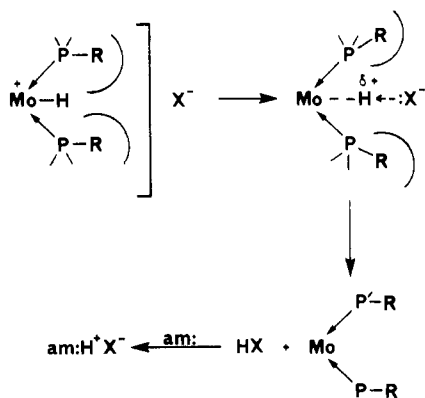


Scheme I



For the neutral amine bases, the rates of deprotonation of $\text{HMo}(\text{CO})_2(\text{P}^-\text{P})_2^+$ are primarily dependent on the size, suggesting that the outer ligand sphere must undergo some rearrangement for the amine lone pair to contact the proton (as in $[\text{Mo}-\text{H}^+\cdots\text{N}]$). There is a marked enhancement of proton transfer to the amine bases in the presence of X^- carriers. The kinetic expression for these mixed-base systems shows no dependence on $[\text{N}]$, but it does depend on $[\text{X}^-]$.

There is a complex dependence on the P^-P ligand involving both steric and electronic factors. The steric environment is reduced in going from 1H^+ to 2H^+ , and this is reflected in the difference in the rate of deprotonation using the strong bulky base DBU. With a smaller base of intermediate strength, py, the electronic factors dominate and the deprotonation of 1H^+ (the stronger acid) is faster than for 2H^+ .

In addition to all the above factors affecting the metalloacid deprotonation rates, solvent dependence is important. The rate

of deprotonation of 1H^+ , using py/ Cl^- , depends on the solvent and varies as $\text{CH}_2\text{Cl}_2 < \text{Me}_2\text{SO} < \text{acetone} < \text{THF}$, spanning a range of at least 2 orders of magnitude. Since the solvent that solvates Cl^- the least produces the fastest rate, we assume this solvation effect to be due to ion-pairing interactions, which vary from solvent to solvent. Jordan and Norton¹¹ found only a small solvent effect, a factor of 2 between CD_3CN and $\text{THF}-d_8$, for the proton-exchange rate between $\text{CpM}(\text{CO})_3\text{H}$ and $\text{K}[\text{CpM}(\text{CO})_3]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) without the presence of any added small anion carriers.

We suggest that the proton-transfer mechanism of the metalloacids, $\text{HMo}(\text{CO})_2(\text{P}^-\text{P})_2^+$, in nonaqueous solvents, has been defined by several probes and that the events are well modeled by Scheme I. An electrostatic interaction of anion with cation precedes coordination sphere rearrangement (in this case most likely a motion of the R substituents on P or an opening of the angle of the P-Mo-P that envelops the Mo-H site) to permit optimum X^- interaction with the acid ($\text{Mo}^{\delta+}-\text{H}$) site. The polarization of Mo-H bond density required for loss of hydrogen as H^+ is proposed to occur in a linear transition state that has less metal-hydrogen bond breaking than hydrogen-anion bond making. The X^- ion then serves to carry out the proton to its thermodynamic sink, the amine base. The slow rates of these reactions (as compared to orders of magnitude more rapid rates of metalloacids such as $\text{CpM}(\text{CO})_3\text{H}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), for example¹¹) is, in our view, highly indicative of the large steric encumbrances in $\text{HMo}(\text{CO})_2(\text{P}^-\text{P})_2^+$.

Acknowledgment. This work was supported by the Robert A. Welch Foundation. Appreciation is expressed to Dr. J. M. Hanchel, who initiated this project.

Registry No. 1H^+ , 63765-16-2; 2H^+ , 102735-00-2; 3H^+ , 94241-76-6; py, 110-86-1; NEt_3 , 121-44-8; DBU, 6674-22-2; Cl^- , 16887-00-6; I^- , 20461-54-5; Br^- , 24959-67-9; OAc^- , 71-50-1; F^- , 16984-48-8; D_2 , 7782-39-0.

