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Note

Synthesis and characterization of ion separated $MU_2(OBu^t)_9$ species where $M = NBu^n{}_4$, PPh_4, Ph_3PMe and K-dibenzo-18-crown-6

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Abstract

Reaction of the molecular species $KU_2(OBu^t)_9$ with bromide salts of non-coordinating counter-cations, MBr ($M = NBu^n{}_4$, PPh_4 and Ph_3PMe) in THF solution results in the precipitation of KBr and the formation of the ion separated $MU_2(OBu^t)_9$ salts. The potassium cation can also be removed from the coordination sphere of the dinuclear uranium anion by reaction with dibenzo-18-crown-6 ether in THF. These compounds have been characterized by ^1H NMR and electronic absorption spectroscopy. ^1H NMR indicates that the dinuclear face-shared bioctahedral structure of the $U_2(OBu^t)_9$ anion is retained in the ion separated species. Comparison of the electronic absorption spectra of $KU_2(OBu^t)_9$ with the dinuclear $U_2(OBu^t)_9$ anion in solution also supports this conclusion.

Introduction

Bioinorganic chemists have developed an innovative technique for discerning the coordination environment of metal ions in enzymes through preparation of model complexes that mimic the properties of the enzyme [1]. Comparison of spectroscopic properties of the models with those of the enzyme can reveal a wealth of information about the coordination environment of the metal ion in the enzyme. This technique has also been used with great utility in the preparation of transition metal alkoxide complexes that serve as models for metal oxides used as catalysts [2]. We are confident that a similar approach will facilitate the characterization and understanding of aqueous actinide species of environmental interest.

The hydroxide ligand [3] is a simple prototype of a large family of alkoxide ligands and actinide alkoxide complexes potentially represent environmentally relevant models for actinide speciation studies [4, 5]. This approach has the advantage that structural characterization by X-ray crystallography is usually unambiguous concerning formulation and that spectroscopic techniques can be used to determine and define solution properties.

Our initial efforts have focused on the U(IV) tert-butoxide system [6]. Gilman and co-workers first investigated the reaction of UCl_4 with KNH_2 in liquid ammonia, followed by alcoholysis of the resulting '$U(NH_2)_4$' with tert-butanol, eqn. (1) [7]. They claimed that this reaction gave green hydrocarbon-soluble $U(OBu^t)_4$ in unspecified yield, while Bradley *et al.* [8] claimed that the reaction actually provided a hydrocarbon-soluble grey–brown uranium(V) complex $UO(OBu^t)_3 \cdot HOBu^t$.

$$\text{'}U(NH_2)_4\text{'} + 4Bu^tOH \longrightarrow \text{'}U(OBu^t)_4\text{'} + 4NH_3 \qquad (1)$$

A reinvestigation of this reaction by Cotton *et al.* led to the isolation and structural characterization of the air-sensitive green potassium salt $KU_2(OBu^t)_9$ [9]. We felt that this and other similar compounds that adopt confacial bioctahedral structures could represent a model system for dinuclear uranium hydroxide species.

A potential criticism of using $KU_2(OBu^t)_9$ as a model for aqueous species is the fact that this compound is soluble in hydrocarbon solvents as a result of tight ion-pairing, a phenomenon that would not be likely in aqueous solution. Therefore, we were interested in preparing compounds containing the $U_2(OBu^t)_9$ anion, but with counterions that would be removed from the coordination environment of the dinuclear uranium anion. In this paper we wish to report the details of our investigations surrounding the preparation of several new $[U_2(OBu^t)_9][M]$ species, where M represents a non-coordinating counterion, and the effects of ion separation on the electronic absorption spectrum of the $U_2(OBu^t)_9$ anion.

Reaction of light green THF solutions of $KU_2(OBu^t)_9$ with an excess of MBr ($M = NBu^n{}_4$, PPh_4 and Ph_3PMe) (eqn. (2)) results in the precipitation of KBr and a barely perceptible color change.

