decrease in C–P–C angles helps to reduce all three $\theta/2$ values and leads to a cone angle of 176°.

In a relatively uncrowded environment, the $(o\text{-tol})_3P$ ligand in $[(o\text{-tol})_3PHgCl\cdot ClO_4]_2$[12] adopts a propeller conformation (Figure 3c) with Hg–P–C–C(H) torsion angles close to 128° and a maximum cone angle of 198° close to the value predicted (194°). The ligand profile (Figure 2d) shows clearly that there are large gaps of the same order of magnitude as those found in the Cy_3P system. When the $(o\text{-tol})_3P$ ligand is subjected to steric stress the propeller conformation is changed considerably to make even bigger gaps between the aromatic rings and to decrease the ligand cone angle (Table I). Figures 2e and 2f show the profiles for $(o\text{-tol})_3P$ in $[(o\text{-tol})_3PHg(OAc)_2]_2$[19] and in $((o\text{-tol})_3P)_2PtI_2$,[20] respectively; the cone angles and torsion angles defining the orientation are given in Table I. That $[(o\text{-tol})_3PHg(OAc)_2]_2$ occurs as a dimer whereas $t\text{-}Bu_3PHg(OAc)_2$ is a monomer clearly reveals that although the $(o\text{-tol})_3P$ ligand has a larger cone angle, the greater gaps between the tolyl rings allow the formation of a dimer which is essentially isostructural with $[Cy_3PHg(NO_3)_2]_2$ and $[Cy_3PHg(OAc)_2]_2$. In the very overcrowded $((o\text{-tol})_3P)_2PtI_2$,[20] one of the tolyl rings is rotated until the Pt–P–C–C(H) torsion angle is close to 0°. The $(o\text{-tol})_3P$ ligand is effectively locked in this conformation by the bulky iodine atoms. Our inability to induce ortho metalation in $((o\text{-tol})_3P)_2PtI_2$ can thus be explained; the ligand conformation is locked, with no methyl group near the platinum, by the bulky iodine atoms. An essentially identical overcrowded conformation is found for $(o\text{-tol})_3P$ in $((o\text{-tol})_3P)_2IrClCO$.[21]

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Registry No. $[Cy_3PHg(SCN)_2]_n$, 67124-77-0; $[Cy_3PHg(NO_3)_2]_2$, 63181-12-4; $[Cy_3PHg(OAc)_2]_2$, 67124-81-6; $(Cy_3P)_2Hg(OAc)_2$, 66161-25-9; $(Cy_3P)_2Hg(ClO_4)_2$, 67124-82-7; $(Cy_3P)_3Pt$, 63175-89-3; $(Cy_3P)_2PtI_2$, 50725-85-4; $t\text{-}Bu_3PHg(OAc)_2$, 66119-71-9; $t\text{-}Bu_3PHg_2(SCN)_4$, 67238-54-4; $t\text{-}Bu_3PNiBr_3^-$, 67124-83-8; $[(o\text{-tol})_3PHgCl\cdot ClO_4]_2$, 67124-85-0; $[(o\text{-tol})_3PHg(OAc)_2]_2$, 67124-86-1; $((o\text{-tol})_3P)_2PtI_2$, 67124-87-2; $((o\text{-tol})_3P)_2IrClCO$, 56487-57-1.

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Contribution from the University of California,
Los Alamos Scientific Laboratory,
Los Alamos, New Mexico 87545

Convenient Multigram Syntheses of Uranium Pentafluoride and Uranium Pentaethoxide

Gordon W. Halstead, P. Gary Eller,* Larned B. Asprey, and Kenneth V. Salazar

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The chemistry of uranium in unusual oxidation states and coordination environments continues to be a subject of great interest.[1] One of the least studied valencies is the +V state, at least in part due to misconceptions concerning the stability of U(V) with respect to disproportionation and the difficulty in preparing suitable uranium(V) precursors for compound synthesis. However, it is becoming clear that pentavalent uranium in the proper ligand and solvent environment is a stable, interesting entity for which an extensive chemistry is developing.[2-4]

