involving cyclopentadienyl rings bonded to transition metals.[25b,27] An appropriate method of handling this particular problem is to treat the rings as hindered rotors, the X-ray scattering by such groups having been given by King and Lipscomb.[28] In the determination of the structure of $(C_5H_5FeS)_4$, Schunn, Fritchie, and Prewitt felt that the Lipscomb-King hindered-rotor scattering expression would describe the thermal motion more accurately than a model based on refinement of individual ellipsoidal atoms. Their resultant average C-C bond distance of 1.43 ± 0.01 Å was in good agreement with the average C-C bond length of 1.43 Å found by Hardgrove and Templeton[29] in ruthenocene (where the molecular packing does not allow libration of the cyclopentadienyl groups) or the average value of 1.419 Å found in the recent survey of cyclopentadienyl complexes of the transition metals.[24] In the present instance, the main concern is with the interaction of the tetrahydroborate ion with the titanium atom. Since in this and other cases individual atom anisotropic refinement does give a satisfactory description of the electron density distribution of the cyclopentadienyl carbon atoms for purposes of structural determination (although a poor description of the geometry of the C_5H_5 rings), the use of the hindered-rotor model was felt to be unnecessary. It may be noted that the individual atom anisotropic refinement model used does result in the carbon atoms of the cyclopentadienyl rings being close to planar (Table II) and a relatively low value for the discrepancy index.

The disorder itself may be thought of in terms of individual molecules containing cyclopentadienyl rings which are in a staggered configuration with respect to each other across the *xy* mirror plane (Figures 1 and 2). Preservation of mirror symmetry for this plane in the lattice is then achieved by alternation of this configuration to the image obtained by a C_2 rotation about the *y* axis. In both forms the mirror symmetry of the individual cyclopentadienyl rings imposed by the crystallographic *yz* mirror plane is maintained, thus giving a $^1/_2$-$^1/_2$ distribution of carbon positions as found experimentally. The average carbon-carbon bond distances for rings 1 and 2 are 1.40 ± 0.13 and 1.37 ± 0.13 Å, respectively, compared to an expected value of 1.43 Å (*vide supra*). The average bond angle found for both rings, 108 ± 10°, is in agreement with the expected value for a planar (Table II) five-membered ring.

Registry No. $(h^5\text{-}C_5H_5)_2Ti(BH_4)$, 12772-20-2.

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Electron-Transfer Reactions of Cobalt(III) and Ruthenium(III) Ammines with Europium(II), Ytterbium(II), and Samarium(II) in Aqueous Solutions

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Kinetic measurements, using the pulse radiolysis technique, have been made on the reaction of Sm(II), Yb(II), and Eu(II) with pentaammine complexes of Co(III) and Ru(III). It has been found that the order of reactivity is Sm(II) > Yb(II) > Eu(II). This order is correlated with the electrode potential $E°$ of the divalent ions. The resulting reactivity patterns are examined with the view of providing a possible kinetic basis for distinguishing between inner- and outer-sphere electron-transfer mechanisms. The reactions of the three divalent lanthanide ions with the hexaammine- and the ethylenediaminecobalt(III) complexes were too slow to be followed by this technique. With the exception of a possible significant contribution of an outer-sphere mechanism to the reduction of the cobalt(III) aquo complex with Sm(II), the reactions of the three Ln(II) ions with the other cobalt pentaammine complexes take place predominantly by an inner-sphere mechanism. Reactivities of corresponding Ru(III) and Co(III) complexes are compared. The electron-exchange rate constants for the Ln(II)-Ln(III) couples were calculated using Marcus' theory of electron-transfer reactions.

Introduction

Previous studies[1] led to the conclusion that the reduction of the cobalt(III) ammine complexes of the type $Co(NH_3)_5X^{3-n}$ (where X^{n-} is one of the ligands NH_3, H_2O, OH^-, F^-, Cl^-, Br^-, I^-, CN^-, NCS^-, N_3^-, etc.) proceeds either by outer-sphere (OS) or inner-sphere (IS) mechanisms.[1] The X^{n-} acts as an inner-sphere bridge for the electron transfer in the latter case.

Several factors, based on kinetic evidence, have been suggested to differentiate between inner-sphere and outer-sphere reducing agents.[2-7] The specific rate of reaction of a series

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Table I. Absorption Spectra of Co(III) Complexes ($R = Co(NH_3)_5$)

Compd as perchlorate	λ, nm (ε, M^{-1} cm^{-1}) Max	Min	Max	Min
RF^{2+}	510 (34)	406 (5)	355 (26)	315 (10)
RCl^{2+}	530 (41)	415 (4.5)	362 (32)	325 (10)
RBr^{2+}	552 (53)	430 (12)		
RI^{2+}	580 (37)	525 (30)	382 (3000)	337 (1200)
$RN_3{}^{2+}$	516 (230)	440 (0)	302 (8100)	245 (300)
$RCNS^{2+}$	495 (182)	420 (45)	304 (1580)	246 (340)
ROH^{2+}	505 (72)	425 (12)	370 (62)	305 (11)
RH_2O^{3+}	492 (8)	405 (8)	345 (45)	285 (6)
$RNH_3{}^{3+}$	475 (55)	390 (10)	340 (45)	285 (9)
$[Co(en)_3]^{3+}$	466 (81)	387 (4)	338 (71)	287 (4.5)
RCN^{2+}	441 (60)	375 (16)	328 (61)	285 (18)

Table II. Absorption Spectra of Ru(III) Complexes ($Ru = Ru(NH_3)_5$)

Compd as perchlorate	λ, nm (ε, M^{-1} cm^{-1}) Max	Min	Compd as perchlorate	λ, nm (ε, M^{-1} cm^{-1}) Max	Min
$RuCl^{2+}$	327 (1810)	250 (110)	$RuOH^{2+}$	298 (1980)	245 (300)
$RuBr^{2+}$	395 (1340)	275 (140)	RuH_2O^{3+}	268 (635)[a]	240 (425)
RuI^{2+}	545 (1960)	420 (100)	$RuNH_3{}^{3+}$	273 (580)	234 (210)

[a] pH 2.

