

of small segments to estimate instantaneous rates of free-radical production during the flash. This analysis was coupled with solutions<sup>20</sup> of the differential rate laws for  $-d[\text{PhCH}_2\cdot]/dt$  and  $d[\text{CrCH}_2\text{Ph}^{2+}]/dt$  to calculate the "initial" value of  $[\text{PhCH}_2\cdot]$  at the time taken as  $t = 0$  in eq 6. This too was done iteratively, the calculation being reported for refined values of  $k_{\text{Cr}}$ . Although not a rigorous solution to the problem, it is adequate for the case at hand since quite minor adjustments in  $[\text{PhCH}_2\cdot]_0$  resulted.

The determination of  $k_{\text{Cr}}$  itself was made on the basis of eq 6, comparing observed and calculated values of  $\Delta[\text{CrCH}_2\text{Ph}^{2+}]_\infty$  in numerous experiments at various  $[\text{Cr}^{2+}]_{\text{av}}$  and  $[\text{PhCH}_2\cdot]_0$ . The success of the procedure is illustrated by the comparison shown in Figure 1. The "best fit" value cited for  $k_{\text{Cr}}$  and an assessment of its precision were found by visual matching.

**Kinetic Spectrophotometry Using Dibenzyl Ketone.** The ketone, characterized by an absorption maximum at 295 nm ( $\epsilon$  220 M<sup>-1</sup> cm<sup>-1</sup>), undergoes photolysis according to eq 4 and 5.<sup>15</sup> Under the conditions used (0.5 mM  $(\text{PhCH}_2)_2\text{CO}$  in 2 M aqueous acetonitrile, 0.05 M  $\text{HClO}_4$  at ionic strength 0.10 M with  $(0.8-4.0) \times 10^{-4}$  M  $\text{Cr}^{2+}$ ),  $[\text{PhCH}_2\cdot]_0$  is estimated to be ca.  $6 \times 10^{-5}$  M. The reaction rate was followed by monitoring the progress of the reaction at 364 nm where  $\text{CrCH}_2\text{Ph}^{2+}$  is the only high-absorbing species present. The evaluation of  $k_{\text{Cr}}$  from the rate law  $d[\text{CrCH}_2\text{Ph}^{2+}]/dt = k_{\text{Cr}}[\text{Cr}^{2+}][\text{PhCH}_2\cdot]$  is, however, not simply a matter of a pseudo-first-order analysis because dimerization of the organic radical also defines  $[\text{PhCH}_2\cdot]$  at any time during the run. The "kinetic observable" thus obeys parallel pseudo-first-order and second-order rate equations, the analysis of which over the entire course of a reaction is complicated in the present

instance by the large uncertainty in  $[\text{PhCH}_2\cdot]_0$ <sup>21</sup> and by the accessible range of  $[\text{Cr}^{2+}]$ . Thus, a modified procedure was adopted. Sufficiently late in the progress of any run, the condition  $[\text{Cr}^{2+}] \gg [\text{PhCH}_2\cdot]$ , will eventually prevail; consequently, the rate of the second-order dimerization reaction will become much smaller than that of the pseudo-first-order component. In practice, only absorbance-time values in the very last segment (with only 2-10% of reaction remaining, depending on the conditions in each run) were used in the kinetic analysis. This subset of the data, analyzed according to standard pseudo-first-order kinetics, yielded a value of  $k_{\text{obsd}}$  that varied linearly with  $[\text{Cr}^{2+}]$ . (The latter was, of course, essentially the value of  $[\text{Cr}^{2+}]$  near the end of the run.) The use of the amplification features of the digitizing oscilloscope was important in acquiring the kinetic data.

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**Registry No.**  $(\text{H}_2\text{O})_3\text{CrCH}_2\text{Ph}^{2+}$ , 34788-74-4;  $(\text{PhCH}_2)_2\text{CO}$ , 102-04-5;  $\text{PhCH}_2\text{Br}$ , 100-39-0;  $\text{Cr}(\text{ClO}_4)_2$ , 13931-95-8;  $\text{Cr}^{2+}$ , 22541-79-3;  $\text{PhCH}_2\cdot$ , 2154-56-5.

(21) The direct determination of  $[\text{PhCH}_2\cdot]_0$  is complicated by the occurrence of reaction 1 during the flash. The formation of highly absorbing  $(\text{H}_2\text{O})_3\text{CrCH}_2\text{Ph}^{2+}$  causes the amount of 290-nm light available to  $(\text{PhCH}_2)_2\text{CO}$  to decrease with time.

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## Kinetics and Mechanism of the Complexation Reaction of Gallium(III) with Tropolone As Studied by a High-Pressure Stopped-Flow Technique. Evidence for a Dissociative-Interchange Mechanism

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The formation kinetics of the 1:1 gallium(III) complex with tropolone (HL) in acidic aqueous media has been studied spectrophotometrically at various temperatures and pressures by means of a stopped-flow technique. The rate law is expressed as  $d[\text{GaL}^{2+}]/dt = (k_{\text{Ga}} + k_{\text{GaOH}}K_{\text{GaOH}}[\text{H}^+]^{-1})(1 + K_{\text{HL}}[\text{H}^+]^{-1})(1 + K_{\text{GaOH}}[\text{H}^+]^{-1})^{-1}[\text{Ga}^{3+}][\text{HL}]$ , with  $k_{\text{Ga}} = 38 \pm 1 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{\text{GaOH}} = (8.2 \pm 0.2) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , and  $K_{\text{GaOH}} = [\text{GaOH}^{2+}][\text{H}^+]/[\text{Ga}^{3+}] = (1.3 \pm 0.1) \times 10^{-3} \text{ M}$  at 25 °C and  $I = 0.50 \text{ M}$  at atmospheric pressure. The activation parameters for the reaction of  $\text{Ga}^{3+}$  ( $k_{\text{Ga}}$  path) and the reaction of  $\text{GaOH}^{2+}$  ( $k_{\text{GaOH}}$  path) are as follows:  $\Delta H^\ddagger_{\text{Ga}} = 61 \pm 10 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger_{\text{Ga}} = -12 \pm 30 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta V^\ddagger_{\text{Ga}} = 4.0 \pm 1.3 \text{ cm}^3 \text{ mol}^{-1}$ ;  $\Delta H^\ddagger_{\text{GaOH}} = 29 \pm 11 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger_{\text{GaOH}} = -74 \pm 38 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta V^\ddagger_{\text{GaOH}} = 2-4 \text{ cm}^3 \text{ mol}^{-1}$ . Positive activation volumes for both the  $k_{\text{Ga}}$  and the  $k_{\text{GaOH}}$  paths point to a dissociative-interchange mechanism.

