sirable to investigate $UF_5.nMF$ systems starting with *uranium initially in the pentavalent state*, in particular, as UF_5.

Since it was known that NH_4F reacts smoothly with UF_4 under anhydrous conditions at 80–130° to form a series of complex fluorides,[5] we investigated the analogous reaction with pentavalent uranium. Both α and β forms of UF_5 react with NH_4F in 1:1 mole ratio to form $UF_5.NH_4F$ at 80–85°. In a typical preparation, ~50 mmol. of freshly prepared α-UF_5 was ground with 50 mmol. of dried NH_4F in a helium atmosphere. The mixture then was placed in a tightly closed polyethylene or Teflon container and heated for 2 days yielding a moisture-sensitive, nearly white product. *Anal.* Calcd. for $UF_5.NH_4F$: U, 64.32; NH_4, 4.86; F, 30.8. Found: U, 64.29; NH_4, 4.9; F, 30.0.

The product of heating NH_4F with UF_5 (1:1) at 85° has a characteristic X-ray powder pattern different from those of the starting materials. It suffers only negligible weight loss on heating several hours in vacuum (1μ) at 150° showing that no free NH_4F is present. It retains the X-ray pattern characteristics of $UF_5.NH_4F$. However, on treatment with water, white $UF_5.NH_4F$ disproportionates instantly, giving a solution containing yellow uranyl(VI) ion and a green solid having the X-ray pattern of rhombohedral $UF_4.NH_4F$.

If 48% HF is used to dissolve $UF_5.NH_4F$, a solution of U(V) is obtained as reported by Rampy.[3] In addition we find that UF_5 can also be dissolved with 48% HF without appreciable disproportionation.

On addition of a saturated solution of RbF dropwise to such solutions of U(V), the new compound $UF_5.RbF$ is precipitated as sizable ice-blue crystals. The X-ray powder patterns of $UF_5.RbF$ made from HF solution and $UF_5.NH_4F$ made under anhydrous conditions show that the two compounds are isostructural.

A pale blue powder is obtained by grinding together anhydrous RbF with UF_5 in a 1:1 mole ratio and heating for 16 hr. in a nickel bomb at 400°. The product gives a powder pattern identical with that of $UF_5.RbF$ obtained from HF solution. Without stabilization by formation of a fluoride complex, UF_5 disproportionates into UF_6 and lower fluorides at this temperature.[6]

The absorption spectra of solid $UF_5.NH_4F$ and $UF_5.RbF$ was measured from 4,000 to 17,000 Å. on a Cary Model 14 spectrophotometer. The spectra of the fluoride complexes containing pentavalent uranium are clearly different from those of fluoride complexes containing tetravalent uranium, particularly in the near infrared region.

Addition of H_2O_2 or Na_2SO_3 to an HF solution containing $UF_5.NH_4F$ causes reduction of U(V) to UF_4 which is insoluble in this medium. Uranyl(VI) is not reduced under these conditions. By this technique it was shown that when UF_5 or $UF_5.NH_4F$ is dissolved in 48% HF, >95% of the uranium is present as soluble U(V).

The technique of treating UF_5 with anhydrous fluorides seems to be generally applicable for preparation of U(V) fluoride complexes. We are in the process of extending this work and characterizing the resulting compounds, in particular those containing ratios of ammonium or alkali fluoride to UF_5 greater than 1:1.

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[5] R. Benz, R. M. Douglass, F. H. Kruse and R. A. Penneman, "Preparation and Properties of Several Ammonium Uranium(IV) and Ammonium Plutonium(IV) Fluorides," being submitted to *Inorg. Chem.*

[6] J. J. Katz and G. T. Seaborg, "Chemistry of the Actinide Elements," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 157.

