The product was washed with 50 ml of acetonitrile, two 100-ml aliquots of ethanol, and finally 100 ml of diethyl ether.

The compound was recrystallized from methylene chloride–hexane solution to yield small colorless blocks (yield 4.30 g, 81%; mp 220–222°, sealed tube, uncorrected). *Anal.* Calcd for $C_{72}H_{70}B_{10}Cu_2P_4$: C, 66.80; H, 5.47; B, 8.35; Cu, 9.82; P, 9.57. Found: C, 66.47; H, 5.56; B, 8.22; Cu, 9.51; P, 9.18. Infrared spectrum (cm^{-1}, Nujol mull): 3090 (m), 2500 (s), 2490 (s), 2480 (s), 2410 (m), 2325 (br), 2230 (br), 1480 (s), 1430 (s), 1320 (w), 1180 (m), 1160 (m), 1100 (s), 1070 (w), 1035 (m), 1010 (m), 925 (w), 850 (w), 750 (vs), 695 (vs). The 80.5-MHz ^{11}B nmr spectrum (in CH_2Cl_2) displayed a doublet at +1.19 ppm (130 ± 20, 1)[27] and a broad singlet at +25.8 ppm (4).[27]

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Registry No. $Cu^I{}_2B_{10}H_{10}$, 52322-30-2; $Cu^I{}_2B_{10}D_{10}$, 52322-31-3; PPh_3, 603-35-0; $[(PPh_3)_2Cu^I]_2B_{10}H_{10}$, 52306-14-6.

[27] The first number in parentheses lists the magnitude of J_{B-H} in Hz; the single integer specifies relative area. The chemical shift given is relative to external $BF_3{\cdot}OEt_2$.

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Kinetic Study of the Reduction of Americium(VI) by Neptunium(V)[1]

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The empirical form of the rate law for the reduction of Am(VI) by Np(V) in aqueous perchlorate media at 25°, $I = 1.0$ *M*, and $0.10\ M < [H^+] < 1.0\ M$, is $-d[Am(VI)]/dt = k'[Am(VI)][Np(V)]$ where $k' = 2.45 \pm 0.04 \times 10^4\ M^{-1}\ sec^{-1}$. The variation of k' with ionic strength and temperature is presented and values calculated for $\Delta H^* = 6.66 \pm 0.08$ kcal/mol and $\Delta S^* = -16.22 \pm 0.27$ eu. The dynamic parameters are compared with those previously reported for the Np(VI)–(V) electron transfer reaction.

There is a variety of evidence consistent with the formulation that the oxo cations of the 5f transition series are isostructural.[3] In particular, the +5 and +6 oxidation states of Am and Np exist as the aquo $O\text{-}M\text{-}O^{+,2+}$ ions in aqueous perchloric acid solutions. The formal potentials of these VI–V couples vary significantly from 1.6 V for Am to 1.14 V for Np.[4]

This note presents the results obtained in a kinetic study of the reaction

$$Am(VI) + Np(V) = Am(V) + Np(VI) \qquad (1)$$

Two of the considerations that prompted this investigation are (a) to determine the effect on the kinetic parameters for reactions of the type noted above when there is a marked difference in the $\Delta F°$ values for the respective reactions and (b) to increase the limited knowledge of the reactivity pattern of the oxidant,[5] Am(VI).

Table I. Rate Parameters for the Reaction Am(VI) + Np(V)[a]

10^4[Am(VI)]$_0$, *M*	10^3[Np(V)]$_0$, *M*	No. of expts	$10^{-4}k'$,[b] M^{-1} sec^{-1}
6.00	1.41	8	2.679 ± 0.069
9.82	1.41	6	2.486 ± 0.119
5.81	3.108	11	2.626 ± 0.014
8.74	2.059	10	2.281 ± 0.043
14.23	0.723	10	2.309 ± 0.068
7.86	1.554	10	2.384 ± 0.040[c]

[a] Temperature 25.0 ± 0.05°, ionic strength 1.0 *M*, and $[H^+] = 0.98\ M$. [b] Uncertainties calculated for 95% confidence level. [c] $[H^+] = 0.10\ M$.

Table II. Temperature Dependence of k'[a]

Temp (±0.05°), °C	$10^{-4}k'$,[b] M^{-1} sec^{-1}	No. of expts
2.27	0.853 ± 0.0083	30
14.1	1.355 ± 0.023	32
25.0	2.454 ± 0.040	55[c]
36.2	4.012 ± 0.043	15

[a] $[H^+] = 0.98\ M$ and ionic strength 1.0 *M*. [b] Initial concentrations of Am(VI) and Np(V) covered same range as in Table I. [c] Includes experiments at $[H^+] = 0.10\ M$.