### Introduction

The kinetic behavior of divalent metal ion  $\text{M}^{2+}$  in complexation reactions in aqueous solution has been mostly interpreted by a dissociative-interchange mechanism,<sup>1</sup> in which the overall formation rate constant  $k_{\text{M}}$  is given by  $K_{\text{os}}k_{\text{M}}^{-\text{H}_2\text{O}}$  where  $K_{\text{os}}$  and  $k_{\text{M}}^{-\text{H}_2\text{O}}$  refer to the formation constant of an outer-sphere complex and the water-exchange rate constant at  $\text{M}^{2+}$ , respectively. This mechanism has been shown to be valid also for complexation reactions involving multidentate ligands having no extra stabilization of an outer-sphere complex and no steric inhibition due to their bulkiness.<sup>2</sup> Merbach and his co-workers have reported the negative values of ac-

tivation volume for the complexation<sup>3</sup> as well as the water exchange at  $\text{V}(\text{H}_2\text{O})_6^{2+}$ .<sup>4</sup> On the basis of these findings they concluded an associative-interchange mechanism for the substitution on this cation.

For trivalent metal ions, on the other hand, the mechanism of complexation reactions is still somewhat in doubt except for chromium(III)<sup>5</sup> and iron(III).<sup>6</sup> This arises mainly from the limited number of ligands suitable for kinetic measurements and from the complicated hydrolysis reactions of the metal ions.<sup>7</sup> The complexation of  $\text{Ga}^{3+}$  has been claimed to

(1) Langford, C. H.; Gray, H. B. "Ligand Substitution Processes"; W. A. Benjamin: New York, 1965.  
(2) Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. In "Coordination Chemistry"; Martell, A. E., Ed.; American Chemical Society: Washington, DC, 1978; ACS Monogr. No. 174, Chapter 1.

(3) Nichols, P. J.; Ducommun, Y.; Merbach, A. E. *Inorg. Chem.* **1983**, *22*, 3993-5.

(4) Ducommun, Y.; Zbinden, D.; Merbach, A. E. *Helv. Chim. Acta* **1982**, *65*, 1385-90.

(5) Stranks, D. R.; Swaddle, T. W. *J. Am. Chem. Soc.* **1971**, *93*, 2783-4.

(6) Ishihara, K.; Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1983**, *22*, 194-8 and references cited therein.

(7) Baes, C. F., Jr.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley: New York, 1976.

proceed via an associative transition state.<sup>8-14</sup> These studies include attempts to assess a possible dependence of the reaction energetics on entering-ligand nature and to compare  $k_{\text{Ga}}/K_{\text{Ga}}$  with  $k_{\text{Ga}}^{-\text{H}_2\text{O}}$  obtained by <sup>17</sup>O NMR measurements.<sup>15,16</sup>

The present paper describes the kinetic results on the complexation reaction of the gallium(III) ion with tropolone as a neutral entering ligand and provides definite mechanistic information on the reaction of this cation, on the basis of the values of activation volume obtained by a high-pressure stopped-flow technique.<sup>6,17-21</sup>

### Experimental Section

**Reagents.** Gallium metal (99.99%) was dissolved in perchloric acid to prepare gallium(III) perchlorate solution. The concentration of excess perchloric acid in the stock solution was determined by means of the Gran plot.<sup>22</sup> 2-Hydroxy-2,4,6-cycloheptatrien-1-one (tropolone, HL) (98%, Aldrich) was purified by sublimation. Sodium 1,2-dihydroxybenzene-3,5-disulfonate (Tiron, Na<sub>2</sub>H<sub>2</sub>A) (Dojin Chemical, Kumamoto, Japan) was purified by recrystallization from distilled water.

Solutions of tropolone and Tiron were prepared by weighing the well-dried reagent prior to each measurement. The solution of sodium perchlorate was prepared as described elsewhere.<sup>23</sup> Perchloric acid of special purity (Wako Junyaku) was used without further purification.

**Measurements.** All experiments were carried out in a room thermostated at 25 ± 0.5 °C. Temperature of the reaction solution was controlled to within ±0.1 °C by using a thermoelectric circulating bath. Ionic strength was maintained at 0.50 M (M = mol dm<sup>-3</sup>) or at 1.00 M with sodium perchlorate and perchloric acid. Solutions of gallium(III) ion and tropolone were prepared in the molar scale, which was converted to the pressure-independent molal (mol kg<sup>-1</sup> = m) scale when necessary.

Equilibrium measurements were made with a highly sensitive spectrophotometer (Type SM 401, Union Giken, Osaka, Japan) with a thermostated cell compartment. Reaction rates of complex formation at atmospheric pressure were followed by a stopped-flow spectrophotometer (RA 401, Union Giken), equipped with a data processor (Union RA 450). The changes in absorbance at 313 nm, a wavelength of the maximum absorption of the 1:1 Ga(III)-tropolone complex, were accumulated to obtain curves with high S/N.<sup>23</sup> The high-pressure stopped-flow apparatus constructed in our laboratory<sup>6,17-21</sup> was used for measurement of the rate of complexation at high pressures.

Hydrogen ion concentration was determined by a pH meter (Orion Digital Ionalyzer 701 A) with a calomel electrode filled with saturated sodium chloride as an internal solution instead of potassium chloride. A 1.000 × 10<sup>-2</sup> M perchloric acid solution containing 0.49 or 0.99 M of sodium perchlorate was employed as a standard of hydrogen ion concentration (-log [H<sup>+</sup>] = 2.000), and the liquid-junction potential was taken into consideration.<sup>24</sup> For the solution of -log [H<sup>+</sup>] < 1, hydrogen ion concentration in solution was calculated from the known amount of perchloric acid in the solution.

**Table I.** Formation Constants for the 1:1 Ga(III)-Tiron Complex and Hydrolysis Constants for the Gallium(III) Ion at Various Temperatures<sup>a</sup>

temp/°C	log (K <sub>GaA</sub> /M)	log (K <sub>GaOH</sub> /M)
15.0	-1.252 ± 0.008	-3.01 ± 0.10
25.0	-1.182 ± 0.006	-2.89 ± 0.03
35.0	-1.134 ± 0.011	-2.89 ± 0.05
45.0	-1.081 ± 0.006	-2.52 ± 0.01

<sup>a</sup> C<sub>Ga</sub> = 2.8 × 10<sup>-3</sup> M, C<sub>A</sub> = 2.0 × 10<sup>-4</sup> M, and I = 0.50 M, where C<sub>Ga</sub> and C<sub>A</sub> denote the total concentrations of gallium(III) and Tiron, respectively.

