Inorg. Chem. **1984**, *23*, 2053–2058 **2053**

Contribution from the Department of Chemistry,
University of Minnesota, Minneapolis, Minnesota 55455

Electrochemical Oxidation of Tetrakis(1,8-diisocyanomenthane)dirhodium(2+) in Nonaqueous Solutions: A Net Two-Electron Oxidation Process

MATTHEW R. RHODES and KENT R. MANN*

Received August 24, 1983

The electrochemical behavior of $[Rh_2(dimen)_4]^{2+}$ (dimen = 1,8-diisocyanomenthane) in the nonaqueous solvents CH_3CN and CH_2Cl_2 has been investigated by cyclic voltammetry, potential-step methods, and double-potential-step chronocoulometry. The appearance of the cyclic voltammogram is dramatically influenced by relatively weak ionic aggregation of the $[Rh_2(dimen)_4]^{2+}$ species with the supporting anion and by the strong complexation of the 2e oxidized species $[Rh_2(dimen)_4]^{4+}$ formed at the electrode. The formal 2e couple $E^{\circ\prime}{}_{4+/2+}$ in CH_2Cl_2 solutions in the presence of ClO_4^- is +0.46 V vs. Ag/AgCl. The relative stabilities of the 2e oxidized species $[Rh_2(dimen)_4(X)_2]^{2+}$ ($X = PF_6^-$, ClO_4^-, and Cl^-) are estimated. The Cl^- and ClO_4^- complexes are respectively 46.6 and 4.6 kcal/mol more stable than the corresponding PF_6^- complex. The differences in the behavior of the $[Rh_2(dimen)_4]^{2+}$ system studied here are compared to the previously studied $[Rh_2(bridge)_4]^{2+}$ system.

Introduction

Since the initial communication[1] in 1977 which reported the photochemical production of hydrogen gas from aqueous solutions of $[Rh_2(bridge)_4]_2^{6+}$ (bridge = 1,3-diisocyanopropane), polynuclear rhodium isocyanide complexes have been investigated extensively with synthetic,[2,3] spectroscopic,[4-15] and structural[16-19] techniques. In contrast, electrochemical methods have been utilized to study the properties of polynuclear rhodium isocyanide complexes in only one report.[20,21] The low solubility of the compounds and the complexity of their electrochemical response have been major factors in the slow development of this aspect of their chemistry.

The original intent of our work in this area was to determine structure/reactivity relationships for the electrochemical response of a series of rhodium isocyanide complexes and to investigate compounds that are capable of net 2e transfers. However, the initial binuclear complex selected for study, $[Rh_2(dimen)_4]^{2+}$ (dimen = 1,8-diisocyanomenthane), exhibited such a rich electrochemical response that it forms the exclusive subject of this report.

Early in the course of our investigations, we were surprised by changes in the appearance of the cyclic voltammograms of this complex with changes in solvent (CH_2Cl_2, CH_3CN) and supporting anion (ClO_4^-, PF_6^-). Additionally, the presence of millimolar concentrations of chloride ion in these solvent/electrolyte systems also influences the cyclic voltammogram of the $[Rh_2(dimen)_4]^{2+}$ cation.

Cyclic voltammetric and chronocoulometric studies indicate the observed changes in the cyclic voltammogram are due to ionic aggregation of $[Rh_2(dimen)_4]^{2+}$ with the supporting anion and to changes in the stability of $[Rh_2(dimen)_4]^{4+}$ as a result of strong axial anion complexation.

Experimental Section

General Considerations. IR spectra were recorded on a Perkin-Elmer 297 infrared spectrophotometer. UV–visible spectra were recorded on a Cary 17D spectrophotometer. Elemental analyses were determined by Galbraith Microanalytical Laboratories, Knoxville, TN. $[Rh(COD)Cl]_2$[22] (COD = 1,4-cyclooctadiene) and 1,8-diisocyanomenthane (dimen)[23] were prepared by standard methods.

Synthesis of Compounds. $[Rh_2(dimen)_4](PF_6)_2$. Synthesis of this compound has been reported previously without experimental detail.[8] To a solution of 1.03 g of $[Rh(COD)Cl]_2$ in 25 mL of CH_2Cl_2 was added 1.80 g of dimen. After complete mixing, the solvent was removed on a rotary evaporator and the residue was dissolved in CH_3OH. The product precipitated as a yellow-orange solid on addition of 0.75 g of NH_4PF_6 dissolved in CH_3OH. Recrystallization from dichloromethane/hexane afforded the product in 91.9% yield (2.42 g).

$[Rh_2(dimen)_4Cl_2](PF_6)_2$. A 100.6-mg amount of $[Rh_2(dimen)_4](PF_6)_2$ was dissolved in 10 mL of CH_3CN. A solution of Cl_2 in CH_3CN was added. The color of the solution changed from intense orange to pale yellow. The solvent was then removed on a rotary evaporator. The yellow product was obtained in 96.6% yield (102.7 mg) after purification from CH_2Cl_2/Et_2O. Anal. Calcd: C, 43.41; H, 5.43; N, 8.44;, Cl, 5.35. Found: C, 42.80; H, 5.73; N, 8.57; Cl, 5.01. IR (Nujol mull): $\nu(CN) = 2206\ cm^{-1}$.

Electrochemistry. Equipment. All electrochemical experiments except double-potential-step chronocoulometry were performed with

---

[1] Mann, K. R.; Lewis, N. S.; Miskowski, V. M.; Erwin, D. K.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, *99*, 5525.

[2] Lewis, N. S.; Mann, K. R.; Gordon, J. G., II; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 7464.

[3] Lewis, N. S.; Mann, K. R.; Gordon, J. G., II; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 7461.

[4] Miskowski, V. M.; Mann, K. R.; Gray, H. B.; Milder, S. J.; Hammond, G. S.; Ryason, P. R. *J. Am. Chem. Soc.* **1979**, *101*, 4383.

[5] Gray, H. B.; Miskowski, V. M.; Milder, S. J.; Smith, T. P.; Maverick, A. W.; Buhr, J. D.; Gladfelter, W. L.; Sigal, I. S.; Mann, K. R. *Fundam. Res. Homogeneous Catal.* **1979**, *3*, 819.

