

the same symmetry character as the π orbitals of the carbonyl bridge;¹⁷ hence, no distortion of the coordination sphere of the reductant is required for overlap. Finally, it appears that the importance of overlap between reductant and bridge orbitals increases sharply as the π system of the bridge is extended by interposition of an aromatic ring in conjugation with the carbonyl function. Thus, the reverse salt effect is not observed in the Cr^{2+} reduction of the μ -pyruvato dimer (IV), in which the bridging group is a lone keto carbonyl, nor in the formate monomer, in which the bridge is a carboxyl carbonyl.²⁰

Acknowledgment. The authors are grateful to Professors James Espenson and Milton Manes for valuable discussions.

Registry No. I, 52362-79-5; II, 52375-30-1; III, R = 2-CHO, 42532-71-8; III, R = 4-CHO, 19743-65-8; IV, 80327-74-8; Cr, 7440-47-3.

(20) Chromium(II) reduction of the 2-formylbenzoato monomer (III, R = 2-CHO) exhibits only the expected positive salt effect. Attack at the aldehyde group has been shown to play only a minor role in this reduction.⁸

Communications

Improved Synthesis of $\text{UCl}_3(\text{THF})_x$ and the Preparation of 15-Crown-5 Derivatives of Trivalent Uranium

Sir:

Since our first report of the synthesis of $\text{UCl}_3(\text{THF})_x$ (THF = tetrahydrofuran),¹ its utility as a starting material for trivalent uranium syntheses has been demonstrated in our laboratories² and in others.³ The sodium hydride reduction of uranium tetrachloride has proved convenient in our hands as a reproducible route to this starting material; however, the variable activity of commercial sodium hydride as well as problems associated with further reduction of the uranium to lower valent species has necessitated exacting control over reaction times as well as solvent amounts. While eliminating some of these problems, an alternative procedure reported by Andersen³ still requires exacting stoichiometric control of reagents since excess sodium naphthalide will easily reduce $\text{UCl}_3(\text{THF})_x$. Also in those instances where naphthalene interferes in subsequent reactions, an additional purification step is required.

In this report we present an improved synthesis of $\text{UCl}_3(\text{THF})_x$, which utilizes excess sodium carbide as the reducing agent and provides marked improvements over the two previously described routes to this key material. A convenient diagnostic for the purity of this reagent is also discussed as part of the chemistry of $\text{UCl}_3(\text{THF})_x$ with 15-crown-5 and benzo-15-crown-5.

Experimental Section. All manipulations were performed under a dry nitrogen atmosphere by using standard Schlenk techniques or by using standard vacuum techniques. All solvents used in this study were reagent grade and were dried prior to use. UCl_4 was prepared by literature procedures.⁴ Sodium carbide was purchased from Alfa Chemicals and used as received. Benzo-15-crown-5 and 15-crown-5 were obtained from Parish Chemical Co. and were used without further purification. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

$\text{UCl}_3(\text{THF})_x$. Uranium tetrachloride (0.38 g, 1 mmol) and Na_2C_2 (0.35 g, 5 mmol) were loaded into a 100-mL reaction vessel in the drybox, and 80 mL of dry, degassed THF was condensed onto the solid. When the mixture was warmed to room temperature, an immediate color change from green to purple was observed. Excess Na_2C_2 , NaCl, and carbon were filtered from the stirred solution after 2 h, and the THF solution of $\text{UCl}_3(\text{THF})_x$ was characterized as previously reported.¹ Such solutions were found to contain ca. 0.8 mmol

of $\text{UCl}_3(\text{THF})_x$. No evidence of further reduction was observed upon stirring the reaction solutions overnight prior to filtration.

$\text{UCl}_3(\text{THF})_x$ + 15-Crown-5. The above solutions of 0.8 mmol of $\text{UCl}_3(\text{THF})_x$ were filtered onto excess (0.5 mL) 15-crown-5 in 15 mL of THF. Quantitative precipitation of red $\text{UCl}_3(15\text{-crown-5})$ occurred as the reaction was stirred overnight, and when the mixture was filtered through a fine frit and the solid was vacuum dried, 0.41 g (0.73 mmol) of product was isolated from the frit. Anal. Calcd for $\text{UCl}_3\text{O}_5\text{C}_{10}\text{H}_{20}$: C, 21.27; H, 3.57; U, 42.15; Cl, 18.84; O, 14.17. Found: C, 21.86; H, 3.85; U, 38.97; Cl, 20.20; O, 15.25. The filtrate from the above reaction was colorless to pale green depending on residual $\text{U}^{\text{IV}} \cdot 15\text{-crown-5}$ present.

