rameters of the CTD–catechol complex relative to the other complexes may signal such an activation, which affords a substrate molecule capable of reacting with dioxygen directly. That such a mechanism is chemically reasonable is supported by recent observations of iron(III)-catalyzed cleavage of catechols in chemical systems.[32,33]

Acknowledgment. This work was supported by the National Institutes of Health (Grant GM 22701-10, E.M.; Grant GM-33162, L.Q.). L.Q. is an Alfred P. Sloan Research Fellow (1982–1986) and an NIH Research Career Development Awardee (1982–1987). We thank Dr. P. Nizin for collecting the Fe(salen)BzO data.

---

(32) White, L. S.; Nilsson, P. V.; Pignolet, L. H.; Que, L., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 8312–8313.

(33) Weller, M. G.; Weser, U. *J. Am. Chem. Soc.* **1982**, *104*, 3752–3754.

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, and Institut für Radiochemie, Technische Universität München, 8046 Garching, West Germany

Rates of Oxidation of Selected Actinides by Cl_2^- [†]

Christoph Lierse,[‡] James C. Sullivan,*[§] and Klaus H. Schmidt[§]

Received September 26, 1986

The Cl_2^- radical produced by pulse radiolysis of aqueous sodium chloride solutions oxidizes U(V), Np(V), Pu(III), and Am(III). The respective rates ($M^{-1}\ s^{-1}$) are $(6.5 \pm 2) \times 10^8$, $(2.38 \pm 0.10) \times 10^6$, $(4.8 \pm 0.4) \times 10^7$, and $(3.2 \pm 0.4) \times 10^5$. The mechanism for the oxidation of U(V) and Np(V) is discussed in terms of the Marcus theory. There is an unexpected linear free energy correlation with the measured rate parameters in the oxidation of U(III), Ti(III), Pu(III), and Am(III).

The pulse radiolysis studies of actinide ions in aqueous solutions[1] have been concerned, predominantly, with the reactions of the primary radicals e_{aq}^- and OH. The salient exception is the study of the reduction of the carbonate radical ion[2] by the carbonato complexes of U(V), Np(V), and Pu(V). That study, as well as the present, was motivated in part to determine if a linear free energy relationship provides an adequate summary of the data over the ranges $\Delta G°$ and log k associated with such reactions. To that end, the present study examines the rates of oxidation of trivalent and pentavalent actinide ions in sodium chloride solutions by the Cl_2^- radical[3] produced by pulse radiolysis techniques. An additional aspect of the present investigation is the attempt to delineate feasible mechanisms for the disappearance of Cl_2^- since the mechanisms[4] of such reactions have not been completely elucidated.

Experimental Section

A stock solution of NaCl (Suprapure, Merck Co., No. 6406) was prepared by the dissolution of weighed quantities of the salt in triple-distilled water. Stock solutions of HCl and NaOH were prepared by dilution of concentrated reagent grade solutions and standardized by conventional techniques. The U(VI) stock solution was prepared by dissolution of a weighed quantity of NBS U_3O_8. The ^{237}Np(V) stock solutions were prepared by dissolution of freshly precipitated neptunium(V) hydroxide and assayed spectrophotometrically by using the peak at 980 nm ($\epsilon = 404\ M^{-1}\ cm^{-1}$). The ^{242}Pu(III) stock solution was prepared by electrolytic reduction of Pu(VI) at a Pt electrode and assayed at 560 nm ($\epsilon = 38\ M^{-1}\ cm^{-1}$). The ^{243}Am(III) solutions were freshly prepared immediately prior to the pulse radiolysis studies (after precipitation as the hydroxide and subsequent washes with triply distilled water) and standardized spectrophotometrically at 503 nm ($\epsilon = 450\ M^{-1}\ cm^{-1}$).

The U(VI) and Np(V) solutions were adjusted to the proper pH by the previously described[5] syringe technique by adding appropriate quantities of HCl or NaOH. The pH of the Pu(III) and Am(III) solutions was adjusted by removing H^+ electrochemically in a special device shown in Figure 1. For all pH measurements, a ROSS electrode (Orion Co.) with 3 N NaCl as filling solution was used.

