formation of the Fe(1)–S(4) bond with concomitant core metric changes. The prismane clusters **1** (L = $X^-$, $RO^-$, $RS^-$) exhibit in cyclic voltammetry a quasi-reversible 3–/4– electron-transfer step implicating a chemically unstable reduced cluster.[1c,e] It remains to be learned if the 4– cluster, isoelectronic with **5**–**7**, undergoes core isomerization or whether tertiary phosphine is obligatory to the stability of this form of $[Fe_6S_6]^{2+}$, presumably by inducing planar-pyramidal $FeS_3P$ coordination sites. It is these sites, present in the two open (nonrhomboidal) $Fe_3S_3$ faces of the core, that appear to impart stability to the $C_{2v}$ arrangement. Conversions d and e reduce core nuclearity, and reaction f is the spontaneous degradation of **3** in solution to the far more stable cluster **5**.

The remaining transformations in Figure 2 are of a formal topological nature, so described because they have not been effected experimentally. Thus, the capping reactions g and h generate the $[Fe_7S_6]$ core of **3**. This is the topological link between the $D_{3d}$ and $C_{2v}$ forms of the $[Fe_6S_6]$ core and the cuboctahedral $[Fe_8S_6]$ core of **2**, derived here by capping reaction i. We note these formal relationships in addition to demonstrated conversions in order to draw attention to the conceivable development of a rational cluster synthesis and conversion chemistry spanning the limits $[Fe_2S_2]$ to $[Fe_8S_6]$. Indeed, certain conversions among smaller cores, viz., $[Fe_2S_2]^{2+} \rightarrow [Fe_4S_4]^{2+}$,[18] $[Fe_2S_2]^{+} \rightarrow [Fe_4S_4]^{2+}$,[18] linear $[Fe_3S_4]^{+} \rightarrow [Fe_4S_4]^{2+}$,[16b] and cuboidal $[Fe_3S_4]^{0} \rightarrow [Fe_4S_4]^{2+}$[19] (with protein clusters), have already been accomplished. Subsequent reports will provide more detailed descriptions of **5**–**7** and related clusters and their reactivities, including core conversions.

**Acknowledgment.** This research was supported by National Institutes of Health Grant GM 28856. X-ray diffraction equipment was obtained by NIH Grant 84-10774.

**Supplementary Material Available:** Tables of atom positional and thermal parameters for $[Fe_6S_6(P(n\text{-}Bu)_3)_4Cl_2]$ (3 pages). Ordering information is given on any current masthead page.

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*Received September 18, 1987*

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## Pulse Radiolysis Studies of Berkelium(III): Preparation and Identification of Berkelium(II) in Aqueous Perchlorate Media[1]

*Sir:*

The chemistry of the transplutonium elements in aqueous solutions has been predominantly concerned with the interactions of the trivalent cations and complexing ligands.[2] Quasi-thermodynamic arguments have been advanced to predict that the +2 and +4 oxidation states of these elements would respectively be very powerful reductants and oxidants.[3] Previous pulse radiolysis investigations in this laboratory have provided evidence for the existence of divalent oxidation states of Am, Cm, and Cf as transient species[4] in aqueous noncomplexing media with the hydrated electron as the reducing agent. There have been a number of elegant solid-state studies that have provided indirect evidence for the existence of Bk(II),[5] but the results obtained in the present investigation provide the first direct evidence for the existence of this oxidation state in aqueous media.

Earlier efforts to search for Bk(II) by pulse radiolysis were hampered by the necessity for relatively high pH for two reasons: (1) a buffer solution cannot be used, so pH adjustment and control are difficult, and (2) aqueous Bk(III) is spontaneously oxidized to Bk(IV) by atmospheric oxygen at relatively high pH since the Bk(IV) hydrolyzes rapidly and precipitates as a hydrous dioxide even at pH 5. These barriers were surmounted by the use of bicarbonate to adjust pH, by maintaining rigorously oxygen free conditions, and by using ethanol to suppress radiolysis products.