Notes

Contribution from the Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya, 464 Japan

Mechanistic Study on the Complex Formation of Aluminum(III), Gallium(III), and Indium(III) Ions in Dimethyl Sulfoxide and *N,N*-Dimethylformamide

Koji Ishihara, Shigenobu Funahashi, and Motoharu Tanaka*

Received November 26, 1985

We have measured the activation volumes for the complexation of iron(III) and nickel(II) ions in aqueous and nonaqueous media.^{1,2} The activation volume for complexation of Ni(II) ion is invariably positive, and it does not largely vary with different solvents, so that the mechanism of the ion remains unchanged within the framework of a dissociative interchange in any solvent. On the other hand, in the case of Fe(III) ion, for which the complexation has been proved to proceed via an associative mode of activation in water, the activation volume does vary to a large extent with entering ligands and coordinated solvents. We have concluded, from these findings, that the bulkiness of reactants is reflected to a larger extent in the activation volume for the complexation with an associative character in water than for the complexation with a dissociative character in aqueous solution.

We report in this paper a study on the high-pressure kinetics of the complex formation of aluminum(III), gallium(III), and

indium(III) ions in Me_2SO in order to understand more thoroughly the effect of the steric bulkiness of reactants and solvents on the reaction mechanism. Al(III), Ga(III), and In(III) ions with isoelectronic configurations in the same column of the periodic table were chosen because we expect to investigate selectively a size effect of metal ions on complexation.

Experimental Section

Due care was given to moisture and explosion of perchlorates.

Solvents. Dimethyl sulfoxide (Me_2SO) and *N,N*-dimethylformamide (DMF) were purified as described previously² and were used within a couple of days after purification.

Reagents. Hydrated Aluminum(III) Perchlorate. A 13-g sample of aluminum (99.99%, Wako Junyaku, Osaka, Japan) was dissolved in 200 cm^3 of 60% HClO_4 (Super Special grade, Wako Junyaku) diluted with 150 cm^3 of distilled water. Concentration of the solution by gentle evaporation yielded hydrated salts.

Hydrated Gallium(III) Perchlorate. A 7-g portion of shot-shaped gallium (99.99%, Wako Junyaku) was dissolved in a 100 cm^3 of 60% HClO_4 by gentle heating.

Hydrated Indium(III) Perchlorate. A 1-g portion of shot-shaped indium (99.98%, Wako Junyaku) in limited amounts was added to 50 g of 60% HClO_4 without heating. *Caution!* Indium dissolves in HClO_4 with vigorous heat evolution. The resultant crystals were recrystallized three times from 60% HClO_4 .

The hydrated salts of Al(III), Ga(III), and In(III) were dried at room temperature under vacuum just before they were converted to the corresponding Me_2SO and DMF salts.

$[\text{Al}(\text{Me}_2\text{SO})_6](\text{ClO}_4)_3$. A 100- cm^3 portion of triethyl orthoformate was poured into the Erlenmeyer flask containing 25 cm^3 of ethanolic solution of hydrated aluminum(III) perchlorate. Under nitrogen atmosphere the solution was stirred for 2 h, and then 10 cm^3 of fresh Me_2SO was added dropwise. Crystals of Me_2SO solvate of aluminum(III) perchlorate were

(1) Ishihara, K.; Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1983**, *22*, 2564.
(2) Ishihara, K.; Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1983**, *22*, 3589.

