Inorg. Chem. **1989**, *28*, 2699-2703

Articles

Contribution from the Institut de Chimie Minérale et Analytique,
Université de Lausanne, Place du Château 3, CH-1005 Lausanne, Switzerland

Water-Exchange Mechanisms on the Terbium to Thulium Octaaqualanthanide(III) Ions: A Variable-Pressure ^{17}O NMR Study[1-3]

Cédric Cossy, Lothar Helm, and André E. Merbach*

Received March 21, 1989

The water-exchange rate on the heavy lanthanide ion series from Tb^{3+} to Tm^{3+} has been determined up to 250 MPa by ^{17}O NMR at 268 K. The calculated activation volumes for the exchange process are -5.7 ± 0.5 cm^3 mol^{-1} for Tb^{3+}, -6.0 ± 0.4 cm^3 mol^{-1} for Dy^{3+}, -6.6 ± 0.4 cm^3 mol^{-1} for Ho^{3+}, -6.9 ± 0.4 cm^3 mol^{-1} for Er^{3+}, and -6.0 ± 0.8 cm^3 mol^{-1} for Tm^{3+} and are representative of a similar interchange associative mechanism for these five ions. A discussion of the kinetic results obtained for the water and DMF exchanges on the lanthanide ions outlines the importance of the steric crowding in these ion solvates. The previously published kinetic results concerning the lanthanide complex formation in aqueous solution are discussed in light of these new mechanistic results reported here for the heavy members of the lanthanide series.

Introduction

The tripositive lanthanide ions (hereafter Ln^{3+}) constitute the longest series of chemically similar elements. This similarity is explained by their almost identical external electronic structure. For each member of the series, the filled 5s and 5p orbitals wrap the partially filled 4f ones, thus avoiding any strong crystal or ligand field effect for the lanthanide complexes. This explains why the structural and kinetic properties of these complexes are mainly governed by electrostatic and steric factors.

The solvation and kinetics of the Ln^{3+} ions in *N,N*-dimethylformamide (hereafter DMF)[4] illustrate well the importance of the steric factors. The mean coordination number (hereafter CN) is 8 for all the ions of the series and there is an equilibrium between octa- and nonasolvated species for the lighter elements (Ce^{3+} to Nd^{3+}). As the ionic radius decreases along the series, this associative tendency disappears for the ions located at the end of the series. The DMF exchange on Tb^{3+} and Yb^{3+} ions even takes place via a dissociative pathway (I_d mechanism for Tb^{3+} to a limiting D for Tm^{3+} and Yb^{3+}).

According to recent reports,[5-9] the determination of structural and mechanistic behavior of the lanthanide ions in aqueous solution seems to be a more difficult task. The data from a recent ^{17}O NMR study[5] have been interpreted as indicative of a constant CN along the whole series. This constancy was suggested by the regular change in the water chemical shift versus reciprocal temperature in solutions of 12 paramagnetic ions. This constant CN was assumed to be 9 according to Lincoln's idea[6] that it is unlikely to find a CN lower than 9 in solution, since stable nonahydrated species exist in the solid state for all ions of the series. The Ln^{3+} ions are however not all nonahydrated in solution. A recent first-order difference neutron scattering study[7] performed in diluted perchlorate solutions has unambiguously established a CN of 8 for Dy^{3+} and Yb^{3+}. Moreover, one can ask whether the CN is really constant along the whole series since the odd temperature dependence of the observed chemical shifts in Sm^{3+} and Eu^{3+} solutions[5] might be due to a change in coordination number with temperature and not to the particular electronic properties of these ions as was initially thought.[5] The idea of a CN change is very attractive since Miyakawa et al.[8] observed a coordination equilibrium in Ce^{3+} aqueous solutions, strongly displaced toward the more coordinated species at room temperature.

Accordingly the assignment of a CN of 8 for the heavy lanthanide ions in aqueous solution can today be considered as firmly documented. The exchange rate and entropy of activation for the water exchange on the Tb^{3+} to Yb^{3+} ions determined by ^{17}O NMR at variable temperature[5] have thus to be recalculated for a CN of 8 instead of 9 (multiply the rate constants reported for a CN of 8 by $^9/_8$ and add 1 J K^{-1} mol^{-1} to activation entropies). The main conclusions from the previous study[5] however remain the same: the water exchange rate decreases regularly along the series going from Gd^{3+} to Yb^{3+}, and the exchange process, characterized by a fairly constant activation entropy, must take place via a similar mechanism for all the ions studied. The nature of this mechanism however remains unknown.

High-pressure kinetic studies have been shown to be particularly successful in the determination of the activation of simple substitution processes.[10] The pressure dependence of the water exchange rates on the lanthanide ions has thus been investigated in order to determine the corresponding activation volumes, a reliable clue for a confident mechanistic assignment of these exchange reactions.

Experimental Section

The lanthanide perchlorate salts and solutions used for relaxation measurements were prepared as previously described.[5] The high-pressure probehead did not allow the use of spherical samples in order to avoid magnetic susceptibility effects on the chemical shifts. ^{17}O enriched 2-methyl-2-propanol (≈1.5 mol %) was thus added as a chemical shift internal reference to the solutions. This reference was prepared by the method of Anbar and Dostrovsky,[11] replacing ^{18}O-enriched water by ^{17}O-enriched water (Yeda, 14.6 atom %, ^{2}H normalized) in the synthesis. The solutions used for the NMR measurements were 0.2 or 0.3 *m* in

---

(1) High-Pressure NMR Study. 38. Part 37: see: Ioset, J.; Helm, L.; Merbach, A. E.; Roulet, R.; Grepioni, F.; Braga, D. *Helv. Chim. Acta* **1988**, *71*, 1458.