Pulse radiolysis was carried out with a beam of 15 MeV electrons at 4–40-ns pulse length. Absorption spectra of the transient species, generated by irradiation of the solutions with single pulses of high-energy electrons, were obtained by the streak camera–tv scanning method described previously.[6] The irradiation procedure and dose measurements were essentially as described earlier.[7] Some of the rate data were obtained by photomultiplier techniques, where the output was digitized in a Biomation 8100 transient recorder and stored in a LSI 11/23 computer. The digital data were then transferred over a local area network to a VAX 11/780 computer, where the data were analyzed.[8] In some cases, a kinetic model program[9] was used to simulate the optical transient, and the simulated signal was compared with the experimental curve.

Results

A. $U(V) + Cl_2^- \rightarrow U(VI) + 2Cl^-$. Since U(V) in solution is not stable, it was produced in situ by reduction of U(VI) by the hydrated electron. We irradiated a He-saturated solution of 10^{-2} M $UO_2(ClO_4)_2$ containing 1 M NaCl, at pH 3, with a pulse of electrons. The following sequence of reactions then occurs:

$$H_2O \rightsquigarrow e_{aq}^-, H, OH \qquad (0)$$

$$e_{aq}^- + UO_2^{2+} \rightarrow UO_2^+ \qquad (1)$$

$$e_{aq}^- + H^+ \rightarrow H \qquad (2)$$

$$OH + Cl^- \rightleftarrows ClOH^- \qquad (3)$$

$$ClOH^- + H^+ \rightleftarrows Cl + H_2O \qquad (4)$$

$$Cl + Cl^- \rightleftarrows Cl_2^- \qquad (5)$$

$$Cl_2^- + UO_2^+ \rightarrow UO_2^{2+} + 2Cl^- \qquad (6)$$

$$Cl_2^- + H \rightarrow H^+ + 2Cl^- \qquad (7)$$

$$Cl_2^- + Cl_2^- \rightarrow Cl_3^- + Cl^- \qquad (8)$$

$$H + H \rightarrow H_2 \qquad (9)$$

At its absorption peak at 340 nm, Cl_2^- is the only strongly ab-

---

[†] Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, U.S. DOE, under Contract No. W-31-109-ENG-38.

[‡] Technische Universität München.

[§] Argonne National Laboratory.

(1) See for example: Sullivan, J. C.; Gordon, S.; Cohen, D.; Mulac, W. A.; Schmidt, K. H. *J. Phys. Chem.* **1976**, *80*, 1684.

(2) Mulac, W. A.; Gordon, S.; Schmidt, K. H.; Wester, D.; Sullivan, J. C. *Inorg. Chem.* **1984**, *23*, 1639.

(3) Jayson, G. G.; Parsons, B. J.; Swallow, A. J. *J. Chem. Soc., Faraday Trans. 1* **1973**, *169*, 1597.

(4) Golub, D.; Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1985**, 641.

(5) Hart, E. J.; Anbar, M. *The Hydrated Electron*; Wiley-Interscience: New York, 1970.

(6) Schmidt, K. H.; Gordon, S.; Mulac, W. A. *Rev. Sci. Instrum.* **1976**, *47*, 356. Schmidt, K. H.; Gordon, S. *Rev. Sci. Instrum.* **1979**, *50*, 1656.

(7) Gordon, S.; Schmidt, K. H.; Hart, E. J. *J. Phys. Chem.* **1977**, *81*, 104.

(8) The nonlinear least-squares fitting program used for rate parameter determination was written by Charles D. Jonah, Chemistry Division, Argonne National Laboratory.

(9) Schmidt, K. H. *Argonne Natl. Lab.*, [Rep.] *ANL* **1966**, *ANL-7199*; **1970**, *ANL-7693*. These programs were modernized and adapted to the VAX 11/780 in 1986.

