TABLE VI

ATOMIC POSITIONAL AND TEMPERATURE PARAMETERS FOR $NO_2(HS_2O_7)$[c]

Atom											
[a]	[b]	x	y	z	U, Å^2	U_{11}, Å^2	U_{22}, Å^2	U_{33}, Å^2	U_{12}, Å^2	U_{13}, Å^2	U_{23}, Å^2
S(1)	S(1)	0.1559 (8)	0.1752 (7)	0.7698 (14)		0.005 (3)	0.014 (3)	0.009 (2)	−0.003 (3)	0.008 (4)	−0.010 (4)
S(2)	S(2)	0.2970 (8)	0.4264 (7)	0.3359 (15)		0.019 (3)	0.013 (3)	0.008 (3)	−0.004 (2)	−0.002 (4)	−0.006 (4)
O(1)	O(1)	0.320 (2)	0.065 (2)	0.742 (5)	0.028 (5)						
O(2)	O(5)	0.079 (2)	0.204 (2)	1.009 (4)	0.026 (5)						
O(3)	O(4)	0.028 (3)	0.153 (3)	0.633 (6)	0.041 (6)						
O(4)	O(6)	0.222 (2)	0.368 (2)	0.625 (5)	0.020 (5)						
O(5)	O(2)	0.417 (2)	0.293 (2)	0.291 (5)	0.022 (5)						
O(6)	O(3)	0.351 (2)	0.595 (2)	0.321 (5)	0.029 (6)						
O(7)	O(7)	0.129 (2)	0.447 (2)	0.186 (4)	0.016 (4)						
O(8)		0.680 (3)	0.093 (3)	0.609 (6)	0.047 (7)						
O(9)		0.773 (3)	0.257 (3)	0.294 (6)	0.032 (6)						
N(1)		0.726 (3)	0.171 (3)	0.465 (6)	0.029 (6)						

[a] Atom corresponding to the convention used in Table IV. [b] Atom given by Steeman and McGillavry.[26] [c] See Table II for explanation.

order of the adjacent bridge bond. This kind of asymmetry has also been observed in a number of pyrophosphates.[24,25]

Appendix

The Refinement of the Structure of $NO_2{}^+HS_2O_7{}^-$

In connection with our work on $Se_4(HSO_7)_2$ we have refined the structure of $NO_2HS_2O_7$ using the X-ray intensities measured by Steeman and MacGillavry,[26,27] who first reported the structure. Since these intensities were already on the same relative scale, only one scale factor was refined, but the reflections designated as unobserved or unreliable by the original authors were omitted in the present work, reducing the number of measurements from about 500 to 360. The positional parameters quoted in the original paper and isotropic temperature factors for all the atoms (except S for which anisotropic temperature factors were used) were allowed to refine using the full-matrix least-squares program CUDLS. Scattering factors for all the atoms were taken from ref 6. As the results were not sensitive to the weighting scheme, unit weights were used throughout. R_1 dropped from 0.16 to 0.125.

The refined atomic parameters are summarized in Table VI, and the molecular geometry of the anion is given in Table IV. Although R_1 was not much reduced, there were some significant changes in the bond distances, notably that of S(1)–O(1) which dropped from the anomalously large value of 1.64 Å to the still large but more likely value of 1.53 Å. The standard errors quoted are those based on the final round of least-squares refinement and are likely to be rather low. The difference in the lengths of the two N–O bonds (0.96 (4) and 1.06 (4) Å) is probably not significant and the O–N–O angle (178 (7)°) does not differ significantly from 180° but the error is large and the conformation of the ion is consistent with the bent model for $NO_2{}^+$ proposed by Cruickshank in $(NO_2)_2S_3O_{10}$.[19] The structure of the anion and the hydrogen-bonding scheme are discussed in the main text.

Acknowledgments.—We thank Dr. C. Calvo for his assistance and useful discussions. This work was supported by the National Research Council of Canada. An Ontario Graduate Fellowship was awarded to D. B. C.

(24) C. Calvo and P. K. L. Au, *Can. J. Chem.*, **47**, 3409 (1969).

(25) C. Calvo, *ibid.*, **43**, 1139 (1965).

(26) J. W. M. Steeman and C. H. MacGillavry, *Acta Crystallogr.*, **7**, 402 (1954).