**Experimental Section.** Sodium bicarbonate, perchloric acid, and ethanol stock solutions were prepared from analytical grade reagents and standardized by conventional techniques. The $^{249}Bk$ ($t_{1/2}$ = 320 days) was purified from its daughter, $^{249}Cf$, by a solvent extraction technique[6] prior to the pulse radiolysis experiments. The purified Bk in a nitric acid–peroxide solution was evaporated to dryness; the Bk was redissolved in $10^{-3}$ M perchloric acid and fumed to dryness. This procedure was repeated, and the berkelium(III) perchlorate salt was dissolved in an aqueous solution containing 0.1 M ethanol to scavenge $OH^{\bullet}$ produced by radioactive decay. The pH was adjusted to 5 by the addition of a solution of 0.1 M sodium bicarbonate–0.1 M ethanol under an atmosphere of Ar.

The rate of disappearance of the hydrated electron was monitored at 600 nm by using the photomultiplier pulse radiolysis technique.[7] The Argonne streak camera system[8] was used to obtain the spectrum of the Bk(II).

**Results and Discussion.** The freshly prepared solution ($2.0 \times 10^{-3}$ M in Bk(III), pH 5, 0.1 M ethanol, Ar saturated) was irradiated with a 4-ns pulse of electrons (ca. 0.7 krad), and from the photomultiplier signal, the resultant first-order rate of decay of the hydrated electron was calculated to be $2.25 \times 10^6$ $s^{-1}$, with the concomitant second-order rate constant of $1.12 \times 10^9$ $M^{-1}$ $s^{-1}$ ± 2.5%. This value is to be compared to $1.6 \times 10^8$ $M^{-1}$ $s^{-1}$ for the reduction of Am(III) and $3 \times 10^9$ $M^{-1}$ $s^{-1}$ for that of Cf(III), by the hydrated electron. The estimated values of the +3/+2 couples are respectively –2.3, –2.8, and –1.6 V for Am, Bk, and Cf. The ordering of log $k$ vs $E°$ is not linear. A comparison with the values that have previously been obtained for the reduction of the 4f transition elements also presents no readily discernible reactivity pattern based on either potential values or electronic structure.[9]

This result led to an attempt to provide direct evidence for the preparation of Bk(II). A Bk(III) solution of the same composition as above was irradiated with a 40-ns pulse of electrons (ca. 5 krad), and a time-resolved absorption spectrum was observed with the streak camera system, with a maximum at about 310 nm. The three-dimensional spectrum is displayed in Figure 1. Because of the experimental constraints on solution composition, the principal reactive radical is the hydrated electron. The observed transient grows in with the same halflife with which that species disappears, i.e. about 0.3 $\mu$s. The absorption is therefore believed

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(1) Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, USDOE under Contract No. W-31-109-ENG-38.

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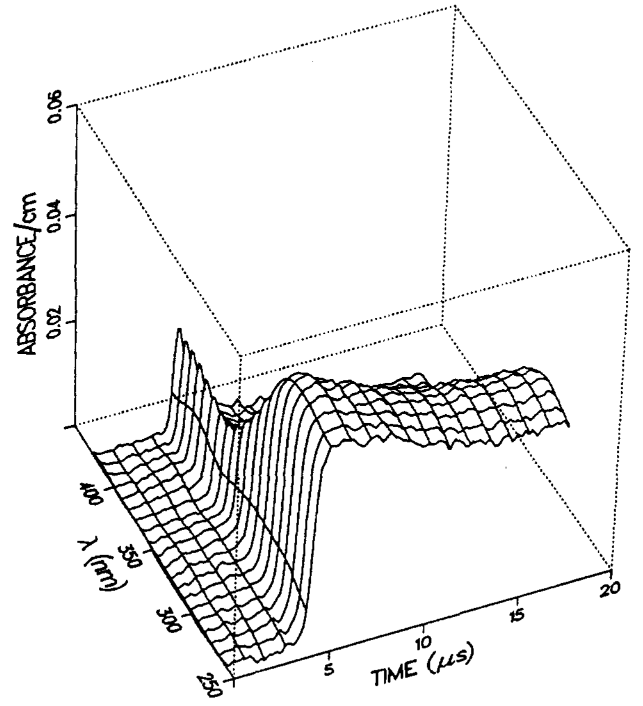

**Figure 1.** Time-resolved absorption spectrum obtained by pulse-irradiating an argon-saturated 2 mM solution of Bk(III) of pH 5, containing 0.1 M ethanol. Note: The rapidly decaying absorption at the long-wavelength end is due to the hydrated electron.