Table III. Ionic Strength Dependence of k'[a]

I, M	10^4[Am(VI)]$_0$, *M*	10^3[Np(V)]$_0$, *M*	$[H^+]$, *M*	No. of expts	$10^{-4}k$, M^{-1} sec^{-1}
0.10	8.38	1.483	0.08	10	0.964 ± 0.011
0.65	4.74	2.35	0.63	8	2.081 ± 0.056
1.00	5.81–14.23	0.723–3.11	0.98	55	2.454 ± 0.040
1.5	7.10	1.483	0.08	11	2.895 ± 0.059
2.0	7.31	1.483	0.08	5	3.865 ± 0.097

[a] Temperature 25.0°; ionic strength varied with $LiClO_4$.

Experimental Section

Reagents. The neptunium(V), americium(VI), and lithium perchlorate and perchloric acid solutions were prepared and standardized as described previously.[5,6]

Kinetic Procedures. A Durrum stopped-flow spectrophotometer was used for the dynamic investigations by monitoring the change in absorbance at 350 nm due to the disappearance of Am(VI). The output from the Durrum instrument was stored in a Biomation 802 transient recorder which was interfaced with a Xerox Sigma V digital computer and the data analysis was carried out as previously described.[5]

Results and Discussion

The formal potentials of the relevant couples provide necessary evidence that reaction 1 will go to completion as written. To demonstrate that unwanted side reactions are not occurring under the experimental conditions used, the value of 0.0097 was obtained for $\{\Delta[Np(V)]_{calcd} - \Delta[Np(V)]_{obsd}\}/\Delta[Np(V)]_{calcd}$ at 25°, 0.96 *M* $HClO_4$, and initial $[Am(VI)] = 5.58 \times 10^{-4}\ M$ and $[Np(V)] = 8.082 \times 10^{-4}\ M$.

The data presented in Table I provide the basis for the empirical form of the rate law

$$-d[Am(VI)]/dt = k'[Am(VI)][Np(V)] \qquad (2)$$

It should be noted that the data presented provide no evidence for a kinetic path dependent upon hydrogen ion concentration.

In Table II the variation of the rate parameter as a func-

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[1] Investigation conducted under the auspices of the U. S. Atomic Energy Commission.

[2] (a) Rosary College. (b) Argonne National Laboratory.

[3] C. Keller, "The Chemistry of the Transuranium Elements," G. E. Spandel, Nuremberg, 1971.

[4] G. Charlot, A. Collumeau, and M. J. Marchon, "Selected Constants and Oxidation-Reduction Potentials of Inorganic Substances in Aqueous Solution," Butterworths, London, 1971.

[5] M. Woods and J. C. Sullivan, *J. Inorg. Nucl. Chem.*, **36**, in press.

[6] R. C. Thompson and J. C. Sullivan, *J. Amer. Chem. Soc.*, **89**, 1096 (1967).

tion of temperature is presented. From these data the values calculated are[7] $\Delta H^* = 6.662 \pm 0.077$ kcal/mol and $\Delta S^* = -16.22 \pm 0.27$ eu.

The variation of the rate parameter with change in ionic strength is presented in Table III.

If the assumption is made that reaction 1 proceeds *via* an outer-sphere path and that the thermodynamic driving force is not large enough to preclude an adiabatic process, it is feasible to use the Marcus cross relations[8] for this reaction. The result of such a calculation[9] $\Delta F^* = 11.0$ kcal/mol is in surprising agreement with the observed value $\Delta F^* = 11.5$ kcal/mol.

The electron-exchange reaction between Np(V) and Np(VI) involves ions of similar charge and structure as those considered in this investigation. A comparison of the dynamic parameters of these systems is of interest in view of the difference in $\Delta F°$ for these reactions, *ca.* 0 compared to -10.61 kcal/mol. The relevant values for Am(VI) + Np(V) and Np(VI) + Np(V) are as follows: k (M^{-1} sec^{-1}) = 2.5×10^4, 96; ΔH^* (kcal/mol) = 6.66 ± 0.08, 7.6 ± 0.4; ΔS^* (eu) = -16.2 ± 0.3, -23.7 ± 1.5. It is apparent, although a rationale is not as obvious, that the difference in thermodynamic driving force is reflected in a lower value for the enthalpy of activation and a more positive value of the entropy of activation in the net reaction. This latter point is reflected in the values for S^* (eu) of -42.2 and -49.9 for the respective $\mathrm{Am^{VI}}$–$\mathrm{Np^{V}}$ and $\mathrm{Np^{VI}}$–$\mathrm{Np^{V}}$ activated complexes. A qualitative explanation of this result is to postulate a different number of water molecules in the respective activated complexes.

Registry No. Am, 7440-35-9; Np, 7439-99-8.

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[7] There were 132 data points correlated by the functional form referenced in K. Reinschmidt, J. C. Sullivan, and M. Woods, *Inorg. Chem.*, 12, 1639 (1973).

[8] R. A. Marcus, *Annu. Rev. Phys. Chem.*, 15, 155 (1964).

[9] For Np(V)–Np(VI), $\Delta F^* = 14.85$ kcal/mol: D. Cohen, J. C. Sullivan, and J. C. Hindman, *J. Amer. Chem. Soc.*, 76, 352 (1954). For Am(V)–Am(VI), $\Delta F^* = 16.86$ kcal/mol, estimated from unpublished data from this laboratory.