(27) J. W. M. Steeman, Doctorate Thesis, Amsterdam, 1953.

Notes

CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA,
LOS ALAMOS SCIENTIFIC LABORATORY,
LOS ALAMOS, NEW MEXICO 87544

The Preparation and Properties of a Chromium(III)–Plutonium(V) Complex[1]

BY T. W. NEWTON* AND MARY J. BURKHART[2]

Received January 29, 1971

It has been known for some time that Cr(III) can form complexes with $UO_2{}^+$ [3] or $NpO_2{}^+$ [4] as ligands. These complexes may be made by the reduction of $UO_2{}^{2+}$ or $NpO_2{}^{2+}$ with Cr^{2+} or, in the case of neptunium, by direct substitution on Cr^{3+}(aq).[4] Attempts to make the corresponding plutonium complex by the reduction of $PuO_2{}^{2+}$ failed, presumably due to the rapid reaction of the complex with Cr^{2+}.[3] We now report the successful preparation of the plutonium complex by the *oxidation* of Pu(IV) by Cr(VI). In agreement with early work[5] we have found that Pu(IV) is oxidized moderately rapidly by excess Cr(VI) in dilute $HClO_4$. However, after the Pu(IV) has been consumed, only about half the total plutonium is Pu(VI);[6] several days are required before all the plutonium appears as Pu(VI). That which is oxidized

---

[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Graduate student summer employee.

[3] T. W. Newton and F. B. Baker, *Inorg. Chem.*, **1**, 368 (1962).

[4] J. C. Sullivan, *ibid.*, **3**, 315 (1964).

[5] R. E. Connick, Chapter 8, "The Actinide Elements," G. T. Seaborg and J. J. Katz, Ed., National Nuclear Energy Series, Division IV-14A, McGraw-Hill, New York, N. Y., 1954, p 260.

[6] D. P. Ames, Report CN-1702m, University of Chicago Metallurgical Laboratory, Chicago, Ill., 1944, quoted in ref 5, reported only 37% oxidation of Pu(IV) to Pu(VI) by a stoichiometric amount of Cr(VI) in 0.5 *M* HNO_3. Although this result was later doubted,[5] it is in agreement with our results.

slowly by Cr(VI) is in the form of a complex which can be recovered by ion exchange. The spectrum of the complex and some of its kinetic properties have been determined.

Experimental Section

Solutions of Cr(VI) were prepared by dissolving weighed amounts of $K_2Cr_2O_7$ (analytical reagent from Mallinckrodt Chemical Works) in doubly distilled water. Ferrous perchlorate solutions were prepared by dissolving pure iron wire in dilute $HClO_4$ followed by reduction on zinc amalgam. Solutions of cerium(IV) perchlorate were made by dilution of a solution from the G. F. Smith Chemical Co. Solutions of Np(VI) were prepared as before.[7] Solutions of Pu(III) were made by dissolving pure plutonium metal in concentrated $HClO_4$ and diluting appropriately. Pu(VI) was made by fuming Pu(III) with $HClO_4$ and Pu(V) was made by reducing Pu(VI) with either I^- or Fe(II). The $HClO_4$, $LiClO_4$, and distilled water were prepared as previously described.[7]

The details of a typical preparation of the complex are as follows. A stoichiometric amount of 0.06 *M* Cr(VI) is added to 0.45 mmol of Pu(III) in about 30 ml of 1.6 *M* $HClO_4$ to give a solution of Pu(IV). This is diluted with H_2O and more Cr(VI) is added so that the final solution is 0.0038 *M* Pu, 0.036 *M* Cr(VI), and 0.38 *M* $HClO_4$. The half-time for the disappearance of Pu(IV) is about 24 min under these conditions, so the mixture is allowed to stand at room temperature for 2.5–3 hr before separation using a 1-cm column, 2 cm long, of Dowex-50 X-2 cation-exchange resin. Excess Cr(IV) is washed out with water and the Cr(III) and Pu(VI) are eluted with 40 ml of 1 *M* $HClO_4$. The complex, which is left on the column as a dark green band, can be eluted with about 40 ml of 2 *M* $HClO_4$. The complex has also been prepared in solutions with $HClO_4$ concentrations ranging from 0.07 to 0.45 *M*. However, if the Pu concentration is too high or the acid concentration is too low, a dark red band forms instead of the green one which cannot be eluted with even 7 *M* $HClO_4$. For example, the red complex was obtained when the original solution was 0.0039 *M* Pu(IV), 0.031 *M* Cr(VI), and 0.19 *M* $HClO_4$. The red complex has not been characterized but may be some sort of polymer.[8]

