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Electrochemical studies on bis(β-diketonato)(dimethyl sulfoxide)dioxouranium(VI) in dimethyl sulfoxide

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Abstract

Electrochemical studies on $U^{VI}O_2$(β-diketonato)$_2$dmso [β-diketonate=dibenzoylmethanate (dbm), trifluoroacetylacetonate (tfacac), hexafluoroacetylacetonate (hfacac), dmso=dimethyl sulfoxide] complexes in DMSO containing tetrabutylammonium perchlorate (supporting electrolyte) have been carried out using cyclic voltammetry (CV) and normal pulse voltammetry (NPV). As a result, it was found that the $U^{VI}O_2$(tfacac or hfacac)$_2$dmso complexes are reduced to U(V) species reversibly and that the $U^{VI}O_2$(dbm)$_2$dmso complex is quasi-reversibly reduced to U(V) species. The formal redox potentials ($E°$/V, vs. Ag/AgCl and vs. ferrocene/ferricinium in parentheses) for the U(VI)/U(V) couple are −0.44 (−0.97) for $U^{VI}O_2$(hfacac)$_2$dmso, −0.52 (−1.05) for $U^{VI}O_2$(tfacac)$_2$dmso, and −0.83 (−1.36) for $U^{VI}O_2$(dbm)$_2$dmso. Furthermore, the $E°$ values were found to correlate with the pK_a values of β-diketones, i.e. the $E°$ values decrease with an increase in the pK_a value. © 1998 Elsevier Science S.A.

Keywords: Electrochemical reactions; Uranyl complexes; U(V) species; Dimethyl sulfoxide

1. Introduction

Electrochemical reactions of uranyl complexes have been studied extensively in aqueous [1] and non-aqueous [2] solutions and reduction mechanisms have been proposed. However, the properties of reduction products, i.e. U(V) complexes, have not been clarified in detail [1,3].

Our previous papers [4,5] report electrochemical and spectroelectrochemical studies on $U^{VI}O_2(CO_3)_3^{4-}$ in Na_2CO_3 solutions, UO_2^{2+} in acidic aqueous solution, and $U^{VI}O_2$(acac)$_2$dmso (acac=acetylacetonate, dmso=dimethyl sulfoxide) complex in DMSO. As a result, it was clarified that these uranyl complexes are reduced quasi-reversibly to U(V) and that the U(V) species formed by reduction of $U^{VI}O_2(CO_3)_3^{4-}$ and $U^{VI}O_2$(acac)$_2$dmso complexes are relatively stable and have small molar extinction coefficients in the visible region, i.e. they are almost colorless. Furthermore, it is expected that the uranyl complexes with bidentate or multidentate ligands at their equatorial sites can form stable U(V) complexes by electrochemical reduction.

In order to examine this expectation, electrochemical studies on $U^{VI}O_2$(β-diketonato)$_2$dmso complexes in DMSO were carried out using cyclic voltammetry (CV) and normal pulse voltammetry (NPV).

2. Experimental

2.1. Materials

The $U^{VI}O_2$(β-diketonato)$_2$dmso [β-diketonate=dibenzoylmethanate (dbm), trifluoroacetylacetonate (tfacac), hexafluoroacetylacetonate (hfacac)] complexes were synthesized by the same methods as described in previous papers [6–8]. Dimethyl sulfoxide (Wako Pure Chemical Ind., Ltd.) was dried and purified according to the reported method [9]. Tetrabutylammonium perchlorate (TBAP, Fulka Chemika) used as supporting electrolyte was purified by recrystallization from ethanol. All other chemicals used were of reagent grade.