Perhaps the most useful precursors for U(V) compound synthesis are uranium pentafluoride[4] and uranium pentaethoxide.[5] The standard synthesis of $U(OC_2H_5)_5$, from UCl_4 and sodium ethoxide in the presence of an oxidant, is a tedious procedure which frequently gives poor yields.[6] Several syntheses of uranium pentafluoride have been reported, but each suffers from certain disadvantages. For example, the reactions of UF_4 and F_2,[7] or of HF with UCl_5 or UCl_6,[8] yield UF_5 but require facilities for handling the highly corrosive materials F_2 and HF. Other reported procedures require elevated temperatures (UF_4 + UF_6)[9] of inconvenient starting materials ($NOUF_6$),[10] produce mixtures (NH_4UF_7 pyrolysis or UF_6 + HBr),[11,12] yield small quantities of product (UF_6 + $SOCl_2$ or photolysis of UF_6),[13,14] or produce impure products.

Recently, we have been investigating pentavalent uranium in a variety of chemical environments[4] and have found UF_5 to have an extensive chemistry in nonaqueous solvents. We report here an easy multigram synthesis of pure β-UF_5 by a method which obviates the necessity for metal vacuum lines or high-temperature apparatuses. Also, we report a convenient one-step synthesis of the useful material $U(OC_2H_5)_5$ from β-UF_5.

Experimental Section

Standard Schlenk, vacuum-line, and inert atmosphere box techniques were used throughout this study for manipulating the air-sensitive samples. Ethanol was dried by distillation from magnesium turnings. Sodium ethoxide was prepared by direct reaction of sodium hydride with dry ethanol, followed by vacuum drying. Uranium hexafluoride was purified by a series of trap-to-trap distillations at −41 °C. Carbon monoxide, 99.9% pure, Matheson Gas Products, was passed through a liquid-nitrogen trap and used without further purification. Uranium was determined gravimetrically as the precipitated uranyl bis(8-hydroxyquinolate), $UO_2(C_9H_6NO)_2\cdot C_9H_7NO$,

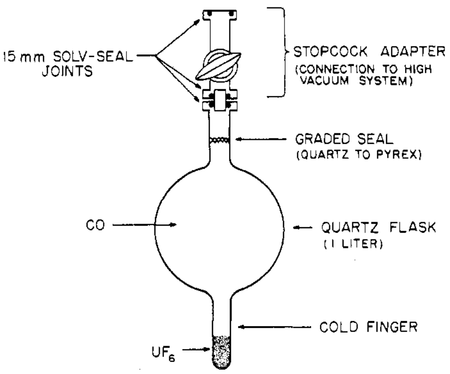

Figure 1. Reaction vessel for preparation of β-UF_5.

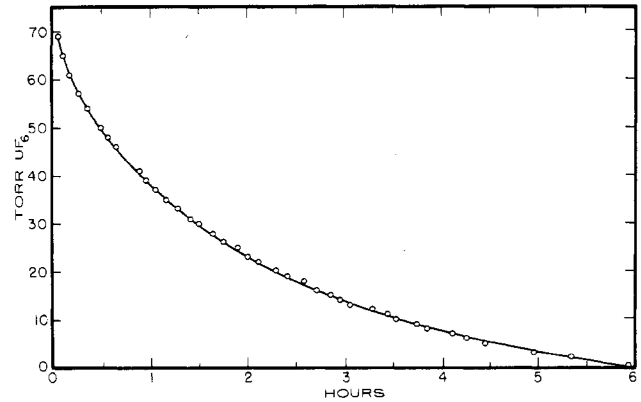

Figure 2. Pressure–time plot for the gas-phase reaction of UF_6 and CO.

after hydrolysis and dissolution of the sample.[15] Fluorine was determined gravimetrically as PbClF by a published procedure.[16] Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Attempts to obtain satisfactory U and F analyses for UF_5 from commercial analytical laboratories were unsuccessful.

