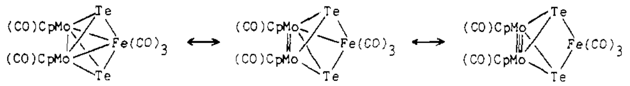
**Table III.** Crystal Data and Refinement Parameters

| | |
|---|---|
| formula | $C_{15}H_{12}FeMo_2O_3Te_2$ |
| cryst syst | monoclinic |
| space group | $P2_1/n$ |
| $a$, Å | 7.137 (1) |
| $b$, Å | 24.012 (3) |
| $c$, Å | 10.457 (3) |
| $\alpha$, deg | 90 |
| $\beta$, deg | 92.43 (2) |
| $\gamma$, deg | 90 |
| $V$, Å$^3$ | 1790.44 |
| $Z$ | 4 |
| $\rho_{calcd}$, $\rho_{obsd}$, g cm$^{-3}$ | 2.76, 2.86 |
| cryst dimens, mm | 0.04 × 0.1 × 0.12 |
| radiation | Mo K$\alpha$ |
| diffractometer | CAD-4 |
| abs coeff, cm$^{-1}$ | 53.4 |
| max, min transmission coeff | 0.7087, 0.5305 |
| $2\theta$ scan range, deg | 2.25 |
| no. of unique data | 1988 ($I > 3\sigma(I)$) |
| no. of data processed | 2682 |
| $R_F$ | 0.0315 |
| $R_{wF}$ | 0.0341 |

$Cp_2Mo_2FeE_2(CO)_x$ ($x$ = 6 or 5; E = S, Te) should be so reactive. An intriguing possibility is that such species contain a reactive multiple bond between the two molybdenum centers, i.e. eq 3.



(3)

## Experimental Section

**Materials and Methods.** The general procedures followed those described in the previous paper.[1] Reagent grade chemicals were obtained commerically. Electrochemical measurements were made by using a BAS-100 instrument and a three-electrode cell with a Pt working electrode. For these measurements $10^{-3}$ M THF solutions of the compound were prepared in a 0.1 M $Bu_4NClO_4$ solution in THF. The data reported here were obtained at a scan rate of 50 mV/s.

**Reactions of $(RCp)_2Mo_2FeTe_2(CO)_7$ with Acetylenes.** In a typical experiment $Cp_2Mo_2FeTe_2(CO)_7$ (0.301 g, 0.363 mmol) was heated at reflux in toluene (125 mL) under a vigorous $C_2H_2$ purge for 1 h. The filtered reaction mixture was reduced to one-sixth volume and diluted with an equal volume of hexane. Flash chromatography (silica gel with 7:3 $CH_2Cl_2$–hexane) of this solution yielded a yellow-green band of the acetylene complex followed by a green band (**1**). The product, 65 mg, was obtained as microcrystals by precipitation with hexane. At ~50% conversion, the yields were ~25%; longer reaction times lead to lower yields. Compound **1** did not react with acetylene even when treated with anhydrous $Me_3NO$ in refluxing THF. Anal. Calcd for $C_{15}H_{12}FeMo_2O_7Te_2$: C, 24.24; H, 1.63; Fe, 7.51. Found: C, 24.01; H, 1.69; Fe, 7.73. FABMS: *m/e* 745 ($M^+$), 719, 691, 661, 634, 613, 602, 585, 557, 520. IR (c-$C_6H_{12}$ solution): 2000 s, 1952 sh, 1946 m cm$^{-1}$. $^{13}C$ NMR ($CDCl_3$ solution): $\delta$ 218.4, 91.6 ($^1J(^1H,^{13}C)$ = 212 Hz, $^2J(^1H,^{13}C)$ = 8 Hz), 47.5 ($^1J(^1H,^{13}C) \approx$ 212 Hz, $^2J(^1H,^{13}C)$ = 8 Hz). $^1H$ NMR ($CDCl_3$ solution): $\delta$ 5.16 s (10 H), 4.37 s (2 H).

