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Electron Transfer in Organouranium and Transuranium Systems

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The preparation of a reduced uranocene derivative, potassium bis([8]annulenediyl)uranate(III), $K^+[(C_8H_8)_2U]^-$, and the 1,1'-dimethyl compound is described. 1,1'-Di-*tert*-butylneptunocene(IV) and -plutonocene(IV) and the potassium salts of the corresponding reduced compounds have been prepared. The 1H NMR spectrum of the plutonocene shows temperature-independent paramagnetism; the other compounds show normal temperature-dependent paramagnetism. Mixtures of each of the bis([8]-annulenediyl)actinide(IV) compounds with the corresponding actinate(III) derivatives show rapid electron exchange on the NMR time scale.

Introduction

We recently found rapid electron exchange between cyclooctatetraene (COT) derivatives of ytterbium(II) and ytterbium(III) with second-order exchange rate constants on the order of $10^7 M^{-1} s^{-1}$.¹ These studies have been extended to related bis([8]annulenediyl)actinide(IV) systems, $(C_8H_8)_2An$, in order to evaluate the generality of such exchange mechanisms in cyclooctatetraene sandwich structures of metals in different oxidation states. The systems that appeared to be the most promising for study are those of uranium, neptunium, and plutonium, because there are reports of bis([8]annulenediyl) compounds of each of these metals in two oxidation states. These reports are reviewed in this introduction because in each system there is something surprising about the reported physical properties of one of the compounds.

Concerning uranium, the reduction product of uranocene was reported in 1981 but not fully characterized; Folcher and co-workers² reported that the reduction product of uranocene could be prepared by the addition of 1 equiv of lithium naphthalene or by treating UCl_3 with COT dianion. The attempted replication of this procedure in our laboratory produced only uranocene.³ The Folcher group reported that the reduction product is brown and that it is oxidized reversibly to uranocene. The ESR spectrum taken at 4 K indicated a paramagnetic compound that was not a uranium(IV) species. The mass spectrum, however, gave a parent ion for uranocene. The reduction product was reported to have a 1H NMR resonance approximately 31 ppm upfield of TMS with a width at half-height of 40 Hz. This resonance is surprisingly sharp for a uranium(III) compound inasmuch as that for uranocene is about 90 Hz wide, and it is expected that a uranium(III) compound, which has an odd number of unpaired electrons, should have a considerably broader NMR resonance than a uranium(IV) compound, which has an even number.

Bis([8]annulenediyl) compounds of plutonium(III) and -(IV) and neptunium(III) and -(IV) have been prepared and characterized. Bis([8]annulenediyl)neptunium(IV), neptunocene, was prepared by Karraker et al.⁴ by addition of neptunium tetrachloride to a tetrahydrofuran (THF) solution of the COT dianion. The product, which was reported to appear yellow as a dilute solution and red as the concentrate, was purified by toluene extraction and characterized by a UV-vis spectrum and by comparison of its IR spectrum and X-ray powder pattern to those of uranocene. The compound is paramagnetic, and its Mössbauer spectrum was determined. Bis(1,3,5,7-tetramethyl[8]-annulenediyl)neptunium(IV) has also been prepared from the reaction of the Me_4COT dianion and neptunium tetrachloride.^{5,6}

Karraker et al.⁴ have also reported the preparation of bis([8]annulenediyl)plutonium(IV), plutonocene, by the addition of bis(tetraethylammonium)plutonium(IV) hexachloride to the COT dianion. The cherry red product was purified and characterized in the same way as for neptunocene, but it was reported that it exhibits an "unusual" type of temperature-dependent diamagnetism. This does not agree with theoretical predictions, based on a simple crystal field model, that plutonocene should have a

$J = 0$ ground state and hence exhibit temperature-independent paramagnetism.^{4,7} Plutonocene has also been prepared by direct reaction of the finely divided metal with COT.⁸ The preparation of 1,1',3,3',5,5',7,7'-octamethylplutonocene has been reported, but the compound almost certainly was potassium bis(1,3,5,7-tetramethyl[8]annulenediyl)plutonate(III).⁹

Potassium bis([8]annulenediyl)neptunate(III) was prepared by the reaction of neptunium tribromide with the COT dianion in THF.¹⁰ The burgundy-colored product was characterized by comparison of its powder pattern to that of potassium bis([8]-annulenediyl)cerate(III). Its magnetic susceptibility indicates two regions of temperature-independent paramagnetism between 2.2 and 5.5 K and between 5.5 and 19 K. Above 19 K it exhibits typical temperature-dependent paramagnetism (*vide infra*). The preparation and characterization of potassium bis([8]-annulenediyl)plutonate(III) are the same as for the neptunate. The turquoise-green plutonium compound exhibits temperature-dependent paramagnetism. Attempts to prepare the neptunate or plutonate from the chloride salts failed, presumably due to the low solubility of these salts. Both of these compounds are extremely water sensitive, in contrast to neptunocene and plutonocene, which are reported to be water stable.¹¹ Traces of oxygen oxidize the trivalent neptunium and plutonium compounds to neptunocene and plutonocene, respectively.