Table III. Spectral Data for Ln(II)

Ln(II)	λ, nm	ε, M^{-1} cm^{-1}
Eu	350	300
Yb	350	500
Sm	565	300

of Co(III) complexes with different reducing cations has been investigated, mainly by the stopped-flow technique.[2-4,7-14] The specific rate of Zn(I), Cd(I), and Ni(I) reactions with a series of Co(III) complexes was measured[15] using the pulse radiolysis technique. The same technique was used to show that divalent ytterbium and samarium ions, formed by reduction of the corresponding trivalent ions by the hydrated electrons, are powerful reducing agents.[16] Oxidation reactions of these ions have been measured.[16]

The rate constants for some Co(III) complexes reacting with Yb(II), prepared by electrolytic reduction of the corresponding trivalent ion, were recently reported.[13] It was, however, established[16] that the half-life of Yb(II) is at most 1 sec. Therefore, it seems that the study of these reactions by means of the stopped-flow technique, used by these authors,[13] is rather difficult. It could be, however, that in the pulse radiolysis studies the decay of Yb(II) was enhanced by the presence of H_2O_2 produced during the radiolysis and by traces of oxygen. Taube, *et al.*,[17-19] showed the importance of comparing the electron-transfer reactions of ruthenium(III) and cobalt(III) complexes with reducing agents such as Cr(II), V(II), and Eu(II). The ruthenium(III) and cobalt(III) ammines are similar in many of their properties (octahedral configuration, redox potential) but different in the respect that in the reduction of the Co(III) the electron enters an e_g orbital, whereas in Ru(III) it enters a t_{2g} orbital and the Ru(II) formed has a low-spin configuration and no electrons in the e_g orbitals. It has been of interest, therefore, to measure the rate constants of Yb(II) and Sm(II) with a series of Co(III) and Ru(III) complexes in order to obtain a better understanding of the reduction properties of these cations and to compare their behavior to that of Eu(II) whose rate constants with these complexes are partially known.[3,19]

Experimental Section

Materials. The water was triply distilled. The chemicals were $Eu(ClO_4)_3$, $Yb(ClO_4)_3$, and $Sm(ClO_4)_3$ ($=Ln(ClO_4)_3$) of 99.9% purity, obtained from Alfa Inorganics Inc. *tert*-Butyl alcohol was "Merck Pro Analysis." All other materials were of analytical grade. All the Co(III) (as perchlorate) complexes, used as oxidants, were prepared using previously reported procedures.[3] The Ru(III) complexes were prepared from $Ru(NH_3)_6Cl_3$ (Johnson Matthey Chemicals Ltd.) using previously reported procedures.[19] Both Co(III) and Ru(III) complexes were purified by recrystallization. The identification and purity of the products were confirmed analytically and spectrophotometrically. The spectra of all complexes (Tables I and II) are in good agreement with previously reported data.[12,19-22] Light-sensitive iodo, azido, cyano, and thiocyanato complexes were prepared and studied in blackened vessels.

Kinetic Measurements. The rate constants of the reactions of Ln(II) with the Co(III) and Ru(III) complexes were determined in solutions usually containing 1×10^{-2} *M* $Ln(ClO_4)_3$, 1×10^{-2} *M tert*-butyl alcohol, and one of the complexes. The Co(III) concentration is in the range 2×10^{-4}–2×10^{-3} *M*; that of Ru(III) is in the range 1×10^{-4}–5×10^{-4} *M* ($\mu = 0.06$–0.07).

The reactions involving $[Co(NH_3)_5H_2O]^{3+}$ and $[Co(NH_3)_5OH]^{2+}$ as oxidants were carried out in solutions containing 5×10^{-2} *M* $Ln(ClO_4)_3$, 1×10^{-2} *M tert*-butyl alcohol, and 1×10^{-3}–2×10^{-3} *M* Co(III) complexes ($\mu = 0.3$). Because of the sensitivity of the reductants to oxygen,[16] solutions were deaerated by continuous bubbling with ultrapure argon gas (Matheson 99.99%) in hypodermic syringes for at least 15 min. This procedure leaves a residual concentration of oxygen of the order of 10^{-7} *M*. All solutions were prepared just before irradiation in order to minimize hydrolysis of the complexes.

For the pulse radiolytic experiments the conditions were 1.0 μsec, 5 MeV, and a 200-mA electron pulse from a linear accelerator, yielding approximately 5×10^{-6} *M* Ln(II). The decays of Eu(II), Yb(II), and Sm(II) were followed spectrophotometrically at the wavelengths given in Table III. The decay process was followed with a multiple-reflection silica cell (1 × 2 × 4 cm) with a light path of 12.5 cm (three passes). A 150-W xenon lamp was used as the analyzing light source, and a Bausch and Lomb high-intensity monochromator, followed by a IP 28A photomultiplier and a Type 556 Tektronix double-beam oscilloscope, fitted with a Polaroid camera, was used for recording the absorption changes in the solutions. To minimize photochemical decomposition of the solute, which could be induced by the analyzing light, filters were introduced between the xenon lamp and the irradiated cell. Jena glass filters, Types WG5 and OG1, were used when the absorption was followed at 350 and 565 nm, respectively. Furthermore, a shutter was also placed between the lamp and the cell and operated mechanically by air pressure. It was kept closed until shortly before the pulse, so that the solutions were kept in the dark.