### Results

**Protonation Equilibrium of Tropolone.** In acidic solution (-log [H<sup>+</sup>] < 1), the absorption spectra of tropolone at various concentrations of hydrogen ion change with isobestic points at 290, 308, 333, and 345 nm. From the plot of the absorbance change at 360 nm vs. -log [H<sup>+</sup>], the logarithmic values of the protonation constant for tropolone K<sub>H<sub>2</sub>L</sub> = [H<sub>2</sub>L<sup>+</sup>][HL]<sup>-1</sup>[H<sup>+</sup>]<sup>-1</sup> at I = 0.50 M were determined to be -0.51 ± 0.10 at 15 °C, -0.48 ± 0.10 at 25 °C, and -0.52 ± 0.05 at 35 °C. The value at I = 1.00 M was also determined to be -0.35 ± 0.05 at 25 °C.

**Complexation Equilibria of Gallium(III) Complexes and Hydrolysis Equilibrium of the Gallium(III) Ion.** Gallium(III) ion forms a 1:1 complex with tropolone (HL) and Tiron (H<sub>2</sub>A<sup>2-</sup>) in acidic solution (-log [H<sup>+</sup>] = 0.5-2.5) where the concentration of gallium(III) ion is in large excess over that of the ligands. Under our experimental conditions only the (tropolonato)gallium(III) (GaL<sup>2+</sup>) is formed quantitatively.

For the Tiron complex, the change in spectra with isobestic points at 244, 276, and 290 nm is attributable to the equilibrium



where Ga' denotes gallium(III) ion not combined with the ligand. Under the present experimental conditions, Tiron is present quantitatively as H<sub>2</sub>A<sup>2-</sup>,<sup>25</sup> whereas gallium(III) ion exists as Ga<sup>3+</sup> and GaOH<sup>2+</sup>.<sup>26,27</sup> In sufficiently acidic medium (-log [H<sup>+</sup>] < 1.5) where gallium(III) ion exists solely as Ga<sup>3+</sup>, the constant for equilibrium 1, K<sub>GaA</sub>, is expressed as

$$K_{\text{GaA}} = [\text{GaA}^-][\text{H}^+]^2[\text{Ga}^{3+}]^{-1}[\text{H}_2\text{A}^{2-}]^{-1} \quad (2)$$

and the plot of {log ([GaA<sup>-</sup>]/[H<sub>2</sub>A<sup>2-</sup>]) - log [Ga<sup>3+</sup>]} vs. -log [H<sup>+</sup>] yields a straight line with a slope of 2 in accordance with eq 2. In a less acidic medium (1.5 < -log [H<sup>+</sup>] < 2.5) where gallium(III) ion exists as Ga<sup>3+</sup> and GaOH<sup>2+</sup>, the conditional formation constant for equilibrium 1, K'<sub>GaA</sub>, is expressed as

$$K'_{\text{GaA}} = [\text{GaA}^-][\text{H}^+]^2[\text{Ga}'^{-1}][\text{H}_2\text{A}^{2-}]^{-1} = \frac{K_{\text{GaA}}}{(1 + K_{\text{GaOH}}[\text{H}^+]^{-1})}$$

where K<sub>GaOH</sub> = [GaOH<sup>2+</sup>][H<sup>+</sup>][Ga<sup>3+</sup>]<sup>-1</sup> is the hydrolysis constant of gallium(III) ion. In such a less acidic medium, the experimental plot of {log ([GaA<sup>-</sup>]/[H<sub>2</sub>A<sup>2-</sup>]) - log [Ga']} vs. -log [H<sup>+</sup>] deviates from the straight line of slope 2 due to the hydrolysis of gallium(III) ion (Figure S1, supplementary material). The analysis of this deviation at 257, 305, and 315 nm as a function of -log [H<sup>+</sup>] enables us to estimate the K<sub>GaOH</sub> value. The formation constants for the 1:1 Ga(III)-Tiron complex and the hydrolysis constants for gallium(III) ion at various temperatures thus estimated are summarized in Table I. The thermodynamic parameters for the hydrolysis reaction were evaluated as ΔH<sup>o</sup><sub>GaOH</sub> = 25 ± 9 kJ mol<sup>-1</sup> and ΔS<sup>o</sup><sub>GaOH</sub> = 30 ± 31 J K<sup>-1</sup> mol<sup>-1</sup>.

- (8) Miceli, J.; Stuehr, J. *J. Am. Chem. Soc.* **1968**, *90*, 6967-72.  
 (9) Kalidas, C.; Knoch, W.; Papadopoulos, D. *Ber. Bunsenges. Phys. Chem.* **1971**, *75*, 106-10.  
 (10) Kawai, Y.; Takahashi, T.; Hayashi, K.; Imamura, T.; Nakayama, H.; Fujimoto, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1417-23.  
 (11) Perlmutter-Hayman, B.; Secco, F.; Tapuhi, E.; Venturini, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2220-3.  
 (12) Corigli, R.; Secco, F.; Venturini, M. *Inorg. Chem.* **1979**, *18*, 3184-7.  
 (13) Perlmutter-Hayman, B.; Secco, F.; Tapuhi, E.; Venturini, M. *J. Chem. Soc., Dalton Trans.* **1980**, 1124-8.  
 (14) Corigli, R.; Secco, F.; Venturini, M. *Inorg. Chem.* **1982**, *21*, 2992-8.  
 (15) Fiat, D.; Connick, R. E. *J. Am. Chem. Soc.* **1968**, *90*, 608-15.  
 (16) Neely, J. W. Ph.D. Thesis, University of California, Berkeley, 1971; cited in ref 2.  
 (17) Funahashi, S.; Ishihara, K.; Tanaka, M. *Inorg. Chim. Acta* **1979**, *35*, L351-2.  
 (18) Funahashi, S.; Ishihara, K.; Tanaka, M. *Inorg. Chem.* **1981**, *20*, 51-5.  
 (19) Ishihara, K.; Funahashi, S.; Tanaka, M. *Rev. Sci. Instrum.* **1982**, *53*, 1231-4.  
 (20) Funahashi, S.; Ishihara, K.; Tanaka, M. *Inorg. Chem.* **1983**, *22*, 2070-3.  
 (21) Ishihara, K.; Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1983**, *22*, 2564-7.  
 (22) Gran, G. *Analyst (London)* **1952**, *77*, 661-71.  
 (23) Yamada, S.; Ohsumi, K.; Tanaka, M. *Inorg. Chem.* **1978**, *17*, 2790-4.  
 (24) Yamada, S.; Nagase, J.; Funahashi, S.; Tanaka, M. *J. Inorg. Nucl. Chem.* **1976**, *38*, 617-21.