(2) This work is part of the Ph.D. Thesis of C.C., University of Lausanne, 1986, and was presented at the 2nd International Conference on the Basic and Applied Chemistry of f-Transition and Related Elements, Lisbon, April 1987. A preliminary account of this work is given in the proceedings of the conference (see ref 3).

(3) Cossy, C.; Helm, L.; Merbach, A. E. *Inorg. Chim. Acta* **1987**, *139*, 147.

(4) Pisaniello, D. L.; Helm, L.; Meier, P.; Merbach, A. E. *J. Am. Chem. Soc.* **1983**, *105*, 4528.

(5) Cossy, C.; Helm, L.; Merbach, A. E. *Inorg. Chem.* **1988**, *27*, 1973.

(6) Lincoln, S. F. *Adv. Inorg. Bioinorg. Mech.* **1986**, *4*, 217.

(7) Cossy, C.; Barnes, A. C.; Merbach, A. E.; Enderby, J. *J. Chem. Phys.* **1989**, *90*, 3254.

(8) Miyakawa, K.; Kaizu, Y.; Kobayashi, H. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 1517.

(9) Cossy, C.; Merbach, A. E. *Pure Appl. Chem.* **1988**, *60*, 1785.

(10) Merbach, A. E. *Pure Appl. Chem.* **1987**, *59*, 161.

(11) Anbar, M.; Dostrovsky, I. *J. Chem. Soc.* **1954**, 1094.

0020-1669/89/1328-2699$01.50/0

Table I. Calculated Parameters of Eq 3 for the Variation of the Chemical Shifts of $Ln(H_2O)_8^{3+}$ Solutions[a]

Ln^{3+}	T, K	$10^{-5}(\Delta\omega_m)_0$, rad s^{-1}	$10^{-5}P_1$, MPa^{-1}
Tb	268.9	11.58 ± 0.05	-3.3 ± 3.2
Dy	268.5	10.12 ± 0.02	-6.1 ± 2.4
Ho	268.8	8.23 ± 0.03	-1.5 ± 1.2
Er	268.9	6.14 ± 0.02	+12.0 ± 3.6
Tm	268.2	3.84 ± 0.02	+11.8 ± 5.2

[a] Errors quoted correspond to one standard deviation.

$Ln(ClO_4)_3$ and 2 m in $HClO_4$. Their exact compositions are given in the supplementary material.

The ^{17}O NMR measurements were made on a Bruker AM-400 spectrometer with a 9.3-T wide bore magnet. A homemade high-pressure probehead[12] tuned at 54.25 MHz was used. A built-in Pt resistor allowed temperature measurement with an accuracy of ±0.5 K after all corrections.[13] The $\pi/2$ pulse length was approximately 15 μs, the number of scans varied from 200 to 10000, and the sweep varied from 10 to 25 kHz. The longitudinal $1/T_1$ and transverse $1/T_2$ relaxation rates were determined by inversion-recovery and Carr–Purcell–Meiboom–Gill pulse sequences, as described earlier.[5] The reliability of this procedure was checked by measuring $1/T_1$ and $1/T_2$ in an acidified $La(ClO_4)_3$ solution. These two parameters only differ by ±2% from each other over the whole pressure range studied.

Results and Data Treatment

The theoretical approach developed for the variable-temperature study[5] was used to characterize the water-exchange kinetics on the Ln^{3+} ions at variable pressure. The difference between the transverse $1/T_1$ and longitudinal $1/T_2$ relaxation rates can be expressed by eq 1, whereas the chemical shift $\Delta\omega_s$ induced by the

$$(1/T_2 - 1/T_1)/P_m = (\Delta\omega_m)^2\tau_m \qquad (1)$$

presence of the metal ion is expressed by eq 2, where P_m is the

$$\Delta\omega_s/P_m = \Delta\omega_m \qquad (2)$$

mole fraction of water bound to the metal, $\Delta\omega_m$ is the chemical shift between free and bulk solvent, and τ_m is the mean lifetime of a water molecule bound to the metal. The inverse of this latter parameter is by definition equal to k, the first-order exchange rate constant.

The variable-pressure dependence of $\Delta\omega_m$ is expected to be negligible. However, Pisaniello et al.[4] found that, for lanthanide ions in DMF solutions, $\Delta\omega_m$ of the formyl proton increased by 10% when the pressure P was varied from 0 to 200 MPa. In order to describe this change, they used the linear relationship (3),

$$(\Delta\omega_m)_P = (\Delta\omega_m)_0(1 + P_1P) \qquad (3)$$

without explaining the physical meaning of the proportionality factor P_1. The variation of $k = 1/\tau_m$ is given, according to the transition-state theory, by eq 4, where ΔV^* is the activation volume

$$\Delta V^* = -RT(\partial \ln k/\partial P)_T \qquad (4)$$

of the exchange reaction. A polynomial relationship between ln k and P is usually assumed,[10] and the pressure dependence of k expressed by eq 5, where k_0 is the zero-pressure rate constant, ΔV^*_0 is the zero pressure activation volume, and $\Delta\beta^*$ is the compressibility coefficient of activation.

