Table II. Bimolecular Rate Constants for the Reaction $^3Pt_2^* + R{-}X \rightarrow [Pt^{II}Pt^{III}{-}X] + R^\bullet$ in Methanol at 25 °C and C–X Bond Energies

R–X	bond energy, kJ mol^{-1} [a]	rate constant, M^{-1} s^{-1}
H–allyl	362	$(5.4 \pm 0.5) \times 10^6$ (cyclohexene)[b]
Br–alkyl	293–286	$(4.4 \pm 0.4) \times 10^7$ (^{n}BuBr)[c]
RS–alkyl	270	$(9.7 \pm 0.8) \times 10^5$ (Me_2S)[d]

[a] *CRC Handbook of Chemistry and Physics*, 67th Ed.; CRC: Boca Raton, FL, 1986–1987. [b] Che, C.-M.; Lee, W. M.; Cho, K.-C., results to be submitted for publication. [c] Reference 1b. [d] This work.

constants (k_q) in methanol deduced from the equation $\tau_0/\tau = 1 + k_q\tau_0[R_2S]$ at 25 °C are summarized in Table I. Since the quenchers do not absorb in the visible region, quenching by an energy-transfer pathway is unlikely. Flash-photolysis experiments give evidence that the reactions occurring between $^3Pt_2^*$ and R_2S are predominately atom transfer in nature[7] as shown in eq 1.

$$^3Pt_2^* + R_2S \rightarrow [Pt^{II}Pt^{III}{-}SR] + R^\bullet \tag{1}$$

The transient difference absorption spectrum recorded instantaneously (5 μs) after the laser flash of a degassed methanolic solution of Pt_2 and Et_2S has an intense band at 390 nm, as shown in Figure 1a. The same spectra are also obtained with $(PhCH_2)_2S$. Figure 1b shows the difference absorption spectrum between $[Pt^{II}Pt^{III}(P_2O_5H_2)_4(SCN)]^{4-}$ and Pt_2.[1c,8] The two spectra are vitually identical, suggesting that the 390-nm peak in Figure 1a is due to the $\sigma(RS) \rightarrow d\sigma^*(PT)$ charge-transfer transition of $[Pt^{II}Pt^{III}{-}SR]$, which is expected to have energy similar to that of the $\sigma(NCS) \rightarrow d\sigma^*(Pt)$ transition of $[Pt^{II}Pt^{III}(P_2O_5H_2)_4(SCN)]^{4-}$. Evidence for the $R^\bullet$ radical in eq 1 also comes from the identification of the $PhCH_2CH_2Ph$ product[9] obtained by broad-band irradiation (λ > 350 nm) of Pt_2 and $(PhCH_2)_2S$ in degassed methanol for 5 h.[10]

Unlike other $[Pt^{II}Pt^{III}(pop)_4X]^{4-}$ complexes (X = Im, H, Cl), which rapidly disproportionate in solution,[2b,8,11] these $[Pt^{II}Pt^{III}{-}SR]$ species remain stable in methanol over a period of 50 ms. The RS ligand is a powerful σ-donor, thus stabilizing the $[Pt^{II}Pt^{III}]$ system through extensive charge-transfer mixing with the dσ-(Pt–Pt) bond. Previous work also indicated that the stability of the $[Pt^{II}Pt^{III}X]$ system increases with increasing nucleophilicity of X, in the order X = Cl < Br < SCN.[1c]

From Table I, the k_q values are in the order $R_2S = (PhCH_2)_2S > Me_2S > {}^tBu_2S > Et_2S$. Except for Me_2S, the k_q values are in parallel with the stabilities of the $R^\bullet$ intermediates.[12] Table II summarizes the rate constants of the reaction $^3Pt_2^* + R{-}X \rightarrow [Pt^{II}Pt^{III}{-}X] + R^\bullet$ together with the C–X bond energies. The unexpectedly low k_q values for R_2S, whose bond energies are the lowest when compared with those for C–H and C–Br bonds, reflect the importance of the steric effect of R_2S in affecting the atom-transfer reactions of $^3Pt_2^*$.