A digitizer (analog to digital converter) served for reading the polaroid pictures and for transferring the data to punched cards, which were then used in a computer program for the analysis of kinetics. All traces were analyzed for first- and second-order decay. Pseudo-first-order rate constants were calculated when a good first-order decay plot was obtained (linear correlation >99%) for at least 3 half-lives. At least ten traces were analyzed for every rate constant. The traces were obtained by pulse radiolyzing ten sample solutions prepared using at least three different stock solutions diluted to three different concentrations of the oxidants. The initial oxidant concentration generally varied over at least a threefold range and first-order dependence on its concentration was confirmed.

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Results

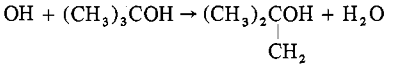
When fast electrons are absorbed in water, the effect may be described by the overall reaction

$$H_2O \rightarrow e_{aq}^-, H, OH, H_2, H_2O_2, H_3O^+ \quad (1)$$

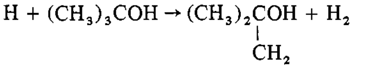
and the ensuing chemistry occurring in an aqueous solution can be accounted for in terms of the reactions of these initial entities. The yields of the products are $G_{e_{aq}^-} = 2.6$, $G_H = 0.55$, $G_{OH} = 2.6$, $G_{H_2} = 0.45$, and $G_{H_2O_2} = 0.75$.

In neutral solutions containing Ln(III) and *tert*-butyl alcohol, the following reactions are expected

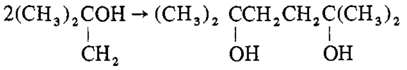
$$e_{aq}^- + Ln(III) \rightarrow Ln(II) \quad (2)$$



$$OH + (CH_3)_3COH \rightarrow (CH_3)_2\underset{CH_2}{\underset{|}{C}}OH + H_2O \quad (3)$$



$$H + (CH_3)_3COH \rightarrow (CH_3)_2\underset{CH_2}{\underset{|}{C}}OH + H_2 \quad (4)$$



$$2(CH_3)_2\underset{CH_2}{\underset{|}{C}}OH \rightarrow (CH_3)_2\,\underset{OH}{\underset{|}{C}}CH_2CH_2\underset{OH}{\underset{|}{C}}(CH_3)_2 \quad (5)$$

$$Ln(II) + H_2O_2 \rightarrow Ln(III) + OH + OH^- \quad (6)$$

$$Ln(II) + H_2O \rightarrow Ln(III) + H + OH^- \quad (7)$$

The first-order decay of Yb(II) and Sm(II) in neutral solutions and in the presence of alcohol is relatively slow[16] ($t_{1/2}$ = 100 and 0.5 msec for Yb(II) and Sm(II), respectively). It is possible to shorten the half-lives to less than 25% of these $t_{1/2}$ values by addition of different oxidants, thus enabling the determination of the specific rate constants of Ln(II) with these oxidants. When a complex (Co(III) for example) is added to the solution, further reactions are expected

$$e_{aq}^- + Co(III) \rightarrow Co(II) \quad (8)$$

$$H + Co(III) \rightarrow Co(II) + H^+ \quad (9)$$

$$Ln(II) + Co(III) \rightarrow Ln(III) + Co(II) \quad (10)$$

Reaction 10 can be studied by following the disappearance of Ln(II) when the added concentration of the complex is low enough to avoid a significant contribution of reaction 8 as compared to reaction 2 (<10%). Additional correction must be made for the decomposition of the complex *via* reaction 9. However, the low yield of H atoms ($G_H = 0.55$) only necessitates a small correction which is within the experimental error.

This assumption was checked by following the changes in the transmittance of an irradiated N_2O-saturated solution containing the complex and *tert*-butyl alcohol without the presence of the La ions. In these solutions all the e_{aq}^- are converted into OH radicals *via* $N_2O + e_{aq}^- \rightarrow N_2 + OH + OH^-$. These OH radicals react *via* reaction 3 and the only possible reaction of the Co(III) complex is *via* reaction 9.

As the changes in the transmittance at the wavelengths studied were observed during and after the pulse, it is concluded that in the determination of the rate constant of reaction 10, reaction 9 contributes very little.

(a) Reactions with Co(III) Complexes. Table IV summarizes the values of the measured second-order rate constants k_{10} defined by

$$-\frac{d[Ln(II)]}{dt} = k_{10}[Ln(II)][Co(III)]$$

where [Co(III)] is the initial concentration of the cobalt(III) complex and [Ln(II)] is the concentration of the reduced lanthanide formed *via* reaction 2. The chosen concentration conditions ensured that the Co(III) complex was always in considerable excess over the Ln(II) (>40-fold), which was sufficient for pseudo-first-order behavior.

The experimental error in most of the rate constants given is within ±10% or better. In a few of these values, approaching the self-decay rate constant of the Ln(II) ion, the error reached ±20%. In some experiments the rate of decay of the Ln(II) was not accelerated by the addition of the complex (maximum amount possible). In these cases only upper limits of the rate constants are given (Table IV).