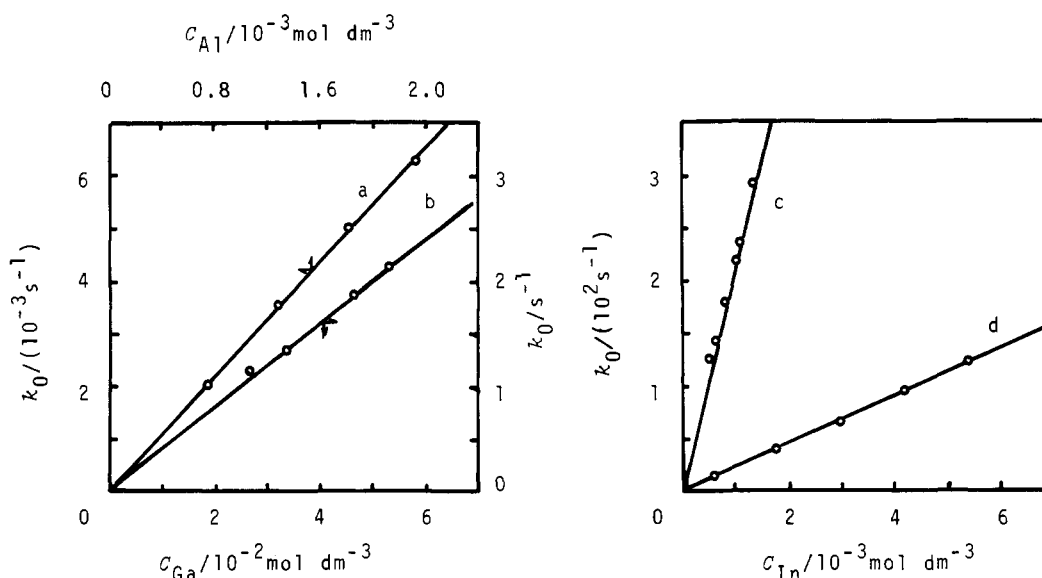


Figure 1. Concentration dependence of the conditional first-order rate constants k_0 . (a) For Al(III) in Me_2SO at 40 °C: $[\text{Hipt}] = 1.16 \times 10^{-4}$ mol dm^{-3} , $[\text{NaClO}_4] = 0.182$ mol dm^{-3} . (b) For Ga(III) in Me_2SO at 35 °C: $[\text{Hipt}] = 3.14 \times 10^{-5}$ mol dm^{-3} , $[\text{NaClO}_4] = 0.158$ mol dm^{-3} . (c) For In(III) in Me_2SO at 24.5 °C: $[\text{Hipt}] = 1.80 \times 10^{-5}$ mol dm^{-3} , $[\text{NaClO}_4] = 4.9 \times 10^{-2}$ mol dm^{-3} . (d) For In(III) in DMF at 16 °C: $[\text{Hipt}] = 3.14 \times 10^{-5}$ mol dm^{-3} , $[\text{NaClO}_4] = 4.93 \times 10^{-2}$ mol dm^{-3} .

Table I. Activation Parameters for Complexation of Al(III), Ga(III), and In(III) Ions with 4-Isopropyltropolone in Me_2SO and DMF

M(III)	$k(25\text{ °C})/\text{mol}^{-1}\text{ dm}^3\text{ s}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1}\text{ K}^{-1}$	$\Delta V^\ddagger/\text{cm}^3\text{ mol}^{-1}$
In Me_2SO				
Al(III)	2.2×10^{-1}	82.3 ± 1.5	18.5 ± 5.0	12.2 ± 1.0 (40 °C)
Ga(III)	3.7×10	74.2 ± 1.6	33.8 ± 5.4	10.6 ± 0.6 (35 °C)
In(III)	1.9×10^4	36.7 ± 0.8	-39.8 ± 2.5	-0.1 ± 0.6 (35 °C)
In DMF				
In(III)	3.5×10^5	36.1 ± 2.4	-17.7 ± 8.1	0.3 ± 0.3 (16 °C)

precipitated by adding diethyl ether. The precipitate was repeatedly washed with diethyl ether.

$[\text{Ga}(\text{Me}_2\text{SO})_6(\text{ClO}_4)_3$ and $[\text{In}(\text{Me}_2\text{SO})_6(\text{ClO}_4)_3]$. When fresh Me_2SO was added to the acetone solution of the hexaaquametal perchlorate ($[\text{Ga}(\text{H}_2\text{O})_6(\text{ClO}_4)_3$ or $[\text{In}(\text{H}_2\text{O})_6(\text{ClO}_4)_3]$), precipitates appeared. The crystals were collected on a G3 glass filter and were recrystallized from Me_2SO solution by adding acetone, washed with hot acetone several times, and dried under vacuum at room temperature.

$[\text{M}(\text{DMF})_6(\text{ClO}_4)_3]$ (M = Al, Ga, In). About a 6-fold excess of DMF over the metal ion was added to the acetone solution of the hydrated salt, and then about a 10-fold excess of diethyl ether was poured into this solution under vigorous stirring. In the case of both Al(III) and Ga(III), a greaselike substance was obtained. After decantation enough DMF was added to dissolve this substance. Addition of diethyl ether produced white powder. Finally, recrystallization from a mixture DMF/diethyl ether (1/10) yielded fine crystals. In the case of In(III), after the phase separation had occurred, the upper diethyl ether layer was discarded by decantation, and then the lower layer was washed with diethyl ether several times until a white powder appeared. The powder turned to fine crystals by recrystallization from a 1/10 DMF/diethyl ether mixture.