The compound $Cp_2Mo_2FeTe_2(CO)_3(PhCCH)$ was prepared similarly from **1**. Anal. Calcd for $C_{21}H_{16}FeMo_2O_7Te_2$: C, 30.79; H, 1.97; Fe, 6.78; Te, 31.15. Found: C, 30.57; H, 2.08; Fe 6.97; Te, 29.3. FABMS: *m/e* 819 ($M^+$), 791, 673, 735, 665, 633. IR (c-$C_6H_{12}$ solution): 2002 s, 1954 m, 1948 m cm$^{-1}$. $^1H$ NMR ($CDCl_3$ solution): $\delta$ 7.31 and 6.84 m (5 H, 5.14 s (10 H), 4.62 s (1 H).

The MeCp–$PhC_2H$ compound was prepared analogously but was an oil and was not obtained in analytically pure form. $^1H$ NMR ($CDCl_3$ solution): $\delta$ 7.19–6.97 m (5 H); 4.97 m, 4.91 m, 4.83 m, and 4.73 m (8 H); 4.45 s (1 H); 1.90 s (6 H).

**Table IV.** Atomic Positions

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| Te(1) | −0.0927 (1) | 0.10762 (3) | 0.6075 (1) |
| Te(2) | 0.4315 (1) | 0.17689 (3) | 0.6271 (1) |
| Mo(1) | 0.2249 (1) | 0.10841 (4) | 0.4803 (1) |
| Mo(2) | 0.2396 (1) | 0.09566 (4) | 0.7324 (1) |
| Fe | 0.0818 (2) | 0.2009 (1) | 0.6286 (1) |
| O(1) | −0.1168 (14) | 0.2178 (4) | 0.8634 (8) |
| O(2) | 0.2414 (12) | 0.3131 (4) | 0.6313 (8) |
| O(3) | −0.164 (1) | 0.2359 (5) | 0.4154 (9) |
| C(1) | 0.2309 (14) | 0.0312 (4) | 0.5888 (10) |
| C(2) | 0.406 (2) | 0.0533 (5) | 0.5932 (10) |
| C(3) | 0.239 (4) | 0.0262 (6) | 0.8849 (1) |
| C(4) | 0.421 (3) | 0.0484 (7) | 0.8883 (13) |
| C(5) | 0.404 (3) | 0.1043 (7) | 0.9305 (12) |
| C(6) | 0.220 (3) | 0.1162 (8) | 0.9512 (12) |
| C(7) | 0.112 (3) | 0.0657 (10) | 0.9258 (14) |
| C(8) | 0.184 (2) | 0.1505 (5) | 0.2778 (10) |
| C(9) | 0.071 (2) | 0.1030 (6) | 0.2773 (11) |
| C(10) | 0.193 (2) | 0.0564 (5) | 0.2923 (10) |
| C(11) | 0.384 (2) | 0.0770 (6) | 0.3036 (11) |
| C(12) | 0.373 (2) | 0.1347 (6) | 0.2943 (12) |
| C(13) | −0.038 (2) | 0.2100 (5) | 0.7728 (11) |
| C(14) | 0.186 (2) | 0.2679 (5) | 0.6338 (11) |
| C(15) | −0.068 (2) | 0.2211 (5) | 0.4971 (11) |

**X-ray Crystallography.** Preliminary X-ray photography of the black rhombic crystals showed monoclinic diffraction symmetry. The space group $P2_1/n$ was assigned on the basis of systematic absences for the $0k0$ ($k = 2n + 1$) and $h0l$ ($h + l = 2n + 1$) reflections. A suitable crystal was epoxied to a thin glass fiber and positioned on a Nonius CAD-4 diffractometer. Unit cell dimensions were derived from a least-squares fit to the setting angles of 25 reflections, obtained by using Zr-filtered Mo K$\alpha$ radiation ($\lambda$ = 0.7107 Å) (Table III). Intensity data were collected by using a variable-width, variable-speed $2\theta/\omega$ scan. there was no significant decay during the data collection, as revealed by monitoring three standard reflections for every one hundred data. Absorption corrections were applied after carefully measuring and indexing each of the ten crystal faces. Fourteen reflections were struck from the data set because of extremely uneven background counts.

The structure was readily solved by locating a trigonal-bipyramidal array of five heavy atoms on the $E$ map with the use of SHELX. Subsequent difference Fourier maps revealed the positions of the remaining eighteen nonhydrogen atoms (Table IV). No attempts were made to refine the hydrogen atom positions, although the acetylenic hydrogens were apparent in the final difference Fourier map.

