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# Reduced Biuranocenylene – a Mixed Valence Organouranium Compound?*

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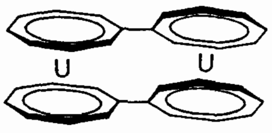
Potassium bis(t-butyl[8]annulene)ytterbate(III) undergoes electron exchange on the $^1$H NMR time scale with its reduction product, potassium bis(t-butyl[8]annulene)ytterbate(II) [1]; the barrier for this exchange appears to be loss of coordinating THF or diglyme solvent. Similarly rapid electron exchange also occurs between bis([8]annulene)cerium(IV) and bis([8]annulene)plutonium(IV) and their respective reduction products; however, there is no electron exchange between uranocene and its reduction product [2].

Bis(bicyclooctatetraenyl)diuranium, biuranocenylene, was prepared and characterized by Miller and Streitwieser in 1981 [3]. We now report the reduction of biuranocenylene, its $^1$H NMR characterization and its electron exchange with biuranocenylene.



Biuranocenylene

## Experimental

$^1$H NMR spectra were obtained on a Bruker 500 MHz AM500 superconducting spectrometer. Chemical shifts are reported in ppm referenced to the upfield residual THF peak set at 3.58 ppm. Bicyclooctatetraenyl and biuranocenylene were prepared by literature procedures [3]. Partial reductions of biuranocenylene were performed by sealing an NMR tube containing a solution of biuranocenylene in THF-$d_8$ with a small piece of potassium. When a desired degree of reduction was obtained the tube was opened in an inert atmosphere box and the solution was transferred to another NMR tube which was then sealed under vacuum. The reduction product was obtained by stirring a solution of approximately 50 mg of biuranocenylene with potassium in THF for 4 days, adding a few drops of diglyme, filtering, and crystallizing by slow diffusion of hexane into the THF–diglyme layer. The microcrystals were pumped dry, and redissolved in THF-$d_8$.

## Results and Discussion

The $^1$H NMR spectrum of biuranocenylene consists of seven peaks at −36.3, −38.0, −42.0, −42.3, −43.5, −48.0 and −99.4 ppm (Fig. 1) indicative of two equivalent rings twisted with respect to each other. A model indicates that if the two joined cyclooctatetraene rings were coplanar there would be considerable steric repulsion between the 2 and 2′ hydrogens. The far upfield resonance is probably that of the 2-*endo* proton that is closest to both uraniums.

Partial reductions of biuranocenylene by potassium in THF-$d_8$ gave the $^1$H NMR spectra B–E in Fig. 1. The first reduction gave spectrum B with six relatively sharp resonances at −34.8, −37.6, −38.8, −40.1, −42.6, −46.5, and a broad far upfield resonance at −85.3 ppm. The appearance of only seven peaks different from those in A demonstrates a rapid intermolecular electron exchange between biuranocenylene and its reduction product, in close analogy to the other bis([8]annulene) f-element systems that we have studied [2]. Further work has shown that uranocene and the corresponding uranate(III) undergo rapid electron exchange on the NMR timescale at room temperature. It is remarkable, however, that such exchange is not observed for uranocene itself

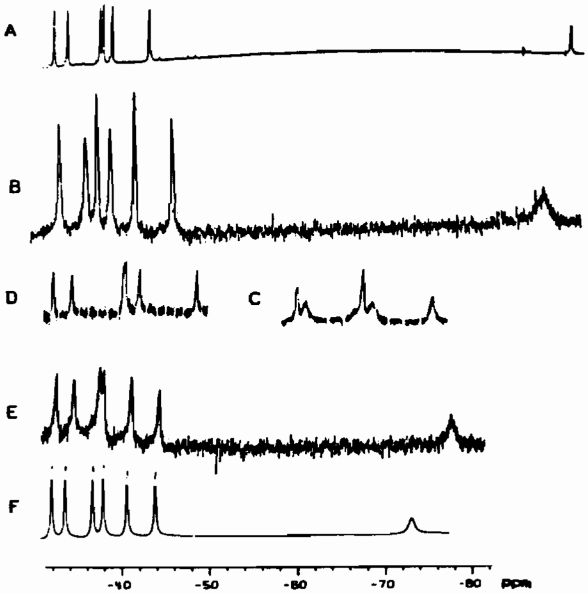


Fig. 1. $^1$H NMR spectra of biuranocenylene reduction.