2.2. Methods

CV and NPV measurements were carried out under

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nitrogen atmosphere with a BAS CV-50W voltammetric analyzer and a BAS CV cell. A three-electrode system was utilized, i.e. a BAS 11-2013 Pt working electrode (area 2 mm^2), a BAS 51-2222 Pt auxiliary electrode, and a BAS RE-1B Ag/AgCl reference electrode. A Fc(ferrocene)/Fc^+ couple was used as the reference redox system in the present study [10]. The potential of the reference electrode was determined to be −0.53 V vs. Fc/Fc^+. All potentials reported are vs. Ag/AgCl and Fc/Fc^+ (in parentheses). All sample solutions were deoxygenated by passing N_2 gas into solutions for at least 10 min prior to starting measurements.

3. Results and discussion

3.1. $U^{VI}O_2(hfacac)_2dmso$ complex system

The CV measurements were carried out for DMSO solution containing $U^{VI}O_2(hfacac)_2dmso$ (1.0×10^{-3} M, $M=mol\,dm-{}^{3}$) and TBAP (1.0×10^{-1} M). The potential was scanned between +0.50 (−0.03) and −0.70 (−1.23) V at different scan rates (v=0.05–0.50 V s^{-1}). The results are shown in Fig. 1. A single cathodic peak (E_{pc}) was observed at −0.47 (−1.00) with a coupled anodic peak (E_{pa}) at −0.41 (−0.94) V. The peak-to-peak separation ($\Delta E_p = E_{pa} - E_{pc}$) was constant and did not depend on the scan rate, i.e. 0.06 V, which is consistent with the theoretical value for the reversible one-electron transfer process. The value of $(E_{pc} + E_{pa})/2$ was also constant, −0.44 (−0.97) V, and was independent of the scan rate. Furthermore, the peak currents (i_{pc}) are found to vary linearly with $v^{1/2}$, as shown in Fig. 2. These results suggest that the $U^{VI}O_2(hfacac)_2dmso$ complex in DMSO is reduced reversibly at the Pt electrode as follows:

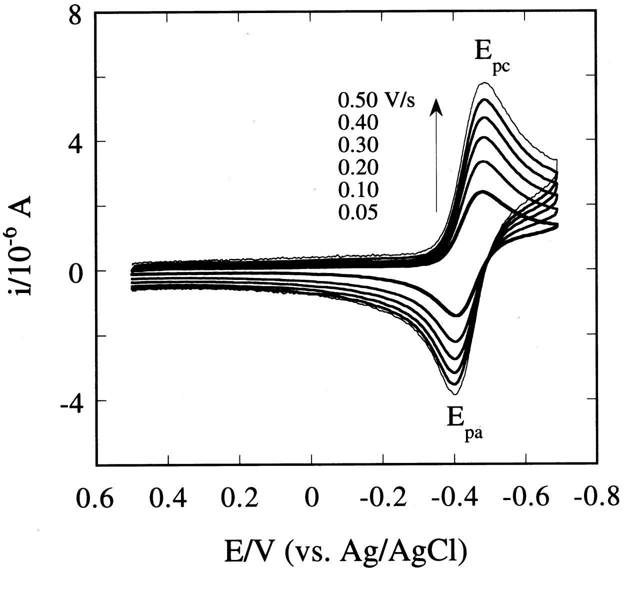

Fig. 1. Cyclic voltammograms of DMSO solution containing $U^{VI}O_2(hfacac)_2dmso$ (1.0×10^{-3} M) and TBAP (1.0×10^{-1} M) measured in the potential range from +0.50 (−0.03) to −0.70 (−1.23) V at different scan rates. Initial scan direction: cathodic.