**Acknowledgment.** This research was supported by the National Science Foundation. T.B.R. is a fellow of the Camille and Henry Dreyfus Foundation. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We thank Professor A. L. Rheingold for his helpful comments on the manuscript. Fast atom bombardment mass spectra were obtained in the University of Illinois Mass Spectrometry Laboratory, which is supported in part by a grant from the National Institutes of General Medical Sciences (Grant No. GM 27029).

**Registry No.** **1**, 94820-11-8; **2**, 104198-45-0; $Cp_2Mo_2FeTe_2(CO)_3(PhC_2H)$, 104198-46-1; $C_2H_2$, 74-86-2; $PhC_2H$, 536-74-3; $(MeCp)_2Mo_2FeTe_2(CO)_7$, 94820-12-9; $(MeCp)_2Mo_2FeTe_2(CO)_3(PhC_2H)$, 104198-47-2.

**Supplementary Material Available:** A table of thermal parameters (1 page); a table of structure factors (9 pages). Ordering information is given on any current masthead page.

---

Contribution from the Central Leather Research Institute,
Adyar, Madras 600 020, India

# Chelation of *cis*-Halo(oxalato)tetraamminechromium(III) Complexes: Evidence for Direct Displacement of a Coordinated Anion by Another

C. Narayanaswamy, T. Ramasami,* and D. Ramaswamy

*Received February 20, 1986*

The factors controlling substitution reactions of octahedral complexes have been extensively investigated and reviewed.[1,2]

---

(1) (a) Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *17*, 214. (b) Swaddle, T. W. *ACS Symp. Ser.* **1982**, *No. 198*, 40. (c) Swaddle, T. W. *Adv. Inorg. Bioinorg. Chem.* **1983**, *2*, 93.

**Table I.** Metal/Ligand Ratios and UV-Visible Spectral Data on Halo(oxalato)tetraamminechromium(III) Complexes, $Cr(NH_3)_4(X)(C_2O_4H)^+$, and Their Chelation Products

| complex | metal/ligand ratio[a] |  |  | $\lambda_{max}$,[b] nm |  |
|---|---|---|---|---|---|
|  | Cr/$NH_3$ | Cr/X | Cr/$C_2O_4$ |  |  |
| $Cr(NH_3)_4(Cl)(C_2O_4H)^+$ | 1/3.97 | 1/1.01 | 1/1.02 | 384 (64.4) | 516 (47) |
| $Cr(NH_3)_4(Br)(C_2O_4H)^+$ | 1/4.03 | 1/0.98 | 1/0.97 | 386 (63.4) | 519 (46.9) |
| $Cr(NH_3)_4(C_2O_4)^+$ | 1/3.96 |  | 1/1.06 | 374 (72.8) | 500 (58.2) |
| $Cr(NH_3)_3(Cl)(C_2O_4)$ | 1/2.94 | 1/1.04 | 1/0.97 | 398 (49) | 535 (44) |
| $Cr(NH_3)_3(Br)(C_2O_4)$ | 1/2.96 | 1/0.95 | 1/1.05 | 397 (46) | 534 (41) |

[a] Average of at least three determinations. [b] Numbers in parenthesis give molar absorption coefficients in $M^{-1}$ $cm^{-1}$.

**Table II.** Product Ratios, *R*, and Rate Constants, $k_{obsd}$, $k_1$, and $k_2$, for the Chelation Reactions of *cis*-$Cr(NH_3)_4(X)(C_2O_4H)^+$ (or Its Conjugate Base) When X = Cl or Br at Different $[H^+]$[a]

|  | X = Cl |  |  |  | X = Br |  |  |  |
|---|---|---|---|---|---|---|---|---|
| $10^3[H^+]$, M | *R* | $10^5k_{obsd}$, $s^{-1}$ | $10^5k_1$, $s^{-1}$ | $10^5k_2$, $s^{-1}$ | *R* | $10^5k_{obsd}$, $s^{-1}$ | $10^5k_1$, $s^{-1}$ | $10^5k_2$, $s^{-1}$ |
| 1.0 | 4.5 | 11.5 | 9.4 | 2.1 | 4.9 | 18.9 | 15.7 | 3.2 |
| 3.16 | 3.1 | 10.6 | 8.9 | 1.7 | 5.9 | 17.2 | 14.7 | 2.5 |
| 10.0 | 6.4 | 9.6 | 8.3 | 1.3 | 7.4 | 15.3 | 13.5 | 2.2 |
| 31.6 | 7.3 | 8.2 | 7.3 | 0.99 | 9.6 | 13.9 | 12.6 | 1.3 |

[a] Temperature = 50 °C; *I* = 1.0 M ($NaClO_4$).