THE EXCHANGE OF CHROMIUM(II) ION AND *cis*-DIAZIDOTETRAAQUOCHROMIUM(III) ION. A DOUBLE-BRIDGED TRANSITION STATE[1]

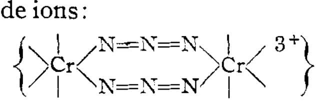
Sir:

Transition-states for many reactions of metal ion oxidizing agents and chromium(II) ion involve bridging between the metal atoms by a single ligand.[2] The possibility of a transition-state with two ligands bridging between the oxidizing agent and chromium(II) ion has been tested directly with negative results in two studies. In the oxidation of chromium(II) ion by either *cis*-diaquotetramminecobalt(III) ion or *cis*-diaquobisethylenediaminecobalt(III) ion, only one water molecule is transferred from the inner coördination sphere of cobalt to the inner coördination sphere of chromium.[3] Reaction of *cis*-difluorotetraaquochromium(III) ion and chromium(II) ion results in inappreciable exchange of chromium between the two species, but instead produces monazidochromium(III) ion, demonstrating the greater stability of a transition-state with one bridging fluoride ion relative to that with two bridging fluoride ions.[4]

In contrast to these results, we have observed direct exchange between chromium(II) ion and *cis*-diazidotetraaquochromium(III) ion:

$$Cr(N_3)_2^+ + {}^*Cr^{2+} = Cr^{2+} + {}^*Cr(N_3)_2^+$$

The only reasonable mechanism for this exchange reaction is "electron-transfer" *via* a transition state involving bridging between the chromium atoms by both azide ions:



If reaction of *cis*-diazidochromium(III) ion and chromium(II) ion had occurred *via* a transition-state with a single azide bridging group, net aquation would have resulted giving monazidochromium(III) ion and hydrazoic acid. The "irreversible" reaction of chromium(II) ion and hydrazoic acid to give nitrogen gas would preclude reentry of azide ion into the first coördination shell of chromium(III) by a pathway involving azide ion, chromium(II) ion and monazidochromium(III) species. Since chromium(II) was not consumed in the kinetic experiments and these

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[1] This work was supported in part by the United States Atomic Energy Commission under Contract AT(11-1)-1168.

[2] H. Taube, in "Advances in Inorganic Chemistry and Radiochemistry," H. J. Emeleus and A. G. Sharpe, editors, Vol. I, 1959, p. 1.

[3] W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **82**, 526 (1960).

[4] Y. T. Chia and E. L. King, *Disc. Faraday Soc.*, **29**, 109 (1960).

TABLE I

EXCHANGE OF CHROMIUM(II) ION AND *cis*-DIAZIDOTETRAAQUOCHROMIUM(III) ION AT 0° AND $I \cong 0.5\ M$

$[H^+]$	$[Cr^{2+}] \times 10^3$	$[Cr(N_3)_2^+] \times 10^3$	$t_{1/2}$, sec.	k,[a] l. mole^{-1} sec.$^{-1}$
0.4	2.4	0.74	3.9	57
.4	1.16	0.74	6.0	61
.45	0.77	1.39	5.3	60
.85	0.78	1.20	5.1	68[b]

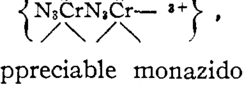
[a] $k = 0.69/([Cr^{2+}] + [Cr(N_3)_2^+])t_{1/2}$. [b] $I \cong 0.9\ M$.

conformed to the usual exponential approach to random mixing of chromium-51 between the chromium species, it can be concluded that this reaction goes *via* a double-bridged transition state.

In addition to several single point experiments which demonstrated exchange, four kinetic experiments involving several points were run. These experiments are summarized in Table I. The second-order rate coefficient for exchange *via* the double-bridged transition state, $k \cong 60$ l. mole^{-1} sec.$^{-1}$ at 0° and an ionic strength of ~ 0.5 molar, is considerably larger than the value $k \cong 1.3$ l. mole^{-1} sec.$^{-1}$ for exchange of monazidochromium(III) ion and chromium(II) ion under these same conditions.[5] The mild increase in rate with a two-fold increase in hydrogen ion concentration can be attributed to the increase of electrolyte concentration.

Although the factors responsible for greater stability of the transition-state involving bridging by two azide ions relative to that with a single bridging azide ion, in contrast to the reverse situation for fluoride ion or water acting as bridging groups, are not obvious, both the electronic structure of azide ion, with its pi bonding, and steric considerations may be relevant. Without great strain, appropriate values for the Cr–N–N angle would be accessible to form a symmetrical double-bridged transition-state.