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Department of Chemistry
University of Hong Kong
Pokfulam Road
Hong Kong

Chi-Ming Che*
Hoi-Lun Kwong

Department of Physics
The Chinese University of Hong Kong
Shatin, New Territories, Hong Kong

Kar-Cheong Cho

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(7) An oxidative-quenching pathway is unlikely since R_2S is electrochemically reduced only with an applied potential less than −2.75 V vs Ag/AgCl. Reductive quenching of $^3Pt^{2*}$ with R_2S will give the $[Pt^{I}Pt^{II}]$ intermediate, which absorbs at 410 nm (Che, C.-M.; Atherton, S. J.; Butler, L. G.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 5143) and is very unstable. This is in contrast to the results of flash-photolysis experiments.

(8) Che, C.-M.; Gray, H. B.; Atherton, S. J.; Lee, W. M. *J. Phys. Chem.* **1986**, *90*, 6747.

(9) $PhCH_2CH_2Ph$ is identified by ^1H NMR spectroscopy and mass spectral analysis.

(10) No $Pt^{III}{}_2$ product was found by ^{31}P NMR spectroscopy. Instead, some decomposition of Pt_2 was observed. Recent studies have shown that $[Pt_2(P_2O_5H_2)X_2]^{4-}$ easily undergoes reduction to $[Pt_2(P_2O_5H_2)_4]^{4-}$ in methanol upon irradiation with UV light (λ > 300 nm) (Che, C.-M., Lee, W. M.; Cho, K.-C. *J. Am. Chem. Soc.* **1988**, *110*, 5407). Thus, it is not suprising to find that steady-state irradiation (λ > 300 nm) of $[Pt_2(P_2O_5H_2)_4]^{4-}$ with R_2S in methanol does not produce $[Pt_2(P_2O_5H_2)_4(R)(SR)]^{4-}$, which is expected to be very reactive toward photochemical reductive elimination.

(11) Roundhill, D. M.; Atherton, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 6829.

(12) Similar reactivities of R_2S with tri-*n*-butyltin hydride have also been found.[5a]

Uranium(VI)-Oxo-Alkoxide Cluster Synthesis via Ligand Redistribution

Sir:

Although a number of well-characterized uranium alkoxide complexes in a variety of formal oxidation states (+3 → +6) have been reported,[1-5] there are few examples of uranyl (UO_2^{2+}) alkoxide complexes[6-11] and only two structurally characterized members of this class.[12,13] There is disagreement in the literature as to the exact composition of binary uranyl alkoxides. Gilman and co-workers[7] proposed complexes of the stoichiometry $UO_2(OR)_2(ROH)_{3-4}$, while Bradley and co-workers[8] reported that uranyl complexes of secondary and tertiary alkoxides disproportionate in alcoholic solution to form compounds of the formula $UO(OR)_4(ROH)$. In both cases, formula assignments were based solely on elemental analyses.

In the course of our investigations of the nonaqueous chemistry of the uranyl ion, we have examined the reactions of anhydrous uranyl halides (UO_2X_2) with alkali-metal alkoxides in aprotic solvents. Addition of a tetrahydrofuran solution of potassium *tert*-butoxide to a stirred THF slurry of anhydrous uranyl chloride results in the slow (8–10 h) formation of a red solution and an insoluble precipitate. Filtration of the suspension, followed by concentration and cooling of the filtrate, results in the isolation of orange-red crystals (**1**) in a yield of ca. 30% based on UO_2Cl_2.[14] The ^1H NMR spectrum of the complex in toluene-d_8 at −35 °C consists of four sharp singlets at δ 2.08, 1.95, 1.66, and 1.55 in a 1:1:2:1 ratio. There are no resonances in the spectrum that can be attributed to free or coordinated tetrahydrofuran. The Nujol mull IR spectrum shows two U–O stretching modes at 931 and 898 cm^{-1}.