The rate constants for the reaction of the Ln(II) ions with the hydroxo and aquo complexes were determined from the dependence of the rate of the Ln(II) decay on the hydrogen ion concentration. The aquo complex hydrolyzes according to

$$RH_2O^{3+} \rightleftharpoons ROH^{2+} + H^+ \quad pK_a = 5.7^{23} \quad (11)$$

where R = $Co(NH_3)_5$.

Thus the oxidation of the Ln(II) with this complex will proceed *via* reactions 12 and 13.

$$Ln(II) + RH_2O^{3+} \rightarrow Ln(III) + Co(II) + 5NH_3 \quad (12)$$

$$Ln(II) + ROH^{2+} \rightarrow Ln(III) + Co(II) + 5NH + OH^- \quad (13)$$

and the contribution of each of these oxidants to the overall rate of decay of Ln(II) will depend on the pH of the solution. Table V represents values obtained for the slope of the first-order decay plot of Sm(II). Those for Yb(II) are shown in Table VI. The rate constants for reactions 12 and 13 were calculated (Table IV) from these values and from the pK_a of reaction 11. The same experiments were carried out in the presence of 1 *M* $NaClO_4$ and 1 *M* NaCl ($\mu = 1$) (Table III). For completeness and comparison Table IV also includes the second-order rate constants of reaction 8 as well as data previously reported in the literature for Eu(II), Yb(II), Cr(II), and $Cr(bipy)_3^{2+}$. Where our measurements overlap earlier ones, good agreement in the rate constants was generally observed.

(b) Reaction with Ru(III) Complexes. Table VII presents second-order rate constants obtained for the reduction of Ru(III) complexes by Ln(II) ions and e_{aq}^-. For comparison, the rate constants for the reduction of these oxidants by Cr(II) and V(II) are also included. Due to photochemical effects occurring during the reaction, the values given for RuI^{2+} (Ru = $Ru(NH_3)_5$) are order of magnitude only. The values for $RuOH^{2+}$ are at pH 6 where the aquo complex is converted to the hydroxo complex ($K_a = 10^{-4.2}$).[23] The values for RuH_2O^{3+} are at pH 2.

It is evident from Table VII that the specific rates of reactions of all reducing agents studied are higher than those obtained with the corresponding cobalt(III) ammines. This difference is attributed to their different electronic configuration.

Discussion

As mentioned above, several kinetic criteria have been suggested to differentiate between inner- and outer-sphere (IS and OS, respectively) mechanisms. It will be assumed, as accepted in the literature, that the reactions of the two hexaammine complexes and $Co(en)_3^{3+}$ with reductants proceed *via* an OS mechanism[1] and that the reactions of other cobalt(III) pentaammine complexes with Cr(II) are IS, whereas the reactions with $Cr(bipy)_3^{2+}$ are OS.[1]

Tables IV and VII show that the behavior of the three lanthanides studied followed the same trend. They also show the order of reactivity of these ions with the Co(III) complexes (Sm(II) > Yb(II) > Eu(II)) is in agreement with their redox potentials.

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Table IV. Second-Order Rate Constants (M^{-1} sec^{-1}) for the Reduction of Co(III) Complexes at 25°

Oxidant $[\mathrm{Co(NH_3)_5} = \mathrm{R}]$	Sm(II)	Yb(II)	Eu(II)	Cr(II)	$\mathrm{Cr(bipy)_3}^{2+}$	$\mathrm{e_{aq}}^{-}$ [a]
RF^{2+}	2.5×10^{7} [b]					
RF^{2+}	2.5×10^{7} [b]	1.1×10^{7} [b]	2.8×10^{3} [b]	2.5×10^{5} [c]	1.8×10^{2} [d]	6.6×10^{10}
	1.1×10^{8} [e]	6.0×10^{7} [e]	1.5×10^{4} [e]	9.0 ± 10^{5} [f]		
	1.8×10^{8} [g]	1.0×10^{8} [g]	2.4×10^{4} [g]			
			2.6×10^{4} [h]			
RCl^{2+}	3.8×10^{7} [b]	4.3×10^{6} [b]	90.0 [b]	6.0×10^{5} [c]	8.0×10^{5} [d]	7.8×10^{10}
	1.7×10^{8} [e]	1.9×10^{7} [e]	4.7×10^{2} [e]	2.6×10^{6} [f]		
	2.3×10^{8} [g]	2.3×10^{7} [g]	5.3×10^{2} [g]			
			3.9×10^{2} [h]			
RBr^{2+}	3.5×10^{7} [b]	3.0×10^{6} [b]	2.5×10^{2} [h]	1.4×10^{6} [c]	5.0×10^{6} [d]	8.0×10^{10}
	1.6×10^{8} [e]	1.4×10^{7} [e]				
	2.5×10^{8} [g]	2.5×10^{7} [g]				
RI^{2+}	5.8×10^{7} [b]		1.2×10^{2} [h]	3.0×10^{6} [c]		
$\mathrm{RN_3}^{2+}$	7.8×10^{7} [b]	1.6×10^{7} [b]	≤ 30 [b]	$\sim 3 \times 10^{5}$ [h]	4.1×10^{4} [d]	7.2×10^{10}
	2.5×10^{8} [i]	2.6×10^{7} [i]	1.9×10^{2} [h]			
RNCS^{2+}	$\leq 1.0 \times 10^{6}$ [b]	$\leq 5.0 \times 10^{4}$ [i]	<10 [b]	19 [h]	1.0×10^{4} [h]	7.3×10^{10}
	$\leq 1.0 \times 10^{6}$ [i]	$\leq 5.0 \times 10^{4}$ [i]	~ 0.7 [h]			
RCN^{2+}	$<3.0 \times 10^{6}$ [b]	3.0×10^{5} [b]	<30 [b]			7.4×10^{10}
ROH^{2+}	1.5×10^{7} [j]	7.7×10^{6} [j]	~ 100 [j]	1.7×10^{6} [k]	3.5×10^{4} [k]	6.0×10^{10}
	5.0×10^{7} [l]	1.9×10^{7} [l]				
	5.0×10^{7} [m]	2.9×10^{7} [m]				
$\mathrm{RH_2O}^{3+}$	6.0×10^{6} [j]	2.2×10^{5} [j]	0.15 [n]	0.5 [k]	6.2×10^{4} [k]	8.0×10^{10}
	8.8×10^{6} [l]	6.4×10^{5} [l]	7.4×10^{-2} [q]			
	2.6×10^{7} [m]	3.2×10^{4} [o]				
$\mathrm{RNH_3}^{3+}$	$<1.0 \times 10^{6}$ [b]	$<5.0 \times 10^{3}$ [b]	2.0×10^{-2} [d]	8.9×10^{-5} [k]	6.9×10^{2} [k]	8.5×10^{10}
	5.0×10^{6} [g]	2.3×10^{3} [o]	1.7×10^{-3} [q]			
$[\mathrm{Co(en)_3}]^{3+}$	$<1 \times 10^{6}$ [b,e,g]	$<5.0 \times 10^{3}$ [b,e,g]	$\sim 5 \times 10^{-3}$ [h]	$\sim 2 \times 10^{-5}$ [p]	1.8×10^{2} [d]	8.5×10^{10}
		4.5×10^{2} [o]				