Multigram Synthesis of β-UF_5. A 1-L quartz flask was connected to a high-vacuum line by an attached stopcock adapter (see Figure 1). The flask was evacuated and carefully flamed with a torch under vacuum to remove any adsorbed water and allowed to cool. Five to ten grams of UF_6 was transferred to the reaction flask by cooling the cold finger in a cold trap, and then 600 Torr of CO was added. The stopcock was closed and the flask was removed from the line and placed 10 cm from an Ace-Hanovia 550-W UV lamp, No. 6515-36, with an aluminum foil reflector placed behind the flask. Irradiation was carried out for 16–18 h to give a large volume of product in the cold finger and as a coating on the flask walls. The flask was placed back on the vacuum line, and the volatile materials (COF_2 and unreacted UF_6) were removed by high vacuum for several hours. The reaction flask was transferred to a drybox, and the fluffy, blue-green β-UF_5 was scraped and shaken into a tared bottle. Yields were as high as 87% with the higher percentage yields being obtained for the smaller UF_6 charges. A charge of 5 g appears to be optimum. An X-ray powder pattern of the product was identical with that of a known sample of β-UF_5.[17] Anal. Calcd for UF_5: U, 71.5; F, 28.5. Found: U, 70.4; F, 27.0.

Gas-Phase Reaction of UF_6 and CO. A 1-L quartz flask equipped with a joint for attachment to a stopcock was connected to a high-vacuum line (see Figure 1). The flask was evacuated and then conditioned for 2 h with 100 Torr of UF_6. The flask was again evacuated and 71 Torr of UF_6 was admitted to the bulb and condensed into the cold finger by means of a −41 °C trap (CH_3CN/N_2). Seventy Torr of CO was then admitted to the flask, the stopcock was closed, and the flask was removed from the vacuum line and placed 10 cm from a 550-W UV lamp. The pressure was then monitored with a pressure transducer during irradiation until the reaction was judged complete (about 6 h). At that point a coating of light green β-UF_5 powder was present on the walls of the flask. The results are presented in Figure 2.

Synthesis of $U(OC_2H_5)_5$ from β-UF_5. Fifteen grams of UF_5 was added to a three-neck reaction flask equipped with a reflux condenser, a nitrogen inlet, and an additional funnel. The flask was cooled to −78 °C and a solution of 15.3 g of $NaOC_2H_5$ in 200 mL of dried, degassed ethanol was added dropwise from the addition funnel. When the addition was complete, the reaction mixture was warmed slowly to room temperature to give a green solution. Refluxing the solution for 4 h gave a brown solution characteristic of $U(OC_2H_5)_5$. The solvent was removed in vacuo yielding a sticky brown solid. The reaction vessel was taken into a drybox and the residue was transferred to a vacuum distillation apparatus with heat tape around the still head. The distillation flask was heated slowly to 170 °C and a clear, brown distillate came over smoothly at a head temperature of 120–130 °C and a pressure of 10^{-2} Torr (lit. value 129–131 °C at 2×10^{-3} Torr[6]). The apparatus was cooled to room temperature and then taken into a drybox, and the liquid $U(OC_2H_5)_5$ was transferred to a tared bottle; yield 12.3 g (60%). Anal. Calcd for $UO_5C_{10}H_{25}$: C, 25.92; H, 5.44. Found: C, 25.74; H, 5.34.

