of the lower component of resonance 3, *i.e.*, the *syn* proton in the (+) configuration. *Therefore, inversion of configuration occurs with syn–anti interchange*, and a σ-bonded intermediate (1-*h*) is implied for the first epimerization process of the *anti*-Ac complex. Similarly, spin saturation labeling experiments and observation of coalescences allow us to conclude that a 1-*h* σ-bonded intermediate is primarily responsible for epimerization of the *syn*-Ac complex. Furthermore, isomerization appears to occur predominantly *via* a 3-*h* σ-bonded intermediate.

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Formation and Reactions of [$(NH_3)_5RuN_2O^{2+}$]

Sir:

When N_2O is added to an aqueous solution of $(NH_3)_5RuOH_2^{2+}$, produced by reduction of $(NH_3)_5RuCl^{2+}$ by Cr^{2+}, Pt–H_2, or Zn(Hg), a new absorption band develops having a maximum at 238 nm (see Figure 1). It increases in intensity when the concentration of N_2O increases, disappears when N_2O is removed by passing argon through the solution, and is restored when N_2O is again added. The rate at which the absorption grows can conveniently be measured spectrophotometrically. Plots of ln $(A_\infty - A_t)$ *vs.* t are found to be strictly linear up to at least 95% completion of reaction. In Figure 2 the values of k_{obsd} as they are obtained from the plots are shown as a function of N_2O concentration.

The data of Figure 2 show that k_{obsd} is given by the relation $k_1 + k_2[N_2O]$. The general observations described above and the kinetic data can be interpreted on the basis that N_2O associates reversibly with $(NH_3)_5RuOH_2^{2+}$.

$$(NH_3)_5RuOH_2^{2+} + N_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (NH_3)_5RuN_2O^{2+} + H_2O \quad (1)$$

On the basis of this interpretation, the rate of approach to equilibrium at constant concentration of N_2O should follow pseudo-first-order behavior, and, moreover, the first-order specific rate k_{obsd} should be given by $k_r + k_f[N_2O]$ (assuming, that is, that the rate laws of the forward and reverse reactions are as indicated in eq 1). Identifying k_1 ($= 1.35 \times 10^{-3}$ sec^{-1}) with k_r and k_2 ($= 9.5 \times 10^{-3}$ M^{-1} sec^{-1}) with k_f, K_1 for reaction 1 at 6.8° and $\mu = 0.023$ (Cl^- as anion) is calculated as 7.0 (using N_2O(aq) rather than N_2O(g) as the standard state for this reactant). It should be noted that the k_r term makes by far the greater contribution to k_{obsd}, and thus the value of k_r is rather well defined by the data. The coefficient k_f is obtained from the slope of the line in Figure 2 and is, therefore, less well defined. The value of k_f suggested by the above data is, however, confirmed by an independent measurement which will now be described.

When Cr^{2+} is present in a solution containing both $(NH_3)_5RuOH_2^{2+}$ and N_2O, the reaction

$$2Cr^{2+} + (NH_3)_5RuOH_2^{2+} + N_2O + 2H^+ = 2Cr^{3+} + (NH_3)_5RuN_2^{2+} + 2H_2O \quad (2)$$

takes place quantitatively. The kinetics of reaction 2 are of particular interest. Though Cr^{2+} is consumed, the reaction rate does not depend on [Cr^{2+}], and the rate law for the reaction is given by

$$\frac{d[(NH_3)_5RuN_2^{2+}]}{dt} = k[(NH_3)_5RuOH_2^{2+}][N_2O] \quad (3)$$

Good kinetic data were obtained following the growth of the nitrogen complex spectrophotometrically at 221 nm. In determining the rate law, N_2O was in excess, but the initial concentration covered the range 8.38×10^{-3}–4.52×10^{-2} M for the series.[1] Chromous ion covered the range 1.2×10^{-4} to 1.2×10^{-3} M; the initial concentration of Ru(II) was fixed at 6×10^{-5} M. The coefficient k at 6.8° is found to be 10.1×10^{-3} M^{-1} sec^{-1}. The form of rate law 3 and the excellent agreement of k with k_f shows that the rate of formation of the N_2O complex is rate determining for reaction 2 and this, in turn, suggests that the N_2O complex is reduced virtually as rapidly as it is formed.