- (25) Morin, M.; Scharff, J. P. *Anal. Chim. Acta* **1972**, *60*, 101-8.  
 (26) Nazarenko, V. A.; Antonovich, V. P.; Nevskaya, E. M. *Zh. Neorg. Khim.* **1968**, *13*, 1574-80.  
 (27) Wilson, A. S.; Taube, H. *J. Am. Chem. Soc.* **1952**, *74*, 3509-12.

Table II. Rate Constants and Activation Parameters for the Reaction of the Gallium(III) Ion with Tropolone

temp/°C	$k_{\text{Ga}}/\text{M}^{-1} \text{s}^{-1}$	$k_{\text{GaOH}}K_{\text{GaOH}}/\text{s}^{-1}$	$k_{\text{GaOH}}/10^3 \text{M}^{-1} \text{s}^{-1}$
15.0	12.4 ± 0.7	4.68 ± 0.05	5.3 ± 0.1
25.0	38 ± 1	10.5 ± 0.3	8.2 ± 0.2
30.0	58 ± 4	15.0 ± 0.3	9.8 ± 0.2
35.0	64 ± 5	21.1 ± 0.4	11.9 ± 0.2

$\Delta H^\ddagger_{\text{Ga}} = 61 \pm 10 \text{ kJ mol}^{-1}$	$\Delta H^\ddagger_{\text{GaOH}} + \Delta H^\circ_{\text{GaOH}} = 54 \pm 2 \text{ kJ mol}^{-1}$	$\Delta H^\ddagger_{\text{GaOH}} = 29 \pm 11 \text{ kJ mol}^{-1}$
$\Delta S^\ddagger_{\text{Ga}} = -12 \pm 30 \text{ J K}^{-1} \text{ mol}^{-1}$	$\Delta S^\ddagger_{\text{GaOH}} + \Delta S^\circ_{\text{GaOH}} = -44 \pm 7 \text{ J K}^{-1} \text{ mol}^{-1}$	$\Delta S^\ddagger_{\text{GaOH}} = -74 \pm 38 \text{ J K}^{-1} \text{ mol}^{-1}$
$\Delta V^\ddagger_{\text{Ga}} = 4.0 \pm 1.3 \text{ cm}^3 \text{ mol}^{-1}$	$\Delta V^\ddagger_{\text{GaOH}} + \Delta V^\circ_{\text{GaOH}} = 5.1 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$	$\Delta V^\ddagger_{\text{GaOH}} = 2-4 \text{ cm}^3 \text{ mol}^{-1}$ <sup>a</sup>

<sup>a</sup> The assumed  $\Delta V^\circ$  value ranges from 0.8 to 3.0  $\text{cm}^3 \text{ mol}^{-1}$  (see the text).

**Reaction of Gallium(III) with Tropolone.** All reactions were first order in gallium(III) ion, which was always held in sufficient excess to ensure the pseudo-first-order kinetics and complete formation of the 1:1 complex. The formation rate of the  $\text{GaL}^{2+}$  complex is proportional to the total concentration of the uncomplexed Ga(III) and tropolone ( $[\text{Ga}']$  and  $[\text{HL}']$ , respectively). Then, the rate is expressed by eq 3, where  $k_{\alpha(\text{H})}$  is a conditional second-order rate constant involving hydrogen ion concentration.

$$d[\text{GaL}^{2+}]/dt = k_{\alpha(\text{H})}[\text{Ga}'][\text{HL}'] \quad (3)$$

Under the present experimental conditions there are four possible paths involving  $\text{Ga}^{3+}$  and  $\text{GaOH}^{2+}$  for gallium(III) ion and HL and  $\text{H}_2\text{L}^+$  for tropolone. Then, the overall rate equation is expressed as eq 4. Since  $[\text{Ga}'] = [\text{Ga}^{3+}](1 +$

$$d[\text{GaL}^{2+}]/dt = k_{\text{Ga}}[\text{Ga}^{3+}][\text{HL}] + k_{\text{GaOH}}[\text{GaOH}^{2+}] \times [\text{HL}] + k_{\text{Ga}}^{\text{H}}[\text{Ga}^{3+}][\text{H}_2\text{L}^+] + k_{\text{GaOH}}^{\text{H}}[\text{GaOH}^{2+}][\text{H}_2\text{L}^+] \quad (4)$$

$K_{\text{GaOH}}[\text{H}^+]^{-1}) = [\text{Ga}^{3+}]\alpha_{\text{Ga}(\text{OH})}$  and  $[\text{HL}'] = [\text{HL}](1 + K_{\text{H}_2\text{L}}[\text{H}^+]) = [\text{HL}]\alpha_{\text{HL}(\text{H})}$ , we obtain eq 5. Values of

$$k_{\alpha(\text{H})}\alpha_{\text{Ga}(\text{OH})}\alpha_{\text{HL}(\text{H})} = k_{\text{Ga}} + k_{\text{GaOH}}K_{\text{GaOH}}[\text{H}^+]^{-1} + k_{\text{Ga}}^{\text{H}}K_{\text{H}_2\text{L}}[\text{H}^+] + k_{\text{GaOH}}^{\text{H}}K_{\text{GaOH}}K_{\text{H}_2\text{L}} \quad (5)$$

$k_{\alpha(\text{H})}\alpha_{\text{Ga}(\text{OH})}\alpha_{\text{HL}(\text{H})}$  obtained at various hydrogen ion concentrations (Table SI, supplementary material) are plotted as a function of  $[\text{H}^+]^{-1}$  in Figure 1. The plots clearly indicate that the  $k_{\text{Ga}}^{\text{H}}$  path is negligible.

From the slope of this plot the rate constant for the  $k_{\text{GaOH}}$  path was determined as in Table II. However, we cannot decide which path is responsible for the reaction, the  $k_{\text{Ga}}$  path or the  $k_{\text{GaOH}}^{\text{H}}$  path. In order to distinguish which of the two paths is really relevant, we now evaluate values of the rate constants  $k_{\text{Ga}}$  and  $k_{\text{GaOH}}^{\text{H}}$  from the intercept of the plot in Figure 1. We calculate the upper limit for  $k_{\text{GaOH}}^{\text{H}}$  assuming  $k_{\text{Ga}}$  to be negligibly small. Thus, the evaluated value of  $k_{\text{GaOH}}^{\text{H}} = 10^{4.95} \text{ M}^{-1} \text{ s}^{-1}$  is almost 1 order of magnitude higher than that of  $k_{\text{GaOH}}$ , for which the mechanism is proven to be dissociative interchange (see Discussion).  $k_{\text{GaOH}}^{\text{H}}$  for the reaction of  $\text{GaOH}^{2+}$  with a positive ligand  $\text{H}_2\text{L}^+$  should be smaller than  $k_{\text{GaOH}}$  for the reaction with a neutral ligand. Therefore, we exclude the  $k_{\text{GaOH}}^{\text{H}}$  path. Then, the complexation rate of gallium(III) ion with tropolone is expressed by eq 6. The

$$d[\text{GaL}^{2+}]/dt = k_{\text{Ga}}[\text{Ga}^{3+}][\text{HL}] + k_{\text{GaOH}}[\text{GaOH}^{2+}][\text{HL}] \quad (6)$$

values of the activation enthalpy and entropy for these two reaction paths are estimated by the Eyring equation, and they are given in Table II.