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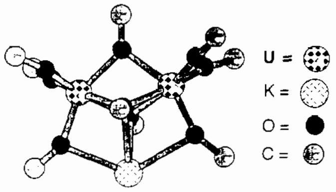
$$KU_2(OBu^t)_9 + MBr \xrightarrow{THF,\ 23\ °C} [U_2(OBu^t)_9][M] + KBr$$

$$M = NBu^n_4,\ PPh_4 \text{ and } Ph_3PMe \qquad (2)$$

Another method commonly used to achieve ion separation and organic solvent soluble salts is through encapsulation of alkali metal ions with crown ethers [1]. For the potassium ion, the maximum binding constant is obtained using an 18-crown-6 ether. Reaction of $KU_2(OBu^t)_9$ with dibenzo-18-crown-6 results in a slight color change and the formation of $[U_2(OBu^t)_9]$[K dibenzo-18-crown-6].

These compounds are all air and moisture sensitive, soluble in ethereal solvents (THF and diethyl ether) and moderately to sparingly soluble in hydrocarbons (hexane, toluene and benzene). The green THF solutions are stable for extended periods of time (weeks) under anaerobic conditions, but rapidly decompose to amber colored solutions when exposed to the atmosphere [6, 9].

The solid-state structure of $KU_2(OBu^t)_9$ has been determined by X-ray crystallography, **I** [9]. The $U_2(OBu^t)_9$ anion is best described as a confacial bioctahedron with the potassium ion coordinated by four oxygen atoms of tert-butoxide ligands. Two of these oxygen atoms are bridging between the uranium atoms and the other two are associated with terminal tert-butoxide ligands of the dinuclear anion, one per uranium.



I (Methyl carbons have been omitted for clarity)

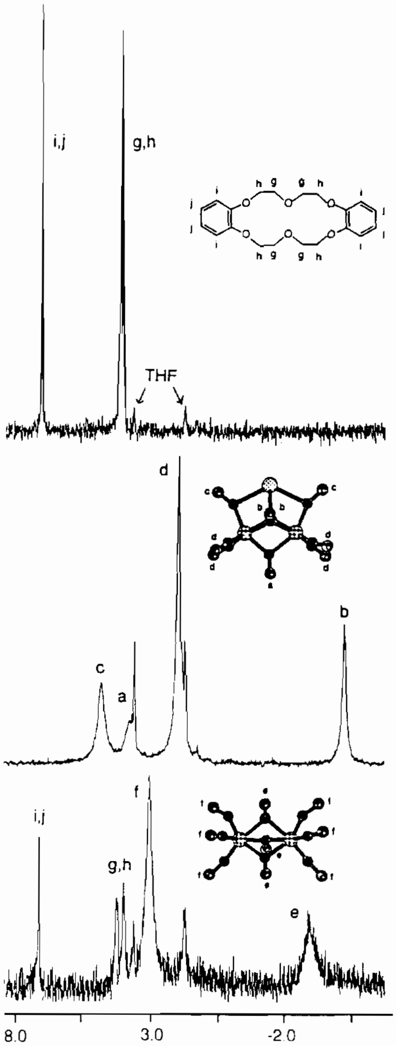


Fig. 1. ^1H NMR spectra (90 MHz, 32 °C) of THF-d_8 solutions containing: (top) dibenzo-18-crown-6; (middle) $KU_2(OBu^t)_9$; and (bottom) $KU_2(OBu^t)_9$ and 1 equiv. of dibenzo-18-crown-6.