In the present paper we report the preparation and isolation of two reduced uranocenes and the 1,1'-di-*tert*-butyl derivatives of neptunocene and plutonocene and their reduction products. The 1H NMR spectra of these compounds and of mixtures are presented and discussed. Some of these results disagree with those reported previously for analogous systems, but the new results are in better agreement with expectation.

Experimental Section

General Data. Air-sensitive compounds were handled under argon either in a Vacuum Atmospheres Model HE 243 Dri-Lab with a Model

- (1) Eisenberg, D. C.; Kinsley, S. A.; Streitwieser, A. *J. Am. Chem. Soc.* **1989**, *111*, 5769.
- (2) Billian, F.; Folcher, G.; Marquet-Ellis, H.; Rigney, P.; Saito, E. *J. Am. Chem. Soc.* **1981**, *103*, 5603.
- (3) Kinsley, S. A. Unpublished results. Reaction of the tetramethylethylenediamine complex of uranium tetrachloride with dipotassium cyclooctatetraenediide in a mixture of THF and toluene at $-78^\circ C$ gives a deep blue color and no uranocene; when the mixture was warmed to room temperature, however, only uranocene was found (Smith, K. A. Dissertation, University of California, Berkeley, 1984).
- (4) Karraker, D. G.; Stone, J. A.; Jones, E. R., Jr.; Edelstein, N. *J. Am. Chem. Soc.* **1970**, *92*, 4841.
- (5) Streitwieser, A., Jr.; Dempf, D.; La Mar, G. N.; Karraker, D. G.; Edelstein, N. *J. Am. Chem. Soc.* **1971**, *93*, 7343.
- (6) Solar, J. P.; Burghard, H. P. G.; Banks, R. H.; Streitwieser, A., Jr.; Brown, D. *J. Am. Chem. Soc.* **1980**, *102*, 2186.
- (7) Hayes, R. G.; Edelstein, N. *J. Am. Chem. Soc.* **1972**, *94*, 8688.
- (8) Starks, D. F.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 3423.
- (9) The preparation is described in ref 6, but the green color indicates that it is the plutonium(III) compound. Presumably on preparation of the powder pattern capillary there was sufficient oxidation to produce a pattern which matched that of the corresponding octamethyluranocene.
- (10) Karraker, D. G.; Stone, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 6885.
- (11) This is mentioned in ref 4, but the stability is probably similar to that of uranocene, which, although originally worked up in degassed water, does decompose with a half-life of 20 h in THF containing 1 M water.

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HE 93A Dri-Train or with use of standard Schlenk line techniques. Unless otherwise noted, materials were obtained from commercial suppliers and used without additional purification. ^1H NMR spectra were obtained on UC Berkeley 200- and 250-MHz superconducting FT spectrometers equipped with Cryomagnets, Inc., magnets and Nicolet Model 1280 data collection systems, a Bruker 500-MHz AM 500 superconducting FT spectrometer with an Aspect 3000 computer system, and a 90-MHz JEOL FX 90Q FT spectrometer. Temperatures were measured with a thermocouple mounted next to the NMR tube. Chemical shifts are reported in ppm with positive shifts reported for peaks downfield of TMS and with peaks referenced to TMS or the upfield residual THF peak taken as 3.58 ppm. Visible spectra were taken on a Cary Model 118 or IBM Model 9430 spectrophotometer. Tetrahydrofuran (THF), toluene, and hexane were distilled from sodium-benzophenone or LiAlH_4 , freeze-thawed three times, and stored over 4A sieves prior to use. We thank BASF for a generous sample of cyclooctatetraene, which was vacuum transferred and stored over 4A molecular sieves prior to use. *tert*-Butylcyclooctatetraene was prepared as described previously¹² and stirred in 4A sieves prior to use.

Handling of Neptunium and Plutonium. Because of the hazards of handling ^{237}Np and ^{242}Pu , multiple levels of containment were used at all times. Air-sensitive work was done either in a glovebox or on a Schlenk line inside a reverse-pressure glovebox while an additional pair of gloves was worn. NMR spectra were taken in double NMR tubes containing an inner Teflon tube and an outer flame-sealed Pyrex tube. ^1H and ^{13}C NMR spectra were obtained on a Bruker 300-MHz superconducting spectrophotometer. Visible and near-IR spectra were obtained on a Cary Model 17 spectrophotometer. The samples were flame-sealed in a Pyrex cuvette, which was mounted in a lead box containing a quartz window.

Potassium Bis([8]annulenediyl)uranate(III). In an argon glovebox 0.50 g (1.1 mmol) of uranocene was dissolved in about 100 mL of THF. Approximately 2 mg (0.2 mmol) of naphthalene and 0.06 g (1.5 mmol) of freshly cut potassium were added, and after several hours the solution turned from green to brown. When the solution had completely changed color, after approximately 8 h, it was filtered into a round-bottomed flask, 10 mL of diglyme was added, and the flask was connected via U-tube to another round-bottomed flask containing approximately 40 mL of pentane. After several days, 0.40 g (58% yield) of reddish brown crystals of the diglyme adduct was obtained. These crystals were all multitwinned and thus unsuitable for X-ray crystallography. ^1H NMR (THF- d_6 , 20 °C): -31.8 (s, about 200 Hz at half-height).