[a] M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotop.*, 18, 493 (1967). [b] $\mu = 0.06$, pH 6, this work. [c] $\mu = 0.1$ (0.1 M $\mathrm{HClO_4}$), ref 8. [d] $\mu = 0.1$, ref 3. [e] $\mu = 1.0$ (1 M $\mathrm{NaClO_4}$), pH 6, this work. [f] $\mu = 1.0$ (0.1 M $\mathrm{HClO_4}$ + 0.9 M $\mathrm{NaClO_4}$), ref 8. [g] $\mu = 1.0$ (1 M NaCl), pH 6, this work. [h] $\mu = 1.0$ (1 M $\mathrm{NaClO_4}$), ref 3. [i] $\mu = 0.5$ (0.5 M $\mathrm{NaClO_4}$), pH 6, this work. [j] $\mu = 0.3$ $[\mathrm{Ln(III)}] = 5 \times 10^{-2}$ M, this work. [k] $\mu = 0.4$, ref 2. [l] $\mu = 1.0$ (1 M $\mathrm{NaClO_4}$), this work. [m] $\mu = 1.0$ (1 M NaCl), this work. [n] A. Zwickel, Ph.D. Dissertation, Chicago University, 1959; cited in ref 3. [o] $\mu = 0.2$, $[\mathrm{H^+}] = 0.005$–0.20 M; ref 13. [p] $\mu = 0.4$, ref 3. [q] $\mu = 0.4$, ref 10.

Table V. First-Order Slope of the Decay Plots of Sm(II) in the Presence of 2×10^{-3} M $\mathrm{RH_2O}^{3+}$ at Different pH Values

	pH				
	6	5.4	3.8	2.5	1.9
Slope, sec^{-1}	2.4×10^{4}	1.8×10^{4}	9.3×10^{3}	8.3×10^{3}	8.3×10^{3}

Table VI. First-Order Slope of the Decay Plots of Yb(II) in the Presence of 2×10^{-3} M $\mathrm{RH_2O}^{3+}$ at Different pH Values

	pH			
	5.5	4.2	3.5	2.0
Slope, sec^{-1}	6.2×10^{3}	8.7×10^{2}	5.5×10^{2}	4.4×10^{2}

(a) **Reactions with Co(III) Complexes.** The relative reaction rate constants of the azido and the thiocyanato complexes is one of the criteria suggested to distinguish between these two mechanisms. Espenson[7] suggested that an IS mechanism should show a great preference for the symmetrical $\mathrm{N_3}^{-}$ over NCS^{-} as found for Cr(II) ($k_{\mathrm{RN_3}^{2+}}/k_{\mathrm{RNCS}^{2+}} = 1 \times 10^{4}$).