The stoichiometry for reaction 2 was checked covering the range [Cr^{2+}]/[Ru(II)] from 1.2 to 10.0 by using Fe^{3+} to quench the reaction, and then developing the color of Fe^{2+} with *o*-phen.[2] Under our conditions, the oxidation by Fe^{3+} of the nitrogen complex was slow compared to that of Cr^{2+} or $(NH_3)_5RuOH_2^{2+}$. By waiting 1 hr after the Fe^{3+} was added, the nitrogen complex was destroyed quantitatively, and the amount of nitrogen liberated was determined by gas chromatography using this reaction. Within the limits of accuracy of the methods, ±5%, the agreement with requirements of eq 2 was exact. The first method was also used to follow the rate of reaction, again in satisfactory agreement with the rates determined spectrophotometrically.

The kinetic measurements were repeated at 20.1°. At the higher temperature, k_r contributes proportionately even more to k_{obsd} than at the lower, and, as before, rather accurate value of this parameter can be obtained. The value of k_f was determined by measuring the rate of reaction 2 at the higher temperature. The values of k_r and k_f obtained, $9.1 \pm .5 \times 10^{-3}$ sec^{-1} and 4.51×10^{-2} M^{-1} sec^{-1}, respectively ($\mu = 0.02$ with Cl^-), combine to yield K_1 at 20.1° as 5.0.

The affinity of $(NH_3)_5RuOH_2^{2+}$ for N_2O was also determined by a vacuum-line method,[3] comparing the partial pressure of N_2O over a solution containing $(NH_3)_5RuOH_2^{2+}$ with that registered in a blank experiment identical in every respect, but with sodium chloride replacing the ruthenium complex. K_1 was measured as 8.3 at 24° and 8.6 at 22°. Because the pressure changes recorded are very small, and because

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[1] The concentration of N_2O in solution was determined using the value of Henry's law constant as obtained from "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p 259.

[2] T. J. Meyer and H. Taube, *Inorg. Chem.*, 7, 2369 (1968); G. Charlot, "Colorimetric Determination of Elements," Elsevier Publishing Co., New York, N. Y., 1964, p 274.

[3] The authors wish to express their appreciation to Mr. P. R. Jones for his assistance with the vacuum-line work.

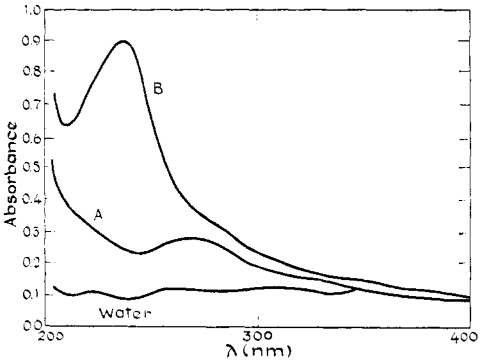

Figure 1. (A) Uv spectrum of $(NH_3)_5RuOH_2^{2+}$. (B) $(NH_3)_5RuN_2O^{2+}$ in equilibrium with $(NH_3)_5RuOH_2^{2+}$. $[(NH_3)_5RuOH_2^{2+}] = 3.29 \times 10^{-4}\ M$, $[HCl] = 1 \times 10^{-2}\ M$, $[N_2O]_{aq} = 2.8 \times 10^{-2}\ M$, $\mu = 0.012$ with Cl^-. Using the value of $K_1 = 5.0$ at 20.1°, the extinction coefficient of the nitrous oxide complex may be calculated as $1.7 \pm 0.2 \times 10^{-4}\ M^{-1}\ cm^{-1}$ at 238 nm.