The procedure was repeated for the reduction of methyluranocene; however, owing to its higher solubility, addition of catalytic naphthalene is not necessary and reduction of the substituted uranocene is complete within 1 h. Typical yields are similar to that of the unsubstituted compound, and crystals suitable for X-ray crystallography were obtained.¹³ ^1H NMR (THF- d_6 , 35 °C): -5.2 (s, 3 H), -29.3 (s, 2 H), -29.9 (s, 1 H), -32.7 (s, 2 H), -35.3 (s, 2 H). Ring peaks are about 210 Hz at half-height, and the methyl peak is about 40 Hz at half-height.

Bis(tetraethylammonium)neptunium(IV) Hexachloride. A 10-mL greenish brown, aqueous solution containing 0.27 g (1.1 mmol) of neptunium, which was present mostly as pentavalent ions, was reduced electrochemically to a light green solution containing tetravalent neptunium. The ratio of peaks at 960 and 980 nm indicated that over 95% of the neptunium was reduced to the tetravalent state. Hydrogen chloride gas was bubbled into this solution; the color changed from green to yellow and a yellow powder precipitated. The product was filtered, washed with ethanol, and pumped dry for several days at about 60 °C to produce 0.55 g (0.78 mmol, 68% yield) of bis(tetraethylammonium)neptunium hexachloride. In several attempts the product of bubbling HCl into the aqueous neptunium(IV) solution varied in color, usually from white to yellow; the X-ray powder pattern calculated contains the lines reported as well as some additional lines.

1,1'-Di-*tert*-butylneptunocene. In an inert-atmosphere glovebox, approximately 0.20 g (5 mmol) of potassium was added to a solution of 0.266 g (1.66 mmol) of *tert*-butylcyclooctatetraene in 30 mL of THF. The solution was stirred for several hours and added to a stirred suspension of 0.53 g (0.75 mmol) of bis(tetraethylammonium)neptunium(IV) hexachloride in 20 mL of THF. The mixture was stirred for several hours, and the solvent was removed in vacuo. The product was dissolved in approximately 20 mL of toluene and filtered, and the solvent was removed in vacuo. The resulting green-brown solid was washed with pentane, yielding approximately 0.15 g (36%) of 1,1'-di-*tert*-butylneptunocene. ^1H NMR (THF- d_6 , 25 °C): -5.15 (s, 150 Hz).

1,1'-Di-*tert*-butylplutonocene. The same procedure was used as that for the neptunocene except that 0.389 g (0.54 mmol) of the hexachloride salt and 0.174 g (1.09 mmol) of *tert*-butylcyclooctatetraene were used and the yield of the blood red product was approximately 0.12 g (40%). UV-vis (THF): 412, 421, 456 nm. ^1H NMR (THF- d_6): 2.15 (s, 9 H), 10.2 (m, 3 H, H4 + H5), 9.9 (d, 2 H, H2), 9.8 (m, 2 H, H3). ^{13}C NMR (THF- d_6 , DEPT, 135°): 95.3, 95.1, 94.0, 89.8, 35.3.

Reduction of Neptunocene and Plutonocene. Reduction was carried out by treating a THF- d_6 solution of the neptunocene or plutonocene with potassium and loading the resulting solution into an NMR tube, which was then sealed. In the case of neptunium the reduction product is violet-red, whereas for plutonium it is light green. ^1H NMR spectrum of potassium bis(1-*tert*-butyl[8]annulenediyl)plutonate(III) (THF- d_6 , 19.3 °C): -2.55 (s), 11 (s), 12.2 (s), 13.8 (s), 14.3 (s). ^1H NMR spectrum of potassium bis(1-*tert*-butyl[8]annulenediyl)neptunate(III) (THF- d_6 , 25 °C): 4.12 (s, 9 H), -6.0 (t, 1 H, H5), -7.1 (t, 2 H, H4), -8.0 (d, 2 H, H2), -8.4 (t, 2 H, H3).

Electron-Exchange Studies. NMR tubes for uranocene exchange were prepared by making a THF solution of a mixture of the uranium(III) and uranium(IV) compounds. NMR tubes for plutonium exchange were prepared by partially reducing a THF solution of the tetravalent compound in THF- d_6 and loading this solution directly into the NMR tube. NMR tubes for neptunium exchange were prepared by partially oxidizing the neptunium(III) compound with Teflon; this oxidation proceeds gradually while the solution is contained in the Teflon NMR tube.