Correspondence

Orbital Energies as Ligand Field Parameters in the Weak-Field Approximation. Application to the Paramagnetic Anisotropy of Bis(2,4-pentanedionato)bis(pyridine)cobalt(II)

AIC40222K

Sir:

In the strong-field approach to ligand field theory (LFT) it is a well-established procedure to treat the one-electron d-orbital energies or the energies of the "mainly d" MO's as parameters. In this approach the real d orbitals, $\mathrm{d^{real}} = \mathrm{d}_{z^2}$, d_{yz}, d_{xz}, d_{xy}, $\mathrm{d}_{x^2-y^2}$, form the basis set and interelectronic interaction effects may be accounted for by computing matrix elements of the type $\langle \Phi | 1/r_{12} | \Phi' \rangle$ between Slater determinantal wave functions Φ based thereon. If it is desired to calculate magnetic properties, for example, g values, the spin–orbit coupling interaction must be added, as can be done with some additional effort by calculating matrix elements of the type $\langle \Phi | \xi \hat{l} \cdot \hat{s} | \Phi' \rangle$, where ξ is the spin–orbit coupling constant. Examples of procedures of this sort abound in the literature.[1]

On the other hand, orbital energies have not generally been employed as parameters in weak-field calculations. In the weak-field approach it is the free-ion term states, which themselves incorporate interelectronic interaction effects, upon which the ligand field perturbation is allowed to act. In this case the basis set involves the many-electron wave functions of the $|L, M_L, S, M_S\rangle$ type. The genesis of the parameters involved in a weak-field calculation most often is a point-charge or point-dipole model.[2] Since these electrostatic models have been shown to be fallacious,[3] these parameters are best viewed as physically meaningless phenomenological variables.

It is the purpose of this correspondence to propose an alternative LF parameterization scheme which involves physically meaningful parameters, namely, one-electron orbital energies. This scheme is applicable to many but not all point symmetries. Furthermore, I wish to outline a generally applicable, symmetry-independent procedure for calculating spectral and magnetic properties for complexes with d^n configurations[4] using the weak-field formalism and including spin–oribit coupling.

The Effective Perturbation Method and Orbital Energies. I recently proposed[5] a new approach to ligand field calculations, which I called the effective perturbation method (EPM). The EPM represents a formal mathematical way of using the results of one-electron MO calculations on transition metal complexes to obtain LF parameters for use in weak-field calculations. Very briefly, the method proceeds as follows. The five eigenfunctions of the "mainly d" MO's are truncated to remove all but the metal 3d contributions. The resulting 5×5 nonorthonormal matrix of column eigenvector coefficients is then symmetrically orthonormalized *via* Lowdin's procedure[6] to yield a 5×5 matrix $\mathbf{C}$, the orthonormal matrix of column eigenvectors which most nearly resembles the original MO coefficient matrix in a least-squares sense.[7] If $\mathbf{E}$ is a 5×5 diagonal matrix whose elements consist of the MO energies, then the desired LF matrix elements $\langle \mathrm{d_i^{real}} | \hat{V}_{\mathrm{LF}} | \mathrm{d_j^{real}} \rangle$ are those of the 5×5 matrix $\mathbf{V}_{\mathrm{eff}}^{\mathrm{real}}$ as defined by eq 1. It is clear that if the real d orbitals are eigen-

$$\mathbf{V}_{\mathrm{eff}}^{\mathrm{real}} = \mathbf{C}\mathbf{E}\tilde{\mathbf{C}} \qquad (1)$$

functions of the LF operator $\hat{V}_{\mathrm{LF}}$, then the $\mathbf{C}$ matrix be-

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[1] See, for example: (a) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, 86, 4580 (1964); (b) W. DeW. Horrocks, Jr., G. R. Van Hecke, and D. DeW. Hall, *Inorg. Chem.*, 6, 694 (1967).

[2] For a recent thorough discussion of LF parameters of this sort see M. Gerloch and R. C. Slade, "Ligand-Field Parameters," Cambridge University Press, Cambridge, U. K., 1973.

[3] For a discussion of this point with regard to 3d electrons see D. S. McClure in "Phonons in Perfect Lattices and Lattices with Point Imperfections," R. W. H. Stevenson, Ed., Oliver and Boyd, Edinburgh, 1966, pp 314–376, and with regard to f electrons see D. J. Newman, *Advan. Phys.*, 20, 197 (1971).

[4] The methods outlined are applicable to f^n configurations as well.

[5] W. DeW. Horrocks, Jr., *J. Amer. Chem. Soc.*, 94, 656 (1972).

[6] P. O. Lowdin, *J. Chem. Phys.*, 18, 365 (1950); *Advan. Phys.*, 5, 1 (1956).

[7] B. C. Carlson and J. M. Keller, *Phys. Rev.*, 105, 102 (1958).