$$\ln k = \ln k_0 - (\Delta V^*_0)P/RT + (\Delta\beta^*)P^2/2RT \qquad (5)$$

Solutions of Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, and Tm^{3+} were investigated.[14] With reference to the previous temperature study,[5] the measurements were done at 268 K, where the kinetic effect on the relaxation rates is large. The pressure effect on the chemical shift $\Delta\omega_s$ was first determined. It was referred to the one measured in a diamagnetic $La(ClO_4)_3$ solution. The magnetic susceptibility effects were avoided by the use of ^{17}O-enriched 2-methyl-2-propanol as an internal reference. The so obtained chemical shifts were then fitted with eq 2 and 3, giving the results reported in Table I. According to eq 3, the change in $(\Delta\omega_m)_p$ with respect to $(\Delta\omega_m)_P$ along the pressure range studied is going from −1.5% (Dy^{3+}) to +3.0% (Er^{3+}), which is less than the experimental accuracy on the $\Delta\omega_s$ measurements (3–5%). The pressure effect on $\Delta\omega_m$ is thus nonsignificant and was neglected in the further treatment.

Table II. Activation Parameters for the Water-Exchange Reaction on $Ln(H_2O)_8^{3+}$[a]

Ln^{3+}	$10^{-7}k^{298}$, s^{-1}	ΔH^*, kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1}	ΔV^*,[b] cm^3 mol^{-1}	$10^2\Delta\beta^*$,[b] cm^3 mol^{-1} MPa^{-1}
Tb	55.8 ± 1.3	12.1 ± 0.5	−36.9 ± 1.6	−5.7 ± 0.5	+0.3 ± 1.6
Dy	43.4 ± 1.0	16.6 ± 0.5	−24.0 ± 1.5	−6.0 ± 0.4	−0.4 ± 1.4
Ho	21.4 ± 0.4	16.4 ± 0.4	−30.5 ± 1.3	−6.6 ± 0.4	−0.6 ± 1.3
Er	13.3 ± 0.2	18.4 ± 0.3	−27.8 ± 1.1	−6.9 ± 0.4	+0.3 ± 1.2
Tm	9.1 ± 0.2	22.7 ± 0.6	−16.4 ± 1.9	−6.0 ± 0.8	+1.2 ± 3.0
Yb	4.7 ± 0.2	23.3 ± 0.9	−21.0 ± 3.3		

[a] Errors quoted correspond to one standard deviation. [b] These parameters were determined at the following temperatures: Tb, 269.1 K; Dy, 268.5 K; Ho, 268.8 K; Er, 268.8 K; Tm, 269.1 K.

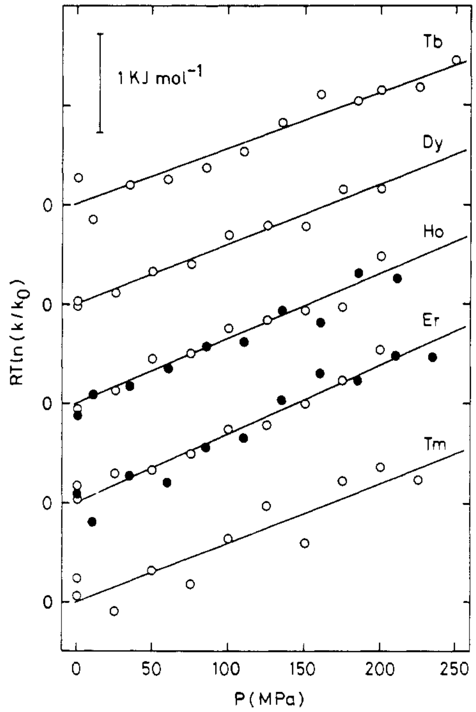


Figure 1. Pressure dependence of $RT \ln (k/k_0)$ for water exchange on Ln^{3+} ions, measured in 0.3 (○) and 0.2 m (●) $Ln(ClO_4)_3/2$ m $HClO_4$ solutions.

The transverse and longitudinal relaxation rates were then measured in 2-methyl-2-propanol free solutions as a function of pressure.[15] These data were fitted by using eq 1 and 5. The parameters adjusted were k_0, ΔV^*_0, and $\Delta\beta^*$. For the five ions studied, $\Delta\beta^*$ was smaller than its associated standard deviation, and sometimes of the opposite sign than ΔV^*_0, and could therefore

---

(12) Frey, U.; Helm, L.; Merbach, A. E. To be submitted for publication.

(13) Meyer, F. K.; Merbach, A. E. *J. Phys. E* **1979**, *12*, 185.

(14) Attempts were made to characterize the water exchange on Yb^{3+} under variable-pressure conditions. Contrary to the other ions studied here, the kinetic effect was not significant with respect to the relatively large experimental uncertainties when measuring in the high-pressure probehead.

(15) The presence of 1.5 mol % of this compound induces an increase of 15–25% on the relaxation rates of water. This could be explained by a change in the viscosity of the solutions, inducing an increase of the reorientation correlation time τ_c of water, and thus of the quadrupolar contribution to longitudinal and transverse relaxation rate. However the observed differences $1/T_2 - 1/T_1$ were independent of the 2-methyl-2-propanol content, and the presence of this chemical shift internal reference was assumed to have no influence on the chemical shift values used in the kinetic treatment.