At 22 °C and 90 MHz the ^1H NMR spectrum of $KU_2(OBu^t)_9$ in benzene-d_6 is consistent with the solid-state structure [6, 9, 10], i.e. four resonances are observed at δ 3.0, 2.8, -0.3 and -1.3 ppm in a 4:2:1:2 ratio. At 32 °C in THF-d_8 (Fig. 1) these same resonances (δ 4.3, 3.4, 1.9 and -4.4 ppm; 2:1:4:2) are considerably broadened and shifted. It should be noted that the chemical shifts of these paramagnetic compounds are highly temperature and solvent dependent [10]. The structure of the $U_2(OBu^t)_9$ anion in the $[U_2(OBu^t)_9][M]$ salts is unambiguously established by ^1H NMR spectroscopy, showing that in each case there are two types of Bu^t groups in a 2:1 ratio, with the Bu^t signals resonating at virtually the same chemical shifts regardless of counterion. This is consistent with a structurally rigid confacial bioctahedral $U_2(OBu^t)_9$ anion in solution. Figure 1 compares the ^1H NMR spectra of THF-d_8 solutions containing dibenzo-18-crown-6, $KU_2(OBu^t)_9$ and $[U_2(OBu^t)_9]$[K dibenzo-18-crown-6]. At 90 Hz/ppm the signals for dibenzo-18-crown-6 are observed as second order A_2B_2 and AA'BB' patterns for the methylene and aromatic resonances, respectively. Upon reaction with $KU_2(OBu^t)_9$, the ratio of $J/(\nu_0\delta)$ for the methylene resonances is decreased from *c.* 0.55 to *c.* 0.25 due to complexation with the potassium ion, but the aromatic resonances remain as a second order pattern with a very large $J/(\nu_0\delta)$ ratio*. It appears that the chemical shifts of the complexed dibenzo-18-crown-6 are not paramagnetically shifted, consistent with the

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*J = coupling constant and $(\nu_0\delta)$ = chemical shift difference in Hz. For a detailed discussion of second order NMR spectra, see ref. 11.

proposed ion separated $[U_2(OBu^t)_9]$[K-dibenzo-18-crown-6] species. Unfortunately, we have been unable to obtain X-ray quality crystals of any of the $[U_2(OBu^t)_9]$[M] salts prepared in this study to confirm the molecular structure in the solid-state*.

Figure 2 compares the electronic absorption spectra of $KU_2(OBu^t)_9$ in THF before and after the addition of a slight excess of dibenzo-18-crown-6. The latter spectrum is virtually indistinguishable from the spectra obtained for the addition of $NBu^n{}_4Br$, PPh_4Br and Ph_3PMeBr. See 'Supplementary material'.

A detailed discussion of the electronic absorption spectra of compounds containing the $U_2(OBu^t)_9$ anion has been presented elsewhere [13]. In that work the sensitivity of the electronic transition energies to the identity of the counter-cation and to the solvation of the counter-cation was demonstrated. The present results lend support to the conclusions drawn in that paper that the spectrum of $[NBu^n{}_4][U_2(OBu^t)_9]$ approximates the spectrum of the dimer anion separated from the influence of the counter-cation. All the non-coordinating counter-cation species investigated in this work produced spectra which were virtually identical to the $NBu^n{}_4$ salt. This indicates that these large cations have no measurable influence on the electronic structure of the uranium centers either through direct electronic interactions or through perturbation of the ligand coordination geometries and these conclusions are consistent with the NMR data.

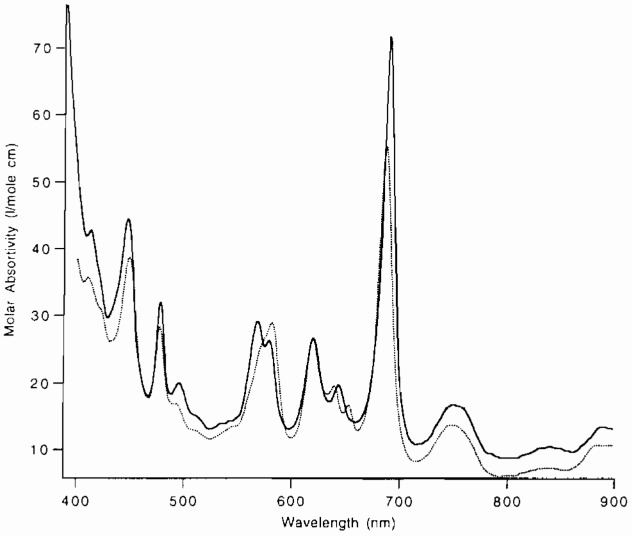

Fig. 2. The electronic absorption spectra of $KU_2(OBu^t)_9$ (light line) and $U_2(OBu^t)_9$ + >1 equiv. of dibenzo-18-crown-6 ether (dark line) in THF. Molar absorptivity coefficients are ±6%.