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(14) IR (Nujol mull): 1365 m, 1356 m, 1225 w, 1193 w, 1166 m, 1021 w, 976 w, 931 s, 898 s, 772 m, 761 w, 719 w, 643 w br, 608 m, 509 w, 498 w, 456 m br cm^{-1}. Anal Calcd for $U_3O_{14}C_{40}H_{90}$: C, 31.8; H, 6.02. Found: C, 31.8; H, 6.07. The crystals decompose at 165 °C without melting.

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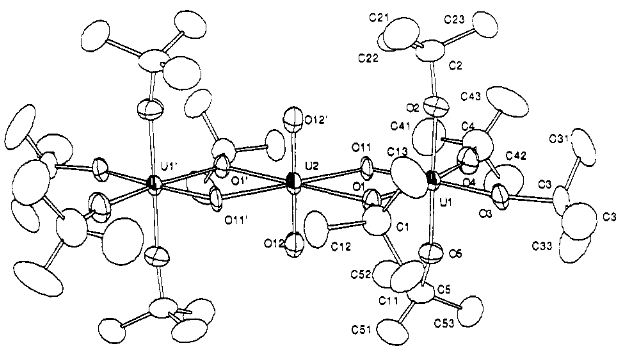
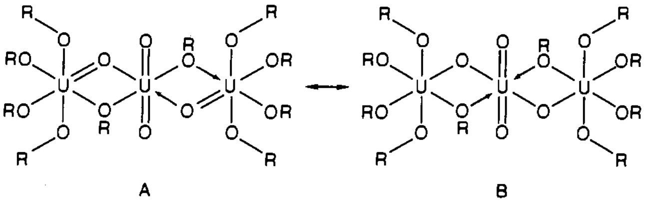


Figure 1. ORTEP drawing of $[UO_2(O\text{-}t\text{-}Bu_2][UO(O\text{-}t\text{-}Bu)_4]_2$ with the atomic numbering scheme. Thermal ellipsoids are at the 30% probability level.

The composition of **1** was determined by single-crystal X-ray crystallography.[15] The solid-state structure of the compound consists of trimeric units (Figure 1) in which a central $UO_2(O\text{-}t\text{-}Bu)_2$ unit is symmetrically ligated by two $UO(O\text{-}t\text{-}Bu)_4$ units. Each uranium atom lies in a nearly octahedral UO_6 coordination environment. The central uranium atom lies on a crystallographic center of symmetry, requiring a rigorously linear disposition of the terminal oxo groups, with U(2)–O(12) equal to 1.753 (6) Å. This distance is within the range reported for other uranyl U–O bond lengths.[16] The U(2)–O(1) bond length, 2.378 (6) Å, is similar to the 2.42 (2) Å average bridging alkoxide U–O distance found in the mixed-valence complex $[UO_2(\mu\text{-}OPh)_2(thf)]_2[U(\mu_3\text{-}O)(OPh)_3(thf)]_2$.[12] The uranyl–bridging oxo distance, U(2)–O(11), is 2.301 (6) Å. In other solid-state structures where U=O groups serve as equatorial ligands to uranyl ions,[17-19] the dative O→U distances generally range from 2.47 to 2.54 Å, suggesting that some resonance delocalization occurs in **1** as indicated in structures A and B.



A

B

The UOX_4 fragment has little structural precedent in uranium chemistry. The solid-state structures of both the α and β forms of UOF_4 have been determined.[20-23] While both forms are plagued by O–F disorder problems in terminal sites, the U–O bond lengths are proposed to be on the order of a typical uranyl U–O bond length (1.70–1.75 Å). The longer bridging uranium–oxo distance in the current structure (U(1)–O(11) = 1.923 (6) Å) is again indicative of resonance delocalization in the complex. The bridging alkoxide U(1)–O(1) bond length of 2.295 (6) Å is longer than the terminal U–O alkoxide distances (2.015 (6)–2.055 (6) Å), as would be expected. The average U–O(terminal) distance of 2.042 (6) Å is similar to the 2.10 Å average found in $U(OMe)_6$.[3]

The average U-O-C angle associated with the terminal *tert*-butoxide ligands is 159.2 (7)° (range 151.6 (7)–163.1 (8)°); large U–O–C angles for terminal alkoxide ligands have been noted in other uranium alkoxides.[2-4] The angle about the bridging oxo group is 117.5 (3)°, while the U–O–U angle about the bridging alkoxide oxygen is 101.4 (2)°.