The Me_2SO and DMF solvates of metal(III) perchlorates obtained above were kept under reduced pressure at room temperature, and their solutions were prepared under an atmosphere of dry nitrogen. The composition of these complexes was confirmed to be that of a hexakis-(solvento)metal(III) perchlorate by the EDTA titration of metal ions.

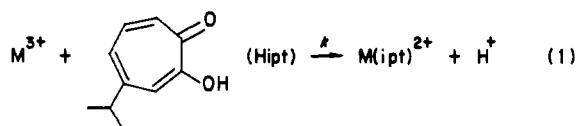
4-Isopropyltropolone (Hipt) was purified by sublimation. Anhydrous sodium perchlorate was prepared by drying the hydrated salt at 100 °C under reduced pressure.

Measurements and Results

Under pseudo-first-order conditions with a large excess of metal ion over the ligand, reactions were followed spectrophotometrically at the wavelength of maximum absorption of the 1/1 complex (375 nm for Al(III) and 378 nm for Ga(III) and In(III)) by the use of a high-pressure stopped-flow apparatus (Type FIT-3).³ The

temperature was controlled to within ± 0.1 °C. It is possible to apply pressure up to 200 MPa. The applied pressure for Me_2SO was restricted by freezing of Me_2SO (Me_2SO freezes at about 120 MPa at 35 °C). All solutions involved a constant concentration of sodium perchlorate.

Pseudo-first-order plots showed good linearity in all systems. As shown in Figure 1, for four reaction systems plots of the conditional first-order rate constant (k_0) against the excess metal ion concentration (C_M) gave straight lines without intercepts. This means that the reverse reaction, i.e., dissociation reaction of the 1/1 complex ($\text{M}(\text{ipt})^{2+}$), is negligible. The studied reaction is expressed by eq 1, where M^{3+} refers to Al^{3+} , Ga^{3+} , or In^{3+} . The



rate law is given by eq 2. The plot of conditional first-order rate

$$d[\text{M}(\text{ipt})^{2+}]/dt = k[\text{M}^{3+}][\text{Hipt}] \quad (2)$$

constant for the reaction of Al(III) and Ga(III) ions with Hipt in DMF vs. metal ion concentration showed a linear relation with an intercept under our experimental conditions. These facts mean that in these reaction systems the reverse reaction cannot be neglected and that the proton released during the reaction would contribute complexity to the reaction. Therefore, we did not carry out further studies on these systems.⁴ The proton released by chelation should not appreciably affect the reaction because of negligible dissociation of the 1/1 complex in the systems except

(3) Ishihara, K.; Funahashi, S.; Tanaka, M. *Rev. Sci. Instrum.* **1982**, *53*, 1231.

(4) We did not vary the hydrogen ion concentration. It does not seem simple to see the effect of H^+ concentration in aprotic solvents such as DMF and Me_2SO .

Table II. Activation Volumes for Ligand Substitution of Trivalent Metal Ions in Water, Me₂SO, and DMF

M(III)	ionic radius ^a r/pm	in H ₂ O		in Me ₂ SO		in DMF	
		Hipt	H ₂ O	Hipt	Me ₂ SO	Hipt	DMF
Al(III)	51		5.7 ± 0.2 ^b	12.2 ± 1.0	15.6 ± 1.4 ^c		13.7 ± 1.2 ^c
Ga(III)	62	4.0 ± 1.3 ^d		10.6 ± 0.6	13.1 ± 1.0 ^c		7.9 ± 1.6 ^c
In(III)	81			-0.1 ± 0.6		0.3 ± 0.3	
Fe(III)	64	-8.7 ± 0.8 ^e	-5.4 ± 0.4 ^f	10.9 ± 1.7 ^g	-3.1 ± 0.3 ^h	5.0 ± 0.4 ^g	-0.9 ± 0.2 ^h

^aWeast, R. C., Ed. *Handbook of Chemistry and Physics*, 60th ed.; CRC: Boca Raton, FL, 1979. ^bReference 9. ^cReference 6. ^dTropolone instead of Hipt was used as a ligand. Reference 8. ^eReference 10. ^fSwaddle, T. W.; Merbach, A. E. *Inorg. Chem.* **1981**, *20*, 4212. ^gReference 2. ^hMeyer, F. K.; Monnert, A. R.; Newman, K. E.; Merbach, A. E. *Inorg. Chem.* **1982**, *21*, 774.

