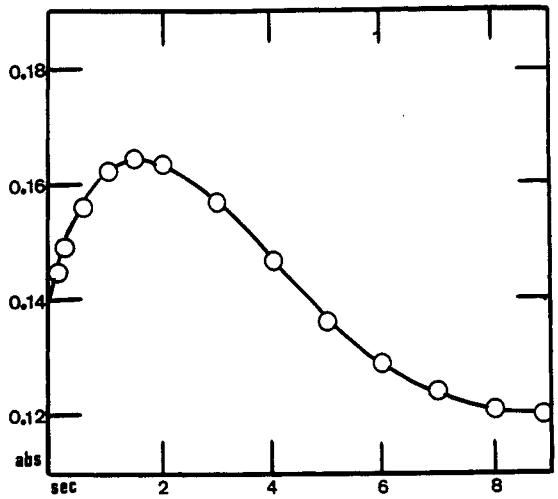


**Figure 1.** Kinetic profile at 600 nm for the reaction of the chromium(V) chelate II (7.5 × $10^{-4}$ M) with $Mo_2O_4^{2+}$ (6.0 × $10^{-3}$ M) at 19 °C. The supporting medium was 0.10 M each in 2-ethyl-2-hydroxybutanoic acid and its sodium salt and 0.60 M in $NaClO_4$; the pH was 3.28. The solid line is the experimental curve, whereas the circles represent absorbances calculated from integration of differential kinetic equations based on sequence 2–5 in the text. The parameters $k_1$ and $k_3$ were taken as 26 and 92 $M^{-1}\ s^{-1}$, and the ratio $k_2/k_4$ was taken as 3.0. Extinction coefficients used ($M^{-1}\ cm^{-1}$): Cr(III), 80; Cr(IV), 152; Cr(V), 96. Mixing time was 0.005 s; optical path length was 2.0 cm.

For steps 4 and 5 we favor outer-sphere paths. It may be argued that an inner-sphere reduction of Cr(IV) is likely to yield a binuclear $Mo^{VI}$–$Cr^{III}$ species. We find no evidence for such a complex among our products, although our experiments with $Cr(H_2O)_6^{3+}$ and $H_2MoO_4$ suggest that it should survive our conditions.

Although we perceive substantial mechanistic versatility among reductions by $(Mo^V)_2$, we remain puzzled by two questions. (1) Why is the kinetic selectivity $k_{Cr(V)}/k_{Cr(IV)}$ reversed upon ligation of $(Mo^V)_2$, and (2) how does this ligation induce an especially rapid route for reaction of the two odd-electron species, Cr(V) and $Mo^VMo^{VI}$? Answers to these questions await more detailed structural information concerning the ligated Mo(V) species in these systems.

Note finally that there is considerable variation in the extinction coefficients for the Cr(IV) intermediates formed by action of various reductants. The value for $\epsilon_{510}$ (407 $M^{-1}\ cm^{-1}$, Table I) for the present system lies close to that recorded for the $Cr^V$–$H_3PO_2$ reaction (4 × $10^2$)[44] and for reduction by hydroquinone (5 × $10^2$)[45] but is less than one-third that for the $Cr^V$–$Fe^{II}$ reaction (1.5 × $10^3$).[11] We suspect that Cr(IV) in the latter case is bound,

---

(40) Richens, S. T.; Helm, L.; Pittet, P.-A.; Merbach, A. E. *Inorg. Chim. Acta* **1987**, *132*, 85.

(41) Hinch, C. W.; Wycoff, D. E.; Murmann, R. K. *Polyhedron* **1986**, *5*, 487.

(42) Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1988**, *27*, 1620.

(43) Gould, E. S. *Inorg. Chem.* **1979**, *18*, 900.

(44) Ghosh, S. K.; Bose, R. N.; Laali, K.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 4737.

