reactions. There is an overall contraction associated with substitution of water for MeCN and an even larger one when Me_2SO is the entering ligand, as can be seen in Figure 5. It is noteworthy that the three ΔV_{-1}^{*} values are equal within experimental error (-1.9 ± 0.4 cm^3 mol^{-1}). It means that the difference in volume between the transition state and the reactants is independent of the leaving group when water is the incoming ligand. Release of MeCN or Me_2SO into the bulk would produce a large expansion. If an interchange mechanism is operating, the ΔV_{-1}^{*} should be modulated depending on the nature of the outgoing molecule, which is obviously not seen. It suggests that the leaving ligand is still tightly bound to the metal center at the transition state, and it follows that, despite the small values of ΔV_{-1}^{*}, the mechanism of these three reactions is probably very associative, if not limiting (A). As pointed out earlier,[8] it also illustrates the importance of drawing the overall volume diagram of a substitution reaction when activation volumes are used for mechanistic classification.

Acknowledgment. Thanks are due to the Swedish Natural Science Research Council and the Swiss National Science Foundation (Grant No. 2.854-0.85) for financial support.

Supplementary Material Available: Spectrophotometric equilibrium measurements at ambient pressure and 298 (Table SI), 288 (Table SII), or 278 K (Table SIII), molar absorptivities for the various complexes at the wavelengths used (Table SIV), spectrophotometric equilibrium measurements at variable pressure (Table SV), observed rate constants at ambient pressure for reaction 1 (Table SVI) and for reaction 2 (Table SVII), and observed rate constants for reaction 1 as a function of pressure at 278.2 K (Table SVII) (11 pages). Ordering information is given on any current masthead page.

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Ligand-Substitutional Nature of Technetium(III). Rate and Mechanism of Ligand Exchange of Tris(acetylacetonato)technetium(III) in Acetylacetone

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Tris(acetylacetonato)technetium(III), ^{99}Tc(acac)$_3$, undergoes ligand exchange in acetylacetone (Hacac) at 125–141 °C. The rate observed by the ^{14}C-labeling method is expressed by rate = k_1[complex] at [complex] = 0.003–0.007 M, [Hacac] = 9.7 M, and [H_2O] = 0.04–0.1 M; $k_1 = (2.1 \pm 0.1) \times 10^{-4}$ s^{-1} at 141 °C. No water catalysis was observed. ΔH^{*} and ΔS^{*} are 119 ± 7 kJ mol^{-1} and -27 ± 18 J K^{-1} mol^{-1}, respectively. The dilution with acetonitrile reduced the rate linearly with [Hacac]. The deuterium isotope effect $k_1(\mathrm{H})/k_1(\mathrm{D})$ was modest (2.3 ± 0.3). The I_a mechanism is assigned to the rate-determining formation of the intermediate containing a one-ended acac$^-$ and a unidentate Hacac. The lability and the mechanism are regarded as reflecting straightforwardly the kinetic nature of Tc^{III} on the basis of the previously reported linear free energy relationship between the present exchange system and the ligand-substitution processes of aqua complexes for various tervalent metal ions (Kido, H.; Saito, K. *J. Am. Chem. Soc.*, **1988**, *110*, 3187–3190). The lability of Tc^{III} with the low-spin d^4 configuration was found to be very close to that of Cr^{III}, much lower than that of Mo^{III}, and slightly higher than that of Ru^{III} and Rh^{III}; Mo^{III} ≫ Tc^{III} > Ru^{III} > Rh^{III}. The mechanism is consistent with that previously proposed for M^{III}(acac)$_3$ complexes, on the basis of an estimated ionic radius of Tc^{III}.