[6] Gray, H. B.; Mann, K. R.; Lewis, N. S.; Thich, J. A.; Richman, R. M. *Adv. Chem. Ser.* **1978**, *No. 168*, 44.

[7] Miskowski, V. M.; Nobinger, G. L.; Kliger, K. S.; Hammond, G. S.; Lewis, N. S. Mann, K. R.; Gray, H. B. *J. Am. Chem. Soc.* **1978**, *100*, 485.

[8] Mann, K. R.; Gray, H. B. *Adv. Chem. Ser.* **1979**, *173*, 226.

[9] Sigal, I. S.; Mann, K. R.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 7252.

[10] Gray, H. B.; Maverick, A. W. *Science (Washington, D.C.)* **1981**, *214*, 1201.

[11] Milder, S. J.; Goldbeck, R. A.; Kliger, D. S.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 6761.

[12] Rice, S. F.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 1593.

[13] Dallinger, R. F.; Miskowski, V. M.; Gray, H. B.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1595.

[14] Kawakami, K.; Okajima, M.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2327.

[15] Yaneff, P. V.; Powell, J. *J. Organomet. Chem.* **1979**, *179*, 101.

[16] Mann, K. R.; Thich, J. A.; Bell, R. A.; Coyle, C. L.; Gray, H. B. *Inorg. Chem.* **1980**, *19*, 2462.

[17] Mann, K. R.; Bell, R. A.; Gray, H. B. *Inorg. Chem.* **1979**, *18*, 2671.

[18] Mann, K. R.; DiPierro, M. J.; Gill, T. P. *J. Am. Chem. Soc.* **1980**, *102*, 3965.

[19] Mann, K. R. *Cryst. Struct. Commun.* **1981**, *10*, 451.

[20] Mann, K. R.; Parkinson, B. A. *Inorg. Chem.* **1981**, *20*, 1921.

[21] Rh_2^{n+} binuclear species with other ligands have been previously investigated by electrochemical techniques: (a) Das, K.; Kadish, K. M.; Bear, J. L. *Inorg. Chem.* **1978**, *17*, 930. (b) Drago, R. S.; Tanner, S. P.; Richman, R. M.; Long, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 2897. (c) Tikkanen, W. R.; Binamira-Soriaga, E.; Kaska, W. C.; Ford, P. C. *Inorg. Chem.* **1983**, *22*, 1147.

[22] Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 4735.

[23] Weber, W. P.; Gokel, G. W.; Ugi, I. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 530.

0020-1669/84/1323-2053$01.50/0

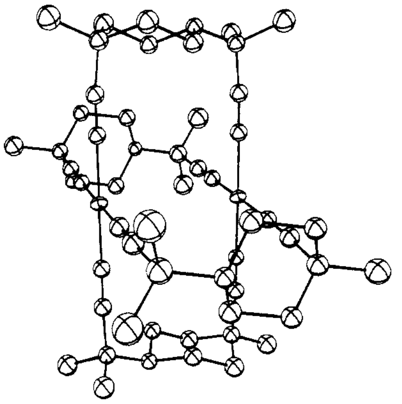

Figure 1. Ball and stick diagram of the $[Rh_2(dimen)_4]^{2+}$ cation.

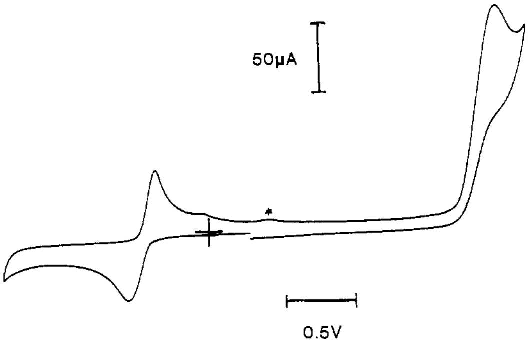

Figure 2. Cyclic voltammogram exhibited by a 0.5 mM solution of $[Rh_2(dimen)_4](PF_6)_2$ in 0.1 M TBAP/CH_2Cl_2. The scan rate is 50 mV/s. The peak labeled with an asterisk is due to a trace Cl^- impurity.

a Princeton Applied Research (PAR) Model 170 electrochemical system. The double-potential-step experiments used a PAR Model 175 universal programmer, a PAR Model 173 potentiostat equipped with a PAR Model 179 digital coulometer, and a Biomation Model 805 waveform recorder. Charge transients obtained on this system were displayed on a Tektronix type 535 oscilloscope before data storage in a Heathkit H89 microcomputer interfaced to the waveform recorder.

Measurements. Electrochemical measurements were performed at 20 ± 2 °C with use of a normal three-electrode configuration consisting of a highly polished glassy-carbon-disk working electrode (typical area ~0.4 cm^2), a platinum-spiral auxillary electrode, and a Ag/AgCl reference electrode containing 1.0 M KCl. The working compartment of the electrochemical cell was separated from the auxiliary compartment by a fritted-glass salt bridge and from the reference compartment by a modified Luggin capillary. All three compartments contained a 0.1 M solution of the supporting electrolyte. The solvents acetonitrile and dichloromethane (Burdick and Jackson) and the supporting electrolytes tetrabutylammonium perchlorate (TBAP) and tetrabutylammonium hexafluorophosphate (TBAH) (Southwestern Analytical Chemicals, Inc.) and benzyltriethylammonium chloride (Aldrich Chemical Co.) were used without further purification.

Electrolyte solutions were prepared and stored over 80–200 mesh activated alumina (Fisher Scientific Co.) prior to use in the experiments. In all cases working solutions were prepared by recording background cyclic voltammograms of 30.0 mL of the electrolyte solution before addition of the depolarizer. The working compartment of the cell was bubbled with solvent-saturated argon to deaerate the solution.