In conclusion, we have been able to prepare a series of $[U_2(OBu^t)_9]$[M] salts from $KU_2(OBu^t)_9$, where M represents non-coordinating counterions. We have also shown that the confacial bioctahedral structure of the anion is retained in solution for these ion separated salts. This demonstrates that the coordination of the K^+ ion by the oxygen atoms of two terminal and two bridging tert-butoxide ligands is not essential for stabilization of the anion. Comparisons of the electronic absorption spectra of the $MU_2(OBu^t)_9$ compounds, where M = $NBu^n{}_4$, PPh_4, Ph_3PMe and K-dibenzo-18-crown-6, support this conclusion.

Supplementary material

Description of experimental procedures, electronic absorption spectra of $[U_2(OBu^t)_9]$[M], where M = PPh_4, Ph_3PMe and $NBu^n{}_4$ (Figs. S4–S6) and ^1H NMR data (Figs. S7 and S8, Table S1) are available from author W.G.V.D.S.

Acknowledgements

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References

1 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry,* Wiley, New York, 5th edn., 1988.
2 M.H. Chisholm, *Inorganic Chemistry: Toward the 21st Century,* ACS Symposium Series No. 211, American Chemical Society, Washington, DC, 1983.
3 J.J. Katz, G.T. Seaborg and L.R. Morss, in *The Chemistry of the Actinide Elements,* Vols. 1 and 2, Chapman and Hall, New York, 2nd edn., 1986, and refs. therein.
4 D.C. Bradley, R.C. Mehrotra and D.P. Gaur, *Metal Alkoxides,* Academic Press, New York, 1978.
5 W.G. Van Der Sluys and A.P. Sattelberger, *Chem. Rev., 90* (1990) 1027.
6 W.G. Van Der Sluys, A.P. Sattelberger and M. McElfresh, *Polyhedron, 9* (1990) 1843.
7 R.G. Jones, G. Karmas, G.A. Martin, Jr. and H. Gilman, *J. Am. Chem. Soc., 78* (1956) 4285.
8 D.C. Bradley, R.N. Kapoor and B.C. Smith, *J. Inorg. Nucl. Chem., 24* (1962) 863.
9 F.A. Cotton, D.O. Marler and W. Schwotzer, *Inorg. Chem., 23* (1984) 4211.
10 J.P. Jesson, in G.N. La Mar, W. DeW. Horrocks, Jr. and R.H. Holm (eds.), *NMR of Paramagnetic Molecules, Principles and Applications,* Academic Press, New York, 1973.

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*It has been shown that the confacial bioctahedral structure of the anion in the tight ion-pair $NaW_2Cl_7(THF)_5$ is retained in the crystallographically characterized ion separated species $[PPh_4][W_2Cl_7(THF)_2]$, see ref. 12.

11 J.W. Emsley, J. Feeney and L.H. Sutcliffe, *High Resolution Nuclear magnetic Resonance Spectroscopy,* Vol. 1, Pergamon, New York, 1965.

12 (a) M.H. Chisholm, B.W. Eichhorn, K. Folting, J.C. Huffman, C.D. Ontiveros, W.E. Streib and W.G. Van Der Sluys, *Inorg. Chem., 26* (1987) 3182; (b) D.J. Bergs, M.H. Chisholm, K. Folting, J.C. Huffman and K.A. Stahl, *Inorg. Chem., 27* (1988) 2950.

13 J.M. Berg, A.P. Sattelberger, D.E. Morris, W.G. Van Der Sluys and P. Fleig, *Inorg. Chem., 32* (1993) 647.