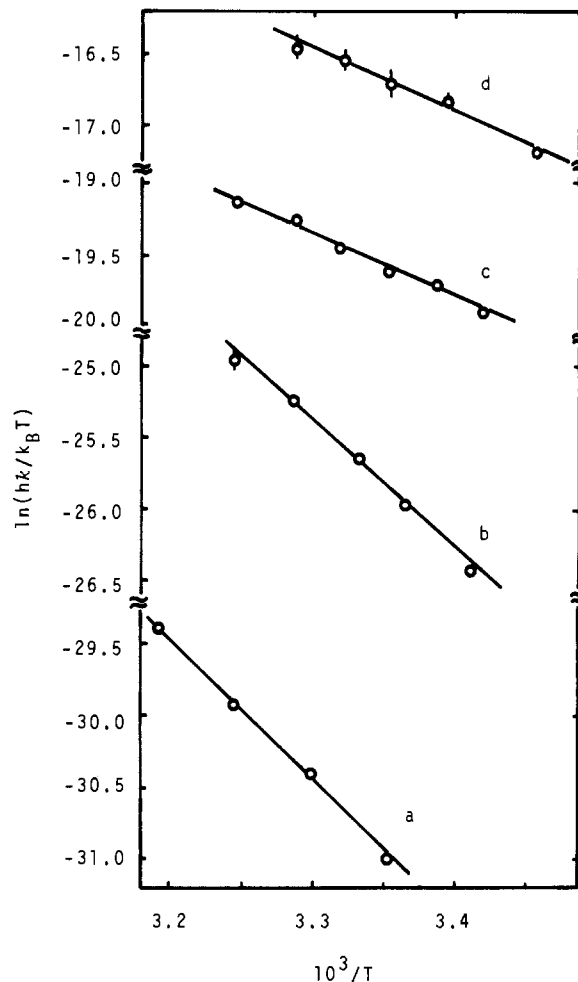


Figure 2. Temperature dependence of the second-order rate constant k . (a) For Al(III) in Me₂SO: [Al(ClO₄)₃] = 4.10 × 10⁻³ mol dm⁻³, [Hipt] = 1.62 × 10⁻⁴ mol dm⁻³, [NaClO₄] = 0.179 mol dm⁻³. (b) For Ga(III) in Me₂SO: [Ga(ClO₄)₃] = 1.87 × 10⁻² mol dm⁻³, [Hipt] = 3.14 × 10⁻⁵ mol dm⁻³, [NaClO₄] = 0.158 mol dm⁻³. (c) For In(III) in Me₂SO: [In(ClO₄)₃] = 1.83 × 10⁻³ mol dm⁻³, [Hipt] = 3.33 × 10⁻⁵ mol dm⁻³, [NaClO₄] = 5.23 × 10⁻² mol dm⁻³. (d) For In(III) in DMF: [In(ClO₄)₃] = 6.91 × 10⁻⁴ mol dm⁻³, [Hipt] = 3.14 × 10⁻⁵ mol dm⁻³, [NaClO₄] = 4.93 × 10⁻² mol dm⁻³.

for those of Al(III) and Ga(III) in DMF.⁵

The second-order rate constant, k , was obtained at various temperatures (Table SI in supplementary material). The variable-temperature results were fitted to the equation $\ln(hk/k_B T)$