For some experiments, an accurate determination of the effective surface area of the working electrode was required. In those cases the electrode area was calibrated[24] from charge transient data obtained in potential-step experiments and from the known diffusion coefficient of ferrocene in CH_3CN.[25]

Ferrocene was used as an internal standard to correct for variations in the junction potentials[26] with different combinations of solvent and supporting electrolyte. This correction employed an $E°'$ value for the $FeCp_2^+/FeCp_2$ couple of 0.400 V vs. NHE,[27] which was assumed to be independent of the medium. All potentials for the Rh-containing compounds are reported vs. corrected AgCl/Ag(aq). The potential of the $FeCp_2^+/FeCp_2$ couple was measured under the various experimental conditions employed: CH_2Cl_2/TBAH, $E°' = 0.450$ V; CH_2Cl_2/TBAP, $E°' = 0.500$ V; CH_3CN/TBAH, $E°' = 0.425$ V; CH_3CN/TBAP, $E°' = 0.435$ V. No IR compensation was used in any of the electrochemical studies.[26]

Double-Potential-Step Chronocoulometry. A general description of double-potential-step chronocoulometry has been given previously.[28,29] Values of the charge ($Q(\tau)$ and $Q(2\tau)$) were collected for various step times (τ). Four determinations were made for each τ value measured. The ratio $Q_r = [Q(\tau) - Q(2\tau)]/Q(\tau)$ was calculated for each determination and averaged (supplementary table I).

The homogeneous rate constant k for the rate-determining step (see the text) was determined by comparing plots of Q_r vs. log ($Ck\tau$) (where C = bulk concentration of $[Rh_2(dimen)_4]^{2+}$) with theoretical curves.[29] The value of k was taken as the value that gave the best visual fit to the experimental values of Q_r.

Results and Discussion

The $[Rh_2(dimen)_4]^{2+}$ cation has the familiar windmill type structure[19] common to other diisocyanide complexes of Rh(I)[16] but contains a long solid-state Rh–Rh distance (4.48 Å), has a relatively rigid "ligand backbone", and is sterically hindered at the ends by the methyl groups (see Figure 1). The PF_6^- salt of the complex is very soluble in CH_2Cl_2 and CH_3CN in the presence of 0.1 M TBAP or TBAH, making it ideal for electrochemical studies.

The cyclic voltammogram exhibited by a 0.5 mM solution of $[Rh_2(dimen)_4](PF_6)_2$ in 0.1 M TBAP/CH_2Cl_2 is shown in Figure 2. There are two main features of interest. The first is a multielectron, irreversible reduction located at $E_{p,c} = -2.10$ V.[30,31] This reduction was not investigated further. The second feature is a quasi-reversible wave[32] at low concentrations (0.1 mM) and slow scan rates (2 mV/s) centered at +0.46 V. Attempts to synthesize this oxidation product and determine n by bulk electrolysis ($E = +1.2$ V) under these conditions led to passivation of the electrode.[33] As an alternate method of evaluating n, $nD^{1/2}$ was measured as 4.28×10^{-3} cm/$s^{1/2}$ from an i vs. $t^{-1/2}$ plot of data obtained in a potential-step experiment ($E_i = 0.0$ V to $E_f = +1.2$ V, $[[Rh_2(dimen)_4]^{2+}] = 0.1$ mM) performed with a freshly polished electrode. Estimation of the diffusion coefficient of $[Rh_2(dimen)_4]^{2+}$ in CH_2Cl_2 from the Stokes-Einstein equation gave $D = 1.01 \times 10^{-5}$ cm^2/s. This calculation[34] used the molecular volume of the $[Rh_2(dimen)_4]^{2+}$ ion to calculate an effective radius (r) of 5.24 Å for the ion. The n value calculated from this estimate of D and the product $nD^{1/2}$ is 1.35 e/$[Rh_2(dimen)_4]^{2+}$ unit. Because this estimation of D does not take into account ionic aggregation, solvation, or deviations from spherical geometry of the $[Rh_2(dimen)_4]^{2+}$ ion, the Stokes–

---

(24) Adams, R. N. "Electrochemisty at Solid Electrodes"; Marcel Dekker: New York, 1969; p 124.

(25) Kuwana, T.; Bublitz, D. E.; Hoh, G. *J. Am. Chem. Soc.* **1960**, *82*, 5811.

(26) Gagné, R. R.; Koval, C. A.; Kisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

(27) Koepp, H. M.; Wendt, H.; Strehlow, H. Z. *Z. Elektrochem.* **1960**, *64*, 483.

(28) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980, pp 199–206.

(29) Hanafey, M. K.; Scott, R. L.; Ridgeway, T. H.; Reilley, C. N. *Anal. Chem.* **1978**, *50*, 116.

(30) With use of 4.58×10^{-6} cm^2 s^{-1} for the diffusion coefficient of $[Rh_2(dimen)_4]^{2+}$ (vide infra in the text) a peak-shape analysis[31] of the totally irreversible reduction yields 3.8 electrons transferred per cation.

(31) Sawyer, D. T.; Roberts, J. L. "Experimental Electrochemistry for chemists"; Wiley: New York, 1974; pp 338–339.

(32) $E_{p,c} - E_{p,a} \approx 60$ mV under these conditions.

(33) Examination by eye of the glassy-carbon-disk electrodes after the bulk electrolysis revealed an apparently passivating film of material on the surface of the electrode. Platinum working electrodes were similarly passivated.

(34) Our calculation follows those of Meyer et al.: Nagle, J. K.; Dressick, W. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 3993.

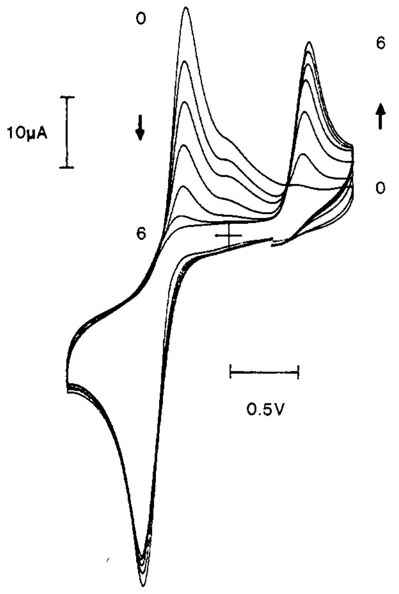

Figure 3. Cyclic voltammograms (scan rate 50 mV/s) of 0.5 mM $[Rh_2(dimen)_4](PF_6)_2$ in 0.1 M TBAP/CH_2Cl_2 as a function of added Cl^-: (0) $[Cl^-]$ = 0.0 mM; (1) $[Cl^-]$ = 0.125 mM; (2) $[Cl^-]$ = 0.250 mM; (3) $[Cl^-]$ = 0.375 mM; (4) $[Cl^-]$ = 0.500 mM; (5) $[Cl^-]$ = 0.625 mM; (6) $[Cl^-]$ = 0.750 mM.