The trimer is fluxional in solution. The low-temperature limiting ^1H NMR spectrum described above is consistent with the solid-state structure of **1**, which possesses idealized C_{2h} symmetry and should therefore show four types of alkoxide ligands in a 2:2:4:2 ratio. As the temperature is raised from −35 °C, the three downfield singlets broaden, while the singlet at δ 1.55 remains sharp. We assign the latter as the resonance associated with the bridging alkoxide ligand. Chemical exchange between the axial and equatorial alkoxides on the terminal uranium atoms accounts for the broadening of the three downfield resonances. These resonances do not completely coalesce until +85 °C, at which point the fourth resonance begins to broaden as well. These spectral properties are reversible. Further heating (>+85 °C) results in the irreversible appearance of new resonances in the spectrum associated with as yet unidentified decomposition products.

The synthesis of **1** may involve initial formation of $UO_2(O\text{-}t\text{-}Bu)_2(thf)_2$, which then decomposes to $UO(O\text{-}t\text{-}Bu)_4$ and (presumably) $UO_3(thf)_x$. Once formed, $UO(O\text{-}t\text{-}Bu)_4$ reacts rapidly with $UO_2(O\text{-}t\text{-}Bu)_2(thf)_2$ to form **1**. Indirect support for the initial formation of $UO_2(O\text{-}t\text{-}Bu)_2(thf)_2$ is based on our observation that mononuclear $UO_2(O\text{-}t\text{-}Bu)_2(OPPh_3)_2$ is the sole isolable product (≥80% yield) when the reaction is carried out in the presence of triphenylphosphine oxide.[24]

It has been suggested[8] that primary uranyl alkoxides are stable with respect to disproportionation in alcoholic solution. We are currently investigating the metathesis reactions of primary and secondary alkoxides in aprotic solvents, with the goal of elucidating the factors controlling assembly of oxo–alkoxide clusters similar to **1**. Such clusters could prove to be useful models in the study of aqueous-phase oxo–hydroxy–uranium(VI) species important in environmental speciation.

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Supplementary Material Available: Tables of atomic positional parameters and isotropic thermal parameters, anisotropic thermal parameters, and selected bond lengths and angles (8 pages). Ordering information is given on any current masthead page.

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(15) The complex crystallizes from toluene in the triclinic space group $P\bar{1}$ with cell parameters a = 9.842 (1) Å, b = 9.761 (4) Å, c = 30.965 (2) Å, α = 94.94 (1)°, β = 89.45 (1)°, γ = 101.87 (2)°, and V = 2900 (2) $Å^3$. There are two independent half-trimers per asymmetric unit, yielding Z = 2 and d(calcd) = 1.73 g cm^{-3}. The geometries of the independent trimers are very similar; only one set of metrical parameters is discussed in the text. The data were collected at room temperature on an Enraf-Nonius CAD4 automated diffractometer, utilizing Mo Kα radiation (λ = 0.71069 Å). Following the application of an analytical absorption correction, the structure was solved by a combination of direct methods and Fourier techniques. All hydrogen atoms were located in a difference Fourier map, then placed in idealized positions; they were not refined. For 4776 reflections with $F_o^2 > 3\sigma(F_o^2)$, R = 0.026 and R_w = 0.029.

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Inorganic and Structural Chemistry Group
(INC-4)
Isotope and Nuclear Chemistry Division
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

C. J. Burns
A. P. Sattelberger*

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