**Reaction of the Gallium(III) Ion with Tropolone at High Pressure.** The conditional second-order rate constants  $k_{\alpha(\text{H})}$  were measured at  $I = 0.51 \text{ m}$  (Table SII, supplementary material) and at  $I = 1.04 \text{ m}$  (Table SIII, supplementary material) at various pressures by a high-pressure stopped-flow technique. A plot of the values of  $k_{\alpha(\text{H})}\alpha_{\text{HL}(\text{H})}$  at a given pressure against the reciprocal molal concentrations of hy-

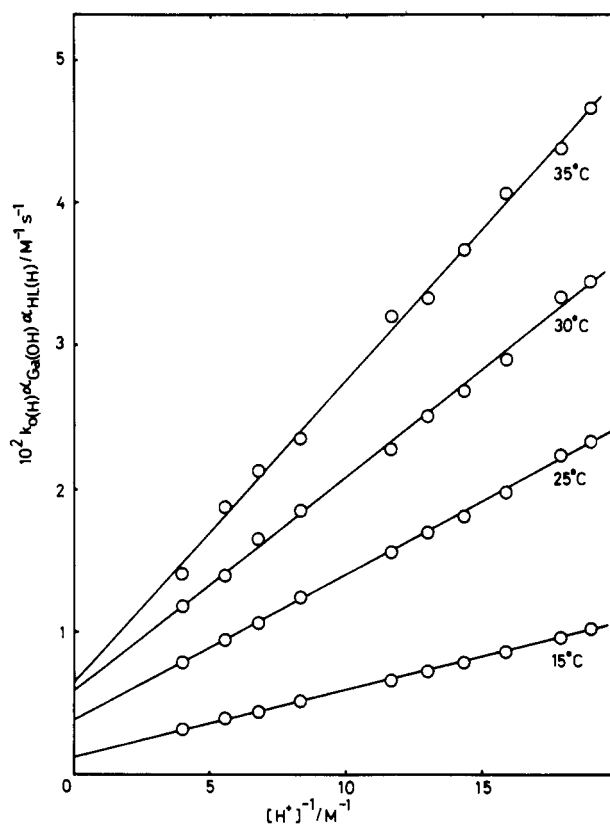


Figure 1. Hydrogen ion dependence of  $k_{\alpha(\text{H})}$  at atmospheric pressure and  $I = 0.50 \text{ M}$ .

drogen ion gives a straight line with a slope of  $k_{\text{GaOH}}K_{\text{GaOH}}$  and an intercept of  $k_{\text{Ga}}$ .<sup>28</sup> With the assumption that activation volume  $\Delta V^\ddagger$  and molar volume change  $\Delta V^\circ$  are independent of pressure,  $\Delta V^\ddagger_{\text{Ga}}$  and  $(\Delta V^\ddagger_{\text{GaOH}} + \Delta V^\circ_{\text{GaOH}})$  are determined by

$$\ln k_{\text{Ga}} = -\Delta V^\ddagger_{\text{Ga}}PR^{-1}T^{-1} + \ln k_{\text{Ga}}^0$$

and

$$\ln (k_{\text{GaOH}}K_{\text{GaOH}}) = -(\Delta V^\ddagger_{\text{GaOH}} + \Delta V^\circ_{\text{GaOH}})PR^{-1}T^{-1} + \ln (k_{\text{GaOH}}^0K_{\text{GaOH}}^0)$$

where  $k^0$  and  $\Delta V^\circ_{\text{GaOH}}$  refer to the rate constant at zero pressure and the reaction volume for the hydrolysis of  $\text{Ga}^{3+}$ , respectively. The plot of  $\ln (k_{\text{GaOH}}K_{\text{GaOH}})$  vs. pressure gave a straight line with a negative slope. Though errors in determining  $k_{\text{Ga}}$  are larger than for  $k_{\text{GaOH}}$ ,  $\ln k_{\text{G}}$  is linearly related to pressure within experimental error. Thus,  $\Delta V^\ddagger_{\text{Ga}}$  and  $\Delta V^\ddagger_{\text{GaOH}} + \Delta V^\circ_{\text{GaOH}}$  are in fact independent of pressure. By the analysis of data in Table SIII, we obtained  $\Delta V^\ddagger_{\text{Ga}} = 4.6$

(28) Since  $\alpha_{\text{Ga}(\text{OH})} \leq 1.02$  over the  $-\log [\text{H}^+]$  range studied at atmospheric pressure, we neglect the term of  $\alpha_{\text{Ga}(\text{OH})}$  in the evaluation of rate constants at high pressure. The term of  $\alpha_{\text{HL}(\text{H})}$  was calculated with the values of  $K_{\text{HL}}$  determined at atmospheric pressure. This treatment is reasonable as judged from the small value of the reaction volume ( $-0.3 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$ ) for the isopropyl derivative.<sup>6</sup>

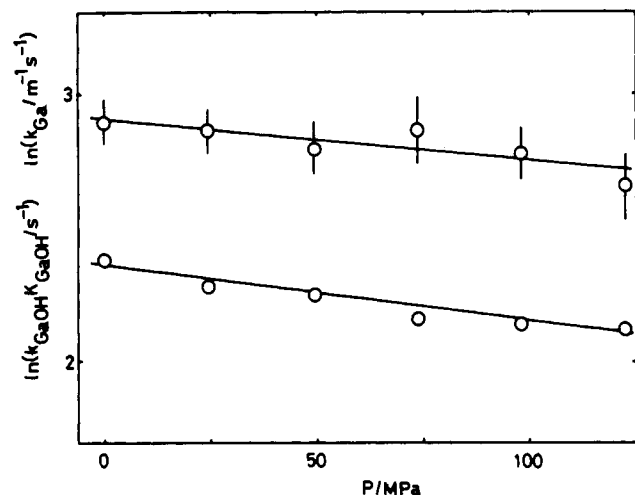


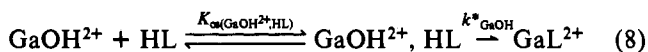
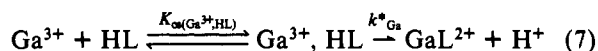
Figure 2. Pressure dependence of  $k_{\text{Ga}}$  and  $k_{\text{GaOH}}K_{\text{GaOH}}$ . Errors are standard deviations.