A thermogravimetric analysis on $\text{UCl}_3(15\text{-crown-5})$ (5.9 mg) indicated decomposition at 308 °C and leveled off at 488 °C with a 50% weight loss. Continued heating under moist oxygen produced 2.89 mg of U_3O_8 , corresponding to 41.5% U.

$\text{UCl}_3(\text{THF})_x$ + Benzo-15-crown-5. Reaction of 0.8 mmol of $\text{UCl}_3(\text{THF})_x$ in 80 mL of THF with 1 g of benzo-15-crown-5 in 20 mL of THF slowly precipitated $\text{UCl}_3(\text{benzo-15-crown-5})$ as a fine red powder. After the mixture was stirred overnight, the precipitate was filtered and vacuum dried, yielding 0.39 g (0.64 mmol) of product and a red filtrate. A quantitative precipitation was observed when 1.5 g or more of benzo-15-crown-5 was used. Anal. Calcd for $\text{UCl}_3\text{O}_5\text{C}_{14}\text{H}_{20}$: C, 27.44; H, 3.29; U, 38.85; Cl, 17.36; O, 13.06. Found: C, 27.21; H, 3.44; U, 39.02; Cl, 17.19; O, 12.85.

Results and Discussion. Reduction of uranium tetrachloride by excess sodium carbide in THF has proved to be a most convenient route to the key starting reagent, $\text{UCl}_3(\text{THF})_x$. Several advantages over previous syntheses are readily discernible, the most important being that no further reduction past U(III) occurs with this reducing agent. In addition, precise control of stoichiometry is not necessary and all by-products (NaCl and C_m , in addition to the excess Na_2C_2) are insoluble and thus easily removed by filtration.

While previous work in our laboratories² had established 18-crown-6 as a good ligand for trivalent uranium, an examination of the cavity diameter of 15-crown-5 suggested an even better match for U(III). Thus the first uranium(III) complexes with 15-crown-5 and benzo-15-crown-5 were prepared. A comparison of the thermal gravimetric analysis on $\text{UCl}_3(15\text{-crown-5})$ with that reported for $\text{UCl}_3(18\text{-crown-6})$ ² supports this contention of increased stability for the 15-crown-5 derivatives in that decomposition occurs at 200 °C for the latter and at 308 °C for the former.

An interesting aside has also resulted from this 15-crown-5 chemistry pertaining to a convenient method of testing the

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(3) Andersen, R. A. *Inorg. Chem.* 1979, 18, 1507.

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purity of $\text{UCl}_3(\text{THF})_x$ reagents generated by various procedures. We have observed that the $\text{UCl}_4 \cdot 15\text{-crown-5}$ adduct is very soluble in THF, probably owing to a ready dissociation of the crown ether, while $\text{UCl}_3(15\text{-crown-5})$ is totally insoluble. This difference allows for direct measurement of residual U(IV) without interference by the U(III) generated. Also the color of the $\text{UCl}_3(15\text{-crown-5})$ varies significantly with minor impurities and provides an additional qualitative measure of the purity of the $\text{UCl}_3(\text{THF})_x$.

Studies are currently continuing on the crown ether derivatives of trivalent uranium and the chemistry of $\text{UCl}_3(\text{THF})_x$ as a synthetic reagent for nonaqueous coordination chemistry as well as organometallic chemistry of uranium(III).

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

Registry No. UCl_4 , 10026-10-5; Na_2Cl_2 , 2881-62-1; $\text{UCl}_3(15\text{-crown-5})$, 71934-08-2; $\text{UCl}_3(\text{benzo-15-crown-5})$, 82583-23-1.

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Received May 7, 1982

Synthesis and Spectroscopic Properties of a New Oligomeric Condensed Phosphite Platinum(II) Complex

Sir:

The synthesis and spectroscopy of luminescent multimetallic transition-metal compounds have become a field of considerable interest. Among the compounds being studied is the bimetallic complex $\text{K}_4[\text{Pt}_2(\text{pop})_4] \cdot 2\text{H}_2\text{O}$ ^{1,2} formed by heating potassium tetrachloroplatinate(II) with phosphorous acid at 100 °C. The complex has evoked interest from the viewpoint of its electronic spectroscopy³ and its photoredox chemistry.⁴ Furthermore, the unusual observation of an intense room-temperature phosphorescence from aqueous solutions of $\text{K}_4[\text{Pt}_2(\text{pop})_4]$ has led to the development of a spectrofluorometric method for the trace-element detection of platinum.⁵ Another interesting feature of the chemistry of this complex is its facility to undergo oxidative addition of halogens and methyl iodide across the dimer to yield metal-metal-bonded biplatinum(III) compounds.⁶ Analogous higher order oligomers would be of interest in order to investigate the effect of extended intermetallic interactions upon the electronic structure in the region between dimeric species (molecular orbital regime) and one-dimensional systems (band theory regime).