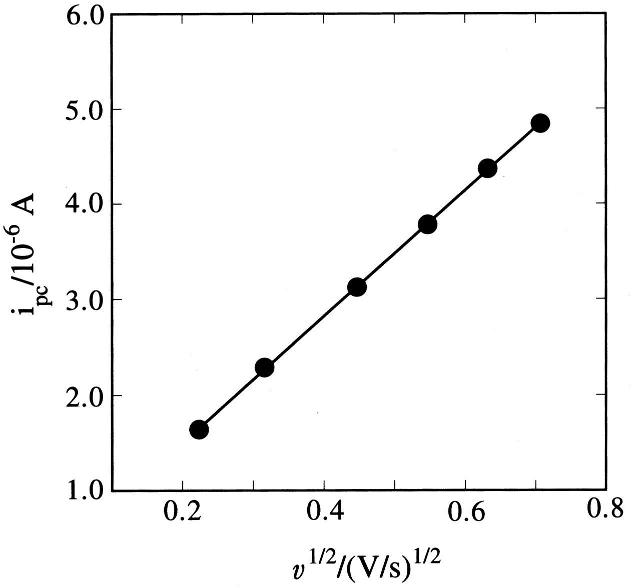

Fig. 2. A plot of peak current (i_{pc}) vs. $v^{1/2}$ for the cyclic voltammograms of Fig. 1.

$$U^{VI}O_2(hfacac)_2dmso + e^- = [U^{V}O_2(hfacac)_2dmso]^- \quad (1)$$

In order to confirm the validity of reaction (1), the electron stoichiometry (n-value) and the half-wave potential ($E_{1/2}$) were measured by NPV. Fig. 3 shows a plot of current (i) versus potential (E) obtained from such a measurement. Generally, the relationship between the potential and the diffusion current (i_d) is expressed as

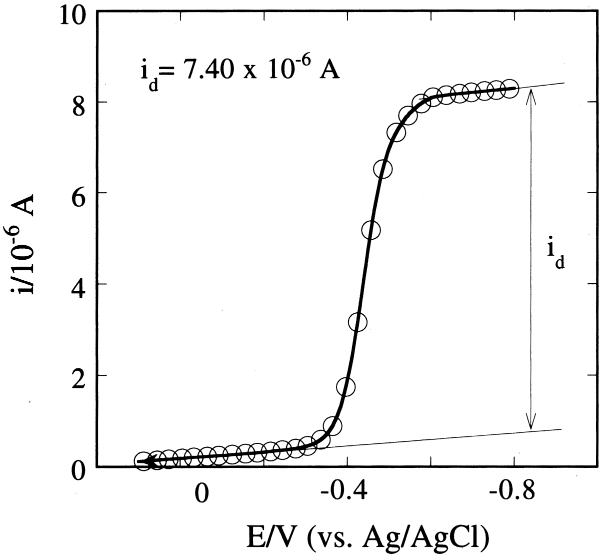

Fig. 3. A plot of current (i) vs. E for the normal pulse voltammetry of DMSO solution containing $U^{VI}O_2(hfacac)_2dmso$ (1.0×10^{-3} M) and TBAP (1.0×10^{-1} M).

$$E = E_{1/2} - \frac{RT}{nF}\ln\frac{i}{i_{\mathrm{d}} - i} \qquad (2)$$

Hence, the values of n and $E_{1/2}$ can be obtained from the slope and intercept of the plot of E vs. $\ln[(i_{\mathrm{d}} - i)/i]$. Such a plot is shown in Fig. 4. The values of n and $E_{1/2}$ were evaluated as 1.0 and −0.45 (−0.98) V, respectively. The $E_{1/2}$ value is compatible with that obtained from CV measurements. From these results it can be concluded that the $\mathrm{U^{VI}O_2(hfacac)_2dmso}$ complex in DMSO is reduced to U(V) species reversibly at the Pt electrode and the formal redox potential ($E°$) is −0.44 (−0.97) V. Furthermore, the electrochemical process is diffusion controlled and the diffusion coefficient (D_0) estimated from the slope of Fig. 2 is $1.50\times10^{-6}\ \mathrm{cm^2\ s^{-1}}$ at 25°C.