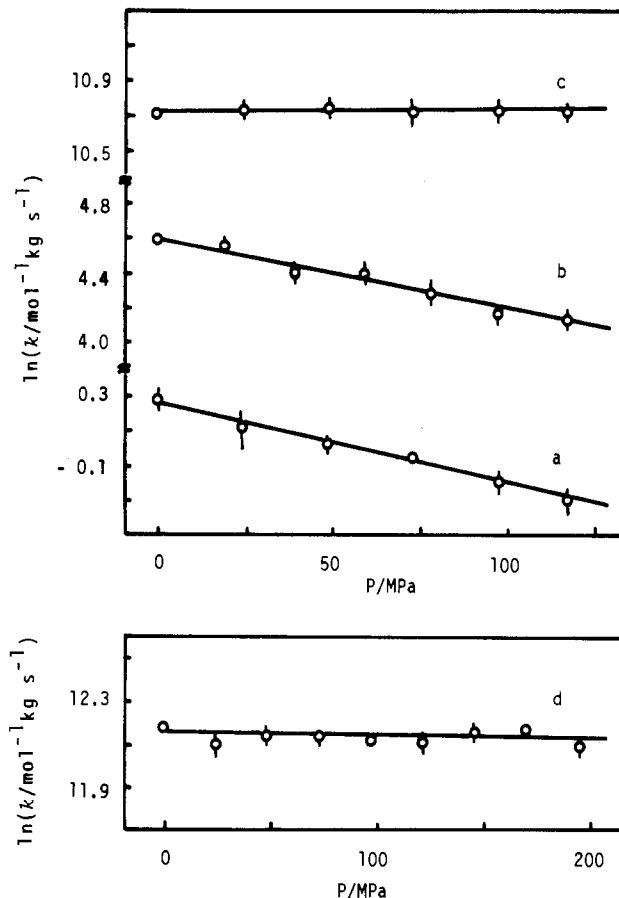


Figure 3. Pressure dependence of the second-order rate constant k . (a) For Al(III) in Me₂SO at 40 °C: [Al(ClO₄)₃] = 3.75 × 10⁻³ mol kg⁻¹, [Hipt] = 1.08 × 10⁻⁴ mol kg⁻¹, [NaClO₄] = 0.169 mol kg⁻¹. (b) For Ga(III) in Me₂SO at 35 °C: [Ga(ClO₄)₃] = 1.74 × 10⁻² and 1.99 × 10⁻² mol kg⁻¹, [Hipt] = 2.90 × 10⁻⁵ mol kg⁻¹, [NaClO₄] = 0.147 mol kg⁻¹. (c) For In(III) in Me₂SO at 35 °C: [In(ClO₄)₃] = 7.50 × 10⁻⁴ and 1.25 × 10⁻³ mol kg⁻¹, [Hipt] = 2.25 × 10⁻⁵ mol kg⁻¹, [NaClO₄] = 4.54 × 10⁻² mol kg⁻¹. (d) For In(III) in DMF at 16 °C: [In(ClO₄)₃] = 6.03 × 10⁻⁴ and 8.03 × 10⁻⁴ mol kg⁻¹, [Hipt] = 3.47 × 10⁻⁵ mol kg⁻¹, [NaClO₄] = 5.40 × 10⁻² mol kg⁻¹. Each point is the average of several determinations.

= $-\Delta H^\ddagger/RT + \Delta S^\ddagger/R$, as shown in Figure 2. Values of activation enthalpy and entropy are summarized in Table I.

Second-order rate constants, determined at various pressures, are given in Table SII (supplementary material). Activation volumes were obtained by applying the least-squares method to plots of $\ln k$ vs. P (illustrated in Figure 3), since the plots were linear within an experimental error, i.e., activation volumes were independent of pressure. The obtained values of activation volume are collected in Table II together with available volumes of activation for complexation in aqueous solution and for solvent exchange.

Discussion

The enthalpies of activation for complexation of Al(III) and Ga(III) ions in Me₂SO are very close to those for the corresponding solvent exchange (82.6 ± 1.2 and 72.5 ± 0.5 kJ mol⁻¹).⁶

(5) Absorption spectra (250–450 nm) of Hipt are the same for all of Me₂SO, DMF, CH₃OH, and CH₃CN solutions. Me₂SO is much more basic than acetonitrile (Barrette, W. C., Jr.; Johnson, H. W., Jr.; Sawyer, D. T. *Anal. Chem.* **1984**, *56*, 1890). Me₂SO is sufficiently basic to absorb the low concentration (at most 2 × 10⁻⁴ mol dm⁻³) of protons released from the free acid Hipt as the complexation reaction proceeds. The rate was not influenced by concentration variation of sodium perchlorate (0.01–0.5 mol dm⁻³). The absence of any salt effect is consistent with Hipt reacting as a noncharged species.