Since major changes in the water structure are needed for reorganization of charged centers, it is generalized that a coordinated anion is not replaced by another anion directly by means of front side attack.[3] Such generalizations do not take into account other thermodynamic considerations like relative strengths of metal-ligand bonds. In order to examine the hypothesis that an anion does not displace another anion directly, complexes of the formula *cis*-halo(oxalato)tetraamminechromium(III), where halide is $Cl^-$ or $Br^-$, have now been synthesized, and the chelation of the oxalate ligand has been investigated. The chelation has to be necessarily by means of a front side attack, and generally associative pathways are believed to dominate chelation processes.[4] The relative ease of the displacement of a halide ion (to give $Cr(NH_3)_4(C_2O_4)^+$) or ammonia ligand (to yield $Cr(NH_3)_3X(C_2O_4)$) by the chelating arm of the oxalate anion has been reported here.

## Experimental Section

**Materials.** The *cis*-halo(oxalato)tetraamminechromium(III) complexes, *cis*-$Cr(NH_3)_4(X)(C_2O_4H)^+$, were prepared in solution from the corresponding *cis*-$Cr(NH_3)_4(X)(H_2O)^{2+}$ (X = Cl or Br) derivatives by means of direct anation processes.[4c] Mixtures containing oxalate buffer (0.6 M, 25 mL) at a pH of 2.5 and the complexes *cis*-$[Cr(NH_3)_4(X)(H_2O)]X_2$ (2 g) were thermostated at 50 °C for 30 min. Then the reaction mixture was cooled to 6 °C, whereupon a portion of free oxalate and (oxalato)tetraamminechromium(III), viz. $Cr(NH_3)_4(C_2O_4)^+$, separated out. The mixture was filtered and the filtrate was loaded on an ice-cooled Dowex 50W-X2 (1.5 × 25 cm) column. The elution with a sodium perchlorate–perchloric acid mixture at $[H^+]$ = 0.01–0.1 M and *I* = 0.8 M gave the desired complex free of the well-characterized $Cr(NH_3)_4(C_2O_4)^+$ as well as other nonionic products.

The starting materials *cis*-$Cr(NH_3)_4(X)(H_2O)^{2+}$ needed for the synthesis of (oxalato)tetrammine derivatives were prepared by using published methods.[5] The complexes of the formulation *cis*-$Cr(NH_3)_4(X)(C_2O_4H)^+$ were characterized in solution by means of electronic spectra as well as Cr/N, Cr/Br and Cr/$C_2O_4$ ratios. The analyses of halide, ammonia, oxalate, and ammonia contents in the complexes were carried out by using standard procedures.[6-9]

**Table III.** Rate Parameters for Halide and Ammonia Displacements in Halo(oxalato)tetramminechromium Derivatives by Various Paths[a]

| complex | reaction path: displacement of | $10^5$ × rate const, $s^{-1}$ |
|---|---|---|
| $Cr(NH_3)_4(Cl)(C_2O_4H)^+$ | $Cl^-$ | 7 ± 0.8 |
| $Cr(NH_3)_4(Cl)(C_2O_4)$ | $Cl^-$ | 10 ± 1.2 |
| $Cr(NH_3)_4(Cl)(C_2O_4H)^+$ | $NH_3$ | 0.8 ± 0.1 |
| $Cr(NH_3)_4(Cl)(C_2O_4)$ | $NH_3$ | 2.3 ± 0.4 |
| $Cr(NH_3)_4(Br)(C_2O_4H)^+$ | $Br^-$ | 12 ± 0.9 |
| $Cr(NH_3)_4(Br)(C_2O_4)$ | $Br^-$ | 16 ± 1.2 |
| $Cr(NH_3)_4(Br)(C_2O_4H)^+$ | $NH_3$ | 0.93 ± 0.12 |
| $Cr(NH_3)_4(Br)(C_2O_4)$ | $NH_3$ | 3.7 ± 0.5 |

[a] Temperature = 50 °C; *I* = 1.0 M ($NaClO_4$).