Preparation and Properties of Compounds

Potassium bis([8]annulenediyl)uranate(III) and potassium bis(methyl[8]annulenediyl)uranate(III) were prepared from the parent uranocenes by potassium reduction of a THF solution. This reaction does not work as well with uranocene as with substituted uranocenes due to the low solubility of the unsubstituted compound; in this case a better synthesis involves reduction catalyzed by a few milligrams of naphthalene. Both reduction products can be crystallized as their diglyme adducts by gaseous pentane diffusion into a THF-diglyme solution, although X-ray-quality crystals could only be obtained from the methyl compound.¹³ The ^1H NMR spectrum in THF- d_6 of potassium bis([8]annulenediyl)uranate(III) at room temperature consists of a single broad resonance of about 200 Hz at half-height at -31.8 ppm. The ^1H NMR spectrum at 35 °C of potassium bis(methyl[8]annulenediyl)uranate(III) consists of a 40-Hz methyl peak at -5.2 ppm and four ring peaks in the ratio of 2:1:2:2 at -29.3 , -29.9 , -32.7 , and -35.3 ppm, which are all about 200 Hz wide. The width of these peaks agrees with expectations for uranium(III) compounds. For comparison, ring proton resonances of 1,1'-dimethyluranocene at the same temperature occur at -31.1 , -33.1 , -34.2 , and -38.2 ppm;¹⁴ the differences in chemical shift are relatively small.

The halogen salts of the actinides are difficult to synthesize, particularly when combined with the hazards of working with transuranium compounds, and we used instead the bis(tetraethylammonium) hexachlorides of neptunium(IV) and plutonium(IV) to prepare neptunocene and plutonocene. These salts have the advantage of being air stable, and the bis([8]annulenediyl)neptunate(III) and -plutonate(III) compounds could then be prepared by potassium reduction of neptunocene and plutonocene. For the electron-exchange studies the *tert*-butyl derivatives were used because we had found in prior work¹ that the *tert*-butyl group serves as a useful NMR marker for paramagnetic compounds as well as improves their solubility properties.

The preparation of bis(*tert*-butyl[8]annulenediyl)plutonium(IV), di-*tert*-butylplutonocene, was straightforward. It began with the preparation of bis(tetraethylammonium)plutonium(IV) hexachloride by bubbling HCl into an aqueous solution of plutonium(IV) containing tetraethylammonium chloride. Treatment of the resulting yellow solid with the *tert*-butylcyclooctatetraene dianion produced the blood red 1,1'-di-*tert*-butylplutonocene. The ^1H NMR spectrum (Figure 1) consists of three ring peaks between 10.3 and 9.8 ppm. The first peak is a multiplet that is the superposition of the H5 and H4 resonances, next is a doublet rep-

(12) Miller, M. J.; Lyttle, M. H.; Streitwieser, A. *J. Org. Chem.* **1981**, *46*, 1977.

(13) Boussie, T. R.; Eisenberg, D. C.; Rigsbee, J. T.; Streitwieser, A.; Zalkin, A. Manuscript in preparation.

(14) Luke, W. D.; Streitwieser, A., Jr. In *Lanthanide and Actinide Chemistry and Spectroscopy*; Edelstein, N. M., Ed.; ACS Symposium Series 131; American Chemical Society: Washington, DC, 1980; pp 93-140.

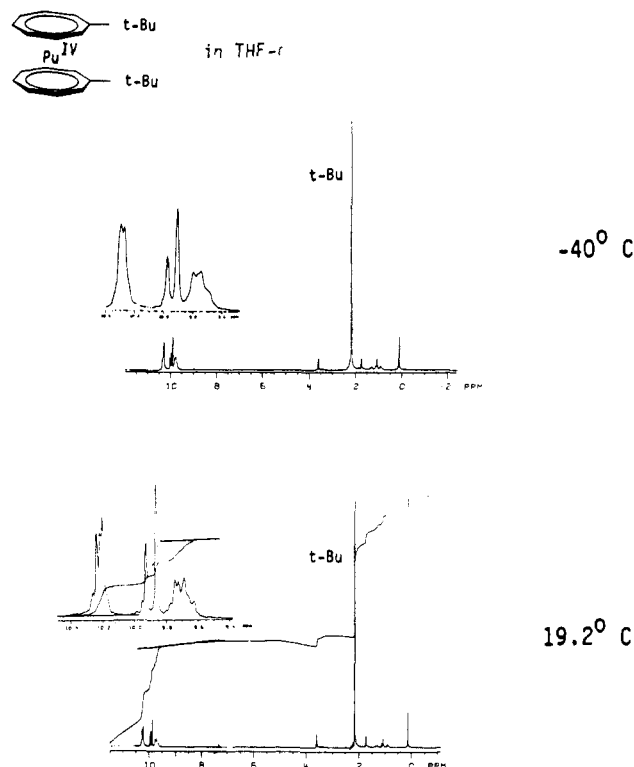


Figure 1. ^1H NMR spectra of 1,1'-di-*tert*-butylplutonocene in $\text{THF-}d_8$.

representing H2, and at 9.8 ppm is a triplet due to H3. The *tert*-butyl resonance appears at 2.15 ppm. These peaks are all sharp and have paramagnetic shifts of about 0.5 ppm for the *tert*-butyl groups and 4.5 ppm for the ring protons compared to the signals for the diamagnetic of 1,1'-di-*tert*-butylthorocene¹⁵ and 1,1'-di-*tert*-butylcerocene.¹⁶ These resonances do not shift as a function of temperature (Figure 1), indicating temperature-independent paramagnetism. The result is in agreement with the predicted $J = 0$ ground state of plutonocene and disagrees with the earlier observation of Karraker et al. (vide supra).