The green complex was analyzed for total plutonium by fuming a known volume with $HClO_4$ and added Cr(VI), to aid in the oxidation of possible organic impurities from the resin. The oxidized solution was diluted to a known volume in 2–3 *M* $HClO_4$ and the plutonium concentration was determined spectrophotometrically using the expression $[\mathrm{Pu}] = [A_{8304} - {}^1/_2A_{8350} - {}^1/_2A_{8250}]/[\mathrm{path} \times 502]$, where the *A*'s are the absorbances at the indicated wavelengths and 502 $M^{-1}\ \mathrm{cm}^{-1}$ is the effective absorptivity, determined using the same procedure on a known sample. Total chromium was determined on a separate sample by treatment with alkaline H_2O_2, filtering off the insoluble substances, boiling to remove excess H_2O_2, making to known volume, and determining the absorbance at 3710 Å. The effective absorptivity at this wavelength was found to be 4690 $M^{-1}\ \mathrm{cm}^{-1}$ using known plutonium–chromium mixtures. The average oxidation state was determined by adding a known excess of Fe(II) to a sample of the complex and back-titrating with standard Ce(IV) to Fe(III), Cr(III), and Pu(IV) in 0.5 *M* H_2SO_4.

Results

Three successive fractions of the complex were eluted from the resin with 2 *M* $HClO_4$ and analyzed as described above. The results, summarized in Table I, indicate that the three fractions have from 5 to 12% Pu(IV) impurity, based on the difference between the oxidizing equivalents and the total plutonium, but that the ratio of total Cr to complexed Pu is unity within the experimental error.

TABLE I

ANALYTICAL AND SPECTRAL RESULTS

Fraction	Vol, ml	10^3 [Total Cr], *M*	10^3 [Total Pu], *M*	10^3 [Ox. agent],[a] *M*	[Total Cr]/[ox. agent]	*A* at 5665 Å[b]	ε, M^{-1} cm^{-1}
I	20	2.99	3.07	2.90	1.03	0.759	52.3
II	20	1.74	1.94	1.76	0.99	0.468	53.2
III	25	0.69	0.75	0.66	1.04	0.178	53.9

[a] Presumably Pu(V), determined by titration as described in the text. [b] Maximum for the complex.

The spectra of the three fractions were determined and a typical example is shown in Figure 1. Also shown is the spectrum of an equimolar mixture of Cr(III) and Pu(V) based on published data.[9,10] A comparison of the two spectra indicates that the plutonium in the complex is in the Pu(V) state.