**Product Analysis.** Solutions of *cis*-$Cr(NH_3)(X)(C_2O_4H)^+$, where X = Cl or Br (50 mL, (2–5) × $10^{-3}$ M), at $[H^+]$ = 0.001–0.0316 M were thermostated at 50 °C for periods ranging from 30 min to 4 h. The solutions were then cooled to ca. 4 °C and loaded on Dowex 50W-X2 (0.8 × 12 cm long) columns. Cationic products were absorbed by the Dowex resin. The nonionic products were separated from other complexes in the reaction mixture by passing the washings of the Dowex 50W-X2 column (after the absorption of cationic species) through Dowex 1-X8 (0.8 × 8 cm) in chloride form. The resulting nonionic and two cationic species obtained after ion-exchange separations were subjected to electronic spectral measurements and analyses of Cr/N, Cr/halide and Cr/N ratios.

**Kinetic Studies.** The kinetics of the chelation reactions of *cis*-$Cr(NH_3)_4(X)(C_2O_4H)^+$, where X = Cl or Br, were carried out at 50 °C, *I* = 1.0 M ($NaClO_4$), and $[H^+]$ = 0.001–0.316 M and 395 (for $Cr(NH_3)_4(Cl)(C_2O_4H)^+$) and 393.5 nm (for $Cr(NH_3)_4(Br)(C_2O_4H)^+$. Since the reactions were slow, chelation was followed to only 2–3 half-lives in order to avoid complications from secondary processes, if any. The monitoring wavelengths 395 and 393.5 nm being isosbestic points in the spectra of $Cr(NH_3)_4(C_2O_4)^+$ and $Cr(NH_3)_3(Cl)(C_2O_4)$ and $Cr(NH_3)_4(C_2O_4)^+$ and $Cr(NH_3)_3(Br)(C_2O_4)$, respectively, the values of optical density at infinity time could be calculated and the first-order plots were linear to 70–80% completion of reaction.

## Results and Discussion

The product analysis revealed that the complexes *cis*-$Cr(NH_3)_4(X)(C_2O_4H)^+$, where X = Cl or Br, underwent chelation to yield only two products, which were identified as $Cr(NH_3)_4(C_2O_4)^+$ and $Cr(NH_3)_3(Cl)(C_2O_4)$. The spectral data and metal–ligand ratios observed for reactants and products are given in Table I. Quantitative analysis of typical product ratios $Cr(NH_3)_4(C_2O_4)/Cr(NH_3)_3(X)(C_2O_4)$, *R*, at 50 °C and $[H^+]$ = 0.001–0.0316 M gave the results presented in Table II. The

---

(2) (a) Margerum, D. W. *ACS Symp. Ser.* **1982**, *No. 198*, 3. (b) Margerum, D. W.; Cayley, G. L.; Weatherburn, D. C.; Pagenkopf, G. W. *Coordination Chemistry, Volume 2*; Martell, A. E., Ed.; ACS Monograph 174; American Chemical Society: Washington, DC, 1978; 1.

(3) Basolo, F.; Pearson, R. G. *Mechanism of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1968; p 177.

(4) (a) Nor, O.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1973**, 1232. (b) Ogino, H.; Shimura, M.; Tanaka, W. *Inorg. Chem.* **1979**, *18*, 2497. (c) Narayanaswamy, C. Ph.D. Thesis, Madras University, 1982.

(5) Hoppenjans, D. W.; Hunt, J. B. *Inorg. Chem.* **1969**, *8*, 505.

(6) Alexeyer, V. *Quantitative Analysis*; Foreign Language Publication House: Moscow, 1964; p 386.

(7) Parnas, J. K.; Wagner, R. *Biochem. Z.* **1921**, *125*, 253.

(8) Vogel, A. J. *Textbook of Quantitative Inorganic Analysis*, 4th ed., ELBS Longman: Harlow, U.K., 1978; p 366.

(9) Haupt, G. W. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1952**, *48*, 414.