Technetium chemistry has been greatly developing in the last decade[1] despite experimental difficulties, in response to radiopharmaceutical demands for ^{99m}Tc compounds[1-3] and in recognition of the key location of the element in the periodic table, a central position of the d block, particularly for understanding the chemistry of 4d and 5d transition series. However, there has been no systematic information on kinetics and mechanisms of simple ligand-substitution reactions of basic complexes despite their basic importance, although some scattered data are available (vide infra). Tris(acetylacetonato)technetium(III), ^{99}Tc(acac)$_3$, can afford a basic understanding of the ligand-substitutional nature of Tc^{III} on the basis of a systematization of the ligand-exchange kinetics of [M^{III}(acac)$_3$] (M = Al, Sc, V, Cr, Mn, Fe, Co, Ga, Mo, Ru, Rh, In).[4]

Tc(acac)$_3$ is known to have the low spin (LS) d^4 configuration.[5] Metal ions with this configuration are classified as substitution inert,[6,7] but a systematic and mechanistic understanding of their ligand-substitution reactions is insufficient.

Table I. Observed First-Order Rate Constants for Ligand Exchange of ^{99}Tc(acac)$_3$ in Acetylacetone

T/°C	[Tc^{III}]/M	[H_2O]/M	$k_1{}^d$/10^{-5} s^{-1}
125	0.0029	0.04	5.3 ± 0.3
	0.0026	0.09	5.1 ± 0.3
133	0.0029	0.04	10.2 ± 0.4
	0.0026	0.09	9.0 ± 0.2
141	0.0023	0.02	22.4 ± 0.5
	0.0030	0.08	21.4 ± 0.8
	0.0071	0.03	21.1 ± 0.6
	0.0027	0.11	14.5 ± 0.4[a]
	0.0029	0.05	9.9 ± 0.9[b]
	0.0029	0.03	4.2 ± 0.2[c]

[a] Hacac[3-$^2H_2$] (deuterium content: 63%). [b] Diluted with CH_3CN; [Hacac] = 4.9 M. [c] Diluted with CH_3CN; [Hacac] = 1.9 M. [d] Errors are calculated at the 70% confidence level.

This paper elucidates the unknown kinetic nature of Tc^{III} with the LS d^4 configuration.

Experimental Section

^{99}Tc(acac[2-^{14}C])$_3$ (100 mg) was prepared by heating a degassed solution of ^{99}Tc(acac)$_3$[5] (200 mg) and Hacac[2-^{14}C][8] (1.5 g) in aceto-

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Table II. Kinetic Parameters and Proposed Mechanism for the Ligand Exchange of $M^{III}(acac)_3$ Complexes in Acetylacetone[a]

M^{III}	CR^b/pm	k_1/s^{-1} (T/K)		$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	effect of [Hacac][c]	mechanism
Co	66.5	2×10^{-10} (298)[d]	2.4×10^{-5} (366)	152 ± 2	+80 ± 25	0	I_d (or D)
Al	67.5	9.1×10^{-5} (298)		85 ± 5	−38 ± 18	1	I[f]
Cr	75.5	4×10^{-10} (298)[d]	1.1×10^{-4} (398)	120 ± 3	−21 ± 10	1	I[f]
Ga	76.0	1.6×10^{-3} (298)		68 ± 9	−71 ± 32	1	I_a
V	78.0	1.4×10^{-4} (298)		73 ± 2	−73 ± 5	1	I_a
Fe	78.5	3.3×10^{-4} (298)[d]	8.9×10^{-4} (283)	60 ± 4	−92 ± 13	1	I_a
Rh	80.5	8×10^{-13} (298)[d]	2.4×10^{-5} (453)	118 ± 2	−79 ± 6		I_a
Ru	82	3×10^{-11} (298)[d]	5.2×10^{-5} (423)	115 ± 8	−61 ± 19		I_a
Tc	(84)[e]	2×10^{-10} (298)[d]	5.2×10^{-5} (398)	119 ± 7	−27 ± 18	1	I_a
Mo		$3._5 \times 10^{-6}$ (298)[d]	1.4×10^{-4} (323)				

[a] References 4b,c. [b] The crystal radius of coordination number 6 (cf. ref 13). [c] Presence (1) or absence (0) of the decrease in k_1 when the system is diluted with CH_3CN ([Hacac] = 2–9.7 M). [d] Extrapolated value. [e] Estimated (see text). [f] I_d–I_a borderline (cf.: Nagasawa, A.; Kido, H.; Hattori, T. M.; Saito, K. *Inorg. Chem.* **1986**, *26*, 4330–4333).