The reduction product potassium bis(*tert*-butyl[8]-annulenediyl)plutonate(III) was prepared by potassium reduction of a $\text{THF-}d_8$ solution of 1,1'-di-*tert*-butylplutonocene. The lime green product was not isolated. Its ^1H NMR spectrum (Figure 2) consists of a *tert*-butyl resonance at -2.6 ppm and four ring peaks in the ratio of 2:2:2:1 between 11 and 15 ppm. The *tert*-butyl peak shifts upfield as the temperature is lowered and the ring peaks shift downfield, indicative of typical paramagnetic behavior.

The preparation of 1,1'-di-*tert*-butylneptunocene is less straightforward than that of the plutonocene because of the uncertainty of the oxidation state of neptunium in solution. In aqueous solution and in the presence of oxygen, neptunium exists in several different oxidation states, so the first step in the preparation is electrochemical reduction to the tetravalent state. The success of this reduction can be monitored by the near-IR spectrum.¹⁷ The bis(tetraethylammonium) hexachloride was prepared as with the plutonium, but with neptunium traces of a different oxidation state appear to change the color and X-ray powder pattern of the putative bis(tetraethylammonium)neptunium(IV) hexachloride. Despite this evidence that higher oxidation states were present, this material was used for the next step because of our expectation that neptunocene is a thermodynamic sink in the system. In any event, the reaction of this neptunium salt with the *tert*-butylcyclooctatetraene dianion in THF produced the

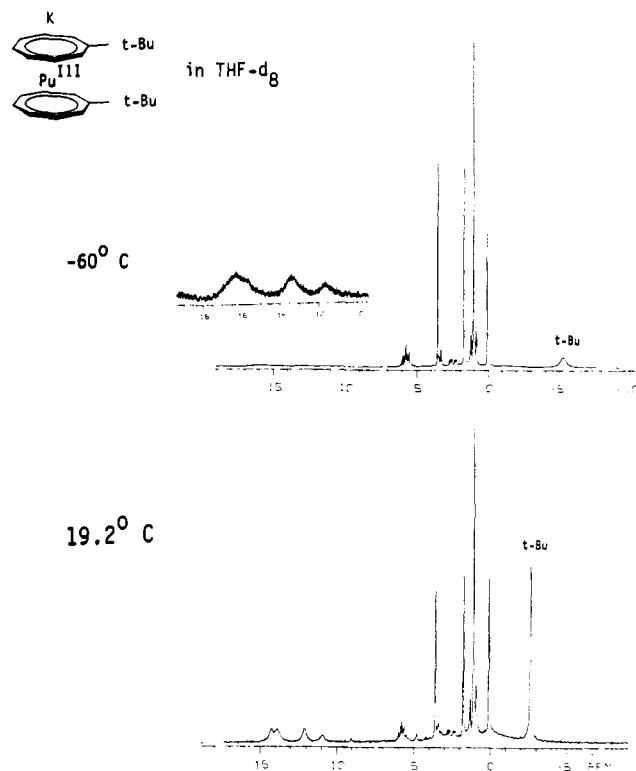


Figure 2. ^1H NMR spectra of potassium bis(*tert*-butyl[8]-annulenediyl)plutonate(III) in $\text{THF-}d_8$.

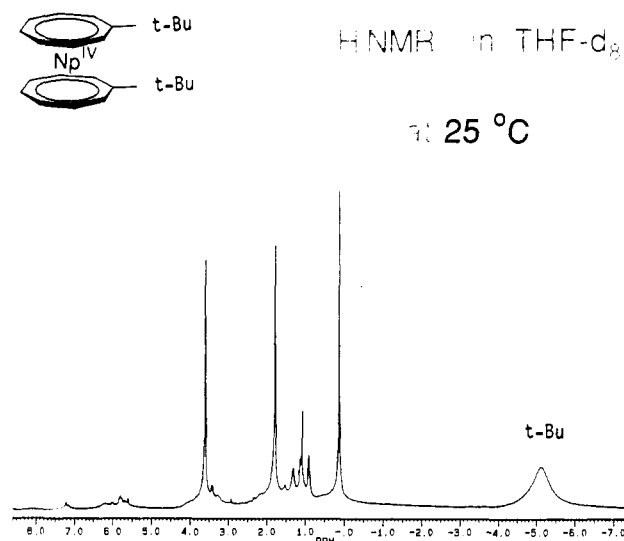


Figure 3. ^1H NMR spectra of 1,1'-di-*tert*-butylneptunocene in $\text{THF-}d_8$.

desired greenish brown product.