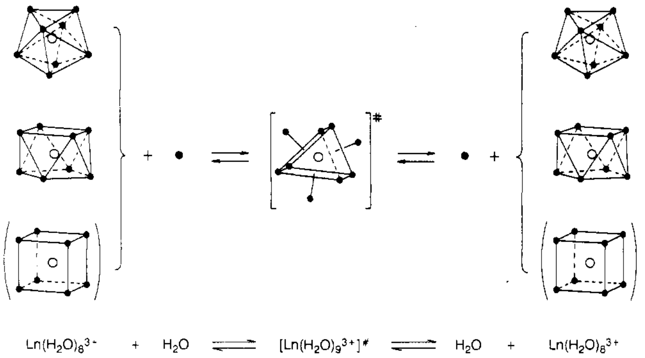


Figure 2. Probable mechanistic description of the water-exchange process on the heavy lanthanide ions.

be discarded. The fits were repeated with $\Delta\beta^\ddagger = 0$, giving pressure-independent $\Delta V^\ddagger$ values. Table II reports the resulting parameters and those determined in the previous variable-temperature study,[5] corrected for a CN of 8. Figure 1 reports the variable-pressure results in a temperature-independent form.

Discussion

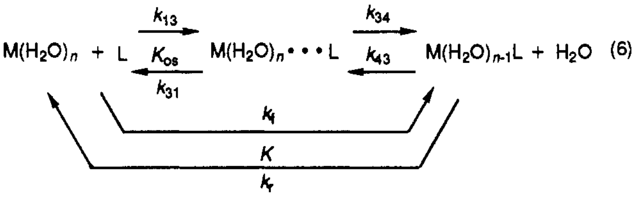
The activation volumes for the water exchange on the heavy lanthanide ions are all negative and close to -6 cm^3 mol^{-1}. A decrease in volume when going from the reactants to the transition state is indicative of an associative activation mode.[10,16] The question is to evaluate whether this negative activation volume corresponds to a concerted I_a pathway (the exchanging ligands enter and leave the complex simultaneously) or to a limiting A mechanism (existence of an intermediate with a higher CN). The semiempirical model of Swaddle[17] allows the calculation of the absolute partial molar volume of the aqua ions in solution, in relation to their coordination number and ionic radius. It can be done for the octahydrated heavy lanthanide ions as well as for the corresponding hypothetical nonahydrated intermediate (present in an A mechanism) by taking the tabulated ionic radii from Shannon.[18] The volume difference between the two solvates corresponds exactly to the addition of one water molecule to the lower coordinated species. The value calculated for the heavy lanthanide ions is -12.9 cm^3 mol^{-1} and agrees well with the reaction volume of -11 cm^3 mol^{-1} reported for the $Ce(H_2O)_8^{3+} + H_2O \rightleftarrows Ce(H_2O)_9^{3+}$ equilibrium.[19] The activation volumes determined here are about 2 times smaller than these limiting values for an A mechanism. The water exchange on the ions Tb^{3+}–Tm^{3+} thus occurs via an identical concerted associative I_a mechanism. This assignment is confirmed by the negative activation entropies previously determined.[5]

The most probable geometries for an octahydrated lanthanide ion are a square antiprism, a dodecahedron, or a cube. According to a recent discussion,[7] this last geometry is less probable but cannot be excluded. A concerted associative water-exchange pathway will involve a nonacoordinated transition state. The most probable geometry for such a species is a trigonal-tricapped prism, since many hydrated salts of the lanthanide exhibit this structure in the solid state.[6,9] Figure 2 shows a probable geometrical description for the exchange process on the octahydrated lanthanide ions.

The effects of the regular decrease in ionic radii along the series Tb^{3+}–Tm^{3+} studied here will have two effects on an associative exchange process. The first one is essentially electrostatic: the smaller the aqua ion is, the stronger is its interaction with the entering ligand. This will lead to an increase of the exchange rate constant across the series. The second effect is due to steric considerations: the smaller the aqua ion is, the larger is the steric hindrance to enter the first coordination sphere. This will correspond to a decrease of the exchange rate along the series. According to the observed regular decrease in the water exchange rates reported in Table II, the steric effects must thus be larger than the electrostatic ones.

The water exchange on $Ln(H_2O)_8^{3+}$ takes place via an I_a mechanism whereas DMF exchanges on $Ln(DMF)_8^{3+}$ via an I_d to D mechanism.[4] This illustrates again the importance of the steric factors for the lanthanide complexes. The observation of an exchange mechanism more dissociative for DMF than for water is not specific to the lanthanide ions but has already been observed for Be^{2+} (A for H_2O, I_d for DMF)[9] and Mn^{2+} (I_a for H_2O, I to I_d for DMF)[20] ions.

At this point it is interesting to compare the water exchange with the complex formation reactions already studied. These reactions have generally been assumed to follow the Eigen–Wilkins[21] mechanistic description, where the complexation occurs in three steps: diffusion of the reactants toward each other, formation of an outer-sphere complex, and, finally, substitution of one water molecule by the entering ligand. The first two steps are usually combined in a single one, giving rise to the scheme in (6).