This fact implies that processes of deprotonation and ring closure of Hipt in the complexation would not be rate-determining. If such processes as deprotonation and/or ring closure are rate-limiting, values of activation parameters are expected to be almost the same regardless of the kind of metal ions. But this is not the case. Here, the reaction of the M^{3+} ion with the entering ligand (Hipt) is represented by eq 3, where K_{os} is the formation



constant of the outer-sphere complex ($M^{3+} \cdots \text{Hipt}$). Interchange of one of coordinated solvents with an entering ligand on the outer-sphere complex should be the rate-limiting step. Thus, the observed second-order rate constant k is given by the product of K_{os} and the first-order rate constant k^* ($K_{os}k^*$), and then the observed volume of activation ΔV^* is given as the sum of ΔV_{os}° and ΔV^{**} , which are the volume change for the first step and the activation volume for the second step, respectively. Usually, ΔV^{**} is split into two terms, ΔV_{intr}^{**} and ΔV_{sol}^{**} . ΔV_{intr}^{**} is an intrinsic volume change, i.e., the change in partial molar volume caused by lengthening of a metal-solvent bond and by partial formation of an entering ligand-metal bond, which is accompanied by a solvational volume change, ΔV_{sol}^{**} . However, since Hipt has no formal charge, its dipole, if any, may be small, ΔV_{os}° and ΔV_{sol}^{**} may not be large,⁷ and they may not differ much for the trivalent metal ions studied in this paper. Therefore, we think that the obtained values of activation volume reflect the intrinsic volume change for the complex formation.

It is noteworthy that the values of activation volume for complexation of Ga(III) and Fe(III) ions in water are quite different (4.0 and $-8.7 \text{ cm}^3 \text{ mol}^{-1}$, respectively), while those in Me_2SO are quite similar to each other ($\Delta V^*/\text{cm}^3 \text{ mol}^{-1}$: 10.6 for Ga(III), 10.9 for Fe(III)). The entering ligand Hipt is neutral, the charge on both metal ions is +3, and their ionic radii are close to each other ($r(\text{Ga(III)}) = 62 \text{ pm}$; $r(\text{Fe(III)}) = 64 \text{ pm}$). Thus, this coincidence of the ΔV^* values would indicate that in Me_2SO their transition states should be geometrically very similar and that the intimate mechanism should be dissociative interchange (I_d) for both Ga(III) and Fe(III) ions.

In a less bulky solvent, i.e. water, both the complexation and solvent exchange at Fe(III) ion exhibit negative values of ΔV^* , which are usually interpreted in terms of associative-interchange (I_a) mechanisms.² Thus the reaction may take place as if the metal-solvent bond was compelled to dissociate by the attack of an incoming ligand on the inner sphere of the metal ion. In bulkier solvents such as DMF and Me_2SO , we would expect a coordinated solvent to be forced to abandon partly the inner sphere of the metal ion, when an entering ligand starts to coordinate. Therefore, activation volumes for the Fe(III) ion largely vary depending on steric bulkiness of ligands and solvents.²

On the other hand, we have already demonstrated that in water the Ga(III) ion reacts through an I_d mechanism.⁸ More recently the mechanism of the water exchange on $\text{Al}(\text{H}_2\text{O})_6^{3+}$ has been demonstrated to be dissociative interchange.⁹ For metal ions like Al(III) and Ga(III) ions, which react via a dissociative-interchange mechanism even in water, it is easy to dissociate the solvent molecule by a collision of reactants, so that the activation volumes vary to a lesser extent with bulkiness of ligands and solvents.

CPK models reveal that coordinated Me_2SO and DMF molecules shield the central metal ion more effectively than water and that Me_2SO molecules in the inner sphere would block the attack of an entering ligand more tightly than DMF. Such a situation has been confirmed, in the iron(III) system, by the fact that the activation volume for complexation of the iron(III) ion with Hipt increases with increasing bulkiness of coordinated solvent

molecules: $-8.7 \text{ cm}^3 \text{ mol}^{-1}$ for water,¹⁰ $5.0 \text{ cm}^3 \text{ mol}^{-1}$ for DMF,² and $10.9 \text{ cm}^3 \text{ mol}^{-1}$ for Me_2SO (see Table II). However, this is not the case for the In(III) system: the activation volumes for In(III) complexation are almost the same in both Me_2SO and DMF. This implies that the In(III) ion having a larger ionic radius than Fe(III) would be crowded to a similar extent with coordinated Me_2SO and DMF molecules.