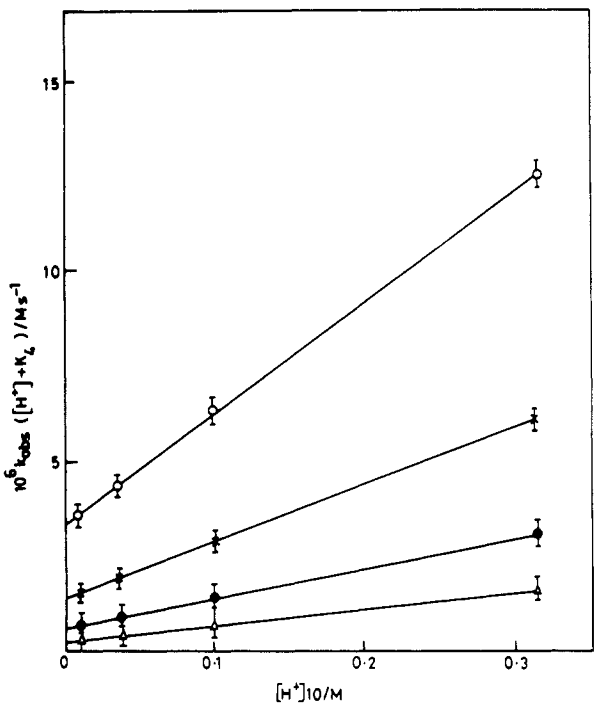


**Figure 1.** Acid dependence of observed rate constants, $k_{obsd}$, for the chelation reaction of *cis*-chloro(oxalato)tetraamminechromium(III) at various temperatures. $T$ (°C): (○) 60; (×) 55; (●) 50; (△) 45.

chelation process may be treated as parallel reactions under these conditions as shown in eq 1 and 2.

$$Cr(NH_3)_4(X)(C_2O_4H)^+ \xrightarrow{k_1} Cr(NH_3)_4(C_2O_4)^+ + X^- + H^+ \quad (1)$$

$$Cr(NH_3)_4(X)(C_2O_4H)^+ \xrightarrow{k_2} Cr(NH_3)_3(X)(C_2O_4) + NH_4^+ \quad (2)$$

The rate constant, $k_{obsd}$, for the first-order decay of $Cr(NH_3)_4(X)(C_2O_4H)^+$ under any condition is therefore given by eq 3 and the product ratio, $R$, by $k_1/k_2$. The values of $k_1$ and

$$k_{obsd} = k_1 + k_2 \quad (3)$$

$k_2$ may be obtained from $k_{obsd}$ by using the experimental values of $R$, and the values of $k_{obsd}$, $k_1$, and $k_2$ at 50 °C for various [H$^+$] are also listed in Table II.

It is evident from Tables II and III that, under all conditions, halide substitution during chelation is the more favored process. Although the formation of $Cr(NH_3)_4(C_2O_4)^+$ does involve the displacement of chloride, the intermediacy of any aquo derivative like $Cr(NH_3)_4\,(H_2O)(C_2O_4H)^{2+}$ (**1**) needs to be ruled out only through other scavenging experiments. This was achieved by using nitrite as a scavenger for any aquo derivative formed during chelation at [H$^+$] = (3–5) × $10^{-4}$ M. Nitrite is known to undergo substitution with metal–oxygen bond retention and N–O bond breaking.[10] Therefore, if aquo compounds like $Cr(NH_3)_4(H_2O)(C_2O_4H)^{2+}$ or $Cr(NH_3)_4(H_2O)(C_2O_4)^+$ were formed, nitrito oxalato derivatives with charge-transfer bands would be expected. There is no evidence for the formation of such nitrito derivatives, and the rate of release of Cl$^-$ paralleled the values of $k_1$ obtained in our study. Therefore the values of $k_1$ and $k_2$ may be assigned to the rate of direct displacement of a halide by the chelating arm of oxalate. The coordinated oxalate anions are known to exhibit protonation behavior in the [H$^+$] region of our study.[11,12] The values of $k_{obsd}$,$k_1$, and $k_2$ exhibited an [H$^+$] dependence typical of equilibrium 4, influencing rate constants for chelation process.

$$Cr(NH_3)_4(X)(C_2O_4H)^+ \overset{K_4}{\rightleftharpoons} Cr(NH_3)_4(X)(C_2O_4) + H^+ \quad (4)$$