3.2. $\mathrm{U^{VI}O_2(tfacac)_2dmso}$ complex system

Fig. 5 shows the cyclic voltammograms of DMSO solution containing $\mathrm{U^{VI}O_2(tfacac)_2dmso}$ (1.0×10^{-3} M) and TBAP (1.0×10^{-1} M) measured at potentials between +0.50 (−0.03) and −0.80 (−1.33) V at different scan rates (v=0.05–0.10 V s^{-1}). As can be seen from Fig. 5, a single cathodic peak (E_{pc}) is observed at −0.55 (−1.08) with a coupled anodic peak (E_{pa}) at −0.49 (−1.02) V. The values of $\Delta E_{\mathrm{p}} = E_{\mathrm{pa}} - E_{\mathrm{pc}}$ and $(E_{\mathrm{pc}} + E_{\mathrm{pa}})/2$ are constant and do not depend on the scan rate, that is 0.06 V and −0.52 (−1.05) V, respectively. Furthermore, the plot of peak current (i_{pc}) vs. $v^{1/2}$ was found to give a linear relationship. These results indicate that the $\mathrm{U^{VI}O_2(tfacac)_2dmso}$ complex in DMSO is reversibly reduced to U(V) species at the Pt electrode as expressed by Eq. (3) and that the process is diffusion controlled

$$\mathrm{U^{VI}O_2(tfacac)_2dmso} + \mathrm{e}^- = [\mathrm{U^{V}O_2(tfacac)_2dmso}]^- \qquad (3)$$

where the formal redox potential ($E°$) is −0.52 (−1.05) V. The diffusion coefficient (D_0) at 25°C was estimated to be $1.37\times10^{-6}\ \mathrm{cm^2\ s^{-1}}$ from the slope of the plot of i_{pc} vs. $v^{1/2}$.

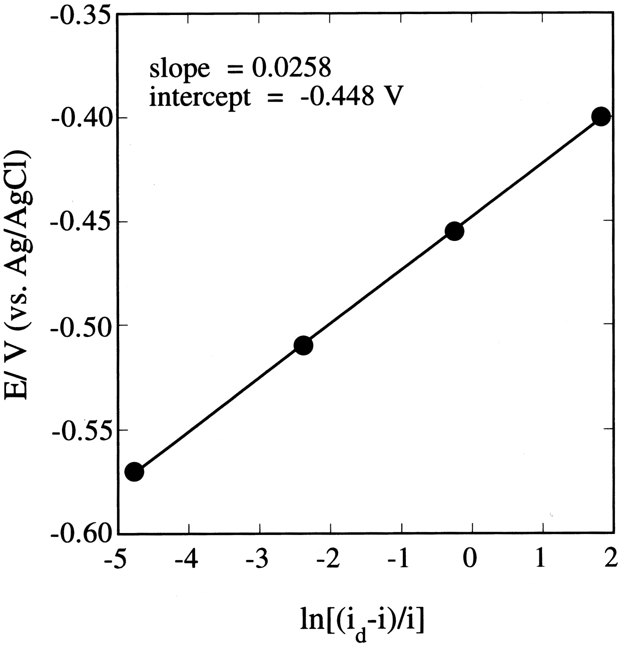

Fig. 4. A plot of E vs. $\ln[(i_{\mathrm{d}} - i)/i]$ for the normal pulse voltammetry of Fig. 3.