Einstein value for D should be considered an upper limit and $n = 1.35$ e is a lower limit. Assuming an effective n value of $n = 2$, D is calculated as 4.58×10^{-6} cm²/s.

The observation of apparent 2e transfers in CV and potential-step experiments can result either from a heterogeneous, two-electron-transfer electrode reaction or from a heterogeneous, one-electron-transfer electrode reaction followed by a homogeneous solution disproportionation reaction. The equations describing these processes are given in parts a and b, respectively of Scheme I. We have not obtained data that can differentiate between these two mechanisms; however, if the disproportionation mechanism obtains, the rate constant k_{disp} is required by data in hand to be large ($k_{disp} > 1.5 \times 10^6$ M^{-1} s^{-1}).

Scheme I

(a) $$[Rh_2(dimen)_4]^{2+} \xrightarrow{k_{het},\ 2e^-} [Rh_2(dimen)_4]^{4+} + 2e^- \qquad (1a)$$

(b) $$[Rh_2(dimen)_4]^{2+} \xrightarrow{k_{het},\ e^-} [Rh_2(dimen)_4]^{3+} + 1e^- \qquad (1b)$$

$$2[Rh_2(dimen)_4]^{3+} \xrightarrow{k_{disp}} [Rh_2(dimen)_4]^{2+} + [Rh_2(dimen)_4]^{4+} \qquad (2)$$

To confirm that the final electrochemical products in this system are indeed due to net 2e oxidation, the isolation and characterization of an oxidation product that could be directly related to the electrochemical experiments was of crucial importance. This situation was realized for a Cl^--containing oxidation product.

Effect of Added Cl^-. Figure 3 displays a series of cyclic voltammograms in which the concentration of Cl^- (benzyltriethylammonium chloride addition) is systematically varied in a 0.5 mM $[Rh_2(dimen)_4]^{2+}$ solution 0.1 M in (TBA)ClO_4/CH_2Cl_2. As the Cl^- concentration is increased, the peaks due to both the oxidative process and the coupled reductive process exhibit changes. The changes observed in the oxidation peak are relatively minor: a cathodic shift of a few millivolts in the peak potential and a slight broadening of the peak. Both changes are consistent with a slight decrease in the heterogeneous electron-transfer rate when Cl^- is present in the solution. More importantly, *no current enhancement for $i_{p,a}$ is observed*[35] with the increase in the Cl^- ion concentration.

The effect of added Cl^- on the coupled reduction peak is more dramatic. After slightly more than 1 equiv of Cl^- has been added, the original peak at +0.32 V disappears completely and a new reduction peak is present in the cyclic voltammogram at −0.59 V; at intermediate $[Cl^-]$ ($0 < [Cl^-] < 1$ equiv) both peaks are present. At a given $[Cl^-]$, variation of scan rate (10–200 mV/s) does not produce any appreciable change in the relative currents corresponding to these reductions. The interconversion rate of the initially formed oxidized species to the Cl^--containing species is very fast compared with the CV time scale.

The synthesis of the oxidized Cl^--containing species responsible for the new reduction peak was accomplished via the chemical oxidation of the $[Rh_2(dimen)_4]^{2+}$ cation in the presence of Cl^-. The reaction of $[Rh_2(dimen)_4](PF_6)_2$ with Cl_2 in CH_3CN solution occurs on mixing and is essentially quantitative. The elemental analysis, UV–vis spectrum, and IR spectrum of the resulting yellow compound indicate conclusively that the compound is the *two*-electron-oxidized product $[Rh_2(dimen)_4Cl_2](PF_6)_2$, which contains a Rh(II)–Rh(II) single bond and two Cl^- ions occupying the axial sites of the cation.[36]

Cyclic voltammograms of a CH_2Cl_2 solution of this oxidized compound exhiibit the reduction at $E_{p,c} = -0.59$ V, but the oxidation peak at $E_{p,a} = +0.64$ V is present *only after the potential is scanned to potentials cathodic of this reduction peak*. This result indicates the electrode processes (the oxidation of $[Rh_2(dimen)_4]^{2+}$ and the reduction of $[Rh_2(dimen)_4Cl_2]^{2+}$) in Cl^--containing solutions are coupled to each other via homogeneous chemical reaction(s).

$[Rh_2(dimen)_4Cl_2]^{2+}$ was confirmed to be the electroactive species responsible for the reduction peak at −0.59 V rather than $[Rh_2(dimen)_4(Cl)(ClO_4)]^{2+}$ by investigating the kinetic properties of $[Rh_2(dimen)_4Cl_2]^{2+}$. The addition of Ag(I) ions to a solution of $[Rh_2(dimen)_4Cl_2]^{2+}$ does not give a AgCl precipitate after several days. The $[Rh_2(dimen)_4Cl_2]^{2+}$ cation is inert to substitution in the electrochemical solutions and is the electroactive species responsible for the $E_{p,c} = -0.59$ V reduction.

The isolation and characterization of the 2e oxidation product of the electrode reaction in the presence of Cl^- ($[Rh_2(dimen)_4Cl_2]^{2+}$) strongly implies that 1e oxidized, odd-electron species ($[Rh_2(dimen)_4]^{3+}$) are unstable as is the $[Rh_2(bridge)_4]^{3+}$ species. However, in the present case, the odd-electron species either undergo an additional 1e heterogeneous electrode oxidation or disproportionate rather than dimerize. Of immediate interest is the lower limit of the possible disproportionation reaction rate relative to the CV time scale. Following the analysis of Saveant et al.,[35] the effective n value measured from the peak current in CV experiments increases from 1.0 to a limiting value of 1.78 as the disproportionation rate is increased (slower scan rates, higher concentrations). The nearly constant value of the product $n^{3/2}D^{1/2}$ in CV experiments as a function of concentration ($[[Rh_2(dimen)_4]^{2+}]$ = 0.1–0.5 mM), the absence of an anodic current enhancement at $E_{p,a}$ when Cl^- ion is added to CV solutions, and the precise identification of the Cl^--containing

---

(35) Mastragostino, M.; Nadjo, L.; Saveant, J. M. *Electrochim. Acta* **1978**, *13*, 721.