(6)

$$M(H_2O)_n + L \underset{k_{31}}{\overset{k_{13}}{\underset{K_{os}}{\rightleftarrows}}} M(H_2O)_n\cdots L \underset{k_{43}}{\overset{k_{34}}{\rightleftarrows}} M(H_2O)_{n-1}L + H_2O \qquad (6)$$

The outer-sphere complex formation is characterized by rates of formation k_{13} and dissociation k_{31}, and by an equilibrium constant K_{os}. The substitution of one bound water molecule by L occurs with a rate k_{34} whereas the reverse process takes place with a k_{43} rate. K is the total stability constant of the ML complex, and k_f and k_r are respectively its global rates of formation and dissociation.

The water exchange is a peculiar case of complexation reaction, where $L = H_2O$ with a rate constant $1/\tau_m$ corresponding to k_{43} in eq 6. k_{34} corresponds to the transfer of one particular water molecule from the outer sphere to the first coordination shell. It is however very difficult to know the number of outer-sphere water molecules. As explained elsewhere,[7] the geometry of the octahydrated heavy lanthanide ions can be a cube, a square antiprism, or a dodecahedron. Assuming that a water molecule is located on each face of these probable coordination polyhedrons, one can have 6 (cube) to 12 (dodecahedron) outer-sphere molecules, or even 16 if each aqua ligand hydrogen bonds to two more waters.[22] This corresponds to a statistical k_{34}/k_{43} ratio varying from $^1/_2$ to $^4/_3$. Both values of k_{34} and k_{43} are thus comparable in the case of the water exchange on the heavy lanthanide ions and a direct comparison between the water exchange rates and the substitution rate k_{34} for other ligands will be possible.

The experimental techniques used for the complex formation studies usually give access to the global rate constants k_f and k_r. If we suppose that the concentration in outer-sphere complex is constant (steady state), k_{34} and k_{43} can be related to k_f and k_r by eq 7 and 8.[23] It is usually assumed that the outer-sphere

$$k_f = \frac{k_{13}k_{34}}{k_{31} + k_{34}} \qquad (7)$$

$$k_r = \frac{k_{31}k_{43}}{k_{31} + k_{34}} \qquad (8)$$

---

(16) Stranks, D. R. *Pure Appl. Chem.* **1974**, *38*, 304.
(17) Swaddle, T. W. *Inorg. Chem.* **1983**, *22*, 2663.
(18) Shannon, R. D. *Acta Crystallogr. Sect. A* **1976**, *32*, 751.
(19) Laurenczy, G.; Merbach, A. E. *Helv. Chim. Acta* **1988**, *71*, 1971.
(20) Cossy, C.; Helm, L.; Merbach, A. E. *Helv. Chim. Acta* **1987**, *70*, 1516.
(21) (a) Eigen, M.; Tamm, K. *Z. Electrochem.* **1962**, *66*, 93. (b) Wilkins, R. G. *Acc. Chem. Res.* **1970**, *3*, 408.
(22) Caminiti, R.; Licheri, G.; Piccaluga, G.; Pinna, G. *J. Chem. Phys.* **1978**, *69*, 1.
(23) Darbani, G. S.; Fittipaldi, F.; Petrucci, S.; Hemmes, P. *Acustica* **1971**, *25*, 125.

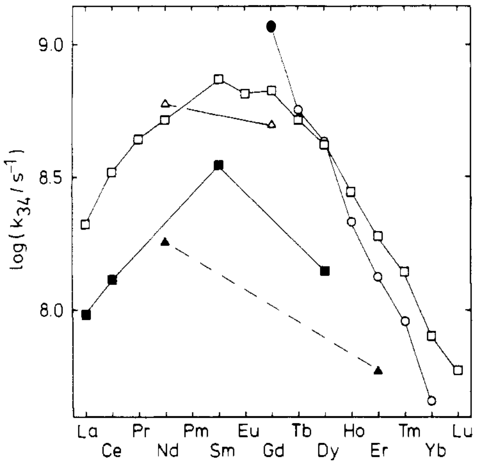


Figure 3. Substitution rate constants k_{34} at 298.15 K for some complex formation reactions on Ln^{3+} ions in water, reported versus reciprocal metal ionic radius: (○) water-exchange rate;[5] (□) sulfate;[26] (■) acetate;[27] (△) nitrate;[28] (▲) nitrate.[29]

processes are much faster than the inner-sphere ones ($k_{34} \ll k_{31}$), and eq 9 and 10 replace eq 7 and 8.

$$k_f = \frac{k_{13}}{k_{31}}K_{34} = K_{os}k_{34} \tag{9}$$

$$k_r = k_{43} \tag{10}$$

For the trivalent lanthanide ions, Darbani et al.[23] calculated k_{31} values varying from 0.8×10^9 to 1.4×10^9 s^{-1}, which is close to the water exchange rate determined in the present work. The assumption of a fast outer-sphere process is thus obviously not respected. Moreover, calculations of k_{34} from k_f will give results of low confidence because the K_{os} values, calculated from the Bjerrum[24] or Fuoss[25] models can vary by 1 order of magnitude, depending on the local dielectric constant value and on the mean distance between metal and outer-sphere water used in the calculation.[23] The k_{34} value reported in Figure 3 should thus be considered with care.