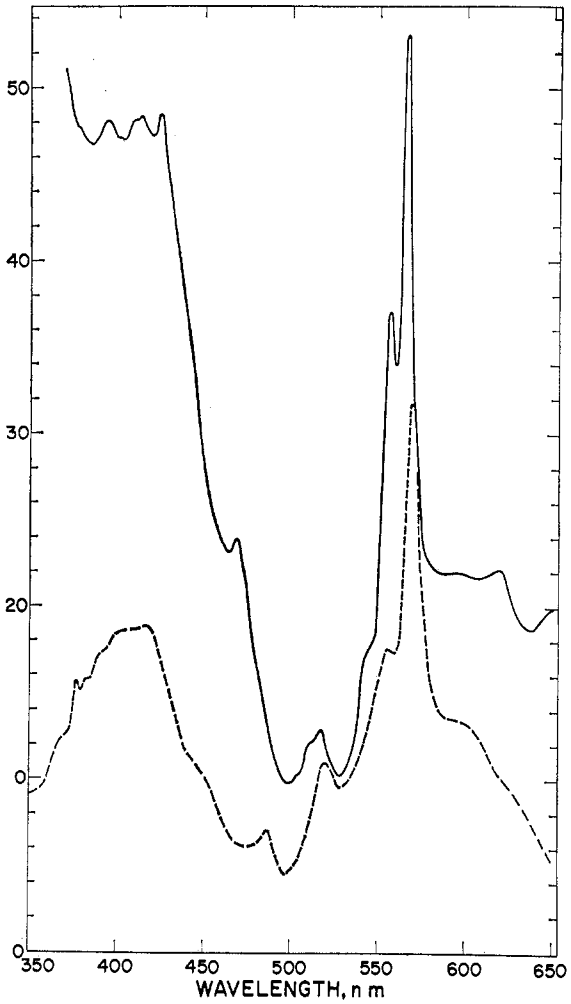

Figure 1.—Spectrum of Cr(III)·Pu(V), ———; ε is based on the concentration of Pu in the complex. Spectrum of an equimolar mixture of Cr(III) and Pu(V), – – – – – –; ε is $\epsilon_{\mathrm{Cr}} + \epsilon_{\mathrm{Pu}}$.

The complex is eluted from Dowex-50 X-2 resin much more slowly than Cr^{3+} but more rapidly than Pu^{4+}. This suggests, but does not prove, that the charge on the complex is 4+, as is indicated for the analogous uranium and neptunium complexes.[3,4]

The rates of disappearance of Pu(IV) were found to be in substantial agreement with the previous work.[5] For example, at 25° in a solution of 1.3×10^{-4} *M* Pu(IV), 0.025 *M* Cr(VI), and 0.1 *M* $HClO_4$, the observed second-order rate constant was 17.8 $M^{-1}\ \mathrm{min}^{-1}$. This is in good agreement with 17.5 $M^{-1}\ \mathrm{min}^{-1}$ from the data of Reas,[11] who used 0.04 *M* Cr(VI)

---

(7) R. B. Fulton and T. W. Newton, *J. Phys. Chem.*, **74**, 1661 (1970).

(8) We thank Professor L. O. Morgan for this suggestion.

(9) E. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1532 (1968).

(10) D. Cohen, *J. Inorg. Nucl. Chem.*, **18**, 211 (1961).

(11) W. H. Reas, Jan 1946, quoted in ref 5.

TABLE II

RATES OF REACTIONS OF Cr(III)·Pu(V) AND OF Pu(V)

Oxidizing agent	Concn × 10^4, *M*	Reducing agent	Concn × 10^4, *M*	Temp, °C	[$HClO_4$], *M*	Rate constant	Comment
Cr(VI)	19	Cr(III)·Pu(V)	2.5	23	1.9	6×10^{-6} sec^{-1}	Based on initial rate
Cr(VI)	38	Cr(III)·Pu(V)	2.5	23	1.9	8×10^{-6} sec^{-1}	Based on initial rate
Cr(VI)	13	Pu(V)	9.3	25	0.1	5.5 M^{-1} sec^{-1}	Initial $t_{1/2}$ = 1.6 min, increased as reaction proceeded
Np(VI)	23–95	Cr(III)·Pu(V)	1.4–2.9	23	2.0	$(2 \pm 0.2) \times 10^{-6}$ sec^{-1}	
Np(VI)	9–55	Cr(III)·Pu(V)	1.3–10	45	2.0	$(5 \pm 0.3) \times 10^{-5}$ sec^{-1}	
Np(VI)	0.9	Pu(V)	0.9	2	1.0	5×10^3 M^{-1} sec^{-1}	68% complete in 5 sec
Ce(IV)	7.5–27	Cr(III)·Pu(V)	1.1–1.8	25	2.0	32 ± 2 M^{-1} sec^{-1}	Stoichiometry[b]
Ce(IV)	8	Cr(III)·Pu(V)	1.5	25	0.46[a]	192 M^{-1} sec^{-1}	
Ce(IV)	0.6	Pu(V)	0.77	23	2.0	$>7 \times 10^5$ M^{-1} sec^{-1}	>99% complete in 2.5 sec
Cr(III)·Pu(V)	8.0	Pu(III)	8.2	23	2.0	120 M^{-1} sec^{-1}	
Cr(III)·Pu(V)	8.0	Pu(III)	8.2	23	1.12[a]	118 M^{-1} sec^{-1}	
Pu(V)	. . .	Pu(III)	. . .	25	1.0	0.05 M^{-1} sec^{-1}	From data in ref 12, first power in [H^+]
Cr(III)·Pu(V)	1.7–2.1	Fe(II)	1.45	5	0.2	920 ± 20 M^{-1} sec^{-1}	
Cr(III)·Pu(V)	1.4	Fe(II)	1.3	5	0.33	1380 M^{-1} sec^{-1}	
Cr(III)·Pu(V)	1.4	Fe(II)	1.3	5	0.13[c]	1520 M^{-1} sec^{-1}	
Cr(III)·Pu(V)	1.4	Fe(II)	1.3	25	0.2	3620 M^{-1} sec^{-1}	
Cr(III)·Pu(V)	1.4	Fe(II)	1.3	25	0.13[d]	4430 M^{-1} sec^{-1}	
Pu(V)	12.5	Fe(II)	15.9	25	0.25[e]	7.2 M^{-1} sec^{-1}	Other experiments show this reaction to be first power in [H^+]