(36) The $[Rh_2(dimen)_4Cl_2]^{2+}$ complex exhibits an intense transition with λ_{max} = 337 nm ($\epsilon_{max} = 5.5 \times 10^4$ M^{-1} cm^{-1}). We assign this transition by analogy to the $[Rh_2(bridge)_4Cl_2]^{2+}$ λ_{max} = 338 nm ($\epsilon_{max} = 5.6 \times 10^4$ M^{-1} cm^{-1}) complex as the $\sigma \rightarrow \sigma^*$ transition of the Rh_2^{4+} unit. The presence of this transition is inconsistent with an encapsulated anion similar to those found in Ni(II) complexes of the dimen ligand (Gladfelter, W. L.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 5909).

Table I[a]

solvent/electrolyte[b]	$E_{p,a}$, V	$E_{p,c}$, V
CH_2Cl_2/TBAP	+0.64	+0.32
CH_2Cl_2/TBAH	+0.75	+0.42
CH_3CN/TBAP	+0.80	−0.28
CH_3CN/TBAH	+1.02	−0.30

[a] Potentials are reported vs. corrected AgCl/Ag: scan rate = 50 mV/s; [$[Rh_2(dimen)_4]^{2+}$] = 0.5 mM. [b] 0.1 M electrolyte.

species as the 2e oxidized product conclusively indicate that the rate of reaction 1a or 2 is fast on the CV time scale.[37]

Before a detailed mechanism is proposed for the formation of $[Rh_2(dimen)_4Cl_2]^{2+}$ under electrochemical conditions, the effects of ionic aggregation and complexation on the CV experiments in the absence of Cl^- will be addressed.

Medium Effects on the Cyclic Voltammogram of $[Rh_2(dimen)_4]^{2+}$ in the Absence of Cl^-. The data at 0.1 mM [$[Rh_2(dimen)_4]^{2+}$] and slow scan rates (2 mV/s) in CH_2Cl_2/(TBA)ClO_4 solution yield an estimate of the $E^{\circ\prime}{}_{4+/2+}$ potential (formally a 2e process) of +0.46 V. Data (Table I, Figure 4) are given for the quasi-reversible wave in CH_3CN/(TBA)ClO_4, CH_3CN/(TBA)PF_6, CH_2Cl_2/(TBA)ClO_4, and CH_2Cl_2/(TBA)PF_6 at 0.5 mM $[Rh_2(dimen)_4]^{2+}$ concentration. The solvent and supporting electrolyte significantly affect the peak potentials ($E_{p,a}$ and $E_{p,c}$) observed in the cyclic voltammograms of $[Rh_2(dimen)_4]^{2+}$. Only stability changes of $[Rh_2(dimen)_4]^{2+}$ and $[Rh_2(dimen)_4]^{4+}$ caused by ionic aggregation and complexation affect the peak potentials because the concentration of the odd-electron, radical species ($[Rh_2(dimen)_4]^{3+}$) is effectively zero at the electrode at all potentials at which it might be generated.[35]

Oxidation Peak. Changes in the stability of $[Rh_2(dimen)_4]^{2+}$ determine the shift in the potential of the oxidation peak, $E_{p,a}$. The effect of medium changes on $E_{p,a}$ is relatively small (~0.38 V full range) and is systematic, with $E_{p,a}$ in CH_3CN greater than $E_{p,a}$ in CH_2Cl_2 for both counterions; $E_{p,a}$ in the presence of PF_6^- is greater than $E_{p,a}$ in the presence of ClO_4^- for both solvents. The order and magnitude of the observed shifts in $E_{p,a}$ are consistent with changes in the predominant species in the solutions, due to changes in the extent of ionic association.

For $[Rh_2(dimen)_4]^{2+}$, no changes in λ_{max} or ϵ_{max} for the lowest ${}^1A_{1g} \rightarrow {}^1A_{2u}$ absorption[8] at 423 nm are observed with changes in solvent, counterion, or counterion concentration. Apparently interactions of $[Rh_2(dimen)_4]^{2+}$ with the medium are weak and an electrostatic model (ion pairing) is sufficient to describe the ionic aggregation equilibria involving this ion. Relevant equilibria are summarized in Scheme II.

Scheme II. Equilibria Involving $[Rh_2(dimen)_4]^{2+}$

$$[Rh_2(dimen)_4]^{2+} + X^- \overset{K_1^{2+}}{\rightleftharpoons} ([Rh_2(dimen)_4]^{2+},X^-)^+ \quad (3)$$

$$([Rh_2(dimen)_4]^{2+},X^-)^+ + X^- \overset{K_2^{2+}}{\rightleftharpoons} ([Rh_2(dimen)_4]^{2+},2X^-) \quad (4)$$

The ionic association constants for equilibria 3 and 4 in Scheme II are expected to be larger in the low dielectric solvent CH_2Cl_2 relative to those in the more polar CH_3CN.[38,39] The predominant species present in each solvent/electrolyte combination cannot be determined from these electrochemical experiments, but previous studies of ionic aggregation suggest the ion trio ($[Rh_2(dimen)_4]^{2+}$,$2X^-$) is the dominant species in CH_2Cl_2 solutions while the ion pair ($[Rh_2(dimen)_4]^{2+}$,X^-)$^+$ is expected to dominate in CH_3CN solutions.

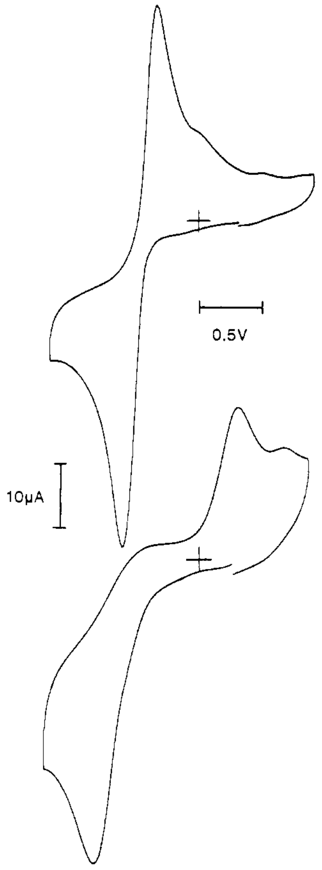

Figure 4. Cyclic voltammograms exhibited by a 0.5 mM solution of $[Rh_2(dimen)_4](PF_6)_2$ in 0.1 M TBAP/CH_2Cl_2 (upper curve) and 0.1 M TBAP/CH_3CN (lower curve). The scan rate is 50 mV/s in both cases.

