X-ray Absorption Spectroscopy of Tricarbonatodioxouranate(V), $[UO_2(CO_3)_3]^{5-}$, in Aqueous Solution

T. I. Docrat,[†] J. F. W. Mosselmans,[‡] J. M. Charnock,[‡,§] M. W. Whiteley,[§] D. Collison,[§] F. R. Livens,*[,§] C. Jones,[||] and M. J. Edmiston[||]

Research & Technology, BNFL Springfields, Preston PR4 0XJ, England, CLRC Daresbury Laboratory,
Warrington WA4 4AD, England, Department of Chemistry, The University of Manchester,
Manchester M13 9PL, England, and Research & Technology, BNFL Sellafield,
Seascale, Cumbria CA20 1PG, England

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Actinyl ions (AnO_2^{+} and AnO_2^{2+}) are strongly complexed by CO_3^{2-} in aqueous solution, and tricarbonato complexes of UO_2^{2+} and NpO_2^{+}, in particular, have been widely studied. Cyclic voltammetry shows that, whereas the Np(V)/Np(VI) couple is reversible in aqueous CO_3^{2-} solution, the analogous U couple is irreversible, suggesting significant conformational change on one-electron reduction of $[UO_2(CO_3)_3]^{4-}$. EXAFS spectroscopy has been used to define the coordination geometry of the reduced species and shows that both axial and equatorial U−O distances increase on reduction, from 1.80 to 1.90 Å and from 2.43 to 2.50 Å, respectively. The basic geometry of the U complex is apparently unchanged by reduction so any conformational change which does occur must be subtle.

Introduction

Little is known of the coordination chemistry of U(V) in aqueous solution since it readily disproportionates, although a few studies have been carried out[1−5] and the UV−visible absorption spectrum of electrochemically generated U(V) in aqueous CO_3^{2-} solution has been reported.[2−4] By analogy with the more stable pentavalent ions of Np, Pu, and Am, it might be expected to form a linear dioxo ion, with axial An−O distances around 0.14 Å longer than those in the comparable dioxo ions of the hexavalent actinides. All of the actinyl(VI) ions, including UO_2^{2+}, are readily complexed in aqueous solution by CO_3^{2-} anions, and this is reflected, inter alia, in very high stability constants[6−8] and, electrochemically, in large negative shifts in reduction potential.[9−14] In addition, the U(VI)/U(V) couple, which is electrochemically reversible in less strongly complexing media, becomes irreversible in aqueous CO_3^{2-} solution.[15] We report the preparation in solution of the $[UO_2(CO_3)_3]^{5-}$ ion by electrochemical methods and its characterization by extended X-ray absorption fine structure (EXAFS) spectroscopy.

Table 1. Principal Multiple Scattering Pathways Used in EXAFS Analysis[a]

$[UO_2(CO_3)_3]^{4-}$			$[UO_2(CO_3)_3]^{5-}$		
pathway	length (Å)	intensity	pathway	length (Å)	intensity
0-1-2-0	7.251	0.176	0-1-2-0	7.534	0.131
0-3-4-0	8.264	0.118	0-3-4-0	8.453	0.105
0-2-3-0	6.592	0.088	0-2-3-0	6.738	0.082
0-3-4-3-0	8.264	0.078	0-3-4-3-0	8.453	0.057
0-1-1a-0	7.199	0.065	0-2-4-3-0	8.988	0.051
0-1-0-1a-0	7.199	0.065	0-1-0-1a-0	7.599	0.049
0-2-4-3-0	8.782	0.062	0-1-1a-0	7.599	0.046
0-1-0-1-0	7.199	0.058	0-1-0-1-0	7.599	0.038
0-2-4-0	8.782	0.045	0-2-4-0	8.988	0.037
0-1-3-0	8.089	0.040	0-1-3-0	8.345	0.036
0-2-3-2c-0	7.410	0.039	0-2-2e-0	9.976	0.035
0-2-2e-0	9.703	0.039			
0-2-0-2e-0	9.715	0.034			

[a] All other pathways have an intensity less than 0.030.

Materials and Methods

Cyclic voltammetric studies of dioxouranate(VI) in aqueous solution were carried out in excess Na_2CO_3 at a final pH of 11.95. Under these conditions, formation of the trimeric $[(UO_2)_3(CO_3)_6]^{6-}$ ion is insignificant.[16,17] All samples were prepared by dissolving solid UO_2Cl_2 (BDH,

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[†] BNFL Springfields.
[‡] CLRC Daresbury Laboratory.
[§] The University of Manchester.
[||] BNFL Sellafield.