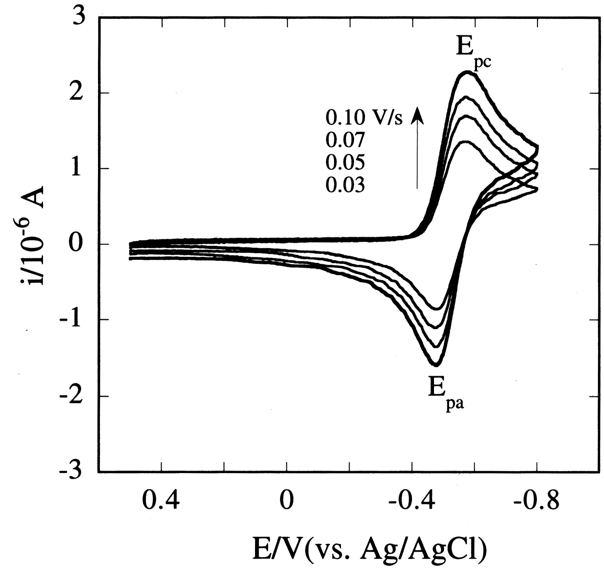

Fig. 5. Cyclic voltammograms of DMSO solution containing $\mathrm{U^{VI}O_2(tfacac)_2dmso}$ (1.0×10^{-3} M) and TBAP (1.0×10^{-1} M) measured in the potential range from +0.50 (−0.03) to −0.80 (−1.33) V at different scan rates. Initial scan direction: cathodic.

3.3. $\mathrm{U^{VI}O_2(dbm)_2dmso}$ complex system

The cyclic voltammograms of DMSO solution containing $\mathrm{U^{VI}O_2(dbm)_2dmso}$ (1.0×10^{-3} M) and TBAP (1.0×10^{-1} M) were measured in the potential range from 0.10 (−0.43) to −1.10 (−1.63) V at different scan rates (v=0.03–0.20 V s^{-1}). The results are shown in Fig. 6. As seen from this figure, a strong cathodic peak (E_{pc1}) and an anodic peak (E_{pa1}) are observed at around −0.87 (−1.40) and −0.79 (−1.32) V, respectively, at scan rates less than 0.1 V s^{-1}, and a weak anodic peak (E_{pa2}) appears at around −0.61 (−1.14) V with an increase in the scan rate. The values of $\Delta E_{\mathrm{p1}} = E_{\mathrm{pa1}} - E_{\mathrm{pc1}}$ increase with increasing scan rate, i.e. 0.075 V at v=0.03 V s^{-1} and 0.092 V at v=0.40 V s^{-1}, which are larger than the theoretical value (0.06 V) for the reversible one-electron transfer process. The value of $(E_{\mathrm{pc1}} + E_{\mathrm{pa1}})/2$ is constant, −0.84 (−1.37) V, and does not depend on the scan rate.

In order to examine the electron stoichiometry (n-value) for the reduction process, NPV measurement was carried out in a similar manner as described for the $\mathrm{U^{VI}O_2(hfacac)_2dmso}$ system. The values of n and $E_{1/2}$

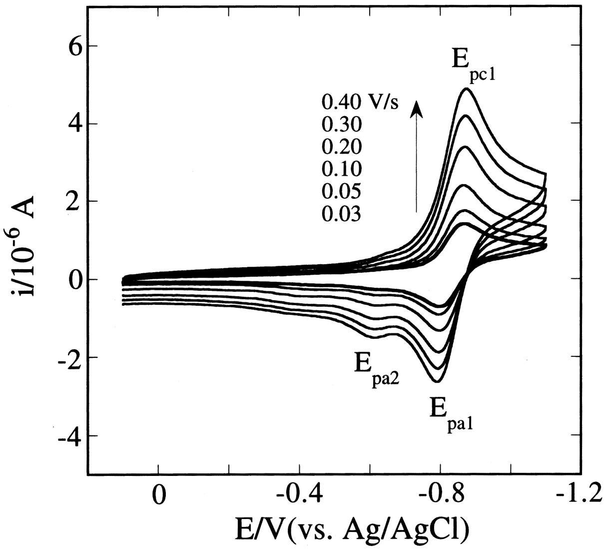

Fig. 6. Cyclic voltammograms of DMSO solution containing $U^{VI}O_2(dbm)_2dmso$ (1.0×10^{-3} M) and TBAP (1.0×10^{-1} M) measured in the potential range from +0.10 (−0.43) to −1.10 (−1.63) V at different scan rates. Initial scan direction: cathodic.

were obtained from the slope and intercept of the plot of E vs. $\ln[(i_d - i)/i]$ and are 1.0 and −0.83 (−1.36) V, respectively.