The ^1H NMR spectrum of the neptunocene (Figure 3) consists of a single broad peak of about 150 Hz at -5.15 ppm. This is consistent with the previously reported spectrum of octamethylneptunocene,⁵ which has methyl peaks 300 Hz wide at $+13$ ppm and ring peaks at -37 ppm of 2000-Hz width. The ring peaks in the *tert*-butyl compound are probably not observable because they are not equivalent; thus, there would not be a single ring resonance as in the octamethyl compound but four different resonances necessarily having reduced intensities. This pattern of change in the direction of paramagnetic shift with each succeeding methyl group has been observed and explained with uranocenes.¹⁴ Neptunocene is isoelectronic with the reduction product of uranocene and might be expected to exhibit similar magnetic properties with differences arising from differences in symmetry, crystal field splitting, spin-orbit coupling, and an expected lower degree of covalency of the uranium(III) compound. Both compounds have broad NMR peaks, although those of the neptunium compounds are much broader (2000 Hz for ring

(15) LeVanda, C.; Streitwieser, A., Jr. *Inorg. Chem.* **1981**, *20*, 656.

(16) Rigsbee, J. T.; Streitwieser, A. Manuscript in preparation.

(17) Hagan, P. G.; Cleveland, J. M. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2905. See: Fahey, J. A. In *The Chemistry of the Actinide Elements*, 2nd ed.; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: New York, 1986; Vol. 1, p 468.

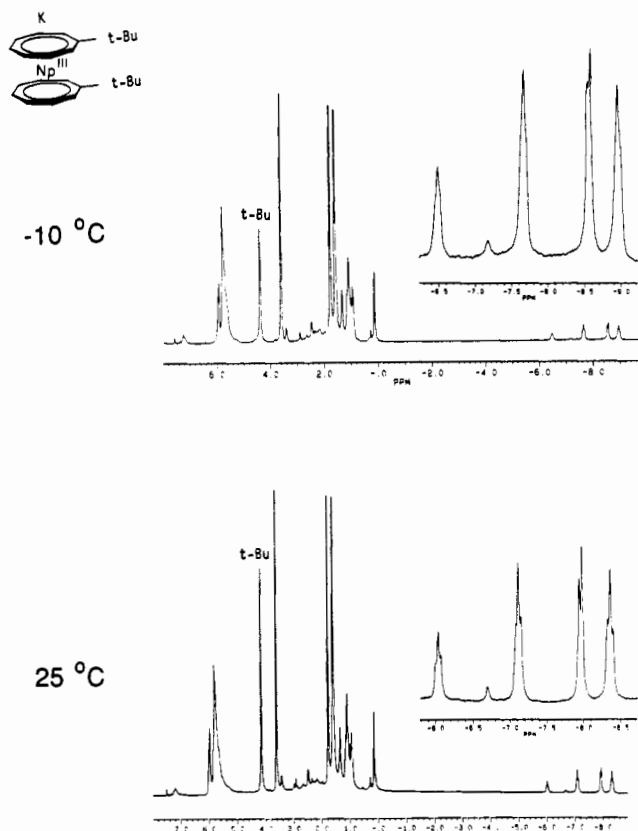


Figure 4. ^1H NMR spectra of potassium bis(*tert*-butyl[8]-annulenediyl)neptunate(III) in $\text{THF-}d_8$.

protons compared to 200 Hz in the uranium compound). The paramagnetic shifts of the two compounds are close for the ring protons (-37 ppm vs -32 ppm) but quite different for the methyl protons ($+13$ ppm vs -5 ppm). These results suggest that some NMR comparisons are qualitatively valid for isoelectronic organoactinides.

The potassium reduction of 1,1'-di-*tert*-butylneptunocene produced burgundy-colored potassium bis(*tert*-butyl[8]-annulenediyl)neptunate(III). Its ^1H NMR spectrum (Figure 4) consists of a sharp resonance at 4.12 ppm for the *tert*-butyl protons and a series of sharp multiplets for the ring protons in the ratio of 1:2:2:2. At -6.0 ppm there is a triplet resulting from H5, at -7.1 ppm a triplet due to H4, at -8.0 a doublet due to H2, and at -8.4 a triplet due to H3. The *tert*-butyl resonance shifts downfield as the temperature is lowered and the ring peaks shift upfield, indicative of typical paramagnetic behavior. The isoelectronic generalization above would suggest that the reduced neptunocene should resemble plutonocene, which has temperature-independent paramagnetism. Karraker has reported that potassium bis([8]annulenediyl)neptunate(III) exhibits two different regions of temperature-independent paramagnetism below 15 K and temperature-dependent paramagnetism above that temperature, possibly indicating a low-lying paramagnetic electronic state that is populated at 15 K. Thus, our results do not disagree with the isoelectronic generalization. Note, for example, that the ^1H resonances of the neptunate(III) are sharp (ring protons about 5 Hz), as are those of the analogous plutonocene.

Also present in many of the NMR spectra are peaks from the solvent (THF) and impurities such as *tert*-butylcyclooctatetraene.