For the $\mathrm{Cr(bipy)_3}^{2+}$ ion, reacting *via* an OS mechanism, this ratio is 4. The data presented in Table IV show the higher reactivity of the azido complex (as compared to thiocyanato) toward the three Ln(II) ions studied ($k_{\mathrm{RN_3}^{2+}}/k_{\mathrm{RNCS}^{2+}}$ ratios are >250, >500, and ∼270 for Sm(II), Yb(II), and Eu(II), re-

Table VII. Second-Order Rate Constants (M^{-1} sec^{-1}) for the Reduction of Ru(III) Complexes at 25°

Oxidant $[\mathrm{Ru(NH_3)_5} = \mathrm{Ru}]$	Sm(II)	Yb(II)	Eu(II)	Cr(II)	V(II)	$\mathrm{e_{aq}}^{-}$
RuCl^{2+}	1.5×10^{8} [a]	1.5×10^{7} [a]	1.5×10^{4} [a]	3.5×10^{4} [b]	3.0×10^{3} [b]	6.0×10^{10} [c]
	4.3×10^{8} [d]	1.8×10^{8} [d]	2.4×10^{4} [b]			
	6.5×10^{8} [e]	2.8×10^{8} [e]				
RuBr^{2+}	1.5×10^{8} [a]	3.3×10^{7} [a]	$\sim 3 \times 10^{3}$ [a]	2.2×10^{3} [b]	5.1×10^{3} [b]	5.0×10^{10} [c]
			1.3×10^{4} [b]			
RuI^{2+}	$\sim 10^{8}$ [a]	$\sim 10^{8}$ [a]		2.6×10^{2} [b]		$\sim 6 \times 10^{10}$ [c]
RuOH^{2+}	4.0×10^{7} [a]	1.3×10^{7} [a]	6.0×10^{4} [a]			5.9×10^{10} [c]
	8.5×10^{7} [b]	2.3×10^{7} [f]	1.0×10^{5} [f]			
	2.2×10^{8} [d]	5.0×10^{7} [d]				
	6.0×10^{8} [e]	1.4×10^{8} [e]				
$\mathrm{RuH_2O}^{3+}$	6.5×10^{7} [g]	1.0×10^{7} [g]	$\leq 2 \times 10^{3}$ [g]			
	1.8×10^{8} [h]	2.9×10^{7} [h]				
	1.3×10^{9} [i]	3.2×10^{8} [i]				
$\mathrm{RuNH_3}^{3+}$	2.5×10^{7} [a]	5.0×10^{6} [a]	$\sim 1 \times 10^{3}$ [a]	2×10^{2} [j]	80 [j]	6.8×10^{10} [k]
	2.0×10^{8} [d]	4.5×10^{7} [d]	2.3×10^{3} [d]			
	8.0×10^{8} [e]	3.0×10^{8} [e]	1.5×10^{4} [e]			

[a] $\mu = 0.06$, pH 6, this work. [b] J. A. Stritar and H. Taube, *Inorg. Chem.*, 8, 2281 (1969). [c] $[(\mathrm{RX}^{n-})^{3-n}] = 1.0 \times 10^{-5}$ M, this work. [d] $\mu = 1.0$ (1 M $\mathrm{NaClO_4}$), pH 6, this work. [e] $\mu = 1.0$ (1 M NaCl), pH 6, this work. [f] $\mu = 0.3$, pH 6, $[\mathrm{Ln(III)}] = 5 \times 10^{-2}$ M, this work. [g] $\mu = 0.3$, pH 2 $[\mathrm{Ln(III)}] = 5 \times 10^{-2}$ M, this work. [h] $\mu = 1.0$ (1 M $\mathrm{NaClO_4}$), pH 2, this work. [i] $\mu = 1.0$ (1 M NaCl), pH 2, this work. [j] J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1686 (1964). [k] J. H. Baxendale, M. A. J. Rodgers, and M. D. Ward, *J. Chem. Soc. A*, 1246 (1970).

spectively). This suggests that Ln(II) ions react *via* an IS mechanism.

The high reactivity of the hydroxo as compared to that of the aquo complex has been cited as an indication for an IS mechanism.[12] For this mechanism high values for the $k_{\mathrm{ROH}^{2+}}/k_{\mathrm{RH_2O}^{3+}}$ ratio have been obtained (for example, in Cr(II), this ratio is 3 × 10^6). Much lower ratios have been found for OS mechanisms, where the aquo is more reactive than the hydroxo complex (0.6 and 0.01 for $\mathrm{Cr(bipy)_2}^{3+}$ and $\mathrm{Ru(NH_3)_6}^{2+}$, respectively). The values for $k_{\mathrm{ROH}^{2+}}/k_{\mathrm{RH_2O}^{3+}}$ are 2-7, 35, and ∿600 for Sm(II), Yb(II), and Eu(II), respectively.

These values are lower than those for Cr(II). However, the higher reactivity (at least for Yb(II) and Eu(II)) of the hydroxo complex suggests that these ions react *via* an IS mechanism.

The value for Sm(II), one order of magnitude lower than that of the Yb(II), may be an indication of some contribution of an OS mechanism in at least one of the two reactions.

This problem can be solved by the chloride ion effect on these Sm(II) rate constants. It has been shown that reactions proceeding *via* an OS mechanism are accelerated by the addition of this ion, whereas minor effects are observed for the IS.[2,14,24] No such effect could be observed on the rate constant of the hydroxo complex. It is therefore suggested that this reaction proceeds *via* an IS mechanism. The aquo complex is influenced by the presence of the Cl^- ion indicating a contribution of an OS mechanism.

The reactions of Ln(II) with the halopentaammine complexes showed that their rate constants vary monotonically as the halide is changed from fluoride to iodide. The "normal" reactivity order (F < Cl < Br < I) was found in Sm(II) and the "inverse" order in Yb(II) and Eu(II). Haim[11] noted that the reactivity order is not a useful indirect criterion for distinguishing between IS and OS mechanisms. Thus, with these rate constants only, no conclusion on the reaction mechanism could be suggested. However, similar to the reaction with the hydroxo complex, no Cl^- ion concentration effect could be observed. This behavior indicates that the reactions proceed *via* an IS mechanism.