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Table 2. Summary of EXAFS Data Fits for Tricarbonato Complexes of Dioxouranate(VI), Dioxouranate(V), and Dioxoneptunate(V)[a]

	$[UO_2(CO_3)_3]^{4-}$			$[UO_2(CO_3)_3]^{5-}$			$[NpO_2(CO_3)_3]^{5-}$	
shell	CN	r (Å)	$2\sigma^2$ (Å^2)	CN	r (Å)	$2\sigma^2$ (Å^2)	CN	r (Å)
1	2 O	1.80 ± 0.02	0.005	2 O	1.90 ± 0.02	0.007	2 O	1.86
2	6 O	2.43 ± 0.02	0.014	6 O	2.50 ± 0.02	0.017	6 O	2.53
3	3 C	2.89 ± 0.04	0.007	3 C	2.94 ± 0.04	0.011	3 C	2.98
4	3 O	4.13 ± 0.04	0.013	3 O	4.23 ± 0.04	0.019	3 O	4.22
edge position (eV)		1 7165.7			1 7163.3			

[a] Coordination numbers were fixed to the known integral values for U(VI), and changes in coordination number by ±1 lead to a significant deterioration in quality of fit for U(V). CN: coordination number. r: interatomic distance. $2\sigma^2$: Debye−Waller factor. Data for $[NpO_2(CO_3)_3]^{5-}$ from ref 21.

Poole, U.K.) in aqueous 1 M Na_2CO_3 (total volume 25 mL), forming the $[UO_2(CO_3)_3]^{4-}$ complex and giving $[UO_2^{2+}]$ of 10 mM. Five milliliters of this solution was transferred to the cyclic voltammetry (CV) cell. Electrochemical data were collected using a Princeton Applied Research PAR Model 173 potentiostat/galvanostat driven by a PAR Model 175 programmer with a PAR Model K0020 hanging mercury drop working electrode (surface area 2.8 mm^2) over the potential range −0.1 to −1.65 V vs SCE, a Pt counter electrode, and a saturated calomel reference electrode.

Solution samples for X-ray absorption spectroscopy (XAS) were prepared immediately before use. The yellow reaction mixture was used directly for XAS of the U(VI) complex. The U(V) complex was generated at a potential of −1.20 V vs SCE using controlled potential coulometry with a PAR Model 362 scanning potentiostat and a mercury pool working electrode. Coulometric measurements showed the number of electrons transferred per U atom to be 1.04 after reduction, and the solution was colorless, as expected.[2−4] The U(V) and U(VI) solutions were transferred to N_2-flushed PTFE XAS cells (4 mm thick × 10 mm high × 25 mm wide with Perspex film windows), using a hypodermic syringe.

Uranium L(III)-edge X-ray absorption spectra were collected on Station 9.3 at the CLRC Daresbury Synchrotron Radiation Source operating at 2 GeV with a typical beam current of 150 mA. A double crystal Si(220) monochromator was used, detuned to 50% of maximum intensity for harmonic rejection. The spectra were recorded in fluorescence mode, using a 13-element Ge detector and collecting a minimum of four scans per sample to improve data quality. The sample cells were purged with Ar gas throughout data acquisition, and all data were collected at room temperature. The U(V) sample was still colorless after data collection. Following energy calibration and background subtraction, edge positions were determined separately for each scan of the reduced solution and found not to have shifted, confirming the sample's stability. The spectra were analyzed with the EXCURV98 program[18] using Rehr−Albers theory.[19] The k^3-weighted EXAFS was simulated using theoretical phase shifts derived from ab initio calculations with Hedin−Lundqvist exchange potentials and von Barth ground potentials. Although there is some uncertainty as to their significance,[20] full cluster multiple scattering calculations were performed using paths up to 10 Å in length and comprising up to three atoms in addition to the central atom in each path. A symmetry of D_{3h} was used, with an O−U−C angle of 26°. The main multiple scattering paths, with their relative importance, are defined in Figure 1 and shown in Table 1.

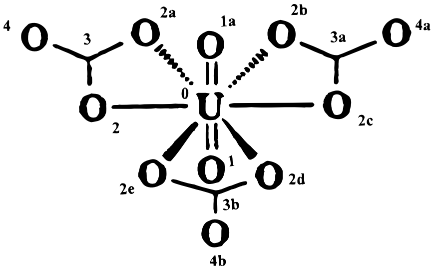

Figure 1. Identification of atoms in the multiple scattering cluster.

Results and Discussion.