(45) Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1988**, *27*, 1620.

via carboxylate bridging, to another cationic center, i.e., that it is present principally as a $Cr^{IV}$–$Fe^{III}$ complex. Analogous dinuclear species may intervene with other cationic reductants.[46] Comparable variability in $\epsilon_{Cr(IV)}$ is encountered with anionic reductants such as thiolactate[15] and 2,3-dihydroxybenzoate.[45] In these instances Cr(IV)–carboxylate association occurs, and this is reflected in the incorporation of carboxyl groups in the resulting Cr(III) products.

**Acknowledgment.** We are grateful to Dr. S. K. Ghosh for help in computational procedures, to Dr. R. N. Bose for valuable discussions, and to Ms. Arla McPherson for technical assistance.

**Registry No.** I, 40804-49-7; [II]Na, 97042-89-2; 2-ethyl-2-hydroxybutanoic acid, 3639-21-2.

**Supplementary Material Available:** Table IV, giving stoichiometric data for the $(Mo^V)_2$–$Cr^V$ reaction, and Table V, listing reaction conditions (2 pages). Ordering information is given on any current masthead page.

---

[46] In addition, association between Cr(IV) and Cr(V) centers in solution may come into play when the latter oxidation state is a major component. When Cr(IV) is generated from Cr(V) chelate II by using a deficiency of $(Mo^V)_2$ in 0.1 M ligand acid, the rate at which Cr(IV) decays (by oxidation of ligand acid) is found to be inversely proportional to [Cr(V)] remaining. The implication here is that the active oxidant is a Cr(IV) species, formed in a preequilibrium involving dissociation of a (predominant) $Cr^{IV}$–$Cr^V$ complex.

---

Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

# Electron Transfer. 104. Reductions of Pyridinecarboxamides with Vitamin $B_{12s}$ (Cob(I)alamin)[1]

S. K. Ghosh, P. N. Balasubramanian, G. Chithambarathanu Pillai, and E. S. Gould*

*Received April 10, 1990*

Vitamin $B_{12s}$ (cob(I)alamin) is oxidized to its $Co^{II}$ analogue by pyridinecarboxamides in aqueous buffers. The amides are reduced in multiples of two units. With $B_{12s}$ in excess, the 3- and 4-$CONH_2$ substituted pyridines consume six units of $Co^I$, whereas the 2-isomer consumes nearly four. With the amide in excess, conversions are principally to a dihydro species which, in the case of nicotinamide, is predominantly a 1,6-dihydro derivative. Further partial conversion to tetrahydro compounds results in nonexponential kinetic profiles which have been treated by numerical integration methods to yield specific rates for both reaction steps. In all cases, that for reduction of the dihydro compound is greater than that for its aromatic precursor. All reactions are accelerated by $H^+$. The various observed [$H^+$] dependencies reflect partition of one or both redox partners into acidic and basic forms and, in some instances, additional contributions from paths involving extraprotonated species which are stoichiometrically minor but exceptionally reactive. The 4-$CONH_2$ amide is reduced about $10^2$ times as rapidly as the 3-$CONH_2$ under comparable conditions, a selectivity similar to that recognized for 1e reductions of these amides but different from that expected for 2e transfers, suggesting that these reactions, although net 2e changes, proceed in 1e steps with the overall rate determined by the initial transfer.

Vitamin $B_{12s}$ (cob(I)alamin, the cobalt(I) analogue of $B_{12a}$), the formal potential of which has been recorded as −0.62 V at pH 5 and −0.50 V at pH 3,[2] is one of the strongest reductants that can be readily handled in aqueous solution.[3] Moreover, it is remarkably diverse in its reactions. In reducing a variety of unsaturated organic species,[4] it functions as a 2e donor, whereas its reactions with the metal centers $Co^{III}$,[5] $Eu^{III}$,[6] $Ti^{IV}$,[6] and $V^{III}$[7] are necessarily 1e transactions. Reductions of organics have been utilized in synthetic procedures,[4a,8] and mechanistic questions have also been considered.[4b,c]

This contribution pertains to the reductions, using $B_{12s}$, of five pyridinecarboxamides, including both the physiologically important 3-$CONH_2$ derivative (niacinamide)[9] and its 4-substituted isomer, which has achieved prominence as a ligand used in fundamental redox studies elsewhere.[10] We present evidence that although these reductions involve net changes of two electrons, both electrons are not transferred in a single act.