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and its reduction product. The broadening of the far upfield resonance relative to the other resonances is attributed to the greater chemical shift difference between the biuranocenylene 2-*endo* proton and the reduced biuranocenylene 2-*endo* proton compared to the other ring hydrogens.

Further reduction results in spectrum C which consists of 6 broad peaks at −37.3, −38.0, −42.7, −43.5 and −48.6 ppm in an approximate ratio of 1:1:2:1:1 with the far upfield resonance now being too broad to observe. D is a spectrum of C at higher temperature; the broad resonances in C have sharpened considerably, indicating exchange in the intermediate to have increased to the fast region. Further reduction results in spectrum E. The far upfield resonance is seen to have reappeared and shifted over 20 ppm downfield from the far upfield resonance of biuranocenylene. The downfield peaks have sharpened and the third peak in C which integrates at twice the area of the other peaks has begun to split.

Complete reduction results in spectrum F, which still shows only seven resonances, six sharp peaks at −31.9, −33.5, −36.6, −37.8, −40.4, −43.5, and a slightly broader far upfield peak at −71.8 ppm. The two joined cyclooctatetraene rings are still equivalent, meaning that intramolecular electron exchange is fast on the NMR time scale. This reduction product is probably the 1-electron product and the two uraniums are effectively equivalent. The NMR linewidth of $(C_8H_8)_2U(III)K$ is about 200 Hz at half height. The two-electron reduction product of biuranocenylene would therefore be expected to have a linewidth substantially greater than the actual value of 100 Hz. If the two uraniums are electronically equivalent, they each must have an intermediate oxidation state of $3\frac{1}{2}$. Alternatively, the compound could be a uranium(IV) ring system joined to a uranate(III) system in which electron transfer between the two uraniums and accompanying movement of the potassium gegenion is rapid on the NMR time scale. To distinguish between these alternatives we studied the electronic spectra.

The visible spectrum of biuranocenylene (B in Fig. 2) is similar to that of dimethyluranocene (A in Fig. 2). If the reduction product were valence localized on the visible time scale, then the visible spectrum of the reduction product would be expected to resemble a superposition of the visible spectrum of uranocene and that of the uranocene reduction product, which has a long UV tail into the visible region. The reduction of biuranocenylene is shown in Fig. 2 where spectrum C represents partial reduction and spectrum D represents complete reduction. The characteristic uranocene cascade of peaks is seen to diminish and finally disappear and the tail into the visible is seen to increase indicating that the mixed valence compound is not valence localized on the visible time scale. That is, we conclude that the reduction product has electronically equivalent uraniums in which the five 5f electrons are delocalized such that each uranium has an intermediate oxidation state of $3\frac{1}{2}$.

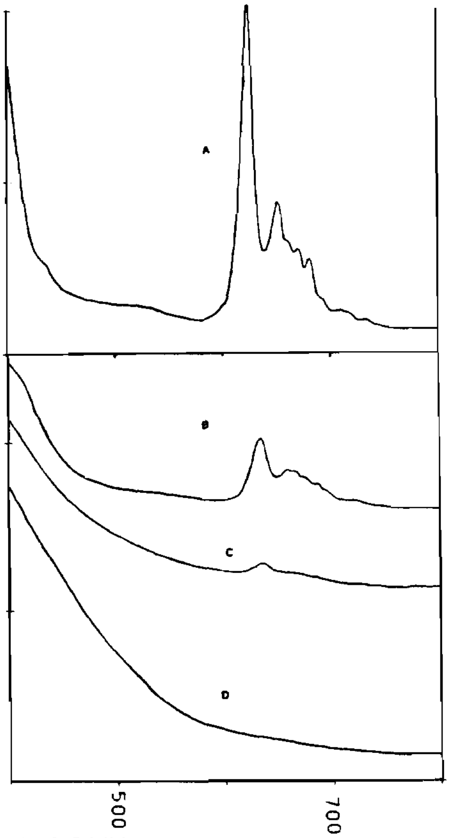

Fig. 2. Visible spectra.

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## References

1 D. C. Eisenberg, S. A. Kinsley and A. Streitwieser, Jr., *Organometallics*, submitted for publication.
2 A. Streitwieser, Jr. *et al.*, to be published.
3 M. J. Miller and A. Streitwieser, Jr., *J. Organomet. Chem.*, *209*, C52 (1981).