In aqueous Cl$^-$ solution, the cyclic voltammetric parameters $E_{1/2}$ (mean of cathodic and anodic potentials) and ΔE_p (peak potential separation) for the U(VI)/U(V) couple are independent of scan rate over the range 10−200 mV s^{-1} with $E_{1/2} = -0.18$ V vs SCE and ΔE_p = 65 mV, consistent with data reported elsewhere.[13,15] By contrast, in aqueous CO_3^{2-} (Figure 2), ΔE_p increases from 390 mV with increasing scan rate and the reduction process occurs at a potential ca. 0.7 V more negative, as observed by other workers.[13] It is noteworthy that the Np(VI)/Np(V) couple is quasi-reversible under comparable conditions of pH and $[CO_3^{2-}]$, with ΔE_p = 89 mV at a scan rate of 20 mV s^{-1}.[9] Controlled potential coulometry (cpc) experiments[15] show that the product of a one-electron reduction of U(VI) in aqueous CO_3^{2-} solution is stable over a period of at least 2 h. These data are consistent with the stoichiometric generation of $[UO_2(CO_3)_3]^{5-}$, which is sufficiently stable to permit spectroscopic characterization.

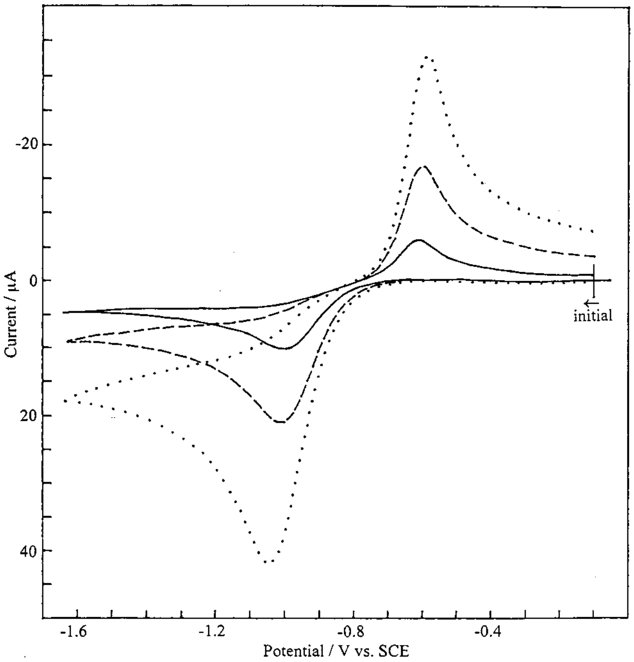

Figure 2. First-scan cyclic voltammogram of 9.94 × 10^{-3} M U(VI) in 1 M aqueous Na_2CO_3 at 21.5 °C, pH = 11.95. Scan rates: 10 (—), 20 (− − −), 50 (•••) mV s^{-1}.

The background-subtracted, k^3-weighted EXAFS for tricarbonato complexes of both dioxouranate(VI) and dioxouranate(V) are shown in Figure 3. The spectra have generally similar