Discussion

High-purity uranium pentafluoride (β form) is formed conveniently in good yield by the room-temperature UV photolysis of UF_6 in the presence of the fluorine scavenger CO (eq 1). The photolytic reduction of UF_6 with CO has been

$$2UF_6 + CO \xrightarrow{h\nu} 2UF_5 + COF_2 \qquad (1)$$

reported before, but on a very small scale.[14] A high-temperature apparatus, a metal vacuum line, or exotic precursors are not required for our procedure. The product was identified as high-purity β-UF_5 by its characteristic color, solubility properties, visible spectrum, X-ray powder pattern, solution NMR, and analysis. Possible impurities, such as intermediate fluorides, oxygen-containing species, and α-UF_5, were not observed. An electronic spectrum of the product in acetonitrile is identical with that of β-UF_5 (prepared by another procedure) in this solvent.[18]

The principal complication preventing the yield from being quantitative in a reasonable length of time is the tendency for the quartz flask to fog with the UF_5 product. Thus, doubling the amount of UF_6 charged to the flask will not double the amount of UF_5 produced. We have also obtained similar yields of β-UF_5 at a comparable rate using SO_2 rather than CO as the fluorine scavenger, but product purity is not as high as with CO. It is posssible to run simultaneously as many as four identical flasks per UV lamp and obtain good yields in each.

We have also investigated the UF_6/CO reaction with both reactants completely in the gas phase. The results are presented in Figure 2. Under these conditions, the reaction appears to have a half-time of 1.2 h. These results are similar to findings for the gas-phase $SOCl_2/UF_6$ reaction.[13]

We have found β-UF_5 to have an extensive nonaqueous solvent chemistry.[4] One of the most useful reactions we have found is its convenient conversion to uranium pentaethoxide, a widely used but tediously prepared precursor to many U(V) and U(VI) organo compounds.[5,6,19] UF_5 reacts cleanly with 5 equiv of $NaOC_2H_5$ to give high-purity $U(OC_2H_5)_5$ in good yield (eq 2). The red-brown liquid was characterized by its

$$UF_5 + 5NaOC_2H_5 \rightarrow U(OC_2H_5)_5 + 5NaF \qquad (2)$$

analysis, boiling point, UV–visible spectrum, and its characteristic ^{13}C NMR spectrum.[19]

In summary, we report new convenient procedures for preparing multigram quantities of UF_5 and $U(OC_2H_5)_5$. These materials have extensive nonaqueous chemistries and form the basis for ongoing studies which will be reported shortly.[4,19]

Acknowledgment. This work was performed under the auspices of the U.S. Department of Energy.

Registry No. β-UF_5, 13775-07-0; $U(OC_2H_5)_5$, 10405-34-2; UF_6, 7783-81-5; CO, 630-08-0.

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Contribution from the
Department of Physical and Inorganic Chemistry,
University of New England, Armidale, N.S.W., 2351, Australia,
and School of Science, Griffith University,
Nathan, Queensland, 4111, Australia

Ferromagnetic Interactions in Sodium Bis(carbonato)cuprate(II)

Anthony K. Gregson*[1a] and Peter C. Healy[1b]

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Simple compounds of copper are well suited to the study of magnetic interactions. None of the complications associated with $S > 1/2$ are present so factors involving cooperative phenomena are readily isolated and characterized. Materials of current interest are those with well-defined structural characteristics where comparisons between the dimensionality of the system and the details of the cooperative transition can be made. Particular systems relevant to the present study include K_2CuF_4, which possesses two-dimensional ferromagnetic intralayer interactions as well as ferromagnetic interlayer coupling,[2] and layered $[CuCl_4]^{2-}$ derivatives[3,4] where the copper atoms form a two-dimensional lattice of ferromagnetically coupled ions with each layer coupled antiferromagnetically. Below the transition temperature T_c these often unusually weak antiferromagnetic interactions can result in complex effects because the spin-flop field can be exceeded by rather smaller magnetic fields than is otherwise possible in normal three-dimensional antiferromagnets.[3]

