Table VII. Comparison of ν(CO) (or ν(C=NR)) and Structural Parameters in CO- (or C=NR-) Bridged "A-Frame" Complexes[a] with Those in **1a**

complex	$\nu(\mu\text{-CO})/\text{cm}^{-1}$	$d_{\text{M-M}}/\text{Å}$	M-C$_\mu$-M/deg	ref
$[\text{Pd}_2(\mu\text{-dpm})_2(\mu\text{-CO})\text{Cl}_2]$	1704			40
$[\text{Pd}_2(\mu\text{-dpm})_2(\mu\text{-C=NCH}_3)(\text{CNCH}_3)_2]^{2+}$ [b]	$(1640\text{–}1680)^c$	3.215 (2)	106 (1)	40
$[\text{Pt}_2(\mu\text{-dpm})_2(\mu\text{-CO})\text{Cl}_2]$	1638			42a
$[\text{Pd}_2(\mu\text{-dam})_2(\mu\text{-CO})\text{Cl}_2]$	1720	3.274 (8)	119 (3)	41
$[\text{Pt}_2(\mu\text{-dam})_2(\mu\text{-CO})\text{Cl}_2]$	1635	3.162 (4)	106 (3)	42b
$[\text{Ir}_2(\mu\text{-S},\mu\text{-CO})(\mu\text{-dpm})_2(\text{CO})_2]$	1760	2.843 (2)	86.7 (6)	17
$[\text{Rh}_2(\mu\text{-Cl},\mu\text{-CO})(\mu\text{-dpm})_2(\text{CO})_2]^+$				
$\quad$ BPh$_4^-$ salt	1863	2.8415 (7)	86.7 (3)	43
$\quad$ RhCl$_2$(CO)$_2^-$ salt	1865	2.838 (1)	86.4 (1)	44
$[\text{Pt}_2(\mu\text{-H},\mu\text{-CO})(\text{dpe})_2][\text{BF}_4]$ (**1a**)	1720	2.716 (1)	84.6 (2)	this work

a dpm = bis(diphenylphosphino)methane; dam = bis(diphenylarsino)methane. *b* As the PF$_6^-$ salt. *c* $\nu(\mu\text{-C=NR})$.

ition, as is also seen in **1$^+$**. A significant variation, however, is seen in the M–C$_\mu$–M angle, which correlates with the M–M separation as indicated in Table VII. The long metal–metal separations of ca. 3.1–3.3 Å involve very little metal–metal bonding[46] and are associated with a wide M–C$_\mu$–M angle, ca. 120°. This is close to that in organic carbonyl compounds, which has led to assignment of the bridging carbonyl group in these complexes as a doubly negatively charged species, i.e. a "demetalated" formaldehyde.[45,46] This requires an increase of the formal oxidation state of the metal by 1 unit: for instance, the complexes thus bridged (Table VII) are regarded as Pt(II)–Pt(II) dimers. Clearly this is *not* the case in the present structure where the Pt–C$_\mu$–Pt angle is 84.6 (2)°, close to that in derivatives where the bridged CO group is taken to be a *two*-electron donor.[46] The structural data thus indicate assignment of these carbonyl- (or isocyanide-) bridged dinuclear cations as protonated Pt(0) dimers. The unusually low stretching absorption for the bridging group is anomalous compared to that in the derivatives listed in Table VI; in these the bridging absorptions occur in the higher range (near 1800

cm^{-1}). This difference is most likely derived from the high degree of electron-releasing ability of the chelating diphosphines in the present dinuclear cations.

Registry No. 1a, 72269-74-0; **1a-d_1**, 86162-52-9; **1b**, 72269-75-1; **2a**, 86162-42-7; **3a**, 86162-43-8; **4a**, 72166-98-4; **4b**, 72166-99-5; **5a**, 72339-25-4; **5a-d_1**, 86162-54-1; **5b**, 72166-96-2; **6a**, 86162-45-0; **6a-d_1**, 86176-86-5; [Pt$_2$H$_3$(dpe)$_2$][BF$_4$], 86176-88-7; [Pt$_2$H$_3$(dpp)$_2$][BF$_4$], 86162-47-2; [Pt$_2$H$_3$(dpb)$_2$][BF$_4$], 86162-49-4; [Pt$_2$H$_3$(dpe)$_2$][I], 86162-50-7; Pt, 7440-06-4; deuterium, 7782-39-0.