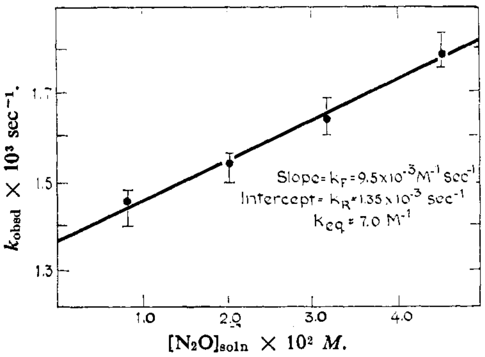

Figure 2. The rate constant governing the approach to equilibrium in the reaction of $(NH_3)_5RuOH_2^{2+}$ with N_2O as a function of $[N_2O]$: $[N_2O]_0 \gg [(NH_3)_5RuOH_2^{2+}]_0$; temperature = 6.8°. $[(NH_3)_5RuOH_2^{2+}] = 6.12 \times 10^{-4}\ M$. $\mu = 0.023$ with Cl^-

there is some net reduction of N_2O during the manipulations, the value of K_1 obtained by this direct method is not considered to be as accurate as that recorded above. The measurement does serve, however, to lend credence to the interpretation of the data which was advanced.

That the variations of K_1 with temperature is small was confirmed by measuring the absorbance of a solution containing N_2O and $(NH_3)_5RuOH_2^{2+}$ at fixed concentration. The ratio of absorbance at 238 nm at 6.8° to that at 20.1° was observed to be 1.39, to be compared to a ratio of 1.4 determined from the values of K_1 above.

Using the values of the equilibrium constant and its temperature coefficient, $\Delta F°$, $\Delta H°$, and $\Delta S°$ for reaction 1 are calculated as −0.9 kcal/mole, −4.2 kcal/mole, and −11 eu, respectively. Combined with the value of $\Delta F°$ (25°) for reaction 4 determined as described below,

$$(NH_3)_5RuOH_2^{2+} + N_2 = (NH_3)_5RuN_2^{2+} + H_2O \qquad (4)$$

$$\Delta F° = -6.5 \text{ kcal}$$

$$(NH_3)_5RuN_2O^{2+} + N_2 = (NH_3)_5RuN_2^{2+} + N_2O \qquad (5)$$

that for reaction 5 can be calculated as −5.6 kcal. This value is significant in showing that the affinity of N_2O for O is diminished when N_2O coordinates to $(NH_3)_5RuOH_2^{2+}$. This outcome was not expected, it having seemed reasonable to conjecture that the back-bonding interaction between N_2 and Ru(II) would increase the negative charge on the terminal nitrogen and thus strengthen the bond to a Lewis acid such as atomic oxygen.

The equilibrium constant for reaction 4 was determined by measuring the rate of loss of nitrogen from $(NH_3)_5RuN_2^{2+}$ in solution, using a stream of Ar to sweep out N_2 as it is formed. Under these conditions both $(NH_3)_5RuOH_2^{2+}$ and $[(NH_3)_5RuN_2Ru(NH_3)_5^{4+}]$ are produced. These were determined spectrophotometrically, the first by developing its color with isonicotinamide[4] and the second using the absorption maximum at 262 nm.[5] Combining the specific rate for the decomposition of the nitrogen complex thus determined, $\sim 1.3 \times 10^{-6}$ sec^{-1} at 25°, with the value measured by Itzkovitch and Page[6] for the rate of formation of the complex, K_4 is calculated as 5.5×10^4. Equilibrium with respect to the bridged nitrogen complex was not attained in these solutions. Other experiments allowing $(NH_3)_5RuN_2^{2+}$ to reach complete equilibrium under nitrogen at 1 atm have led to a value of $\sim 5 \times 10^4$ for K_4 at 25° ($\mu = 0.1$ with chloride) and indicate that the quotient $[(NH_3)_5RuN_2Ru(NH_3)_5^{4+}]/([(NH_3)_5RuN_2^{2+}][(NH_3)_5RuOH_2^{2+}])$ at equilibrium is of the order of 10^4.

The slow reduction of N_2O by $(NH_3)_5RuOH_2^{2+}$ has already been referred to. In a solution with $[(NH_3)_5RuOH_2^{2+}] = 3.3 \times 10^{-4}\ M$ and $[N_2O] = 0.028\ M$, no significant loss of reducing power is observed within 0.5 hr. But on the time scale of days, $(NH_3)_5RuN_2^{2+}$, $[(NH_3)_5Ru]_2N_2^{4+}$,[7] $(NH_3)_5RuOH_2^{3+}$, and $(NH_3)_5RuCl^{2+}$ (chloride medium) are formed. In contact with amalgamated Zn or platinum wire, the reduction of N_2O by $(NH_3)_5RuOH_2^{2+}$ is greatly accelerated.