$\pm 0.9 \text{ cm}^3 \text{ mol}^{-1}$  and  $\Delta V^*_{\text{GaOH}} + \Delta V^\circ_{\text{GaOH}} = 5.1 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$ . Since tropolone reacts as a noncharged ligand, we utilized all data in Tables SII and SIII (supplementary material) and then we obtained  $\Delta V^*_{\text{Ga}} = 4.0 \pm 1.3 \text{ cm}^3 \text{ mol}^{-1}$  and  $\Delta V^*_{\text{GaOH}} + \Delta V^\circ_{\text{GaOH}} = 5.1 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$ , as shown in Figure 2.

### Discussion

**Effect of Pressure on Complexation Rates.** The study of the effect of pressure on the rate of complexation reaction leads to the volume of activation,  $\Delta V^*$ , which has been proven to be useful in the diagnosis of reaction mechanism. Where values of  $\Delta V^*$  are not complicated by charge effects, bond stretching in a dissociative activation mode gives rise to an increase in volume, i.e.  $\Delta V^*$  is positive. Conversely, bond formation occurring in an associative activation mode will lead to a negative  $\Delta V^*$ .<sup>29</sup>

Under the present experimental conditions, the complexation of gallium(III) ion with tropolone (HL) proceeds via the  $k_{\text{Ga}}$  and  $k_{\text{GaOH}}$  paths, which are given by eq 7 and 8, where  $k^*_{\text{Ga}}$



and  $k^*_{\text{GaOH}}$  denote the rate constants of substitution at  $\text{Ga}^{3+}$  and  $\text{GaOH}^{2+}$ , respectively. Since the process of chelate-ring closure is usually much faster than the coordination of the first donor in the entering ligand, the observed second-order rate constant  $k_{\text{Ga}}$  is given by  $k_{\text{Ga}} = K_{\text{os}}(\text{Ga}^{3+}, \text{HL})k^*_{\text{Ga}}$ . Then, the overall activation volume is given by

$$\Delta V^*_{\text{Ga}} = \Delta V^\circ_{\text{os}(\text{Ga}^{3+}, \text{HL})} + \Delta V^*_{\text{Ga}}$$

where  $\Delta V^\circ_{\text{os}(\text{Ga}^{3+}, \text{HL})}$  and  $\Delta V^*_{\text{Ga}}$  are the reaction volume for  $K_{\text{os}}(\text{Ga}^{3+}, \text{HL})$  and the activation volume for  $k^*_{\text{Ga}}$ , respectively. Since HL has no formal charge, if any, its dipole may be small and  $\Delta V^\circ_{\text{os}(\text{Ga}^{3+}, \text{HL})}$  should be substantially zero.<sup>30</sup> Then,  $\Delta V^*_{\text{Ga}} \approx \Delta V^*_{\text{Ga}} = 4.0 \text{ cm}^3 \text{ mol}^{-1}$ . This small positive value of  $\Delta V^*_{\text{Ga}}$  indicates that a volume increase caused by lengthening of the bond of a water molecule coordinated in the inner sphere of  $\text{Ga}^{3+}$  is largely compensated by a volume decrease due to the entering of the donor atom of HL into the inner sphere.

From the pressure dependence of the conditional rate constants, we obtain the composite activation volume,  $\Delta V^*_{\text{GaOH}} + \Delta V^\circ_{\text{GaOH}} = 5.1 \text{ cm}^3 \text{ mol}^{-1}$ . Unfortunately no reaction

Table III. Values of Kinetic Parameters for the Reactions of the Gallium(III) Ion with Various Ligands at 25 °C<sup>a</sup>

ligand ( $L^{n-}$ ) <sup>b</sup>	$\log(k_{\text{Ga}}/M^{-1} s^{-1})$	$\log(k^*_{\text{Ga}}/s^{-1})$	$\Delta H^\ddagger_{\text{Ga}}/kJ \text{ mol}^{-1}$	$\log(k_{\text{GaOH}}/M^{-1} s^{-1})$	$\log(k^*_{\text{GaOH}}/s^{-1})$
tropolone (HL) <sup>c</sup>	1.58	2.1	61	3.89	4.4
Tiron ( $H_2L^{2-}$ ) <sup>d</sup>	1.16	1.7		3.39	3.9
NSAL ( $HL^-$ ) <sup>e</sup>	2.61	1.9		3.81	3.5
PCV ( $H_3L^-$ ) <sup>f</sup>	1.81	2.3	52	3.94	4.4
SAL ( $HL^-$ ) <sup>g</sup>	2.82	2.1		4.53	4.2
SXO ( $H_2L^{2-}$ ) <sup>h</sup>	2.84	2.1		4.08	3.8
$SO_4^{2-}$ <sup>i</sup>	4.32	1.3		5.00	3.0
$SO_4^{2-}$ <sup>j</sup>	3.81	0.7			
$H_2O$ <sup>k</sup>		3.3	26		
$H_2O$ <sup>l</sup>		2.9	69		

<sup>a</sup> Distinction between reaction paths with proton ambiguity is made by checking the reasonableness of the rate constants calculated as in the present system. <sup>b</sup> Ligand abbreviation; PCV = pyrocatechol violet; NSAL = 5-nitrosalicylic acid; SAL = salicylic acid; SXO = semixylenol orange. <sup>c</sup> This work at  $I = 0.5 \text{ M}$  (Na,H)- $\text{ClO}_4$ . <sup>d</sup> Yamada, S.; Tanaka, M., unpublished result at  $I = 0.5 \text{ M}$  (Na,H)- $\text{ClO}_4$ . <sup>e</sup> Reference 13, at  $I = 0.1 \text{ M}$  (Na,H)- $\text{ClO}_4$ . <sup>f</sup> Reference 12, at  $I = 0.2 \text{ M}$  (Na,H)- $\text{ClO}_4$ . <sup>g</sup> Reference 11, at  $I = 0.1 \text{ M}$  (Na,H)- $\text{ClO}_4$ . <sup>h</sup> Reference 10, at  $I = 0.1 \text{ M}$  (Na,H)- $\text{ClO}_4$ . <sup>i</sup> Reference 8, at  $I = 0$ . <sup>j</sup> Reference 9, at  $I = 0$ . <sup>k</sup> Reference 15, at  $I = 1.7 \text{ M}$   $\text{Ga}(\text{ClO}_4)_3$ ,  $0.2 \text{ M}$   $\text{Co}(\text{ClO}_4)_2$ , and  $0.6 \text{ M}$   $\text{HClO}_4$ . <sup>l</sup> Reference 16,  $0.6 \text{ M}$   $\text{Mn}(\text{ClO}_4)_2$  was used as a relaxation reagent instead of  $\text{Co}(\text{ClO}_4)_2$  in ref 15.