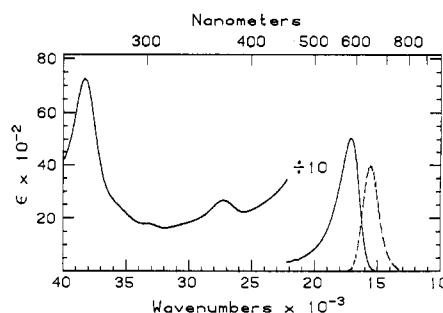


Figure 1. Room-temperature absorption (—) and luminescence (---) spectra of the oligomeric platinum(II) complex in aqueous 1 M HCl.

We now find that, when the synthesis of $\text{K}_4[\text{Pt}_2(\text{pop})_4]$ is carried out at a temperature of 170 °C rather than 100 °C, the bimetallic complex is not the final product. Instead reaction proceeds beyond the bimetallic stage and a new species is formed as dark green powder.⁷ This compound is soluble only in aqueous medium and decomposes within a few hours in solution to first $\text{K}_4[\text{Pt}_2(\text{pop})_4]$ and finally $\text{Pt}\{\text{OP}(\text{OH})_2\}_4\text{H}_2$. The maximum solution stability is realized when the solution is acidified to an approximate pH of 0. Blue solutions of this new complex exhibit an intense red luminescence at room temperature.

The ³¹P NMR spectrum of this complex in acidified aqueous solution shows a broad overlapping multiplet ($\nu_{1/2} = 112$ Hz) centered at δ 62.1 and flanked by satellite peaks due to coupling with ¹⁹⁵Pt ($^1J(\text{Pt-P}) = 3250$ Hz). The broadness of the lines not only is due to overlapping resonances from inequivalent phosphorus nuclei but also is caused by the considerable line multiplicity from second-order effects in the spectrum. The ¹⁹⁵Pt NMR spectrum shows two poorly resolved sets of quintet resonances of unequal intensity. The sets of peaks are centered at δ -4936 ($^1J(\text{Pt-P}) = 3250$ Hz) and δ -4948 ($^1J(\text{Pt-P}) = 3300$ Hz).⁸ The rate of complex decomposition precludes collection of sufficient data to resolve the ²J(Pt-P) coupling, but the resolved ¹J(Pt-P) coupling into sets of quintets confirms that each platinum atom is tetracoordinated by phosphorus atoms. Comparison of the ³¹P and ¹⁹⁵Pt shift positions and the magnitude of the ¹J(Pt-P) coupling shows a close similarity to those values found for the platinum(II) complex, $\text{K}_4[\text{Pt}_2(\text{pop})_4]$, but quite a difference from those of the analogous platinum(III) compounds.⁶ From these NMR spectral observations we believe the complex has a linear arrangement of divalent platinum atoms. Magnetic susceptibility and EPR studies indicate that the platinum atoms are all diamagnetic in contrast to the mixed-valence rhodium oligomers⁹ and platinum blues.¹⁰

The electronic absorption spectrum of the complex in aqueous 1 M HCl solution (Figure 1) shows an exceptionally intense band at 580 nm ($\epsilon = 5.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). No intense absorption bands were observed in the near-infrared region. The large red shift of the low-energy intense absorption band from 368 nm in $\text{K}_4[\text{Pt}_2(\text{pop})_4]$ upon an increase of the metallic chain length has also been observed in the solution aggregation of rhodium isocyanide complexes.^{9,11,12} By analogy with

(1) The abbreviation pop represents $[(\text{HO})(\text{O})\text{POP}(\text{O})(\text{OH})]^{2-}$.
(2) (a) Sperline, R. P.; Dickson, M. K.; Roundhill, D. M. *J. Chem. Soc., Chem. Commun.* 1977, 77-79. (b) Filomena Dos Remedios Pinto, M. A.; Sadler, P. J.; Neidle, S.; Sanderson, M. R.; Subbiah, A. *Ibid.* 1980, 13-15.
(3) Fordyce, W. A.; Brummer, J. G.; Crosby, G. A. *J. Am. Chem. Soc.* 1981, 103, 7061-7064.
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(7) In addition to this green complex a vermilion red compound is found in variable yield. This additional compound is insoluble in water and organic solvents. The nature of this compound is presently completely uncertain. These higher oligomers of $\text{K}_4[\text{Pt}_2(\text{pop})_4]$ have also been observed by others (Gray, H. B., personal communication).
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