In contrast to $(NH_3)_5RuOH_2^{2+}$, the reducing agent Cr^{2+} reacts extremely rapidly with $(NH_3)_5RuN_2O^{2+}$. By taking account of the fact that the rate of reaction 2 is independent of $[Cr^{2+}]$ even at the lowest concentration used, a lower limit for the rate of reaction Cr^{2+} with the species $(NH_3)_5RuN_2O^{2+}$ of $10^2\ M^{-1}$ sec^{-1} is calculated. The reaction of Cr^{2+} with N_2O is very much slower, requiring a time period of the order of days for half-reaction.[8] Preliminary measurements (Cr^{2+} at 0.01 M, N_2O at 0.028 M), assuming a second-order reaction, show the specific rate to be $\sim 10^{-5}\ M^{-1}$ sec^{-1}. Product studies on reaction 2 using ion-exchange techniques to identify Cr(III) species show that Cr^{3+} and $CrCl^{2+}$ are the dominant products. Thus a one-electron, rather than a two-electron reduction of the coordinated N_2O, is indicated. Because, as shown by $\Delta F°$ for reaction 5, the N–O bond is weakened when N_2O associates with $(NH_3)_5RuOH_2^{2+}$, the increase in reactivity toward Cr^{2+} of the coordinated oxide is not unexpected. It is possible also that Cr^{2+} and Ru(II) interact on N_2O in concert, and that the increase in reactivity is partly attributable to this. This point cannot be settled, however, without further experimentation.

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(4) R. G. Gaunder, Ph.D. Thesis, Stanford University, Stanford, Calif., June 1969.

(5) D. F. Harrison, E. Weissberger, and H. Taube, *Science*, **159**, 320 (1968).

(6) I. J. Itzkovitch and J. A. Page, *Can. J. Chem.*, **46**, 2743 (1968).

(7) Molecular nitrogen complexes of pentaammineruthenium(II) have been prepared by reducing $(NH_3)_5RuCl^{2+}$ in the presence of N_2O: A. A. Diamantis and G. J. Sparrow, *Chem. Commun.*, **23**, 469 (1969).

(8) R. G. S. Banks, R. J. Henderson, and J. M. Pratt, *J. Chem. Soc., A*, 2886 (1968); W. Traube and W. Passerge, *Ber.*, **49**, 1692 (1916).

The value of the second-order specific rate for formation of the N_2O complex may be compared with the formation rates of other $(NH_3)_5Ru^{II}L^{2+}$ complexes at 25°. For L = N_2, $(NH_3)_5RuN_2{}^{2+}$, N_2O, CO, pyridine, and isonicotinamide, $k = 7.1 \times 10^{-2}$,[6] 4.2×10^{-2},[6] 7.21×10^{-2}, 12×10^{-2},[9] 11.8×10^{-2},[10] and 6×10^{-2} $M^{-1}\ \mathrm{sec}^{-1}$.[11]

Acknowledgment. Financial support by the National Institutes of Health, Grant No. GM 13638-03, and the National Science Foundation, Grant No. GP 5322, is gratefully acknowledged.

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(9) D. F. Harrison, Ph.D. Thesis, Stanford University, Stanford, Calif., Jan 1969.

(10) A. R. Allen, R. Hintze, and P. C. Ford, to be submitted for publication.

(11) J. N. Armor, unpublished result.

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Synthesis of Cyclooctatetraenyleuropium and Cyclooctatetraenylytterbium

Sir:

The preparation of bis(cyclooctatetraenyl)uranium(IV),[1] which has received the trivial name "uranocene," has renewed interest in new types of compounds containing cyclooctatetraene. Aside from uranocene, compounds of formula $M(Cot)_2$, with M = V, Ti, have been known for some time. Several compounds of formula M(Cot) are also known,[2] as is one mixed cyclopentadienyl–cyclooctatetraenyl compound, Co(cp)(Cot),[3] and many Cot–carbonyl compounds. We report here the preparations and some properties of cyclooctatetraene compounds of Yb and Eu. We believe these to be the first reported cyclooctatetraene complexes of rare earth elements.