volume datum is available for the first hydrolysis reaction of  $\text{Ga}^{3+}$ . However, for  $\text{Fe}^{3+}$ , which has almost the same ionic radius (64 pm) as  $\text{Ga}^{3+}$  (62 pm),<sup>31</sup> the available  $\Delta V^\circ_{\text{FeOH}}$  value ranges from 0.8 to  $3.0 \text{ cm}^3 \text{ mol}^{-1}$ .<sup>32-34</sup> Thus, if we assume that the  $\Delta V^\circ_{\text{GaOH}}$  value is close to that of  $\text{Fe}^{3+}$ , we have  $\Delta V^*_{\text{GaOH}} = 2-4 \text{ cm}^3 \text{ mol}^{-1}$ . This result shows that the complexation of the hydrolyzed gallium ion proceeds via a dissociative-interchange ( $I_d$ ) mechanism.

**Water-Exchange Rate at  $\text{Ga}^{3+}$  and  $\text{GaOH}^{2+}$ .** The following criteria have been invoked for a "normal" dissociative-interchange mechanism:<sup>35</sup> (1)  $k_M/K_{\text{os}}$  values of ligands having different charge and different numbers of donor sites are reasonably constant. (2) Values of  $k_M/K_{\text{os}}$  (apart from a statistical factor that is not far from unity<sup>36</sup>) are not very different from the values of  $k_M^{-\text{H}_2\text{O}}$ , which are usually measured by NMR methods. (3) Activation enthalpies for the complex formation are reasonably similar to that for the solvent exchange.

We calculated rate constants  $k^*_{\text{Ga}}$  and  $k^*_{\text{GaOH}}$  for our system and others. The results are summarized in Table III in which are also given the second-order rate constants for complexation reactions. The  $K_{\text{os}}$  values were calculated from the Fuoss equation<sup>37</sup> with  $a$ , the distance of closest approach, = 500 pm, on the assumption that a negatively charged group removed from the eventual coordination site is unimportant in the calculation of  $K_{\text{os}}$  values.<sup>38</sup> Values of  $\log k^*_{\text{Ga}}$  are all low in comparison with the value of  $\log k_{\text{Ga}}^{-\text{H}_2\text{O}}$  of 3.3 and 2.9 obtained by <sup>17</sup>O NMR measurements. However, except for  $L = \text{SO}_4^{2-}$ , for which the estimation of  $K_{\text{os}}$  is extremely critical in the evaluation of  $k^*_{\text{Ga}}$ , they seem to be ligand independent, as claimed for the dissociative-interchange mechanism. However, in reactions with a modest dissociative character,

(31) Weast, R. C., Ed. "Handbook of Chemistry and Physics", 60th ed.; CRC Press, Boca Raton, FL, 1979.

(32) Jost, A. *Ber. Bunsenges. Phys. Chem.* **1976**, *80*, 316-21.

(33) Hasinoff, B. B. *Can. J. Chem.* **1979**, *57*, 77-82.

(34) Swaddle, R. W.; Merbach, A. E. *Inorg. Chem.* **1981**, *20*, 4212-6.

(35) Coetzee, J. F. "Solute Solvent Interactions"; Coetzee, J. F.; Ritchie, C. D., Eds.; Marcel Dekker, New York, 1976; Vol. 2, Chapter 14.

(36) Neely, J.; Connick, R. *J. Am. Chem. Soc.* **1970**, *92*, 3476-8.

(37) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059-61.

(38) Cassatt, J. C.; Wilkins, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 6045-50.

(29) Palmer, D. A.; Kelm, H. *Coord. Chem. Rev.* **1981**, *36*, 89-153.

(30) Hemmes, P. J. *Phys. Chem.* **1972**, *76*, 895-900.

the entering-ligand dependence, though small it may be, cannot be excluded as in the case of a set of substituted salicylic acid systems.<sup>14</sup>

**Enhanced Reactivity of GaOH<sup>2+</sup>.** As seen from Table III,  $k_{\text{GaOH}}^*$  is almost 2 orders of magnitude higher than  $k_{\text{Ga}}^*$ . The effect of bound ligands on the ease of replacement of the remaining water molecule has been interpreted by their ability to donate electrons to the central metal ion.<sup>23,39,40</sup> This effect is also reflected in the lower activation enthalpy for the  $k_{\text{GaOH}}$  path than for the  $k_{\text{Ga}}$  path (Table II).

For the complexation reactions dissociatively activated, values of  $k_{\text{M}}/K_{\text{os}} = k_{\text{M}}^*$  and  $k_{\text{MA}}/K_{\text{os}} = k_{\text{MA}}^*$  do not differ much from  $k_{\text{M}}^{-\text{H}_2\text{O}}$ , the rate constant of water exchange at M, and  $k_{\text{MA}}^{-\text{H}_2\text{O}}$ , the rate constant of water exchange at MA, respectively, if the compared rate constants are determined under similar conditions.<sup>2,41</sup> The bound-ligand effect on the water exchange has been interpreted by eq 9,<sup>23,39,40</sup> where  $E(\text{A})$

$$\log k_{\text{MA}}^{-\text{H}_2\text{O}} = \log k_{\text{M}}^{-\text{H}_2\text{O}} + \gamma E(\text{A}) \quad (9)$$

refers to the electron donor constant of the coordinated ligand

(39) Tanaka, M. *J. Inorg. Nucl. Chem.* **1973**, *35*, 965-71.

(40) Tanaka, M.; Yamada, S. *J. Chem. Soc., Chem. Commun.* **1976**, 178-9.

(41) Tanaka, M. *Inorg. Chim. Acta* **1983**, *76*, L243-4.

A and  $\gamma$  is a constant characteristic of the metal ion M. Taking into account the statistical factor arising from the number of water molecule available for exchange, the water-exchange rate constant at GaOH<sup>2+</sup> is expressed as

$$\log (k_{\text{GaOH}}^{-\text{H}_2\text{O}}/5) = \log (k_{\text{Ga}}^{-\text{H}_2\text{O}}/6) + 1.65\gamma$$

where 1.65 is the electron donor constant of OH<sup>-</sup> as proposed by Edwards.<sup>42</sup> By the use of the rate constants listed in Table III, the  $\gamma$  value for Ga(III) is estimated to be 1.3. As stated previously,<sup>23,40</sup> a hard metal ion such as Ga(III) has higher  $\gamma$  value than less hard metal ions such as Co(II) ( $\gamma = 0.47$ ), Ni(II) ( $\gamma = 0.40$ ), and Zn(II) ( $\gamma = 0.30$ ).