The above electrochemical behavior is similar to that for the $U^{VI}O_2(acac)_2dmso$ complex system reported in a previous paper [5]. Furthermore, in the CV measurement of the DMSO solution containing $U^{VI}O_2(dbm)_2dmso$, TBAP, and free dibenzoylmethane (Hdbm), the E_{pa2} peak was found to disappear.

From these results, it is concluded that the $U^{VI}O_2(dbm)_2dmso$ complex is reduced quasi-reversibly to U(V) species at the Pt electrode, and it is considered that the reduction process proceeds via the same mechanism as proposed for the electrochemical reactions of the $U^{V}O_2(acac)_2(dmso)$ system as follows [5]:

$$U^{VI}O_2(dbm)_2dmso + e^- = [U^{V}O_2(dbm)_2dmso]^- \quad E_{pc1}/E_{pa1} \tag{4}$$

$$[U^{V}O_2(dbm)_2dmso]^- + x\text{DMSO} \xrightarrow[\text{fast}]{} [U^{V}O_2(dbm)(\text{uni-dbm})(dmso)_{x+1}]^- \tag{5}$$

$$[U^{V}O_2(dbm)(\text{uni-dbm})(dmso)_{x+1}]^- + \text{DMSO} \xrightarrow[\text{fast}]{} U^{V}O_2(dbm)(dmso)_{x+2} + dbm^- \tag{6}$$

where uni-dbm and x symbolize the dbm ligand coordinated to UO_2^{2+} as unidentate and any number of coordinated dmso, respectively. In this mechanism, the disappearance of the E_{pa2} peak in CV measurements in the presence of free Hdbm can be reasonably explained by the retardation effect of free Hdbm on reaction (6). Therefore, peak E_{pa2} is considered to correspond to the oxidation of $U^{V}O_2(dbm)(dmso)_{x+2}$ (Eq. (7)) followed by the coordination and chelation reactions of uni-dbm (Eqs. (8) and (9))

$$U^{V}O_2(dbm)(dmso)_{x+2} \rightarrow [U^{VI}O_2(dbm)(dmso)_{x+2}]^+ + e^- \quad E_{pa2} \tag{7}$$

$$[U^{VI}O_2(dbm)(dmso)_{x+2}]^+ + dbm^- \xrightarrow[\text{fast}]{} U^{VI}O_2(dbm)(\text{uni-dbm})(dmso)_{x+1} + \text{DMSO} \tag{8}$$

$$U^{VI}O_2(dbm)(\text{uni-dbm})(dmso)_{x+1} \xrightarrow[\text{fast}]{} U^{VI}O_2(dbm)_2dmso + x\text{DMSO} \tag{9}$$

4. Summary

The results obtained from the present and previous studies [5] are summarized in Table 1 with the pK_a values of β-diketones. From this table, the $E°$ values decrease with an increase in the pK_a values of β-diketones. This means that the reduction of $U^{VI}O_2(\beta\text{-diketonato})_2dmso$ complexes becomes difficult with an increase in the basicity of the coordinated β-diketonate.

References

[1] (a) B. McDuffie, C.N. Reilley, Anal. Chem. 38 (1966) 1881. (b) M. Mastragostino, L.M. Saveant, Electrochim. Acta 13 (1968) 751. (c) J. Kuta, E. Yeager, J. Electroanal. Chem. 31 (1971) 119. (d) L. Sipos, L.J. Jeftic, M. Branica, Z. Galus, J. Electroanal. Chem. 32 (1971) 35. (e) K.U. Din, J. Kuta, L. Pospisil, Electrochim. Acta 22 (1977) 1109. (f) D.W. Wester, J.C. Sullivan, Inorg. Chem. 9 (1980) 2838. (g) D. Hodko, V. Pravdic, Electrochim. Acta 30 (1985) 1341.