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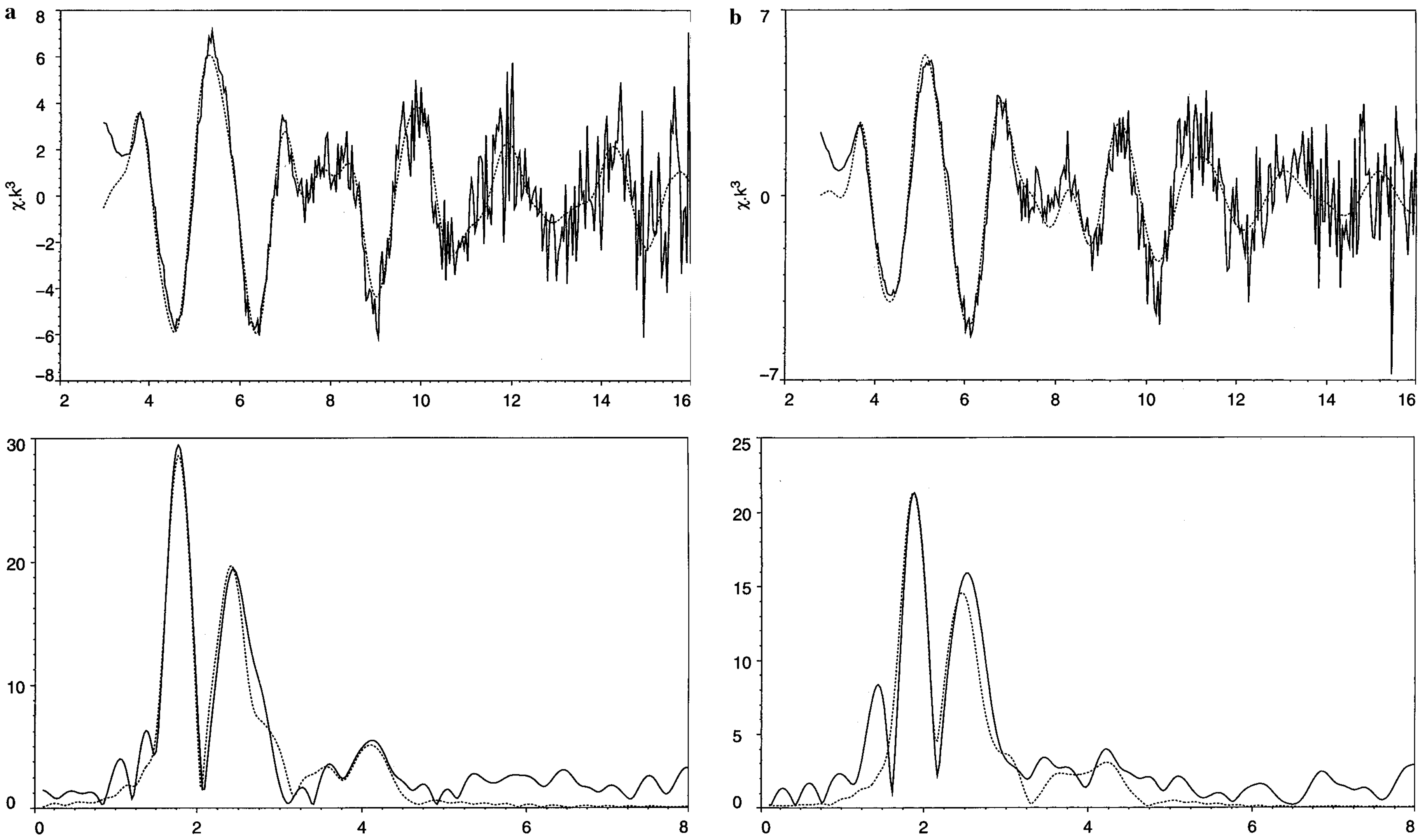

Figure 3. EXAFS spectra and Fourier transforms for the (a) tricarbonatodioxouranate(VI), $[UO_2(CO_3)_3]^{4-}$, and (b) tricarbonatodioxouranate(V), $[UO_2(CO_3)_3]^{5-}$, complexes in aqueous solution. Both experimental and modeled data are shown. Fourier transforms are phase shift corrected to the first shell.

profiles, and the relative intensities of the major features of the Fourier transforms are also similar, suggesting that the geometry and coordination number of the U center is not substantially affected by reduction. The relatively minor differences in the Fourier transforms at r < 1.5 Å arise from differences in background subtraction and those around 3.5 Å from multiple scattering effects. However, the interatomic distances in the inner coordination shells are greater in the U(V) complex than in the U(VI) species. Edge positions, calculated coordination numbers, and interatomic distances for both complexes are given in Table 2, together with data from an EXAFS analysis of $[NpO_2(CO_3)_3]^{5-}$ for comparison.[21]

The one-electron reduction of $[UO_2(CO_3)_3]^{4-}$ to $[UO_2(CO_3)_3]^{5-}$ causes a shift in the U L(III)-edge position from 17165.7 to 17163.3 eV, consistent with the decrease in Z_{eff}. The coordination environment of the dioxouranate(VI) ion in solution, as determined here, is very similar to that found by other workers in the solid state using both XAS[16] and X-ray crystallographic[22−26] methods. The axial U−O distances increase by 0.10 Å on reduction, rather less than the 0.15 Å difference observed for tricarbonato complexes of NpO_2^{2+} and NpO_2^{+} in the solid state.[27,28] The distances of all equatorial ligand atoms from the U center increase by about 0.10 Å, suggesting that the geometry of the CO_3^{2-} ligands is not substantially changed. The U−O(axial) distance is longer in the U(V) complex than in the analogous Np(V) species, as might be expected from the U atom's larger size, but the interatomic distances in the equatorial plane are very similar.[21]

The geometric similarity of the $[UO_2(CO_3)_3]^{4-}$ and $[UO_2(CO_3)_3]^{5-}$ ions apparent from the profiles of the EXAFS spectra makes it difficult to rationalize the change in electrochemical behavior which occurs on complexation with CO_3^{2-}. In other contexts,[29] such behavior is indicative of a substantial conformational change. In the case of the tricarbonatodioxouranate ions described here, such a change could arise from a twist about the U−C direction which moves the coordinated O atoms out of the equatorial plane, as has been observed in the solid state for $[UO_2(CO_3)_3]^{4-}$ compounds.[22−26]

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