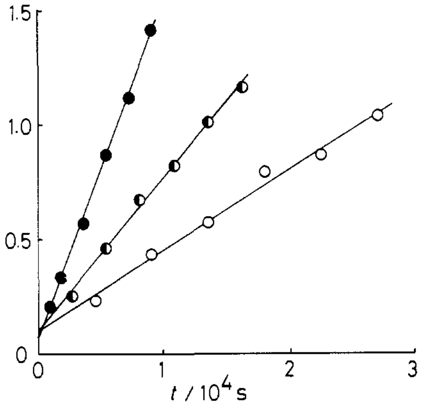


Figure 1. Mckay plots of ligand exchange of $^{99}Tc(acac)_3$ in acetylacetone at 141 (closed), 133 (half-closed), and 125 °C (open) at the lowest $[H_2O]$ (cf. Table I), where F is the fraction of the exchange.

nitrile (4 mL) at 147 °C for 96 h[9] in a sealed tube, recrystallized from acetylacetone (2 mL) and n-hexane (25 mL), and spectrophotometrically checked in dry acetonitrile. λ_{max}/nm (ϵ/M^{-1} cm^{-1}): 535 (4900), 505 (4900), 375 sh (7600), 348 (10 500), 283 sh (16 300), 270 (17 800) [lit.[5] 535 (4600), 505 (4600), 375 sh (7300), 348 (10 300), 283 sh (16 500), 270 (18 000)]. Hacac[3-$^2H_2$] (63% deuteriated at the methylene moiety) was prepared by the reported method.[10] The exchange rate was measured as follows.[4b,10] Solutions of the ^{14}C-labeled complex (10 mg) in Hacac (10 mL) were dispensed and sealed in eight glass tubes after degassing, and the tubes were heated in a thermostat. The tubes were withdrawn one by one at appropriate time intervals and chilled with cold water. From each solution, Hacac was collected in small tubes in a liquid-nitrogen bath by distillation in vacuo at room temperature and submitted to scintillation counting (^{14}C).

Results

McKay plots gave straight lines over 70% of the completion of the exchange with small intercepts (Figure 1). The visible absorption spectra and the water content (determined by Karl Fischer titration) of the reaction mixture did not vary throughout the exchange. Hence, the reaction

$$^{99}Tc(^*acac)_3 + Hacac \rightleftharpoons {}^{99}Tc(acac)_3 + H^*acac \qquad (1)$$

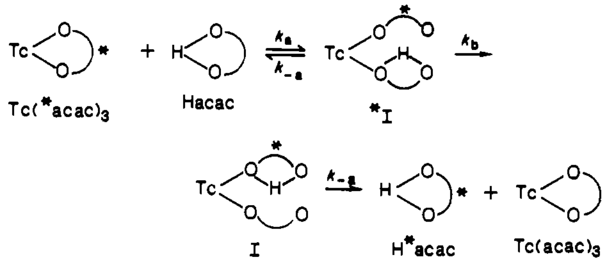
takes place exclusively (* denotes ^{14}C-labeling). The observed rate was proportional to the concentration of the complex at 141 °C (Table I):

$$\text{rate} = k_1[\text{complex}] \qquad (2)$$

where k_1 is the observed first-order rate constant, which was independent of $[H_2O]$ (Table I). The temperature dependence of k_1 gave $\Delta H^\ddagger = 119 \pm 7$ kJ mol^{-1} and $\Delta S^\ddagger = -27 \pm 18$ J K^{-1} mol^{-1}. On deuteriation (63%) of the acidic hydrogen of Hacac, k_1 decreased(Table I) and $k_1(H)/k_1(D)$ was 2.3 ± 0.3. When Hacac was diluted with CH_3CN to make [Hacac] = 4.9 and 1.9 M, k_1 decreased linearly (Table I).