[a] $\mu = 2.0$ *M* ($LiClO_4$). [b] Stoichiometry given by 4Ce(IV) + Cr(III)·Pu(V) = 4Ce(III) + Cr(VI) + Pu(VI) if Ce(IV) is in excess. [c] $\mu = 0.33$ *M* ($LiClO_4$). [d] $\mu = 0.20$ *M* ($LiClO_4$). [e] $\mu = 1.0$ *M* ($NaClO_4$).

but tracer concentrations of plutonium. Significant complexing between Cr(VI) and Pu(IV) was also observed.

Kinetic experiments have shown that reactions in which the complex is oxidized by Cr(VI), Np(VI), or Ce(IV) are much slower than the corresponding oxidations of uncomplexed Pu(V). Conversely, the reduction of the complex by either Pu(III) or Fe(II) is significantly faster than the corresponding reactions of Pu(V). The results of these experiments are summarized in Table II.

The reaction between the complex and Np(VI) is essentially zero order in Np(VI), so the observed first-order rate constant is a measure of the rate of dissociation of the complex. At 45° this constant is probably independent of the concentration of the complex but may increase as much as 10% between 1.3×10^{-4} and 1×10^{-3} *M*. From this the second-order rate constant for the disproportionation of the complex to give Pu(IV) and Pu(VI) might be as large as 6×10^{-3} M^{-1} sec^{-1}. The corresponding rate constant for the disproportionation of Pu(V) is about 3×10^{-2} M^{-1} sec^{-1} at 45° in 1 *M* $HClO_4$, calculated from the data of Rabideau.[12]

The stoichiometry of the Ce(IV)–Cr(III)·Pu(V) reaction requires further discussion. Since the reaction between Cr(III) and Ce(IV) is relatively rapid in $HClO_4$ the rate constants for the Ce(IV)–Cr(III)·Pu(V) reaction given in Table II were calculated using $dx/dt = k(A - 4x)(B - x)$, where $A = [\mathrm{Ce(IV)}]_0$, $B = [\mathrm{Cr(III)\cdot Pu(V)}]_0$, and $x = [\mathrm{Pu(VI)}]$. This is based on the assumption that the stoichiometry is given by

$$4\mathrm{Ce(IV)} + \mathrm{Cr(III)\cdot Pu(V)} = 4\mathrm{Ce(III)} + \mathrm{Cr(VI)} + \mathrm{Pu(VI)} \qquad (1)$$

However, runs made with Cr(III)·Pu(V) in excess produced more Pu(VI) than required by eq 1; the results are summarized in Table III.

TABLE III

STOICHIOMETRIC RATIOS[a]

10^4[Ce(IV)]$_0$, *M*	10^4[Cr(III)·Pu(VI)]$_0$, *M*	10^4[Pu(VI)]$_\infty$, *M*	[Ce(IV)]$_0$/Pu(VI)$_\infty$ Calcd[b]	Obsd
1.90	1.84	0.932	1.91	2.04
3.78	1.84	1.47	2.61	2.57
5.66	1.84	1.756	3.31	3.22

[a] Conditions: 2.0 *M* $HClO_4$, 25°. [b] Calculated using the mechanism given in the text, with $k_1 = k_2$.