0020-1669/87/1326-1408$01.50/0 © 1987 American Chemical Society

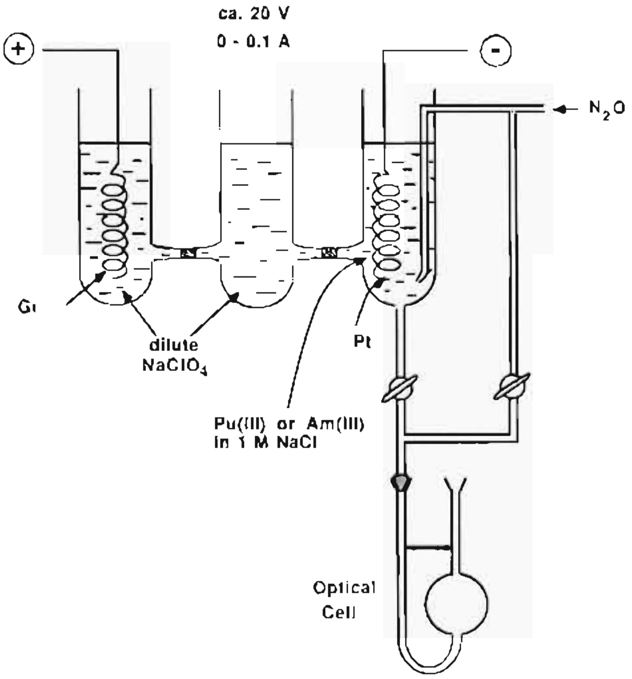

Figure 1. Electrolytic cell used for adjusting the pH of the Pu(III) and Am(III) solutions.

sorbing species in the system. Since the published values of k_8 and $\epsilon(Cl_2^-, 340\ nm)$ vary over a wide range,[10c] we first determined these values under our experimental conditions by irradiating a N_2O-saturated solution of 1 M NaCl at pH 3. N_2O converts e_{aq}^- into OH

$$e_{aq}^- + N_2O \rightarrow N_2 + OH + OH^- \qquad (10)$$

thus greatly reducing the importance of reactions 2, 7, and 9. We obtained $k_8 = (2.25 \pm 0.1) \times 10^9\ M^{-1}\ s^{-1}$ and $\epsilon(Cl_2^-, 340\ nm) = 8100\ M^{-1}\ cm^{-1}$. After this, we determined k_7 using the same solution but saturated with He. For all other rate constants, sufficiently accurate literature values[10] were available. The above determinations were made by means of the kinetic modeling program, and the unknown parameters were varied until one consistent set of parameters produced a fit for both "blank" solutions. We obtained $k_7 = (8.0 \pm 1.2) \times 10^9\ M^{-1}\ s^{-1}$. This compares well with a literature value[11] of $k_7 = (7 \pm 1) \times 10^9\ M^{-1}\ s^{-1}$.

Our evaluation of k_6 is illustrated by Figure 2. The experimental decay curve A lies between the model curves B ($k_6 = 0$) and C ($k_6 = 7.5 \times 10^8\ M^{-1}\ s^{-1}$). From these and additional curves, we interpolate $k_6 = (6.5 \pm 2) \times 10^8\ M^{-1}\ s^{-1}$.

B. $Np(V) + Cl_2^- \rightarrow Np(VI) + 2Cl^-$. Dioxoneptunium(V) is the phenomenologically stable oxidation state in aqueous solutions. Therefore, it was feasible to study the reaction

$$Np(V) + Cl_2^- \rightarrow Np(VI) + 2Cl^- \qquad (11)$$

in 1 M NaCl, at pH 3, for initial concentrations [Np(V)] = 0.001, 0.0113, and 0.114 M. Since the decrease in absorbance at 340 nm could adequately be described by a concurrent (pseudo-) first- and second-order decay (of Cl_2^-), the pseudo-first-order rate ($k^{(1)}$) of reaction 11 for each Np(V) concentration was determined by a combined first- and second-order computer fit with the second-order component, which corresponds to reaction 8, fixed. The respective values of the pseudo-first-order rate parameters $k^{(1)}$ (s^{-1}) were as follows for initial concentrations of Np(V) (M) 0.001, 0.0223, and 0.114 (two measurements for each): 7.67×10^3, 7.65×10^3; 3.09×10^4, 3.07×10^4; 2.77×10^5, 2.75×10^5. The second-order rate parameter for reaction 11 was then determined as the slope of the least-squares best straight line through a plot of $k^{(1)}$ vs. [Np(V)], resulting in a value of $k_{11} = (2.38 \pm 0.10) \times 10^6\ M^{-1}\ s^{-1}$.