The plots of $k_{obsd}$([H$^+$] + $K_4$) against [H$^+$] were linear and are shown in Figure 1 for the chloride system. Similar results were also observed when ([H$^+$] + $K_4$)$k_1$ or ([H$^+$] + $K_4$)$k_2$ was plotted against [H$^+$] when $K_4$ = 4.9 × $10^{-3}$ M at 50 °C and X = Cl or Br. Statistical analysis of $k_1$ and $k_2$ using the rate laws of the form shown in eq 5, run on an IBM 370 computer and Los Almos

$$k_1 \text{ or } k_2 = \frac{a[H^+] + bK_4}{[H^+] + K_4} \quad (5)$$

program, gave the values of $a$ and $b$. The values of $a$ and $b$ correspond to the first-order rate constants for the halide as well as ammonia displacements at 50 °C from dissociated and undissociated oxalato tetraammine derivatives and are listed in Table III. The similarity of rate constants observed in this study for the reaction of protonated and dissociated forms is as reported earlier for other related systems.[11]

It is evident from Table III that direct substitution of halide by the dissociated arm of oxalate does occur in preference to the substitution of neutral ammonia ligand, and the rate constants for the displacement of Cl$^-$ and Br$^-$ by carboxylates in the oxalato derivatives studied in case of oxalato-*O,O′* derivatives are nearly the same. The activation parameters obtained for various pathways show that ammonia displacement has a higher enthalpy of activation $\Delta H$ (ca. 2.5–5.0 kcal mol$^{-1}$ higher than that for halide displacement).[12] Therefore entropy advantages that anions may enjoy against their direct substitution by another anion do not seem to override the enthalpic components to substitution reactivity, even when associate pathways occur.

**Registry No.** *cis*-$Cr(NH_3)_4Cl(C_2O_4H)^+$, 104130-06-5; *cis*-$Cr(NH_3)_4Br(C_2O_4H)^+$, 104130-07-6; $Cl_2$, 7782-50-5; $Br_2$, 7726-95-6; $NH_3$, 7664-41-7.

---

[10] (a) Basolo, F.; Hammaker, *Inorg. Chem.* **1962**, *1*, 1. (b) Matts, T. C.; Moore, P. *J. Chem. Soc. A* **1971**, 1632. (c) The reactions of aquo complexes like $Cr(H_2O)_6^{3+}$ with nitrite have been shown to be relatively rapid.

[11] (a) Ramasami, T.; Wharton, R. K.; Sykes, A. G. *Inorg. Chem.* **1975**, *14*, 359. (b) Andrade, C.; Taube, H. *Inorg. Chem.* **1966**, *5*, 1087.

[12] Narayanaswamy, C.; Ramasami, T.; Ramaswamy, D., unpublished results.

---

Contribution from the Science Research Laboratory,
3M Corporate Research Laboratories,
St. Paul, Minnesota 55144

# Ternary Rhodium–Tungsten–Sulfur Clusters

A. R. Siedle* and W. B. Gleason

*Received March 25, 1986*

We have previously reported the syntheses and structures of clusters and nets derived from the dithiotungstate(2–), $WO_2S_2^{2-}$, and tetrathiotungstate(2–), $WS_4^{2-}$, ions and metals of the copper group (Cu, Ag, Au). Exemplary are $[(Ph_2PMe)Au]_2WS_4$,[1] in which gold bridges alternate edges of the $WS_4$ tetrahedron to form a netlike structure; $([(Ph_2PMe)Ag]_2WS_4)_2$[2] and $([(p\text{-tolyl})_3PCu]_2WOS_3)_2$,[3] which contain 12-atom cages formed by dimerization of units in which two metals bridge adjacent edges on the thiometalate tetrahedra; and $(Et_3P)_2PtWS_4$,[4] in which

---

[1] Huffman, J. C.; Roth, R. S.; Siedle, A. R. *J. Am. Chem. Soc.* **1976**, *98*, 4340.

[2] Stalick, J. K.; Siedle, A. R.; Mighell, A. D.; Hubbard, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 2832.

[3] Doherty, R.; Hubbard, C. R.; Mighell, A. D.; Siedle, A. R. *Inorg. Chem.* **1979**, *18*, 2991.

[4] Siedle, A. R.; Hubbard, C. R.; Mighell, A. D.; Stewart, J. D.; Doherty, R. *Inorg. Chim. Acta* **1980**, *38*, 197.