The use of the Ln(II) ions as reducing agents is another example where the reaction products are ligand labile. This fact makes the differentiation between the IS and OS mechanisms by a direct analysis rather difficult. It seems, therefore, that although kinetic evidence has been advanced for the IS mechanism in practically all the redox reactions studied (except $\mathrm{RNH_3}^{3+}$ and $\mathrm{Co(en)_3}^{3+}$), this conclusion is not as safe as that suggested for the classical IS mechanism found in Cr(II).

(b) Reactions with Ru(III) Complexes. The lack of data for the fluoro complex and the uncertainty of the values given for the iodo complex make the interpretation by the sequence of reactivity of the halopentaammine complexes criterion[3] rather difficult. Nevertheless, the mechanism involved in the reactions of the Ln(II) ions with these complexes can be distinguished by the chloride ion catalytic effect.[2] As no such effect on the rate constants of the halopentaammines could be observed it is suggested that the reaction of Ln(II) ions with these complexes proceeds *via* an inner-sphere mechanism.

As mentioned above, the relative reaction rate constants of the hydroxo and the aquo complexes of Co(III) were cited as being an indication for the differentiation.[12] Assuming that the above Ru(III) complexes follow the same behavior, then one has another criterion. The ratio $k_{\mathrm{RuOH}^{2+}}/k_{\mathrm{RuH_2O}^{3+}}$, at the same ionic strength (μ = 1.0), was found to be 1.2, 1.7, and >50 for Sm(II), Yb(II), and Eu(II), respectively.

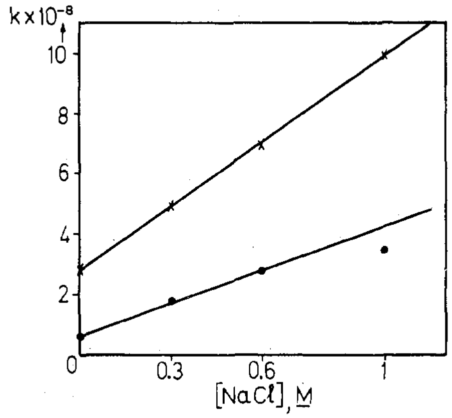

Figure 1. Variation of the rate constants for the reactions of $\mathrm{Ru(NH_3)_6}^{3+}$ with Sm(II) and Yb(II), with Cl^- concentration at constant ionic strength (μ = 1): ×, Sm(II); •, Yb(II).

The high value for Eu(II), similar to that for the corresponding Co(III) complexes, suggests that the Eu(II) ion reacts with these Ru(III) complexes *via* an inner-sphere mechanism. No mechanism for the reactions of Yb(II) and Sm(II) could be suggested at this stage due to their relatively low values of the ratio $k_{\mathrm{RuOH}^{2+}}/k_{\mathrm{RuH_2O}^{3+}}$. However, as shown in Table VII, the reactions of the hydroxo- and the aquoruthenium(III) complexes with Sm(II) and Yb(II) have a Cl^- catalytic effect (similar to that of the $\mathrm{RuNH_3}^{3+}$). It is therefore suggested that both Yb(II) and Sm(II) react with these complexes *via* an outer-sphere mechanism. As the catalytic effect is more pronounced in the reaction of the aquo complex, the reaction with the hydroxo complex might have a contribution of an inner-sphere mechanism.

Sm(II), Yb(II), and Eu(II) react *via* an outer-sphere mechanism with $\mathrm{RuNH_3}^{3+}$. This is supported by the effect of the Cl^- ions on the rate constants as shown in Table VII and Figure 1.

(c) Correlation with the Marcus Theory. Marcus[25] proposed a relation among the rate of the redox reaction proceeding *via* an outer-sphere mechanism, the rates of electron exchange for the component couples, and the driving force of the reaction. According to Endicott and Taube,[4] the work terms for the reaction between ammine and aquo complexes are small and Marcus' relation will be given by

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{I}$$

where

$$\ln f = (\ln K_{12})^2/[4 \ln (k_{11}k_{22}/Z^2)]$$

and k_{12} is the observed rate constant of the redox reaction, k_{11} and k_{22} are the electron-exchange rate constants for the component couples, K is the equilibrium constant for the redox reaction, and Z the collision frequency for the uncharged species taken to be 10^{11} M^{-1} sec^{-1}. The specific rates of the electron-exchange reaction (k_{22}) of the Ln(II)-Ln(III) couples could be evaluated from Marcus' equation. However, for rate constants (k_{obsd}) approaching the diffusion-controlled limit (k_{diff}) the eq II must also be taken into consideration.[26]

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Table VIII. Electron Exchange Rate Constants for Sm(II), Yb(II), and Eu(II)

Reaction	k_{obsd},[a] M^{-1} sec^{-1}	$k = k_{\mathrm{act}}$,[a] M^{-1} sec^{-1}	k_{11},[b] M^{-1} sec^{-1}	K_{12}	k_{22}(calcd), M^{-1} sec^{-1}
$Ru(NH_3)_6^{3+}$ + Sm(II)	3.5×10^6	3.6×10^6	8.2×10^2	9.2×10^{27}	5×10^{-12}
$Ru(NH_3)_6^{3+}$ + Yb(II)	5.7×10^5	5.6×10^5	8.2×10^2	1.5×10^{21}	3×10^{-9}
$Ru(NH_3)_6^{3+}$ + Eu(II)	1.1×10^2	1.1×10^2	8.2×10^2	9.6×10^8	1×10^{-7}