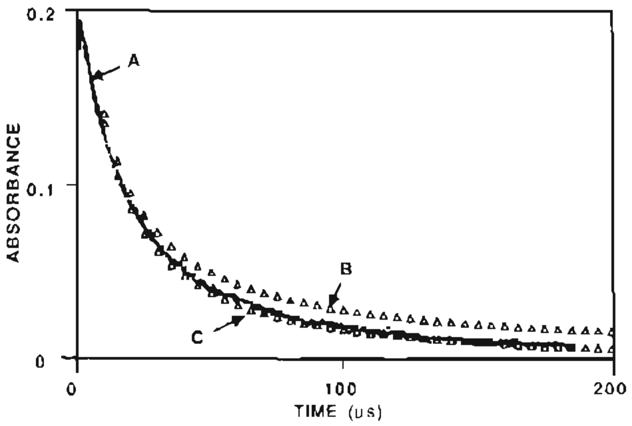

Figure 2. Decay of the absorption at 340 nm (Cl_2^-): (A) experimental curve; (B) curve calculated for $k(Cl_2 + U(V)) = 0$; (C) curve calculated for $K(Cl_2^- + U(V)) = 7.5 \times 10^8\ M^{-1}\ s^{-1}$.

C. $Pu(III) + Cl_2^- \rightarrow Pu(IV) + 2Cl^-$. The trivalent Pu ion is a hydrated species in aqueous solutions with eight molecules of water in the primary coordination sphere. Pu(III) is stable with respect to oxidation by normal concentrations of dissolved oxygen at pH values ≤2. Solutions of 0.001 and 0.01 M Pu(III), 1 M in NaCl, N_2O saturated, were irradiated with 3.6–9 krd of electron pulses and the resulting transients monitored over the wavelength range of 250–450 nm. From the decay of the absorption at 340 nm, the variation of the pseudo-first-order rate parameters as a function of [Pu(III)] resulted in a calculated value of $k(Cl_2^- + Pu(III)) = (4.8 \pm 0.4) \times 10^7\ M^{-1}\ s^{-1}$.

D. $Am(III) + Cl_2^- \rightarrow Am(IV) + 2Cl^-$. The aquo americium(III) ion is the thermodynamically stable oxidation state in aqueous solutions. Solutions 0, 0.01, and 0.1 M in Am(III), 1 M in NaCl, N_2O saturated, were irradiated with doses from 0.7 to 9 krd and the resulting transient absorption spectra monitored from 250 to 450 nm. The change in absorptivity with time at 340 nm disappeared via a pseudo-first-order process. The respective values were ($10^4\ s^{-1}$) 2.98, 3.18, 6.67, and 5.64 for initial concentrations of 0, 0.01, and 0.1 M (two independent duplicate experiments). From these values, a second-order rate parameter of $(3.2 \pm 0.4) \times 10^5\ M^{-1}\ s^{-1}$ was calculated.

Discussion

The formal potential for the Np(VI/V) couple in 1 M HCl[12] is 1.14 V. From the measured rates[18a] a value of $3.5 \times 10^2\ M^{-1}\ s^{-1}$ was calculated[18b] for the Np(VI/V) exchange in 1 M chloride. These data and the value of 2.09 V for the $Cl_2^-/2Cl^-$ couple[13] are used to calculate an apparent self-exchange rate for this couple of $k_{22} = 1 \times 10^{-6}\ M^{-1}\ s^{-1}$ from the Marcus cross relation. The potential for the U(VI/V) couple is ca. 0.06 V, and if one assumes that the self-exchange rate for U(VI/V) is the same order of magnitude as that of the Np couple, a value of $k_6 = 10^{15}\ M^{-1}\ s^{-1}$ is estimated. It is therefore evident that an outer-sphere electron-transfer mechanism in terms of the cross relation is not a satisfactory interpretation of these results. This could be caused by operating in a region of large $\Delta G°$ values where the ΔG^* vs.

---

(10) (a) Natl. *Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1973**, *NSRDS-NBS 43*, 67. (b) *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1977**, *NSRDS-NBS 59*, 122. (c) *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1979**, *NSRDS-NBS 65*, 62. (d) *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1975**, *NSRDS-NBS 51*, 56.

(11) Naravatnam, S.; Parsons, B. J.; Swallow, A. J. *Radiat. Phys. Chem.* **1980**, *15*, 159.

(12) Hindman, J.; Magnuson, L.; Lachapelle, T. *J. Am. Chem. Soc.* **1949**, *71*, 687.

(13) Jayson, G. G.; Parsons, B. T.; Swallow, A. T. *J. Chem. Soc., Faraday Trans. 1* **1975**, *69*, 1597.

(14) Martinat, L.; Fuger, J. In *Standard Potentials in Aqueous Solution*; Bard, A. J., Parsons, R., Jordan, S., Eds.; Marcel Dekker: New York, 1985; pp 663–664.

(15) Schwarz, H. A.; Dodson, R. W. *J. Phys. Chem.* **1984**, *88*, 3643.