[2] (a) H. Bildstein, H. Fleischer, V. Gutmann, Inorg. Chim. Acta 2 (1968) 347. (b) E.A. Kanevskii, B.V. Rengevich, G.R. Pavlovskaya, Radiokhimiya 17 (1975) 534. (c) P. Zanello, A. Cinquantini, G.A.

Table 1
Electrochemical reduction of $U^{VI}O_2(\beta\text{-diketonato})_2dmso$ complexes in DMSO

U(VI)/U(V) couple		$E°$/V	pK_a^a	Ref.
$U^{VI}O_2(hfacac)_2dmso + e^- = [U^{V}O_2(hfacac)_2dmso]^-$	Reversible	−0.44 (−0.97)	6.0	This work
$U^{VI}O_2(tfacac)_2dmso + e^- = [U^{V}O_2(tfacac)_2dmso]^-$	Reversible	−0.52 (−1.05)	8.3	This work
$U^{VI}O_2(acac)_2dmso + e^- = [U^{V}O_2(acac)_2dmso]^-$	Quasi-reversible	−0.91 (−1.44)	12.7	[5]
$U^{VI}O_2(dbm)_2dmso + e^- = [U^{V}O_2(dbm)_2dmso]^-$	Quasi-reversible	−0.83 (−1.36)	13.8	This work

[a] pK_a values of β-diketone compounds (H. Yokoi, T. Kishi, Chem. Lett. (1973) 749).

Mazzocchin, Inorg. Chim. Acta 21 (1977) 195. (d) P. Zanello, A. Cinquantini, P.D. Bernardo, L. Magon, Inorg. Chim. Acta 24 (1977) 131. (e) P. Zanello, A. Cinquantini, G.A. Mazzocchin, O. Traverso, Inorg. Chim. Acta 27 (1978) 157. (f) P. Zanello, A. Cinquantini, G.A. Mazzocchin, J. Electroanal. Chem. 131 (1982) 215. (g) R. Seeber, P. Zanello, J. Chem. Soc. Dalton Trans. (1985) 601. (h) S. Marouani, A.L.M. Gross, Electrochim. Acta 33 (1988) 147. (i) L. Bahadur, J.P. Pandey, J. Electrochem. Soc. 137 (1990) 3755.

[3] (a) G. Gritzner, J. Selbin, J. Inorg. Nucl. Chem. 30 (1968) 1799. (b) D. Cohen, J. Inorg. Nucl. Chem. 32 (1970) 3525. (c) J.T. Bell, H.A. Friedman, M.R. Billings, J. Inorg. Nucl. Chem. 36 (1974) 2563. (d) C. Miyake, Y. Yamana, S. Imoto, H.O. Nishiguchi, Inorg. Chim. Acta 95 (1984) 17. (e) C. Miyake, T. Kondo, S. Imoto, H.O. Nishiguchi, J. Less Common Met. 122 (1986) 313. (f) S.P. Best, R.J.H. Clark, R.P. Cooney, Inorg. Chim. Acta 145 (1988) 41.

[4] K. Mizuguchi, Y.-Y. Park, H. Tomiyasu, Y. Ikeda, J. Nucl. Sci. Technol. 30 (1993) 52.

[5] S.-H. Lee, K. Mizuguchi, H. Tomiyasu, Y. Ikeda, J. Nucl. Sci. Technol. 33 (1996) 190.

[6] G.M. Kramer, E.T. Maas, Inorg. Chem. 20 (1981) 3514.

[7] G.M. Kramer, M.B. Dines, R.B. Hall, A. Kaldor, A.J. Jacobson, J.C. Scanlon, Inorg. Chem. 19 (1980) 1340.

[8] L. Sacconi, G. Giannoni, J. Chem. Soc. (1954) 2368.

[9] Y. Ikeda, H. Tomiyasu, H. Fukutomi, Bull. Chem. Soc. Jpn. 56 (1983) 1060.

[10] G. Gritzner, J. Kuta, Pure Appl. Chem. 56 (1984) 461.