Reduction Peak. The potential of the reduction peak $E_{p,c}$ is determined by the stability of $[Rh_2(dimen)_4]^{4+}$. Large shifts occur for the coupled reduction peak with solvent change ($E_{p,c}$ = −0.28 V in CH_3CN/TBAP and $E_{p,c}$ = +0.32 V in CH_2Cl_2/TBAP solutions; see Figure 4). These shifts are of larger magnitude (~600 vs. ~300 mV) than the oxidation peak shifts: stability changes of $[Rh_2(dimen)_4]^{4+}$ with medium are of larger magnitude than those of $[Rh_2(dimen)_4]^{2+}$. In CH_2Cl_2 solution, these stability changes are likely to involve strong anion complexation in the two open, axial binding sites of the $[Rh_2(dimen)_4]^{4+}$ ion. In CH_3CN soltuions, CH_3CN coordination is required to explain the large shift in $E_{p,c}$ and the independence of $E_{p,c}$ on the nature of X^-. Relevant complexation equilibria for CH_2Cl_2 solutions are given in Scheme III. It has been established previously that $[Rh_2(dimen)_4Cl_2]^{2+}$ has high kinetic and thermodynamic stability. Binding constants for covalent complexes of the weaker ligands[40] PF_6^- and ClO_4^- present in the CV solutions are expected to be less stable, with $K^{4+}(ClO_4^-) > K^{4+}(PF_6^-)$ and $K_1^{4+}(X^-) > K_2^{4+}(X^-)$. The complexed, oxidized ion will also undergo ionic aggregation to an extent comparable to that for the reduced form. The complexity of the situation (two complexation equilibria and two ionic aggregation equilibria) precludes a detailed analysis of the results, but the CH_2Cl_2 data indicate the stability of

---

(37) With use of the appropriate equation from ref 36 ($\lambda_d = k_{disp}C^\circ RT/n\nu F$) and an estimate for the onset of an observable decrease in λ_d (the kinetic parameter) of ~1×10^4, C° = 0.5mM, and ν = 0.002 V/s, a lower limit of 1.5×10^6 M^{-1} s^{-1} is calculated for k_{disp}.

(38) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(39) (a) Boggess, R. K.; Zatko, D. A. *J. Chem. Educ.* **1975**, *10*, 649. (b) Popovych, O.; Tomkins, R. P. T. "Nonaqueous Solution Chemistry"; Wiley: New York, 1981; pp 264–286. (c) Janz, G. J.; Tomkins, R. P. T. "Nonaqueous Electrolytes Handbook; Academic Press: New York, 1972; Vol. I.

(40) Mayfield, H. G.; Bull, W. E. *J. Chem. Soc. A* **1971**, 2279.

the complexed ions $[Rh_2(dimen)_4X_2]^{2+}$ increases in the order $PF_6^- < ClO_4^- < Cl^-$, with the ClO_4^- complex about 4.6 kcal/mol more stable than the PF_6^- complex and the Cl^- complex 46.6 kcal/mol more stable than the PF_6^- complex.[41] The data for CH_3CN solutions are more difficult to interpret because CH_3CN is a viable ligand for the $[Rh_2(dimen)_4]^{4+}$ ion. In this case, it is likely that at least one of the binding sites is occupied by CH_3CN rather than the weakly coordinating ClO_4^- or PF_6^- anions.

Scheme III.
Complexation Equilibria Involving $[Rh_2(dimen)_4]^{4+}$

$$[Rh_2(dimen)_4]^{4+} + X^- \overset{K_1^{4+}}{\rightleftharpoons} ([Rh_2(dimen)_4]^{4+},X^-)^{3+} \qquad (5)$$

$$([Rh_2(dimen)_4]^{4+},X^-)^{3+} + X^- \overset{K_2^{4+}}{\rightleftharpoons} ([Rh_2(dimen)_4]^{4+},2X^-)^{2+} \qquad (6)$$

$$X^- = PF_6^- \text{ or } ClO_4^-$$

Proposed Mechanism for the Formation of $[Rh_2(dimen)_4Cl_2]^{2+}$ in CH_2Cl_2 Solutions. A proposed mechanism for the formation of $[Rh_2(dimen)_4Cl_2]^{2+}$ under electrochemical conditions in CH_2Cl_2 solution is given in Scheme IV. The oxidation product $[Rh_2(dimen)_4(ClO_4)_2]^{2+}$ is formed at the electrode either by the direct 2e oxidation of $([Rh_2(dimen)_4]^{2+},2ClO_4^-)$ or via the disproportionation of the odd-electron $([Rh_2(dimen)_4ClO_4]^{2+},ClO_4^-)^+$ species.

Scheme IV

$$([Rh_2(dimen)_4]^{2+},2ClO_4^-) \xrightarrow{k_{het},\ 2e^-} [Rh_2(dimen)_4(ClO_4)_2]^{2+} + 2e^- \qquad (7a)$$

or

$$([Rh_2(dimen)_4]^{2+},2ClO_4^-) \xrightarrow{k_{het},\ 1e^-} ([Rh_2(dimen)_4]^{3+},2ClO_4^-)^+ + e^- \qquad (7b)$$

$$2([Rh_2(dimen)_4]^{3+},2ClO_4^-)^+ \xrightarrow{k_{disp}} [Rh_2(dimen)_4(ClO_4)_2]^{2+} + ([Rh_2(dimen)_4{}^{2+},2ClO_4^-)] \qquad (8)$$

followed by

$$[Rh_2(dimen)_4(ClO_4)_2]^{2+} + Cl^- \xrightarrow{k_{subs1}} [Rh_2(dimen)_4(Cl)(ClO_4)]^{2+} + ClO_4^- \qquad (9)$$

$$[Rh_2(dimen)_4(Cl)(ClO_4)]^{2+} + Cl \xrightarrow{k_{subs2}} [Rh_2(dimen)_4Cl_2]^{2+} + ClO_4^- \qquad (10)$$

In either case, qualitative cyclic voltammetric data indicate the rate-limiting step for the formation of the final product, $[Rh_2(dimen)_4Cl_2]^{2+}$, must be either reaction 9 or 10 (ligand substitution reactions at the axial positions of the $[Rh_2(dimen)_4]^{4+}$ ion). Quantitative data that could be used to derive the value of k for the rate-limiting step (either (9) or (10)) were not obtained by cyclic voltammetry; instead, data collected under purely diffusion-limited conditions (i.e. double-potential-step chronocoulometry[28,29]) were utilized to test Scheme IV.