Sulfate substitution[26] and water exchange rates are very similar. This agreement is surprising with respect to the associative process operative for these reactions, where some effect due to the nature of the entering ligand is expected. The lanthanide ions are thus similar to the Mn^{2+} ion[30] with respect to their kinetic nonselectivity. According to the HSAB principle,[31] these ions are hard Lewis acids without any ligand field stabilization. The selectivity of such hard metal centers toward various ligands must be poor, whatever the charge and the polarizability of the ligands might be.

The other kinetic results concerning the lanthanide ions in aqueous solution were only reported in term of total rate constant k_f. These results, illustrated in Figure 4, do not allow direct comparison with the water-exchange rate constants. The observed k_f values are varying by several orders of magnitude for the same metal ion. The existence of an associative pathway for the complex formation reactions (in agreement with the I_a mechanism observed for the water exchange) might be an explanation for the ligand influence on the rates of these reactions. This might however be due to various other factors. The ligands do not all have the same charge and will have very different outer-sphere parameters. Furthermore, the data reported were not all collected at the same temperature. It should also be recalled that these ligands are all weak bases, and competition may occur between protonation and metal bond formation on the ligand basic sites: this is exemplified by the case of monoprotonated *trans*-1,2-diaminocyclohexane-*N,N,N′,N′*-tetraacetato complexation on the lanthanide ions,[39] where the complexation rate constants (≈3 dm^3 mol^{-1} s^{-1} at 298.2 K; not reported in Figure 4) are governed by the ligand last deprotonation. One has finally to mention a very important parameter that certainly affects the reported k_f values: the largest number of the studied ligands are multidentate, and the observed rate constants are probably due to the ring closure step (chelation) and not to the first substitution step. This is certainly the case for the murexide,[32] oxalate,[36] and anthranilate[37] complexation occurring with a similar rate for almost all the lanthanide ions although these ligands do not have the same charge and thus not the same K_{os}.

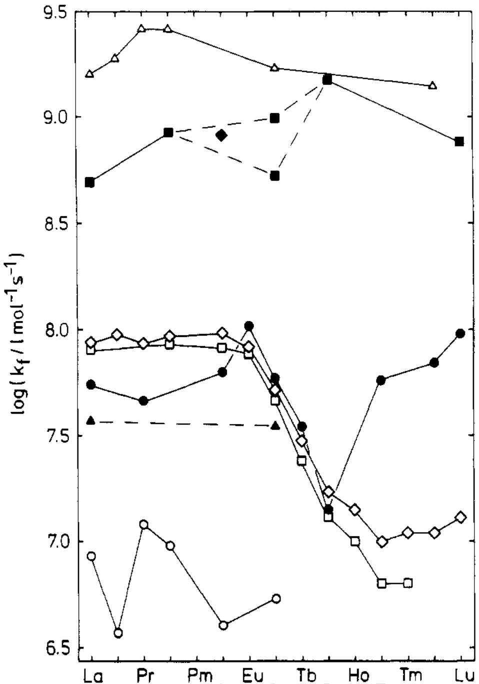


Figure 4. Complex formation rate constants k_f for some reactions on Ln^{3+} ions in water, reported versus reciprocal metal ionic radius: (◇) murexide at 285.2 K;[32] (◆) murexide at 298.2 K;[33] (○) xylenol orange at 298.2 K;[34] (□) oxalate at 298.2 K;[35] (●) anthranilate at 285.2 K;[36] (△) nitrate at 298.2 K;[23] (▲) methyl red at 293.2 K;[37] (■) picolinate at 293.2 K.[38]

The most recent discussions[7,8] concerning the coordination of the lanthanide aqua ions conclude to a probable change in CN occurring from Sm^{3+} to Gd^{3+}. This may explain the observed change along the series in the rate of almost all the complexation reactions illustrated in Figures 3 and 4. The maxima is substitution rates observed around Sm^{3+} and Eu^{3+} in Figure 3 are close to the diffusion limits. This might be indicative of a very easy substitution pathway for these ions, due to the almost identical energies of the octa- and nonacoordinated species. Moreover, the observation of an associative water-exchange mechanism on the octahydrated heavy Ln^{3+} ions (the smallest of the series according to their ionic

---

(24) Bjerrum, N. *K. Dan. Vidensk. Selsk. Skr. Naturvidensk. Math. Afd.* **1926**, *7*, 9.
(25) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.
(26) Fay, D. P.; Litchinsky, D.; Purdie, N. *J. Phys. Chem.* **1969**, *73*, 544.
(27) Garza, V. L.; Purdie, N. *J. Phys. Chem.* **1970**, *74*, 275.
(28) Garnsey, R.; Ebdon, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 50.
(29) Silber, H. B.; Scheinin, N.; Atkinson, G.; Grecsek, J. J. *J. Chem. Soc. Faraday Trans. 1* **1972**, *68*, 1200.
(30) Ducommun, Y.; Newman, K. E.; Merbach, A. E. *Inorg. Chem.* **1980**, *19*, 3695.
(31) Pearson, R. G. *Science* **1966**, *151*, 172.
(32) Geier, G. *Ber. Bunsen-Ges. Phys. Chem.* **1965**, *69*, 617.
(33) Farrow, M. M.; Purdie, N.; Eyring, E. M. *Inorg. Chem.* **1974**, *13*, 2024.
(34) (a) Yatsimirskii, K. B.; Budarin, L. I. *Chem. Abstr.* **1968**, *69*, 70243e. (b) *Coordination Chemistry, Vol. 2*; Martell, A. E., Ed., ACS Monograph 174; American Chemical Society: Washington, DC, 1978.
(35) Graffeo, A. J.; Bear, J. L. *J. Inorg. Nucl. Chem.* **1968**, *30*, 1577.
(36) Silber, H. B.; Farina, R. D.; Swineheart, J. H. *Inorg. Chem.* **1969**, *8*, 819.
(37) Eriksen, T. E.; Grenthe, I.; Puigdomênech, I. *Inorg. Chim. Acta* **1986**, *121*, 63.
(38) Eriksen, T. E.; Grenthe, I.; Puigdomênech, I. *Inorg. Chim. Acta* **1987**, *126*, 131.
(39) Nyssen, G. A.; Margerum, D. W. *Inorg. Chem.* **1970**, *9*, 1814.