Discussion

Exchange Mechanism. Since the reaction system is very simple, consisting substantially of two components, the complex and the solvent, the possible mechanism is limited to the previously proposed one, which is common for the exchange of $M^{III}(acac)_3$ complexes in Hacac (M = Al, V, Cr, Fe, Co, Ga, Ru, Rh).[4b,c]



(3)

The exchange proceeds in three steps consisting of two elementary processes. The first step is the substitution of the free ligand for one end of the chelate to give the intermediate *I (k_a). The second is the intramolecular proton transfer between the unidentate ligands in *I (k_b). The third is the reverse of the first (k_{-a}). The observed rate law without the $[H_2O]$ term (eq 1), the deuterium isotope effect ($k_1(H)/k_1(D) = 2.3 \pm 0.3$) in acetylacetone, and the decrease of k_1 by dilution with CH_3CN do not conflict with the mechanism. The concentration of *I is reasonably considered to be very low as compared with that of the original complex, since the visible absorption spectrum of the reaction mixture just after heating is the same as that in CH_3CN. The steady-state approximation to *I gives eq 4, where the branching ratio $k_b/(k_{-a}$

$$k_1 = k_a \frac{k_b}{k_{-a} + k_b} \qquad (4)$$

$+ k_b)$ is the probability for the accomplishment of the exchange from *I, and its value can be estimated from the analysis of the deuterium isotope effect in our previous paper.[4b,11] The analysis is based on the reasonable assumptions that only k_b is subject to the effect and that $k_b(H)/k_b(D) \simeq 9$. The modest value of $k_1(H)/k_1(D)$ in the present system as compared with those in $Sc(acac)_3$ (ca. 5),[11] $In(acac)_3$ (ca. 5),[4c] and $Th(acac)_4$ (9)[12] systems indicates that $k_b/(k_{-a} + k_b)$ is very close to unity (0.9) and hence $k_b \simeq 10k_{-a}$. We can thus conclude that $k_a \ll k_{-a} \ll k_b$ and that the first substitution step is substantially rate-determining and

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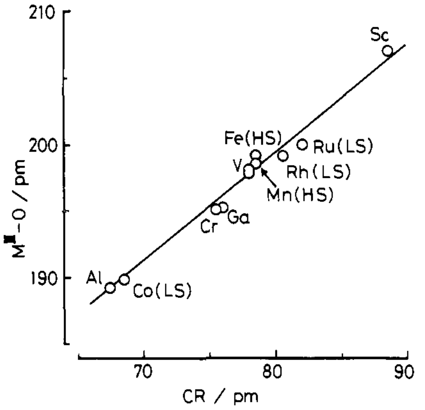

Figure 2. Linear relationship between averaged M^{III}–O distances of $M^{III}(acac)_3$ complexes[15] and the crystal radii (CR)[13] of M^{III} in coordination number 6. HS = high spin; LS = low spin.

responsible for the activation parameters.

Ligand Substitution Mechanism. The negative $\Delta S^{\ddagger}$ value and the rate dependence on [Hacac] indicate the I_a mechanism for the k_a step, comparable with that for other $M^{III}(acac)_3$ complexes (Table II), for which the mechanisms were previously assigned by independent comparison of kinetic parameters within each M^{III}.[4b,c] Since the ionic radius of Tc^{III} has not been given, we estimated it to be ca. 84 pm as the crystal radius (CR)[13] of coordination number (CN) 6 by interpolating the averaged Tc^{III}–O distance in $^{99}Tc^{III}(acac)_3$, which was kindly supplied by Hashimoto and Omori as 202.5 pm,[14] to a linear relationship between the averaged M^{III}–O distance of $M^{III}(acac)_3$[15] and the CR of M^{III} in CN 6 (Figure 2). The estimated radius is regarded to be sufficiently large to accept an incoming ligand as a seventh one in the activated state.[4b,c]