(16) Gordon, S.; Mulac, W. A.; Schmidt, K. H.; Sjoblom, R. K.; Sullivan, J. C. *Inorg. Chem.* **1978**, *17*, 294.

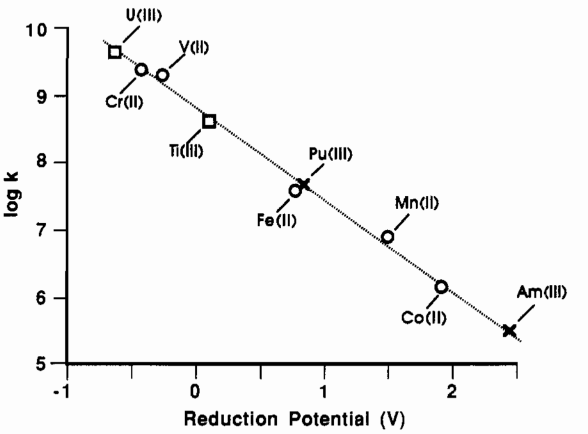

Figure 3. Rates of reaction of Cl_2^- with several di- and trivalent metal ions vs. oxidation potential: (○, □) published values; (×) this work.

$\Delta G°$ function is approaching a maximum. The results could also be used to suggest that the mechanism for the oxidation might involve an atom-transfer mechanism. These considerations will be explored in the contemplated studies with the dioxo cations of Pu and Am.

The trivalent cations provide a series of simple aquo species that are used to explore the reactivity patterns of Cl_2^-. The present results, along with those previously reported for the oxidations of U(III)[4] and Ti(III),[13] are plotted in Figure 3 vs. the formal reduction potentials. The linear free energy correlation not only is valuable for the systemization but can also be used with confidence for predictive purposes.

There are a number of additional important aspects to be considered.

(1) The values reported for the rates of oxidation of the divalent (5d) transition elements by Cl_2^- are correlated by the same linear $E°$ function as the trivalent cations. This observation can be used to imply that any electrostatic interactions do not have a significant influence on the dynamics of oxidation of these cations by Cl_2^-.

(2) A linear relation between log k and $\Delta G°$ is generally assumed as a necessary condition for an outer-sphere electron-transfer mechanism to be a valid description of a series of reactions with a common reagent. However, since $Cr^{2+} + Cl_2^- \rightarrow Cr^{3+} + 2Cl^-$ proceeds equally via inner- and outer-sphere mechanisms while $V^{2+} + Cl_2^- \rightarrow V^{3+} + 2Cl^-$ proceeds by an outer-sphere diffusion-controlled mechanism,[17] it is evident that the observed linearity is not also a sufficient condition.

Acknowledgment. C.L. acknowledges financial support provided by J. I. Kim and W. T. Carnall. We also gratefully acknowledge the technical assistance of D. Ficht and G. Cos, who operated the linear accelerator, and M. F. Williams, who assured radiation safety for the operations.

---

(17) Lawrence, G. S.; Thornton, A. T. *J. Chem. Soc., Dalton Trans.* **1974**, *11*, 1142.

(18) (a) Cohen, D.; Sullivan, J. C.; Hindman, J. C. *J. Am. Chem. Soc.* **1955**, *77*, 4964. (b) The rates of the isotopic exchange reactions between Np(VI) and Np(V) were measured as a function of chloride concentration at 0.0, 4.78, and 9.84 °C. At an ionic strength of 3.0, the values at 1 M Cl^- were extrapolated to 25 °C. From the measured ionic strength dependencies, the 25 °C value was corrected to unit ionic strength.

Contribution from the Laboratoire de Synthèse et d'Electrosynthèse Organométallique,
Associé au CNRS (UA 33), Faculté des Sciences "Gabriel", Université de Dijon, 21100 Dijon, France,
and Department of Chemistry, University of Houston, Houston, Texas 77004

First Example of 1:1 Actinide–Phthalocyanine Complexes: Synthesis, Electrochemical, and Spectral Characterization of Bis(diketonato)thorium(IV) and -uranium(IV) Phthalocyaninates

R. Guilard,*[1a] A. Dormond,[1a] M. Belkalem,[1a] J. E. Anderson,[1b] Y. H. Liu,[1b] and K. M. Kadish*[1b]

Received October 24, 1986

The synthesis of $(Pc)Th(acac)_2$ and $(Pc)U(acac)_2$, where Pc is the dianion of phthalocyanine and acac is the anion of 2,4-pentanedione, is reported. These are the first examples of 1:1 actinide–phthalocyanine complexes. NMR data suggest that the metal is out of the plane of the porphyrin ring and that the two acac ligands are in a cis geometry about the metal. Electrochemical, spectroelectrochemical, and ESR studies on these complexes were performed and demonstrate that both $(Pc)U(acac)_2$ and $(Pc)Th(acac)_2$ can undergo two ring reductions and two ring oxidations.