The negative volume of activation for solvent exchange on the Fe(III) ion in Me_2SO and DMF indicates that the associative character is still maintained in these solvents. The activation volumes for complexation with Hipt in Me_2SO and DMF are more positive than the respective volume of activation for solvent exchange. It has been concluded that Hipt should be bulkier than Me_2SO and DMF as entering ligands. But this is not the case for Ga(III) complexation in Me_2SO . Since Ga(III) has an intimate dissociative character in water as described above, the activation volume varies to a lesser extent with different solvents.

As generally expected, the rate is higher for large metal ions (Table I). As is obvious from Table I, on going from Al(III) to Ga(III) to In(III) the activation volume for complexation in Me_2SO decreases. Larger metal ions tend to accept more easily an entering ligand: the larger the ionic radius, the less dissociative the mechanism. Quite similarly, the less bulky the solvent, the less dissociative the activation process. When we compare ions with isoelectronic configurations in the same column of the periodic table, the dissociative character of complex formation in a given solvent should decrease, as the activation enthalpy decreases, on going down the column.

Acknowledgment. Financial support from the Ministry of Education, Science, and Culture through a Grant-in-Aid for Scientific Research (No. 59430010) and a Grant-in-Aid for Special Project Research (No. 60129031) is gratefully acknowledged.

Registry No. $[\text{Al}(\text{Me}_2\text{SO})_6](\text{ClO}_4)_3$, 16788-31-1; $[\text{Ga}(\text{Me}_2\text{SO})_6](\text{ClO}_4)_3$, 29519-19-5; $[\text{In}(\text{Me}_2\text{SO})_6](\text{ClO}_4)_3$, 58528-07-7; $[\text{Al}(\text{DMF})_6](\text{ClO}_4)_3$, 16040-05-4; $[\text{Ga}(\text{DMF})_6](\text{ClO}_4)_3$, 51921-91-6; $[\text{In}(\text{DMF})_6](\text{ClO}_4)_3$, 13927-82-7; Al, 7429-90-5; Ga, 7440-55-3; In, 7440-74-6; 4-isopropyltropolone, 499-44-5.

Supplementary Material Available: Listings of numerical data of rate constants at various temperatures (Table SI) and at various pressures (Table SII) (6 pages). Ordering information is given on any current masthead page.

(10) Ishihara, K.; Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1983**, *22*, 194.

Contribution from the Ministero della Pubblica Istruzione of Italy, Dipartimento di Chimica, University of Modena, 41100 Modena, Italy, Istituto di Chimica Generale e Inorganica, Centro di Studi per la Strutturistica Diffraattometrica del CNR, University of Parma, 43100 Parma, Italy, and Istituto di Chimica, Facoltà di Medicina Veterinaria, University of Bari, 70126 Bari, Italy

Tridentate Facially Coordinated L-Aspartate Ion Complexation with the Copper(II) Ion: Spectroscopic and Structural Properties of Aqua(L-aspartato)(1,10-phenanthroline)copper(II) Tetrahydrate

L. Antolini,^{1a} L. P. Battaglia,^{1b} A. Bonamartini Corradi,^{1b} G. Marcotrigiano,^{1c} L. Menabue,^{*1a} G. C. Pellacani,^{1a} M. Saladini,^{1a} and M. Sola^{1a}

Received January 17, 1986

In solid complexes of copper(II) and aspartate of glutamate ions, thus far studied crystallographically, polymeric chain

(6) Ammann, C.; Moore, P.; Merbach, A. E.; McAteer, C. H. *Helv. Chim. Acta* **1980**, *63*, 268.

(7) Hemmes, P. *J. Phys. Chem.* **1972**, *76*, 895.

(8) Yamada, S.; Iwanaga, A.; Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1984**, *23*, 3528.

(9) Hugi-Cleary, D.; Helm, L.; Merbach, A. E. *Helv. Chim. Acta* **1985**, *68*, 545.