The data suggest the mechanism

$$\mathrm{Ce(IV)} + \mathrm{Cr(III)\cdot Pu(V)} = \mathrm{Ce(III)} + \mathrm{Cr(III)} + \mathrm{Pu(VI)} \quad k_1$$

$$\mathrm{Ce(IV)} + \mathrm{Cr(III)} = \mathrm{Ce(III)} + \mathrm{Cr(IV)} \quad k_2$$

followed by rapid reactions with an overall stoichiometry given by

$$2\mathrm{Ce(IV)} + \mathrm{Cr(IV)} = 2\mathrm{Ce(III)} + \mathrm{Cr(VI)}$$

This mechanism leads to the simultaneous equations $dx/dt = k_1(A - 4x + 3y)(B - x)$ and $dy/dt = dx/dt - k_2(A - 4x + 3y)y$, where $y = [\mathrm{Cr(III)}]$ and *A*, *B*, and *x* are as above. These equations were solved numerically using the Runge-Kutta method, trial values of k_1 and k_2 were used with the experimental values of *A* and *B*, and it was found that $k_1 = k_2$ leads to stoichiometric ratios in reasonable agreement with the observed ones, as shown in Table III. When Ce(IV) is in excess according to eq 1, the buildup of Cr(III) during the reaction is relatively unimportant. Calculations show that the apparent second-order rate constant based on eq 1 is 17% high when Ce(IV) is in excess by 75%.

Discussion

The fact that complexing PuO_2^+ with Cr^{3+} slows its rates of oxidation by Ce(IV) and Np(VI) is in agreement with the effect of similar complexing of NpO_2^+

---

[12] S. W. Rabideau, *J. Amer. Chem. Soc.*, **79**, 6350 (1957).

on its oxidation by Co(III). It was shown[13] that Np(V) reacts with Co(III) about 150 times faster than Cr(III)·Np(V) does in 1 *M* $HClO_4$-1 *M* $LiClO_4$ at 25°. A more interesting observation is that reactions in which Cr(III)·Pu(V) is reduced by Pu(III) or Fe(II) are zero order in $[H^+]$ as well as being considerably faster than the corresponding reactions of Pu(V) which are first power in $[H^+]$. These observations lead to the plausible suggestion that Cr(III), in the complex, weakens and lengthens the Pu–O bonds, which are broken on reduction but shortened on oxidation. Electrostatic and steric effects can also contribute to the relative slowness of the oxidation of the complex by cations.

The reduction reactions of PuO_2^+ and other actinide-(V) ions usually show first-power $[H^+]$ dependences and may be interpreted to involve protonated species such as $HOPuO^{2+}$. Apparently Cr^{3+} plays a role similar to that of H^+ in these reactions. The relative effectiveness of these two ions may be seen by considering as an example the purely formal process $[HOPuOPu^{5+}]^* + Cr^{3+} = [CrOPuOPu^{7+}]^* + H^+$, where the formulas but not necessarily the structures of the activated complexes are implied. The "equilibrium" quotient for this process is $Q^* = k_{Cr}Q/k_H$, where k_{Cr} is the rate constant for the reduction of the complex by Pu(III), k_H is the rate constant for the $[H^+]$-dependent reduction of PuO_2^+, and Q is the association quotient for $CrOPuO^{4+}$ which for the corresponding Np complex is $2.6 \pm 0.5\ M^{-1}$ at 25° and $\mu = 8\ M$.[4] The values of k_{Cr} and k_H from Table II are 120 M^{-1} sec^{-1} and 0.05 M^{-2} sec^{-1} giving Q^* a value of about 2×10^3. The corresponding value for reduction by Fe(II) is about 200, if a reasonable ionic strength dependence is assumed for the reaction between Fe^{2+} and $CrOPuO^{4+}$. These rather large values for Q^* show that, *based on the aqueous ions*, Cr^{3+} is much more effective than H^+ in promoting the reduction of Pu(V) either by Pu(III) or by Fe(II).

Acknowledgments.—The authors gratefully acknowledge helpful discussions with Dr. J. C. Sullivan and with Dr. C. E. Holley, Jr., under whose general direction this work was done.