Supplementary Material Available: Tables A–C, listing hydrogen atom coordinates, thermal parameters, and calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

Notes

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Pulse Radiolysis Studies of Californium(III) in Aqueous Perchlorate Solution. Evidence for the Preparation of Californium(II)[1]

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The solution chemistry of the transplutonium elements Am, Cm, Bk, and Cf has been limited primarily to the reactions of these elements in the +3 oxidation state.[2] Quasi-thermodynamic arguments have been advanced to predict that the +2 and +4 oxidation states of these elements are respectively powerful reductants and oxidants.[3] We have previously demonstrated that the divalent and tetravalent oxidation states of Am and Cm can be prepared as transient species[4] in aqueous

noncomplexing media with the hydrated electron as reductant and the OH radical as oxidant. In this report we present evidence for the production of the hitherto undescribed aqueous oxidation state Cf(II) and the results of attempts to prepare Cf(IV) by pulse radiolysis techniques.

Experimental Section

Sodium hydroxide, perchloric acid, and *tert*-butyl alcohol stock solutions were prepared from analytical grade reagents and standardized by conventional techniques. The ^{249}Cf ($t_{1/2}$ = 350 years) was obtained as the product of the β^- decay of several milligrams of ^{249}Bk ($t_{1/2}$ = 314 days), which had been produced by Oak Ridge National Laboratory. The ^{249}Cf was purified by a series of ion-exchange procedures previously detailed,[5] followed by evaporation to dryness and precipitation of the hydroxide (immediately prior to the pulse irradiation), which was then washed and finally dissolved in the minimum amount of perchloric acid. This procedure was adopted to minimize introduction of impurities by the self-radiolysis of the solutions of the ^{249}Cf (9×10^6 disintegrations min^{-1} μg^{-1}). The Cf concentrations in the stock solutions were determined by α assays of aliquots with a 51% geometry α proportional counter.

After the pH was adjusted to 5.1–5.3 with NaOH solution, the Cf(III) solutions (5.5×10^{-4} M) were introduced into the gas-satu-

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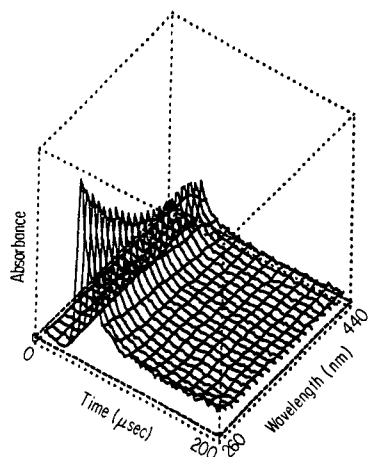
Figure 1. Time-resolved optical absorption signal obtained by pulse irradiating a He-saturated solution of 5×10^{-4} M $Cf(ClO_4)_3$ (pH 5.3) containing 0.1 M *tert*-butyl alcohol. Spectrum is interpreted as that of Cf(II).
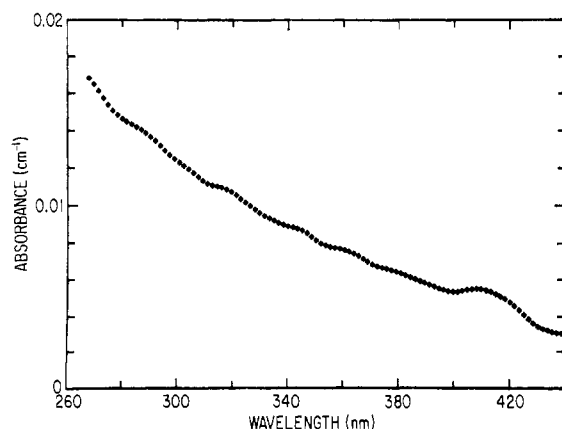
Figure 2. Transient absorption signal of Cf(II) observed 20 μs after the electron pulse (for conditions see Figure 1).