Inorg. Chem. **1989**, *28*, 2703-2710

radii) leads to the presumption of a larger CN for the light elements, thus reinforcing the idea of a CN change in the middle of the series.

Acknowledgment. We thank Prof. G. Geier for stimulating discussions. This work was financially supported by the Swiss National Science Foundation (Grant No. 2.672-0.87).

Registry No. $Tb(H_2O)_8^{3+}$, 121096-88-6; $Dy(H_2O)_8^{3+}$, 121096-89-7; $Ho(H_2O)_8^{3+}$, 63213-08-1; $Er(H_2O)_8^{3+}$, 63118-71-8; $Tm(H_2O)_8^{3+}$, 63118-73-0; $Yb(H_2O)_8^{3+}$, 63118-75-2; H_2O, 7732-18-5.

Supplementary Material Available: Listings of sample composition (Table S1), pressure dependence of chemical shifts (Table S2), and pressure dependence of relaxation rates (Table S3) (9 pages). Ordering information is given on any current masthead page.

Contribution from Inorganic Chemistry 1, Chemical Center, University of Lund, S-221 00 Lund, Sweden, and Chemistry Department, Royal Veterinary and Agricultural University, DK-1871 Frederiksberg C, Denmark

Kinetics and Mechanism for Reaction between Ammine- and Haloamminegold(III) Complexes and Thiocyanate. Competitive Electron Transfer and Substitution

Sofi Elmroth,[1a] L. H. Skibsted,*[,1b] and Lars I. Elding*[,1a]

Received January 6, 1989

The reactions in acidic aqueous solution between thiocyanate and each of the gold(III) complexes $Au(NH_3)_4^{3+}$, *trans*-$Au(NH_3)_2Cl_2^+$, and *trans*-$Au(NH_3)_2Br_2^+$ have been studied by use of potentiometric pH measurements and sequential-mixing stopped-flow spectrophotometry. The reactions give a common gold(I) product whereas the rate-controlling steps are different. The reaction between $Au(NH_3)_4^{3+}$ and thiocyanate takes place via rate-controlling substitution of an ammine ligand by thiocyanate with $k = 7.6 \pm 0.1$ M^{-1} s^{-1}, $\Delta^{\ddagger}H^{\circ} = 61 \pm 1$ kJ mol^{-1}, and $\Delta^{\ddagger}S^{\circ} = 26 \pm 3$ J mol^{-1} K^{-1} at 25.0 °C, followed by rapid reduction to gold(I) with the overall stoichiometry

$$3Au(NH_3)_4^{3+} + 6SCN^- + 4H^+ + 4H_2O \rightarrow 2Au(SCN)_2^- + Au(SCN)(CN)^- + SO_4^{2-} + 12NH_4^+ \qquad \text{(i)}$$

For *trans*-$Au(NH_3)_2X_2^+$ (X = Cl, Br), thiocyanate replaces halide in two rapid consecutive and reversible substitution steps without an observable solvent path prior to the slower reduction:

$$\textit{trans}\text{-}Au(NH_3)_2X_2^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \textit{trans}\text{-}Au(NH_3)_2XSCN^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \textit{trans}\text{-}Au(NH_3)_2(SCN)_2^+ \qquad \text{(ii)}$$