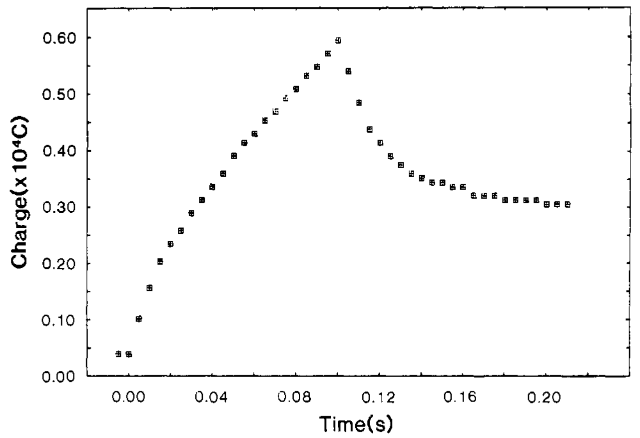

Figure 5. Typical double-potential-step charge transient produced by pulsing a solution of 0.5 mM $[Rh_2(dimen)_4](PF_6)_2$ and 0.7 mM benzyltriethylammonium chloride in 0.1 M TBAP/CH_2Cl_2 with a 0.1-s potential step from E = 0.1 V to E = +1.2 V and back.

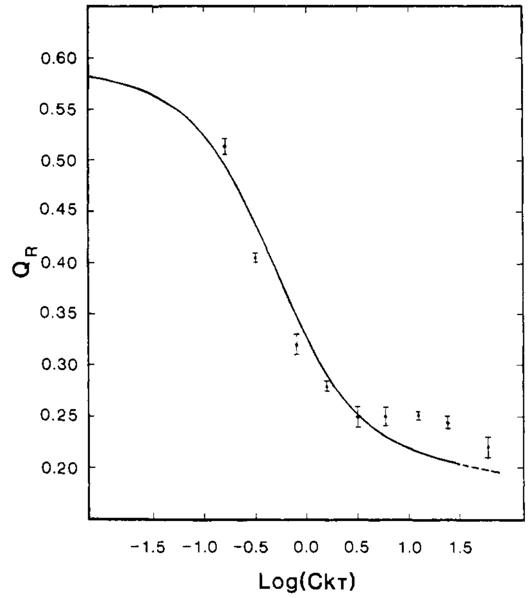

Figure 6. Plot of Q_r vs. log ($Ck\tau$) for experimental data (points with error bars) and theoretical curve with $k_{subs2} = 1.12 \times 10^4\ M^{-1}\ s^{-1}$ (solid line).

Solutions 0.5 mM in $[Rh_2(dimen)_4]^{2+}$ and 0.7 mM in Cl^- were subjected to square wave potential steps from +0.1 to +1.2 V and back for varying lengths of time (τ). Each trial produces a charge transient similiar to the one shown in Figure 5. The data are manipulated to yield a plot of $Q_r = [Q(\tau) - Q(2\tau)]/Q(\tau)$ vs. log ($Ck\tau$), where $Q(\tau)$ and $Q(2\tau)$ are the charges passed at times τ and 2τ and C is the initial concentration of the electrogenerated reagent species. Comparison of the experimental Q_r vs. log ($Ck\tau$) plot with theoretical response curves (Figure 6) available from the literature[29] allows a feasibility test of the mechanism and an estimation of the rate constant k for the rate-limiting chemical step. As expected, the theoretical curves that correspond to k_{disp} (eq 8) as the rate-limiting step give poor agreement with the data. Similarly, theoretical curves that utilize k_{subs1} as the rate-limiting step also give poor agreement. However, the data are consistent with the theoretical curve appropriate for k_{subs2} as the rate-limiting step with $[Cl^-]/[[Rh_2(dimen)_4(Cl)(ClO_4)]^{2+}] = 0.4$. This curve is appropriate if eq 9 lies essentially to the right. The value for k_{subs2} that gives a good visual fit to the experimental data is $(1.12 \pm 0.7) \times 10^4\ M^{-1}\ s^{-1}$.

---

[41] The ΔG's are calculated by utilizing the shift in the reduction peak potentials as a measure of the shift in $E°$ for the $E°'_{4+/2+}$ potentials. n is assumed to be 2 for these calculations. The data enable a rough estimate of 15 kcal/mol to be made for the Rh(II)–Cl bond; for comparison, the Rh(I)–Cl bond dissociation energy in $Rh_2(CO)_4Cl_2$ has been measured to be 24 kcal/mol while the Rh(III)–Cl bond dissociation energy in $RhCl_3$ is 43 kcal/mol (Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71).