[13] J. C. Sullivan and R. C. Thompson, *Inorg. Chem.*, **6**, 1795 (1967). It should be noted that the hydrogen ion dependence of the rate of the reaction of the complex is predominantly $[H^+]^{-1}$ but that of NpO_2^+ is $[H^+]^0$.

CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Incomplete Conformational Averaging in Tris(ethylenediamine)platinum(IV) Ion

BY LUCILLE H. NOVAK AND JAMES K. BEATTIE*

Received September 30, 1970

The nmr spectra of tris(ethylenediamine)metal complexes provide evidence for a free energy difference between the δ and λ conformations of the coordinated ethylenediamine ligands.[1-4] The δ conformation is assumed to be more stable for the Λ configuration of the three ligands about the metal ion,[5,6] in accord with observed crystal structures,[7] conformational preferences of related propylenediamine complexes,[8] and calculations of nonbonded interactions within the complex.[5,9] About 60–75% of the ligands are in the δ conformation, estimated from the comparison of chemical shifts between propylenediamine and ethylenediamine complexes of ruthenium(II),[10] comparisons of vicinal coupling constants between tris(ethylenediamine)rhodium(III) ion and related molecules,[3] and observation of the temperature dependence of contact shifts in tris(ethylenediamine)nickel(II) ion.[1]

No evidence for a conformational preference in tris-(ethylenediamine)platinum(IV) ion appears to have been reported and arguments from optical activity data suggest that none exists.[11] The previously reported[2,12] 60-MHz nmr spectrum of N-deuterated $Pt(en)_3^{4+}$ consists of a single sharp peak of about 1-Hz width, together with equally sharp satellites due to coupling with ^{195}Pt. No chemical shift difference is observed which could be attributed to a conformational preference, although from comparison with the spectra of $Pt(pn)_3^{4+}$ any chemical shift difference is expected to be small.[10] At the higher magnetic field strength of the 220-MHz spectrum, however, a chemical shift difference is observed.

A chemical shift difference between protons in an optically inert tris-ethylenediamine complex does not necessarily indicate incomplete conformational averaging.[12] Even if there is no conformational preference and each ligand spends an equal amount of time in the δ and λ conformations, there exists in principle a chemical shift difference. The positions of the protons in the δ and λ conformations are not related by the symmetry of the complex due to the presence of the other two chelate rings. Consequently, an AA′BB′ spectrum is expected even if there is no conformational preference. The magnitude of the chemical shift difference arising from this inherent magnetic nonequivalence is unknown. A recent analysis of the spectrum of $Rh(en)_3^{3+}$ yields an indirect estimate of 0.02 ppm in that complex.[3] In the present work we suggest on the basis of observed differences in platinum–proton coupling constants that the chemical shift difference due to inherent magnetic nonequivalence is negligible in $Pt(en)_3^{4+}$ and that the observed chemical shift difference is better explained by incomplete conformational averaging.

Experimental Section

Tris(ethylenediamine)platinum(IV) chloride was prepared as

---

[1] F. F.-L. Ho and C. N. Reilley, *Anal. Chem.*, **42**, 600 (1970).

[2] J. K. Beattie and H. Elsbernd, *J. Amer. Chem. Soc.*, **92**, 1946 (1970).

[3] J. L. Sudmeier and G. L. Blackmer, *Inorg. Chem.*, **10**, 2010 (1971).

[4] J. L. Sudmeier and G. L. Blackmer, *J. Amer. Chem. Soc.*, **92**, 5238 (1970).

[5] E. J. Corey and J. C. Bailar, Jr., *ibid.*, **81**, 2620 (1959).

[6] For a description of the nomenclature of conformations see *Inorg. Chem.*, **9**, 1 (1970).

[7] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *ibid.*, **7**, 842 (1968).

[8] F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **85**, 2913 (1963).

[9] J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, **9**, 576 (1970); J. R. Gollogly, C. J. Hawkins, and J. K. Beattie, *ibid.*, **10**, 317 (1971).

[10] J. K. Beattie and L. H. Novak, *J. Amer. Chem. Soc.*, **93**, 620 (1971).

[11] S. F. Mason and B. J. Norman, *J. Chem. Soc. A*, 307 (1966).

[12] T. G. Appleton, J. R. Hall, and C. J. Hawkins, *Inorg. Chem.*, **9**, 1299 (1970).