Second-order rate constants (M^{-1} s^{-1}) at 2.0 °C are as follows: for X = Cl; $k_1 = (9.0 \pm 1.4) \times 10^3$, $k_{-1} = (0.6 \pm 0.2)$, $k_2 = (1.56 \pm 0.21) \times 10^5$, $k_{-2} = (3.4 \pm 0.6) \times 10^2$; for X = Br, $k_1 = (8.9 \pm 0.3) \times 10^4$, $k_{-1} = (1.32 \pm 0.20) \times 10^3$, $k_2 = (1.4 \pm 0.4) \times 10^5$, $k_{-2} = (1.0 \pm 0.7) \times 10^4$. Temperature variation of k_1 gave the following values: for X = Cl; $\Delta^{\ddagger}H^{\circ} = 33 \pm 7$ kJ mol^{-1}, $\Delta^{\ddagger}S^{\circ} = -48 \pm 21$ J K^{-1} mol^{-1}; for X = Br, $\Delta^{\ddagger}H^{\circ} = 30 \pm 11$ kJ mol^{-1}, $\Delta^{\ddagger}S^{\circ} = -50 \pm 30$ J K^{-1} mol^{-1} at 25.0 °C. Parametrization of the substitution rate constants shows that the nature of the entering ligand is even more important than the trans effect for these complexes, in marked contrast to isoelectronic Pt(II) complexes. The relative stability constants for these short-lived complexes, $K_n = k_n/k_{-n}$, were obtained from the rate constants and are as follows: for X = Cl, $K_1 = (1.5 \pm 0.5) \times 10^4$, $K_2 = (4.6 \pm 0.5) \times 10^2$; for X = Br, $K_1 = 67 \pm 12$, $K_2 = 12 \pm 3$. The ratio K_1/K_2 shows a nonstatistical distribution for the chloro–thiocyanato system, indicating a increased thermodynamic stability for the complex *trans*-$Au(NH_3)_2ClSCN^+$, whereas the bromo–thiocyanato system is approximately statistically distributed. An UV–vis spectrum for the intermediate short-lived complex *trans*-$Au(NH_3)_2BrSCN^+$ was calculated from continuous-flow spectra. Reduction to gold(I) takes place via three parallel paths subsequent to establishment of the rapid substitution equilibria (ii). Each gold(III) complex *trans*-$Au(NH_3)_2X_{2-n}(SCN)_n^+$ is reduced by outer-sphere thiocyanate in second-order reactions. The second-order rate constants, k_{rn} ($n = 0, 1, 2$), at 25.0 °C are as follows: for X = Cl, $k_{r1} = (2.7 \pm 0.5) \times 10^3$, $k_{r2} = (2.2 \pm 0.4) \times 10^2$; for X = Br, $k_{r0} = 10 \pm 5$, $k_{r1} = (3.0 \pm 0.5) \times 10^2$, $k_{r2} = (2.5 \pm 0.4) \times 10^2$ M^{-1} s^{-1}. Temperature variation of k_{r2} gave $\Delta^{\ddagger}H^{\circ} = 66 \pm 4$ kJ mol^{-1} and $\Delta^{\ddagger}S^{\circ} = 21 \pm 12$ J mol^{-1} K^{-1} at 25.0 °C. The mixed chloro– and bromo–thiocyanato complexes are reduced most rapidly, indicating that an asymmetric distribution of electrons along the trans-axis facilitates reduction. It is concluded that reduction takes place by attack of outer-sphere thiocyanate on the sulfur of a coordinated thiocyanate. In keeping herewith, the two complexes *trans*-$Au(NH_3)_2XSCN^+$ (X = Cl, Br), which contain a loosely bound halide ligand in the ground state, also substitute this halide ligand for thiocyanate most rapidly (k_2). A unified mechanism for competitive electron transfer and ligand substitution for the reaction between gold(III) complexes and reducing ligands is suggested.

Introduction

Reactions between gold(III) complexes and efficient nucleophiles such as iodide, thiocyanate, thiosulfate, thiourea, and alkyl sulfides in aqueous solution result in reduction to gold(I).[2-7] As a rule, this type of reaction takes place via rapid ligand substitutions in the gold(III) complexes, followed by an electron-transfer step, which in most cases is slow compared to the initial substitution.[8] For very efficient nucleophiles like iodide attacking complexes with favorable electronic properties, such as $AuBr_4^-$ and possibly also $AuCl_4^-$, reduction might take place directly without any prior substitution.[2,3] For other combinations of nucleophile and substrate, the initial substitution is necessary and rate-controlling for reduction.[8] Examples of this latter type are the reactions between $Au(NH_3)_4^{3+}$ and iodide[3] and possibly also those between $AuCl_4^-$ and anions of carboxylic acids.[9]

For reactions between gold(III) complexes and thiocyanate, there is a subtle balance between the rates of substitution and the rate of electron transfer.[4] The reaction between AuX_4^- (X = Cl, Br) and thiocyanate is complicated with four consecutive substitution steps. Each step gives substitution products, which might participate in the subsequent electron transfer. A complete resolution of the overall kinetics with five parallel electron transfer

---

(1) (a) Lund University. (b) The Royal Veterinary and Agricultural University.

(2) Elding, L. I.; Olsson, L.-F. *Inorg. Chem.* **1982**, *21*, 779.

(3) Elding, L. I.; Skibsted, L. H. *Inorg. Chem.* **1986**, *25*, 4084.

(4) Elding, L. I.; Gröning, A.-B.; Gröning, Ö. *J. Chem. Soc., Dalton Trans.* **1981**, 1093.

(5) Nord, G.; Skibsted, L. H.; Halonin, A. S. *Acta Chem. Scand., Ser. A* **1975**, *A29*, 505.

(6) Makotchenko, E. V.; Peschchevitskii, B. I.; Novoselov, R. I. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1978**, *14*, 44; **1981**, *9*, 47, 52, 56.

(7) Annibale, G.; Canovese, L.; Cattalini, L.; Natile, G. *J. Chem. Soc., Dalton Trans.* **1980**, 1070.

(8) Skibsted, L. H. *Adv. Inorg. Bioinorg. Mech.* **1986**, *4*, 137.

(9) Maritz, B. S.; van Eldik, R. *Inorg. Chim. Acta* **1976**, *17*, 21; **1976**, *20*, 43; *J. Inorg. Nucl. Chem.* **1976**, *38*, 1545, 1749, 2124; **1977**, *39*, 1935.

0020-1669/89/1328-2703$01.50/0