Electron Exchange

When uranocene is mixed with its reduction product in $\text{THF-}d_8$, the resulting peak has a chemical shift at room temperature that is the weighted average of the chemical shifts of the two species individually. The line width also is approximately the weighted average of uranocene and its reduction product. When dimethyluranocene is mixed with its reduction product, the same situation results. With both of these systems it has not been possible thus far to freeze out the exchange. This is not surprising

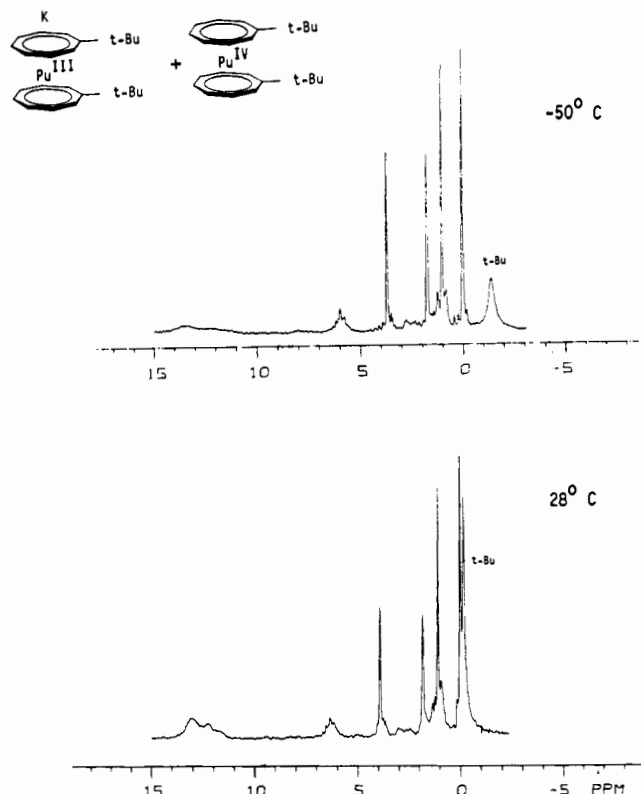


Figure 5. ^1H NMR spectra of a mixture of 1,1'-di-*tert*-butylplutonocene and potassium bis(*tert*-butyl[8]-annulenediyl)plutonate(III).

because near the coalescence temperature the line width varies approximately linearly with the difference in chemical shifts between the two species in hertz and with the rate constant. Comparable electron exchange between cyclooctatetraene derivatives of Yb(III) and Yb(II) is in the slow-exchange region at about -70 °C at 200 MHz.¹ At this temperature the difference in chemical shifts between the two Yb species is approximately 26 ppm. The difference in chemical shifts between uranocene and its reduction product is only about 5 ppm; hence, if the exchange rate for the two systems is about the same, the uranium case will require a lower temperature or a higher field to reach the slow-exchange region in the NMR spectrum.

Partial reduction of di-*tert*-butylplutonocene led to an NMR spectrum (Figure 5) at 28 °C containing a sharp resonance at -0.12 ppm and a series of broad resonances between 11 and 14 ppm. As the temperature was lowered to -50 °C, the broad ring resonances broadened further into the base line and the sharp resonance due to the *tert*-butyl protons broadened and shifted upfield to -1.5 ppm. This upfield shift occurs because the *tert*-butyl resonance of the trivalent plutonium compound shifts upfield as the temperature is lowered, while the tetravalent compound exhibits no change in chemical shift versus temperature, so the net effect for the exchanging peak is an upfield shift combined with broadening.

Partial oxidation of the neptunate produced an NMR spectrum containing a broadened peak at 3.9 ppm due to the *tert*-butyl protons. The signals for the ring protons, which are shown in Figure 6, broadened to the point of being barely distinguishable above the base line. When the temperature was lowered to -20 °C, the peaks sharpened considerably so that four definite peaks could be seen in the ratio of 1:2:2:2 with a width of approximately 70 Hz. The much sharper ring proton signals of the pure neptunate(III) are also shown in this figure for comparison.

Due to the small chemical shift differences between the peaks for the plutonium(III) and -(IV) compounds it was not possible to freeze out this exchange. In the neptunium system, however, the ring peaks for the tetravalent compound should be near the reported resonances for octamethylneptunocene at -37 ppm. Since the ring peaks for the trivalent compound appear between -6 and -8.4 ppm, this gives a difference for the 300-MHz spectrometer