rating and cell-filling device previously described.[6] The time-resolved spectra of the transient species produced by single 13-MeV pulses of electrons in He- or N_2O-saturated solutions were obtained by using the streak camera–TV scanning method described in a previous publication.[7] Transient conductivity measurements were also carried out by a procedure previously described.[8]

Results and Discussion

When a solution of Cf(III) (ca. 5×10^{-4} M) in dilute perchloric acid, containing 0.1 M *tert*-butyl alcohol to scavenge OH, adjusted to pH 5.3, is irradiated with a 3-μs electron pulse, a transient absorption is observed that decays with a half-life of approximately 10 μs (Figures 1 and 2). Because of the experimental constraints imposed, the principal reactive radical in the solution is e_{aq}^-. We therefore identify the absorption as due to Cf(II). The estimated rate constant for the reaction of e_{aq}^- with Cf(III) is greater than or equal to 3×10^9 M^{-1} s^{-1}. We calculate a value for the absorptivity of $\epsilon \approx 500$ M^{-1} cm^{-1} at λ 270 nm. This is not inconsistent with the calculations of Carnall,[9] who predicts a strong absorption for Cf(II) that extends from ca. 380 nm into the ultraviolet region.

The polarographic reduction of Cf(III) to Cf(II) in acetonitrile solution has been previously reported.[5] Paralleling this experiment were calculations that led to an estimate of the

standard aqueous reduction potential for Cf(III)/Cf(II) of ca. 1.6 V.[10] Since the estimate of the potential for the reaction

$$e_{aq}^- + H_3O^+(aq) = {}^1/_2 H_2 + H_2O \qquad (1)$$
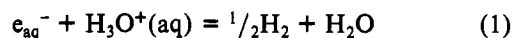
is -2.86 V,[11] it can be seen that all available evidence is consistent with the identification of the transient absorption as that of Cf(II).

The Cf(II) disappears via an apparent first-order process, with a rate parameters of $(7 \pm 1) \times 10^4$ s^{-1}. We should note that this value is similar to that previously determined for the oxidation of Am(II)[4b] $(9.7 \times 10^4$ $s^{-1})$ despite the $5f^7$ configuration of the latter compared to $5f^{10}$ for Cf(II). We plan to investigate the reactions of Bk(III) with e_{aq}^- to determine if the dynamic stability of the +2 oxidation state is indeed essentially independent of the 5f configuration.

When an N_2O-saturated, aqueous solution of 5×10^{-4} M Cf(III), pH 5.1, was subjected to the same irradiation, no transient absorption was observed over the range 240–600 nm. The predominant radical species produced in this environment is the OH radical, a powerful oxidant. Thus, there is no spectrophotometric evidence for the production of Cf(IV) in aqueous perchlorate media. With the same experimental constraints of solution composition, there was no evidence for an oxidation process from transient conductivity measurements.

There has been a previous report of the preparation of Cf(IV) in aqueous solutions of potassium phosphotungstate.[12] The absorption spectrum of the Cf(IV) prepared in this medium has a broad band that extends from ~ 1000 nm and increases to 390 nm, the limit of the reported observation. This is not consistent with the spectral results we have obtained. In addition, the values for the estimated potentials of OH as an oxidant (2.65 V)[11] and that for the Cf(IV)/Cf(III) couple (3.2 V)[3] are not consistent with the preparation of Cf(IV) via OH oxidation.

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Structure of (Urea)mercury(II) Chloride and the Effects of Strain on Ligand Properties of Urea

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Along with the accumulation of the data on the structure of complexes with molecular ligands, there is a growing interest in a search for general features in cation bonding by a particular ligand. The urea molecule, one of the most common multifunctional ligands, coordinates most cations with the carbonyl oxygen.[2] The exceptions are Pt(II) and Pd(II) for which coordination at an amide nitrogen was assigned on the basis of IR absorption data.[3] In the urea complexes with

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