Diazidotetraaquochromium(III) ion was prepared by oxidation of chromium(II) ion with a large excess of azide ion[6] present as a sodium azide–hydrazoic acid buffer (0.1–0.2 M in each constituent). Product species of charge +1, the isomeric diazidochromium(III) ions, were separated from reaction products of higher charge (monoazidochromium(III) ion, aquochromium(III) ion, and amminochromium(III) species[3]) by ion-exchange. At the electrolyte concentrations employed, ions of charge +1 pass directly through the column. After freeing this solution of uncomplexed azide by acidification and aeration with nitrogen, it was treated with chromium(II) ion. This procedure, designed to convert *trans* diazidochromium(III) ion to monoazidochromium(III) ion *via* a transition state



$\left\{N_3CrN_3Cr—^{3+}\right\}^{\ddagger}$,

did produce appreciable monazidochromium(III) ion. The excess chromium(II) ion was treated with iron(III) ion or oxygen, and residual diazidochromium(II) ion, presumably the *cis* isomer, was separated from other chromium and iron species by ion-exchange. Analysis of two independent batches of complex prepared in this way gave values of azide/chromium of 1.96 and 2.14.

Aliquots of reaction mixture in kinetic experiments were quenched into a dilute solution of hydrogen peroxide at 4–5 times ranging from 3 to 18 seconds after mixing. Diazidochromium(III) ion, the only chromium species of charge +1 in the quenched solution was separated from other chromium species by ion-exchange. Visual inspection of the column containing light colored ion-exchange resin showed no detectable monazidochromium(III) ion. An analysis for chromium(II) ion performed at the end of each experiment corresponded closely to the amount added.

The fraction exchange was calculated using either a directly measured infinity-time specific activity or a value calculated from the specific activity of the chromium(II) ion and the solution composition. In two experiments, an appreciably better correlation of data was obtained using the former quantity.

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BRIDGE ADDUCTS—THE INTERACTION OF BF_3 WITH TRANSITION METAL CYANIDE COMPLEXES

Sir:

This communication reports the general Lewis basicity of some transition metal cyanide complexes. One example of this phenomenon is afforded by the compounds formed between boron trifluoride and $K_2Ni(CN)_4$. Spectral evidence, stoichiometry of formation, and magnetic data indicate the presence of cyanide bridges (*e.g.*, $—Ni—C{\equiv}N—BF_3$) in this new class of compounds.

Potassium tetracyanonickelate(II)[1] was dried by heating the solid under high vacuum (less than 10^{-4} mm.); and boron trifluoride addition was accomplished by three methods. (1) It was found that purified BF_3[2] at a pressure of *ca.* 50 mm. slowly added to $K_2Ni(CN)_4$ which was maintained at 85°. After about two hours absorption appeared to slow down.[3] In a typical run 1.30 millimoles of $K_2Ni(CN)_4$ absorbed 1.29 millimoles of BF_3 (as indicated by P, V and T measurement of BF_3); also weight increase of the solid corresponded to an uptake of 1.28 millimoles BF_3. (2) A 1:1 adduct also was obtained by the interaction of dry $K_2Ni(CN)_4$ with an excess of practical grade 47% boron trifluoride etherate. The infrared spectrum and color of this product indicated it was less pure than that produced by procedure one. (3) Boron trifluoride at greater than one atmosphere pressure was allowed to react with $K_2Ni(CN)_4$ in a sealed glass tube for two weeks at room temperature.

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(5) R. Snellgrove and E. L. King, forthcoming publication.

(6) With only an equivalent amount of azide present at much lower concentrations, the reaction products include chromium(III)-ammine species (M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2816 (1962)).

(1) $K_2Ni(CN)_4$ was prepared by the method of W. C. Fernelius and J. J. Burbage, *Inorg. Syntheses*, **2**, 227 (1946).

(2) H. C. Brown and R. B. Johannsen, *J. Am. Chem. Soc.*, **72**, 2937 (1950).