Summary and Conclusions

The electrochemical response of $[Rh_2(dimen)_4]^{2+}$ has been studied by cyclic voltammetry, potential-step methods, and double-potential-step chronocoulometry. The appearance of the CV is dramatically influenced by relatively weak ionic aggregation of the $[Rh_2(dimen)_4]^{2+}$ species and the strong complexation of the 2e oxidized species $[Rh_2(dimen)_4]^{4+}$ formed at the electrode. The potential odd-electron intermediate ($[Rh_2(dimen)_4]^{3+}$) is quite unstable. It either is oxidized further at the electrode or undergoes rapid disproportionation. This behavior is in contrast with the behavior of $[Rh_2(bridge)_4]^{3+}$, which has previously been found to dimerize at the diffusion limit to form the stable $[Rh_2(bridge)_4]_2^{6+}$ ion.[4,5,8]

The observed differences in the behavior of the bridge and dimen systems are intriguing, because they must involve the interplay of several factors: differences in the Rh–Rh bond length of the $[Rh_2(L)_4]^{3+}$ complexes, the changes in stability caused by axial complexation, and steric restraints in the dimen system along the Rh–Rh bond axis which might preclude dimerization to the $[Rh_2(L)_4]_2^{6+}$ species. The observed propensity of the $[Rh_2(dimen)_4]^{2+}$ system to undergo net 2e jumps in oxidation state indicates that it may have importance in solar energy storage schemes. Studies designed to test the viability of this idea are currently in progress.

Acknowledgment. M.R.R. gratefully acknowledges the National Science Foundation for a fellowship. In addition we also wish to thank Barbara Moriarity and Prof. John Evans for several very helpful discussions and for the use of the equipment needed for the double-potential-step experiments. This research was supported in part by a grant from the DOE Corrosion Center.

Registry No. $[Rh_2(dimen)_4](PF_6)_2$, 72478-06-9; $[Rh_2(dimen)_4Cl_2](PF_6)_2$, 90269-63-9; $[Rh_2(dimen)_4]^{2+}$, 72478-05-8; $[Rh_2(dimen)_4Cl_2]^{2+}$, 90269-62-8; $[Rh_2(dimen)_4(ClO_4)_2]^{2+}$, 90269-64-0; $[Rh_2(dimen)_4]^{4+}$, 90269-65-1; $[Rh_2(dimen)_4(PF_6)_2]^{2+}$, 90269-66-2; Rh, 7440-16-6; Cl_2, 7782-50-5; benzyltriethylammonium chloride, 56-37-1.

Supplementary Material Available: A listing of Q_r ratios for double-potential-step chronocoulometry (1 page). Ordering information is given on any current masthead page.

Contribution from Rocketdyne, A Division of
Rockwell International, Canoga Park, California 91304

Coordinatively Saturated Fluoro Cations. Oxidative Fluorination Reactions with KrF^+ Salts and PtF_6

KARL O. CHRISTE,* WILLIAM W. WILSON, and RICHARD D. WILSON

Received August 24, 1983

The usefulness of KrF^+ salts and PtF_6 as oxidative fluorinators for the syntheses of the coordinatively saturated complex fluoro cations NF_4^+, ClF_6^+, and BrF_6^+ was studied. The syntheses of NF_4SbF_6, NF_4AsF_6, NF_4BF_4, and $NF_4TiF_5{\cdot}nTiF_4$ from KrF_2–Lewis acid adducts and NF_3 were investigated under different reaction conditions. The fluorination of NF_3 by $KrF^+SbF_6^-$ in HF solution was found to proceed quantitatively at temperatures as low as −31 °C, indicating an ionic two-electron oxidation mechanism. An improved synthesis of $KrF^+MF_6^-$ (M = As, Sb), Raman data and solubilities in HF, and the existence of a $Kr_2F_3^+{\cdot}nKrF_2BF_4^-$ adduct in HF at −40 °C are reported. Attempts to fluorinate OF_2, CF_3NF_2, and ClF_4O^- with KrF^+ salts were unsuccessful. Whereas KrF^+ is capable of oxidizing NF_3, ClF_5, and BrF_5 to the corresponding complex fluoro cations, PtF_6 was shown to be capable of oxidizing only NF_3 and ClF_5. Since the yield and purity of the NF_4^+ fluoroplatinate salts obtained in this manner were low, NF_4PtF_6 was also prepared from NF_3, F_2, and PtF_6 at elevated temperature and pressure. General aspects of the formation mechanisms of coordinatively saturated complex fluoro cations are discussed briefly.

Introduction

The preparation of coordinatively saturated complex fluoro cations presents a great challenge to the synthetic chemist. The nonexistence of the corresponding parent molecules preempts the normally facile cation formation by a simple F^- abstraction from a parent molecule, and an F^+ addition to a lower fluoride is ruled out by the fact that fluorine is the most electronegative element and therefore F^+ cannot be generated by chemical means.[1] In view of these difficulties it is not surprising that at the present time only three coordinatively saturated fluoro cations, NF_4^+,[2,3] ClF_6^+,[4,5] and BrF_6^+,[6] are known to exist. In addition to their challenge to the synthetic chemist, the formation mechanism of these cations represents an intriguing and as yet unsolved puzzle.[7]

These problems were complicated by the facts that each of the three known coordinatively saturated fluoro cations had been prepared by a different method[2-6] and that these methods could not readily be transferred from one cation to another. The purpose of this study was to examine whether the synthesis of each coordinatively saturated fluoro cation is indeed limited to a specific method and whether these methods possess any commonalties.

Experimental Section

Apparatus. Volatile materials used in this work were handled in a stainless steel–Teflon FEP vacuum line. The line and other hardware used were well passivated with ClF_3 and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry-nitrogen atmosphere of a glovebox. Metathetical reactions and solubility measurements were carried out in HF solution with use of an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter.[8]

Infrared spectra were recorded in the range 4000–200 cm⁻¹ on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl windows in an

---

(1) Christe, K. O.; Wilson, W. W.; Curtis, E. C. *Inorg. Chem.* **1983**, *22*, 3056.

(2) Christe, K. O.; Guertin, J. P.; Pavlath, A. E. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 83.

(3) Tolberg, W. E.; Rewick, R. T.; Stringham, R. S.; Hill, M. E. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 79.

(4) Roberto, F. Q. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 737.

(5) Christe, K. O. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 741.

(6) Gillespie, R. J.; Schrobilgen, G. J. *J. Chem. Soc., Chem. Commun.* **1974**, 90; *Inorg. Chem.* **1974**, *13*, 1230.

(7) Christe, K. O.; Wilson, R. D.; Goldberg, I. B. *Inorg. Chem.* **1979**, *18*, 2572 and references cited therein.

(8) Christe, K. O.; Schack, C. J.; Wilson, R. D. *Inorg. Chem.* **1977**, *16*, 849.

0020-1669/84/1323-2058$01.50/0 © 1984 American Chemical Society