Introduction

Lanthanide or actinide metalation reactions with phthalocyanines typically result in formation of the bis(phthalocyanine) complexes (Pc)M(PcH) or (Pc)M(Pc), where Pc is the dianion of phthalocyanine and M is a lanthanide or actinide metal in the +3 or +4 oxidation state and is located at the top of an antiprism. Lanthanide bis(phthalocyanine) complexes are typified by Nd(III), Pr(III), Er(III), and La(III) complexes, which were first described[2] in 1965, followed by numerous detailed studies of their physicochemical, spectroscopic, and photoconductive properties.[3–25] The actinide bis(phthalocyanine) complexes are typified by $(Pc)_2Np$,[26] $(Pc)_2Th$, $(Pc)_2U$,[27] and a proactinium complex[28] whose sandwich

---

(1) (a) Université de Dijon. (b) University of Houston.

(2) (a) Kirin, I. S.; Moskalev, P. N.; Makashev, Y. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1965**, *10*, 1065. (b) Kirin, I. S.; Moskalev, P. N.; Makashev, Y. A. *Zh. Neorg. Khim.* **1967**, *12*(3), 707. (c) Kirin, I. S.; Moskalev, P. N.; Ivannikova, N. V. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1967**, *12*, 497.

(3) Misumi, S.; Kasuga, K. *Nippon Kagaku Zasshi* **1971**, *92*, 335.

(4) Moskalev, P. N.; Kirin, I. S. *Zh. Fiz. Khim.* **1967**, *41*, 497.

(5) Moskalev, P. N.; Kirin, I. S.; Shapkin, G. N. *Zh. Neorg. Khim.* **1973**, *12*, 3229.

(6) Lux, F. *Proc. Rare Earth Res. Conf., 10th* **1973**, 871.

(7) Moskalev, P. N.; Alimova, N. I. *Zh. Neorg. Khim.* **1975**, *20*, 2664.

(8) Moskalev, P. N. USSR Patent 497302, 1976.

(9) Moskalev, P. N.; Mishin, V. Y.; Rubksov, E. M.; Kirin, I. S. *Zh. Neorg. Khim.* **1976**, *21*, 2259.

(10) Yamana, M. *Nippon Kagaku Kaishi* **1977**, *1*, 144.

(11) Pyatosin, V. E.; Sevchenko, A. N.; Solovev, K. N.; Tsvirko, M. P. *Dokl. Akad. Nauk. SSSR* **1977**, *234*, 578.

(12) Moskalev, P. N. USSR Patent 525318, 1978.

(13) Moskalev, P. N.; Shapkin, G. N.; Misko, Y. S. *Radiokhimiya* **1978**, *20*, 343.

(14) Pyatosin, V. A.; Sevchenko, A. N.; Tsvirko, M. P. *Izv. Akad. Nauk. SSSR, Ser. Fiz.* **1978**, *42*, 588.

(15) Yamana, M. *Res. Rep. Tokyo Denki Univ.* **1977**, *25*, 39.

(16) Nicholson, M. M.; Galiardi, R. V.; Pizzarello, F. A.; Layman, G. A. *U.S. NTIS, AD Rep.* **1980**, A086691.

(17) Corker, G. A.; Grant, B.; Clecak, N. J. *J. Electrochem. Soc.* **1979**, *126*, 1339.

(18) Kasuga, K.; Tsutsui, M.; Petterson, R. C.; Tatsumi, K.; Van Opdenbasch, N.; Pepe, G.; Meyer, E. F., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 4835.

(19) Kasuga, K.; Tsutsui, M. *Coord. Chem. Rev.* **1980**, *32*(1), 67.

(20) Kapinus, E. I.; Smykalova, L. I.; Dilung, I. I. *Zh. Neorg. Khim.* **1980**, *25*, 412.

0020-1669/87/1326-1410$01.50/0 © 1987 American Chemical Society