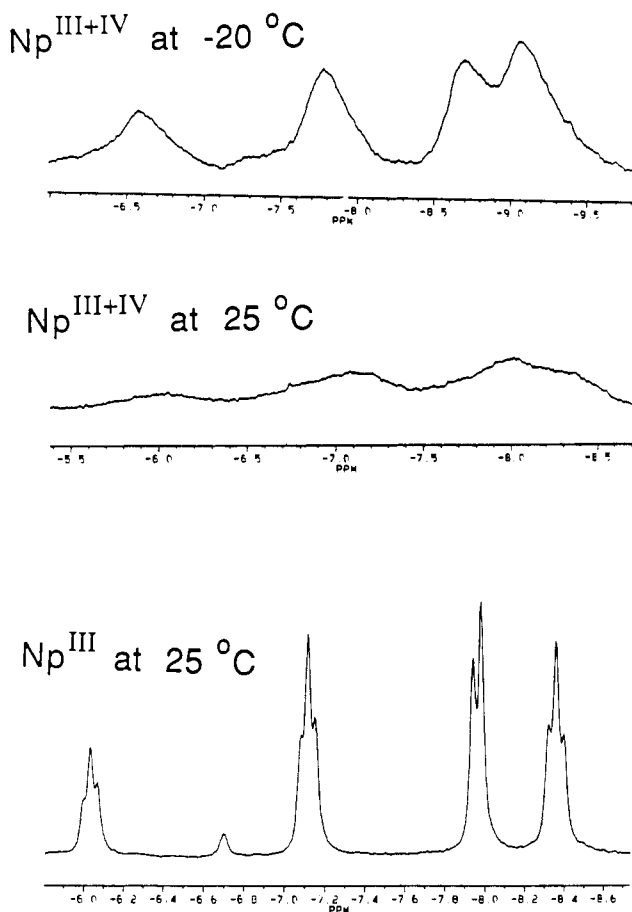


Figure 6. ^1H NMR spectra of ring protons in potassium bis(*tert*-butyl)[8]annulenediylneptunate(III) and its mixture with 1,1'-di-*tert*-butylneptunocene.

that was available for this transuranium work of about 9000 Hz. This is almost twice as large as the difference in the previously studied ytterbium system. Unfortunately, this spectrometer is only equipped to go down to -20°C , but at that temperature the ring peaks do sharpen considerably as can be seen in Figure 6, indi-

cating that the slow-exchange region has almost been reached.

These results, although not as quantitative as desired, do nevertheless demonstrate that the rates of electron exchange between actinide(III) and actinide(IV) derivatives of cyclo-octatetraene are on the same order of magnitude as those for the ytterbium system.¹ The former case may be considered as involving electron transfer between an ion pair (the potassium bis([8]annulenediyl)actinide(III) salt) and a neutral actinide(IV) compound, whereas the ytterbium exchange involves an ion pair (the potassium bis([8]annulenediyl)ytterbate(III) salt) and a triple ion (the dipotassium bis([8]annulenediyl)ytterbate(II) salt). In both systems, however, electron exchange is accompanied by transfer of a potassium cation. This cation probably requires partial desolvation in the exchange transition state, a feature in ion aggregate electron exchange systems that complicates the possible application of Marcus theory.¹ The fast exchange found for the present cases does nevertheless demonstrate a commonality of exchange processes for both actinide and lanthanide f-element systems.

Conclusions

Electron transfers in THF between the III and IV oxidation states of the [8]annulene sandwich compounds of uranium, neptunium, and plutonium are rapid on the NMR time scale and appear to be qualitatively comparable to the exchange between the ytterbium(II) and -(III) oxidation states studied previously.¹

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Registry No. K[U(C₈H₈)₂], 124020-90-2; K[U(MeC₈H₇)(C₈H₈)], 124020-91-3; K[Pu(*t*-BuC₈H₇)₂], 124020-94-6; K[Np(*t*-BuC₈H₇)₂], 124020-95-7; uranocene, 11079-26-8; methyluranocene, 124020-89-9; bis(tetraethylammonium)neptunium(IV) hexachloride, 12080-88-5; *tert*-butylcyclooctatetraene, 61593-18-8; 1,1'-di-*tert*-butylneptunocene, 124020-92-4; 1,1'-di-*tert*-butylplutonocene, 124020-93-5; bis(tetraethylammonium)plutonium(IV) hexachloride, 33393-76-9.

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Conversion of $[\text{MoS}_4]^{2-}$ to $[\text{Mo}_2\text{S}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ by Organic Disulfides: The Mechanism of an Induced Redox Reaction

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The kinetics of the reaction of tetrathiomolybdate, $[\text{MoS}_4]^{2-}$, with organic disulfides, RSSR, to produce the Mo(V) dimer $[\text{Mo}_2\text{S}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ have been investigated. The reaction involves an internal redox process and occurs in two stages. The overall rate of reaction is dependent on the electron-withdrawing properties of the disulfide such that diphenyl disulfide < bis(*p*-chlorophenyl) disulfide < bis(*p*-carboxyphenyl) disulfide. The first stage involves rapid equilibrium formation of an EPR-inactive, green intermediate. The reaction of $[\text{MoS}_4]^{2-}$ with diphenyl disulfide or bis(*p*-chlorophenyl) disulfide is first order in tetrathiomolybdate and first order in organic disulfide. However, the reaction of $[\text{MoS}_4]^{2-}$ with bis(*p*-carboxyphenyl) disulfide is more complex. Analysis of the molybdenum X-ray absorption spectrum of the green intermediate indicates the likelihood of a mononuclear species with two to three short Mo-S interactions at 2.16 Å and three to four longer Mo-S interactions at 2.41 Å. The rate-determining step of the second stage of the reaction involves first-order rearrangement or dissociation of the green intermediate. This is followed by rapid reaction of the resultant complex with another molybdenum species to produce $[\text{Mo}_2\text{S}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$. Mechanisms are proposed that are consistent with these findings and that provide potential insight into the use of oxidants to prepare new lower valent transition-metal sulfur-containing complexes from tetrathiomolybdate starting materials.

Transition-metal sulfur-containing sites in enzymes and heterogeneous catalysts undergo redox during catalysis.¹⁻³ Although

many of these redox reactions are metal-centered, some involve processes that are localized on the sulfur ligands.^{4,5} Moreover,