Comparison with Related Reactions. The linear free energy relationship (LFER) between k_1 of the present exchange system and the first-order rate constant of the exchange and/or anations of the aqua complexes $[M^{III}L_5(H_2O)]^{3+}$ (L = H_2O or NH_3) for various metal ions (M = Al, Sc, V, Cr, Mn, Fe, Co, Ga, Mo, Ru, Rh, In)[4c] suggests the constant for Tc^{III}–aqua complexes to be most probably 10^{-5} s^{-1} at 298 K.

The present k_1 is closest to that of Cr^{III} (Table II). This fact and the LFER indicate that the lability of Tc^{III} complexes of these types is close to that of Cr^{III} complexes. This will be a helpful standard when a new Tc^{III} complex is going to be prepared from a known Tc^{III} complex by the "substitution route".[1] $Tc(acac)_3$ could be a good starting material for the preparation of some aqua complexes, as is $Cr(acac)_3$, which affords *cis*- and *trans*-$[Cr(acac)_2(H_2O)_2]^+$, $[Cr(acac)(H_2O)_4]^{2+}$, and $[Cr(H_2O)_6]^{3+}$.[16]

When k_1 values are compared within the second transition series (Table I), the order of lability

$$\underset{d^3}{Mo^{III}} \gg \underset{d^4,LS}{Tc^{III}} > \underset{d^5,LS}{Ru^{III}} > \underset{d^6,LS}{Rh^{III}}$$

is obtained. For the first transition series, the order of lability for the cyanide exchange of $[M^{III}(CN)_6]^{3+}$ in aqueous solution was reported[17] as

$$\underset{d^4,LS}{Mn^{III}} \gg \underset{d^3}{Cr^{III}} > \underset{d^5,LS}{Fe^{III}} \sim \underset{d^6,LS}{Co^{III}}$$

and interpreted in terms of the crystal field activation energy (CFAE) for the octahedral wedge activated complex.[18,19] It is noteworthy that the present system inverts d^3 and d^4,LS. It is attributable to the difference in the ligand or in the transition series. The present order of lability conflicts with the theoretical indication for the octahedral wedge based on the CFAE and the ligand field activation energy (LFAE)[20] but is consistent qualitatively with that for the pentagonal-bipyramid (PBP) activated complex obtained by the LFAE calculation,[20] Mo ≫ Tc ~ Ru ~ Rh. Larger M^{III} in the second transition series than those in the first may form preferably PBP complexes rather than the octahedral wedge activated complexes. Extended calculations are in progress.

The rate and the activation parameters of the aquation of $[Tc^{IV}Cl_6]^{2-}$ in acidic aqueous media,[21] the rates of the base hydrolysis of $[Tc^{IV}Cl_2(acac)_2]$ in aqueous acetonitrile in the course of the decomposition to pertechnetate[22] and the solvolysis of *cis*-$[Tc^{V}O(8\text{-quinolinolate})_2Cl]$ in methanol,[23] and the spectral changes associated with the ligand substitution of a few $[Tc^{V}O(OCH_2CH_2O)_2]^-$-type complexes with 1,2-dithiols in methanol[24] were reported. However, more information is necessary to know the effect of the oxidation state of Tc on the lability.

In conclusion, Tc^{III} is found for the first time to have a lability very close to that of Cr^{III} and to undergo I_a ligand substitution. The order of lability for M^{III} of the second transition series and with d^3 to d^6 configurations (low spin) is first defined: $Mo^{III} \gg Tc^{III} > Ru^{III} > Rh^{III}$.

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