[a] At $\mu \rightarrow 0$. [b] T. J. Meyer and H. Taube, *Inorg. Chem.*, 7, 2369 (1968).

$$\frac{1}{k_{\mathrm{obsd}}} = \frac{1}{k_{\mathrm{act}}} = \frac{1}{k_{\mathrm{diff}}} \qquad \text{(II)}$$

The activation-controlled rate constant (k_{act}) is the one calculated by eq I. The diffusion-controlled rate constant (k_{diff}) was calculated using the Debye equation.[27]

The value obtained is 1.1×10^8 M^{-1} sec^{-1}. As this calculated value is given for zero ionic strength, the observed values k_{obsd} for $RuNH_3^{3+}$ were corrected accordingly using Davies' equation[28] (Table VIII); thus, only k_{act} for Sm(II) was corrected by eq II (Table VIII). The calculated values of k_{22} (Table VIII) show that the rate of electron transfer between the lanthanide ions is very slow and reflect the fact that the exchanging electron of these ions is in an f orbital. The k_{22} value for the Eu(II)-Eu(III) couple is in good agreement with that of Meier and Garner.[29]

Knowing the k_{22} value, it is possible to calculate the specific rate constants of the Ln(II) ions studied with the $Co(NH_3)_6^{3+}$ complexes. Assuming a value of 1×10^{-9} M^{-1} sec^{-1} for the exchange reaction of the $Co(NH_3)_6^{3+}$-$Co(NH_3)_6^{2+}$ couple,[4] the values obtained are 33, 3, and 2×10^{-4} M^{-1} sec^{-1} for Sm(II), Yb(II), and Eu(II), respectively. The result obtained for Eu(II) is in agreement with the accepted value.[9] These low values corroborate the fact that in the pulse radiolytic measurements these reactions could not be followed.

Registry No. Table I RF^{2+}, 36126-23-5; RCl^{2+}, 15156-18-0; RBr^{2+}, 14591-65-2; RI^{2+}, 14972-83-9; RN_3^{2+}, 14283-04-6; $RCNS^{2+}$, 15663-42-0; ROH^{2+}, 18885-27-3; RH_2O^{3+}, 13820-81-0; RNH_3^{3+}, 13820-83-2; $[Co(en)_3]^{3+}$, 14977-29-8; RCN^{2+}, 14216-98-9. Table II $RuCl^{2+}$, 36273-18-4; $RuBr^{2+}$, 36273-19-5; RuI^{2+}, 36273-20-8; $RuOH^{2+}$, 36388-18-8; RuH_2O^{3+}, 36273-21-9; $RuNH_3^{3+}$, 36273-22-0. Eu, 7440-52-0; Yb, 7440-64-4; Sm, 7440-19-9.

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Notes

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Preparation of Dimethylaminodimethylphosphine and Cleavage to Dimethylcyanophosphine by Hydrogen Cyanide[1]

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The compound $(CH_3)_2PCN$ has been prepared recently by the action of AgCN on $(CH_3)_2PCl$ in acetonitrile.[2] The success of the reactions of HX (where X is Cl, Br, or I) with $(CH_3)_2NP(CH_3)_2$ to produce the corresponding alkylhalophosphines[3,4] suggested the analogous cleavage by HCN

$$(CH_3)_2NP(CH_3)_2 + 2HCN \rightarrow (CH_3)_2PCN + (CH_3)_2NH_2CN$$

Present work utilizing ^1H nmr data and vacuum-line manipulation shows that this reaction proceeds as written providing good yields of the cyanophosphine. Dialkylaminophosphines can be obtained by the alkylation of dialkylaminochlorophosphines with Grignard reagents,[3,5] alkylaluminum compounds,[6] or organolithium reagents;[7,8] however, the only reported synthesis of $(CH_3)_2NP(CH_3)_2$ employed CH_3MgBr and $(CH_3)_2NPCl_2$.[3] We have found this procedure to be optimum after studying the reactions of the methylating agents CH_3MgX (where X is Cl, Br, or I) and CH_3Li with either $(CH_3)_2NPCl_2$ or $(CH_3)_2NPBr_2$.

Experimental Section

General Information. All reactions were conducted under either high-vacuum conditions or a dry nitrogen atmosphere using anhydrous, freshly purified materials. Infrared spectra were recorded using a Beckman Model 257 spectrophotometer operating from 4000 to 625 cm^{-1}. Proton magnetic resonance data were obtained with a Varian Associates T-60 nmr spectrometer at 37° using tetramethylsilane dissolved in the sample for reference.

Materials. Diethyl ether solutions of CH_3MgBr and CH_3Li and a tetrahydrofuran solution of CH_3MgCl were supplied by Alfa Inorganics, while CH_3MgI was prepared by standard methods. Hydrogen cyanide prepared from KCN and H_2SO_4 was purified by vacuum fractionation using −63, −78, −83, and −196° cold traps. Pure HCN was retained at −83° as indicated by infrared, vapor pressure, and molecular weight data.

Dimethylaminodichlorophosphine.[3] To 267 g of PCl_3 dissolved in 164 g of pyridine and 650 ml of Et_2O at 0° was slowly added, with stirring, a solution of 90 g of $(CH_3)_2NH$ in 300 ml of Et_2O. The $(CH_3)_2NPCl_2$ was isolated by distillation under reduced pressure followed by distillation under atmospheric pressure. The boiling range of the product was observed to be 149-152°. *Anal.* Calcd for

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