Sodium bis(carbonato)cuprate(II) is best described[5] (Figure 1) as a two-dimensional polymeric network of $[Cu(CO_3)_2{}^{2-}]_\infty$ with each copper in an approximately square-planar environment coordinated by the four symmetry-related binuclear bridging carbonate groups. Successive layers of $[Cu(CO_3)_2{}^{2-}]_\infty$ are bound ionically by the sodium ions. The two-dimensional structure of $Na_2Cu(CO_3)_2$ contrasts with the chain-like structures and magnetic properties of $Na_2Cu(CO_3)_2{\cdot}3H_2O$[6,7] and $Cu(NH_3)_2CO_3$.[8,9]

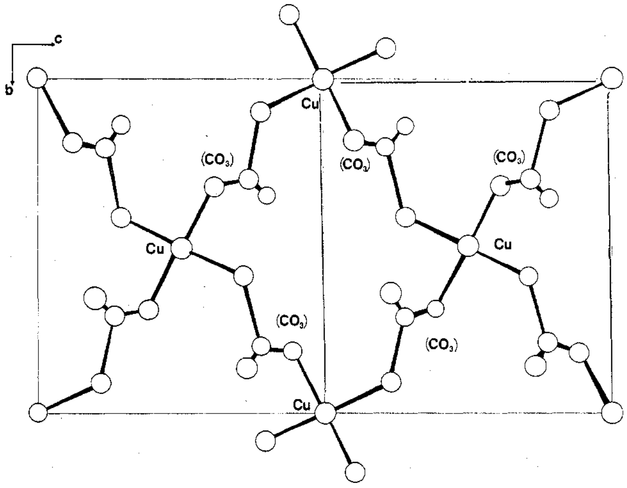

Figure 1. Unit cell of $Na_2Cu(CO_3)_2$.

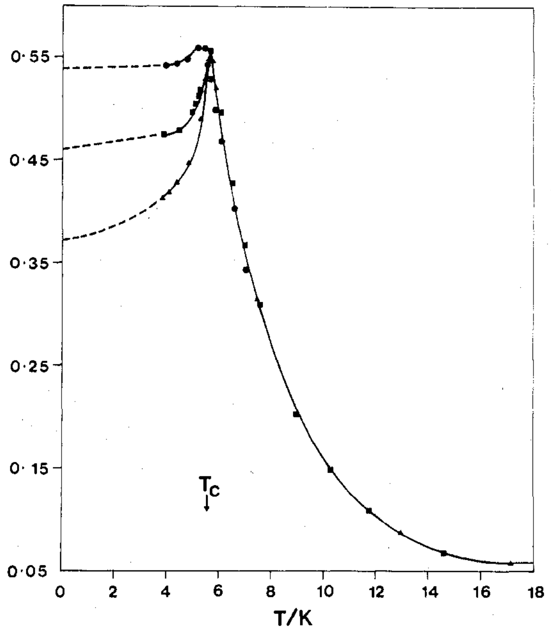

Figure 2. Average susceptibility of a powdered sample of $Na_2Cu(CO_3)_2$ in various applied magnetic fields: ▲, 1.7 mT; ■, 28.7 mT; ●, 346.7 mT. Solid lines are a guide to the eye; dashed lines are extrapolations to $T = 0$ K.

Experimental Section

$Na_2Cu(CO_3)_2$ was prepared by previously published methods.[5] The magnetization and susceptibility of a powdered sample were determined using the SQUID susceptometer described recently.[10] No corrections for the diamagnetism of the substituent atoms have been made, the corrections below 70 K being negligible.

Results and Discussion

The average powder susceptibility of $Na_2Cu(CO_3)_2$ between 4 and 18 K is plotted in Figure 2. Above the transition temperature of 5.6 ± 0.2 K the susceptibility is characteristic of a ferromagnetic system. It increases more rapidly than expected for a simple paramagnetic ion although it is nearly field independent over the range of applied fields (1.7–350 mT) except near T_c where the maximum becomes less distinct and appears to move to lower temperatures in the highest field. The data between 15 and 70 K can be fitted by the Curie–Weiss expression $\chi = C/(T - \Theta)$, where $C = Ng^2\beta^2/4k$, with

0020-1669/78/1317-2969$01.00/0