**Acknowledgment.** The authors thank Dr. Koji Ishihara for helpful discussions and assistance with the kinetic measurements by the high-pressure stopped-flow apparatus.

**Registry No.** Gallium, 7440-55-3; tropolone, 533-75-5.

**Supplementary Material Available:** Listings of conditional rate constants  $k_{\text{OH}}$  at atmospheric pressure (Table SI) and at high pressure (Tables SII and SIII) and a plot of  $\{\log ([\text{Ga}^+]/[\text{H}_2\text{A}^{2-}]) - \log [\text{Ga}^+]\}$  vs.  $-\log [\text{H}^+]$  (Figure S1) (7 pages). Ordering information is given on any current masthead page.

(42) Edwards, J. O. *J. Am. Chem. Soc.* **1954**, *76*, 1540-7.

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## Reactivity of Decamethylvanadocene with Phenyl Isothiocyanate and Carbonyl Sulfide: Reactions Related to the Desulfurization of the Thiocarbonyl Group

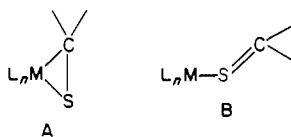
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The reaction of decamethylvanadocene (I) with phenyl isothiocyanate gave  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{V}(\text{PhNCS})]$  (II) containing a  $\eta^2\text{-C}_5\text{S}$ -bonded isothiocyanate unit. The X-ray structure of II showed that the CS fragment is accommodated in the cavity provided by the two bent  $\text{C}_5\text{Me}_5$  ligands [ $\text{V}-\text{C} = 2.042$  (7) Å;  $\text{V}-\text{S} = 2.444$  (2) Å;  $\text{C}-\text{S} = 1.745$  (7) Å]. Complex II is thermally labile, and it undergoes a thermal transformation occurring with the migration of the metal-bonded carbon to one of the  $\text{C}_5\text{Me}_5$  rings. The resulting complex was  $[(\eta^5\text{-C}_5\text{Me}_5)\text{V}(\text{PhN}-\text{C}(\text{S})-\text{C}_5\text{Me}_5)_2]$  (III) whose structure was determined by an X-ray analysis. Complex III is a vanadium(III) derivative ( $\mu_{\text{eff}} = 2.98 \mu_{\text{B}}$  at 297 K) containing a  $\eta^5\text{-C}_5\text{Me}_5$  ring and two bidentate chelating thioamido groups [ $\text{V}-\text{S} = 2.458$  (4),  $2.449$  (3) Å;  $\text{V}-\text{N} = 2.154$  (4),  $2.150$  (4) Å]. Carbonyl sulfide reacted with  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{V}]$  to form a rather labile crystalline adduct  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{V}(\text{COS})]$  [ $\nu(\text{C}=\text{O}) = 1625 \text{ cm}^{-1}$ ] undergoing thermal transformation to  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{V}(\text{S}_2)]$  and  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{V}(\text{CO})]$  by a pathway that is probably different from that of PhNCS. Crystallographic details for complex II: space group  $P2_1/n$  (monoclinic),  $a = 9.876$  (3) Å,  $b = 14.650$  (5) Å,  $c = 16.784$  (6) Å,  $\beta = 94.40$  (3)°,  $Z = 4$ ,  $V = 2421$  (1) Å<sup>3</sup>,  $D_{\text{calcd}} = 1.25 \text{ g cm}^{-3}$ . The  $R$  final factor was 0.052 for 1686 observed reflections. Crystallographic details for complex III: space group  $Pbca$  (orthorhombic),  $a = 29.971$  (7) Å,  $b = 14.292$  (4) Å,  $c = 18.698$  (5) Å,  $Z = 8$ ,  $V = 7961$  (4) Å<sup>3</sup>,  $D_{\text{calcd}} = 1.21 \text{ g cm}^{-3}$ . The  $R$  final factor was 0.045 for 2644 observed reflections.

### Introduction

The thiocarbonyl functional group has been largely used for modeling studies concerning the desulfurization of substrates like thioketones, isothiocyanates, and carbonyl sulfide promoted by mononuclear<sup>1-6</sup> or polynuclear<sup>5b</sup> metal complexes. Such a reaction proceeds via a preliminary coordination to the metal of the  $>\text{C}=\text{S}$  unit, which can display either a  $\eta^2\text{-C}_5\text{S}$  (A) or a  $\eta^1\text{-S}$  (B) bonding mode.



Both kinds of ( $>\text{C}=\text{S}$ )-(metal) interactions have been identified and structurally proven in thioketones,<sup>6-8</sup> while the side-on coordination is preferred by isothiocyanates<sup>9</sup> and carbonyl sulfide.<sup>10</sup> Other bonding modes for thioketones have

- (1) Alper, H.; Paik, H. N. *J. Am. Chem. Soc.* **1978**, *100*, 508-512.
- (2) Alper, H. *J. Org. Chem.* **1975**, *40*, 2694; *J. Organomet. Chem.* **1974**, *73*, 359-364.
- (3) Werner, H. *Coord. Chem. Rev.* **1982**, *43*, 165-185.
- (4) Fehlhammer, W. P.; Mayr, A. *J. Organomet. Chem.* **1980**, *191*, 153-159.
- (5) (a) Omae, I. *Coord. Chem. Rev.* **1979**, *28*, 97-115. (b) Adams, R. D. *Acc. Chem. Res.* **1983**, *16*, 67-72. Adams, R. D.; Dawoodi, Z.; Foust, D. F.; Segmüller, B. E. *Organometallics* **1983**, *2*, 315-323.
- (6) Pasquali, M.; Leoni, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1983**, *22*, 841-844.
- (7) Alper, H.; Silavve, N. D.; Birnbaum, G. I.; Ahmed, F. R. *J. Am. Chem. Soc.* **1979**, *101*, 6582-6588.
- (8) Gingerich, R. G. W.; Angelici, R. J. *J. Organomet. Chem.* **1977**, *132*, 377-386. Karcher, B. A.; Jacobson, R. A. *Ibid.* **1977**, *132*, 387-393. Dettlaf, G.; Behrens, U.; Weiss, E. *Ibid.* **1978**, *152*, 95-99.
- (9) Bianchini, C.; Masi, D.; Mealli, C.; Meli, A. *J. Organomet. Chem.* **1983**, *247*, C29-C31.

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