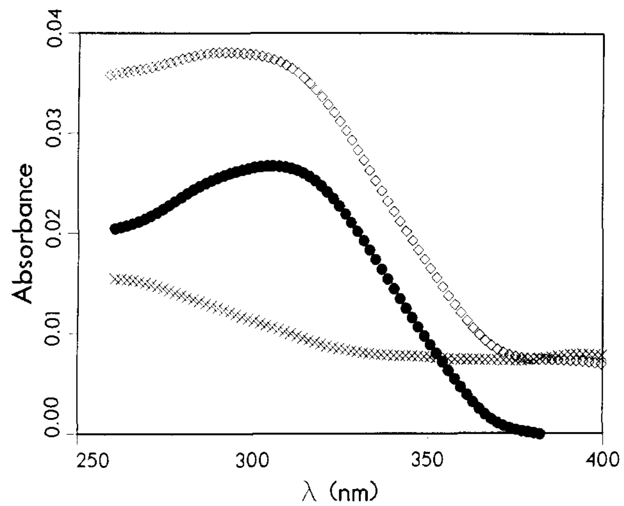

**Figure 2.** Derivation of Bk(II) spectrum: diamonds, spectrum at signal maximum obtained from data in Figure 1; crosses, spectrum of the ethanol radical from the blank experiment, containing the same (small) contribution from the hydrated electron absorption; filled circles, difference spectrum, ascribed to Bk(II).

to be characteristic of Bk(II). In order to obtain the undistorted shape of the Bk(II) spectrum, a correction was made for the absorption of the ethanol radical produced by the reaction of the OH radicals with the ethanol. Figure 2 shows the measured absorption spectrum at the time peak of the signal (diamonds), the absorption spectrum of the ethanol radical determined with a blank solution (crosses), and the difference spectrum (solid circles) with its absorption maximum at 310 nm and a molar absorptivity at this wavelength of $\epsilon = (2.3 \pm 0.2) \times 10^3$ cm$^{-1}$ M$^{-1}$. We ascribe this spectrum to Bk(II). This assignment is consistent with theoretical considerations advanced by Carnall and Crosswhite[10] that would predict strong absorption in the visible and near-UV regions analogous to that observed for $Tb^{2+}$.

Bk(II) is in an unstable oxidation state in aqueous solution. Its rate of disappearance, determined from the time profile at 310 nm, is $(1.53 \pm 0.25) \times 10^5$ s$^{-1}$, a value to be compared to $9.7 \times 10^4$ s$^{-1}$ for the disappearance of Am(II) and to $7 \times 10^4$ s$^{-1}$ for that of Cf(II).

The logarithms of the rate constants for the oxidation of the divalent Am, Bk, and Cf (4.94, 5.18, and 4.85, respectively) are satisfactorily correlated with the values of the potentials for the +3/+2 couples. However, the value reported for the rate of disappearance of Cm(II) is smaller than that for any of these other divalent transplutonium ions in aqueous solution. This deviation from the systematics is particularly noticeable because of the estimated value of −3.7 V for the potential of the $Cm^{3+}/Cm^{2+}$ couple and warrants further investigation.

**Acknowledgment.** We are indebted for the use of the $^{249}$Bk to the Office of Basic Energy Sciences, Division of Chemical Sciences, USDOE, through the transplutonium element production facilities at Oak Ridge National Laboratory. We also gratefully acknowledge the technical assistance of D. F. Ficht and G. Cox, who operated the linear accelerator, and M. F. Williams, who ensured radiation safety for the operations.

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*Received October 14, 1987*

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## Monomeric and Dimeric Ruthenium(II) $\eta^2$-Dihydrogen Complexes with Tricyclohexylphosphine Coligands

*Sir:*

We have recently described the preparation and some reactions of $RuH_6(PCy_3)_2$ (**1**), the first hexahydride of ruthenium.[1] Its exact structure was unknown. In view of the discovery of the $\eta^2$-$H_2$ ligand in thermally stable, group 6 metal complexes by Kubas' group[2,3] and later on in group 8 and 9 metal complexes by other groups,[4-14] we were led to reinvestigate the structure of **1** as well as those of other polyhydrido tricyclohexylphosphine complexes. We report here that **1** is likely to be the second thermally stable complex to contain two $\eta^2$-dihydrogen ligands. We have also characterized spectroscopically the first dinuclear complexes to contain an $\eta^2$-$H_2$ ligand.

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