It is well known that solutions of ytterbium and europium in liquid ammonia may be used to prepare the respective cyclopentadienides.[4] The cyclooctatetraene derivatives of these elements were successfully synthesized using similar techniques. Because of the almost explosive air oxidation of both compounds, all studies were carried out under anaerobic conditions. Also, in contrast to $U(Cot)_2$,[1] both compounds undergo immediate hydrolysis in the presence of water.

One would expect to obtain compounds of the type M(Cot) from Yb and Eu, since these elements both have stable +2 oxidation states. This expectation is fulfilled. Analysis of the Yb compound substantiates the formulation Yb(Cot). The Yb compound is, furthermore, diamagnetic. The Eu compound has an epr spectrum visible at 77°K, which is consistent only with Eu^{2+}. The epr spectrum of the powdered compound consists of a strong resonance 4 kG wide, peak-to-peak, centered on $g = 2.00$.

The compounds appear to have strong interactions with solvents, which affect their appearance markedly. The unsolvated Yb compound is, for example, pink. It is insoluble in ammonia, but becomes orange. Removal of excess ammonia at atmospheric pressure yields a compound which is a very intense blue. Removal of ammonia under vacuum yields the original compounds. Yb(Cot) is insoluble in hydrocarbons and ethers but dissolves in more basic solvents, such as pyridine and dimethylformamide. The solutions are deep red and the solids in contact with them are nearly black. These solvents may be removed under vacuum.

Both compounds are stable to 500° under vacuum. Neither sublimes at 500° and 10 μ.

There is no marked difference between the epr spectra of unsolvated Eu(Cot) and the compound solvated with NH_3. This means only that there has been no remarkable change in the electrical asymmetry of the environment of the Eu^{2+} in the two cases.

The compounds were prepared by the dropwise addition of cyclooctatetraene to ytterbium or europium metal dissolved in anhydrous ammonia. The reactions were carried out under a purified nitrogen atmosphere. In a typical reaction, 0.01 mole of cyclooctatetraene was added slowly to 0.01 mole of the metal, yielding an orange or light green precipitate for ytterbium or europium, respectively. After stirring for 2 hr, the remaining ammonia was removed and a bright blue or light green product recovered. Upon heating to 200° at 10^{-3} mm, a pink (Yb) or orange (Eu) product was obtained. Carbon and hydrogen analyses were slightly off, but consistent with a 1:1 complex. *Anal.* Calcd: C, 34.7; H, 2.9. Found: C, 30.5; H, 3.0. Metal analysis, carried out in the same manner as that for ytterbium cyclopentadienide,[5] gave excellent agreement for a 1:1 complex. *Anal.* Calcd for Yb(Cot): Yb, 62.4. Found: Yb, 62.1. Analysis of the pink Yb(Cot) indicated that less than 0.5% nitrogen was present. All solvents used were purified by refluxing over calcium hydride or by contact with potassium mirrors. Electron paramagnetic resonance measurements were performed on a Varian V-4502-15 X-band spectrometer, and magnetic susceptibilities were determined with a simple Gouy balance using $HgCo(NCS)_4$ as a standard.

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(1) A. Streitwieser, Jr., and U. Müller-Westerhoff, *J. Am. Chem. Soc.*, **90**, 7364 (1968).

(2) H. Breil and G. Wilke, *Angew. Chem. Intern. Ed. Engl.*, **5**, 898 (1966).

(3) A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Jap.*, **33**, 425 (1960).

(4) E. O. Fischer and H. Fischer, *J. Organometal. Chem.*, **3**, 181 (1965).

(5) J. M. Birmingham and G. Wilkinson, *J. Am. Chem. Soc.*, **78**, 42 (1956).

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Fluxional Behavior of (*Trihapto*cycloheptatrienyl)(*pentahapto*cyclopentadienyl)monocarbonyliron

Sir:

We recently reported the preparation of a substance which was assigned the structure of a 7-*monohapto*cycloheptatrieneiron complex.[1] Further examination of this substance and a comparison of its nmr spectrum

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(1) D. Ciappenelli and M. Rosenblum, *J. Am. Chem. Soc.*, **91**, 3673 (1969).