**Table I.** Stoichiometries of the Reactions of Vitamin $B_{12s}$ (Cob(I)alamin) with Pyridinecarboxamides[a]

| amide (Py–R) | mmol of PyR × $10^4$ | mmol of $B_{12s}$ × $10^4$ | Δmmol of $B_{12s}$ × $10^4$ | $\Delta[B_{12s}]/\Delta[PyR]$ |
|---|---|---|---|---|
| 2-$CONH_2$ | 2.6 | 16.0 | 10.4 | 4.0 |
| | 4.0 | 24 | 15.3 | 3.8 |
| | 2.0 | 24 | 7.8 | 3.9 |
| 3-$CONH_2$ | 0.33 | 4.0 | 2.04 | 6.1 |
| | 0.66 | 4.0 | 4.0 | 6.1 |
| | 0.45 | 4.0 | 2.66 | 5.9 |
| 3-$CONHCH_3$ | 1.00 | 8.0 | 4.0 | 4.0 |
| | 1.50 | 8.0 | 6.0 | 4.0 |
| | 0.50 | 8.0 | 2.1 | 4.2 |
| 4-$CONH_2$[b] | 0.40 | 4.0 | 2.5 | 6.3 |
| | 0.50 | 4.0 | 3.1 | 6.2 |
| | 0.67 | 4.0 | 3.9 | 5.6 |
| 1-$CH_3$-4-$CONH_2$,[b,c] | 1.33 | 8.0 | 7.4 | 5.6 |
| | 0.80 | 8.0 | 4.6 | 5.8 |
| | 0.67 | 8.0 | 3.9 | 5.8 |

[a] Reactions were carried out in solutions buffered with 0.05 M each of glycine and its hydrochloride, unless otherwise indicated, and were monitored at 470–500 nm. [b] Faster reactions carried out in HOAc–$OAc^-$ buffer. [c] 1-Methyl-4-carbamoylpyridinium perchlorate.

---

[1] Sponsorship of this work by the National Science Foundation (Grants 8313253 and 8619472) is gratefully acknowledged.

[2] Rubinson, K. A.; Parekh, H. V.; Itabashi, E.; Mark, H. B., Jr. *Inorg. Chem.* **1983**, *22*, 458. This potential is strongly dependent on acidity at low pH but nearly independent in the pH range 5–12.

[3] By way of comparison, the strongest reductant among readily preparable hydrated metal cations is $U^{3+}$ ($E° = -0.63$ V) (Ahrland, S.; Liljenzin, J. O.; Rydberg, J. *Comprehensive Inorganic Chemistry*; Pergamon: Oxford, U.K., 1973; Vol. 5, p 519).

[4] (a) Schrauzer, G. N.; Holland, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 4060. (b) Pillai, G. C.; Reed, J. W.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 4734. (c) Pillai, G. C.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 4740.

[5] Kaufmann, E. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1977**, *99*, 7051.

[6] Pillai, G. C.; Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1988**, *27*, 1868.

[7] Pillai, G. C.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 3120.

[8] (a) Fischli, A. *Helv. Chim. Acta* **1982**, *65*, 1167, 2697. (b) Dolphin, D. *Methods Enzymol.* **1971**, *18C*, 34.

[9] See, for example: (a) York, J. L. In *Textbook of Biochemistry*; Devlin, T. M., Ed.; Wiley: New York, 1982; p 156. (b) Robinson, F. A. *The Vitamin Co-Factors of Enzyme Systems*; Pergamon: Oxford, U.K., 1966; Chapter IV.

[10] See, for example: (a) Nordmeyer, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1162. (b) Itzkowitz, M. M.; Nordmeyer, F. *Inorg. Chem.* **1975**, *14*, 2124. (c) Akhtar, M. J.; Haim, A. *Inorg. Chem.* **1988**, *27*, 1608.

0020-1669/91/1330-0487$02.50/0 © 1991 American Chemical Society