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Association of Tris(acetylacetonato)chromium(III) with Chlorinated Phenols in the Liquid-Liquid Partition System

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The liquid–liquid partition behavior of tris(acetylacetonato)chromium(III) ([Cr(acac)$_3$]) between heptane and 0.10 mol dm^{-3} aqueous sodium perchlorate solutions has been studied in the presence of a series of chlorinated phenols (HA) at 298.2 K. A large enhancement of the partition coefficient of [Cr(acac)$_3$] with HA has been observed, e.g., it rises by about 1000-fold in the presence of 0.02 mol dm^{-3} 3,5-dichlorophenol in the organic phase. This effect is ascribable to the association of [Cr(acac)$_3$] with HA in the organic phase. From a partition-equilibrium analysis, the association complexes have been identified as being [Cr(acac)$_3$]$\cdot i$HA (i=1,2), and the association constants ($\beta_{\mathrm{ass},i}$) determined. The $\beta_{\mathrm{ass},i}$ value increases with an increase of the acid-dissociation constant of HA in the family of HA with the same combination of substituents at the 2,6-positions, i.e., the association is due to hydrogen bonding of the hydroxyl hydrogen atom of HA to [Cr(acac)$_3$]. A linear free-energy relationship has been found between the $\beta_{\mathrm{ass},i}$ values of [Cr(acac)$_3$] and those of [Co(acac)$_3$] previously reported.

The liquid–liquid partition of electrically neutral metal chelates is the most important process governing the extractability and separation efficiency of metal ions with a chelating agent in both solvent extraction and liquid chromatography. Suzuki and his coworkers have studied the partition coefficients of a large number of metal chelates, and have shown that the solvent effect on the partition coefficient can generally be interpreted in terms of regular solution theory.[1–4)] In the case of acetylacetonato (2,4-pentanedionato) complexes, however, even for coordinatively saturated complexes such as tris(acetylacetonato)chromium(III) ([Cr(acac)$_3$]) and -cobalt(III) ([Co(acac)$_3$]), the effect of some solvents, such as chloroform and 1-octanol, could not be interpreted quantitatively.[3)] This may be due to a specific interaction, such as hydrogen bonding between the metal acetylacetonates and the solvents. The hydrogen bonding between metal complexes and organic compounds might be very important for not only the partition behavior, but also regarding other chemical properties, such as the solubility and reactivity of metal complexes.[5)] There have been a few studies concerning the interaction between metal β-diketonates and proton-donor solvents, such as chloroform and methanol.[1,5,6)] However, the interaction observed in their systems was rather weak. The specific interaction between these chelates and chlorinated phenols, which are considered to be strong proton donors, has not yet been studied, except for our previous work, in which it was found that [Co(acac)$_3$] forms highly stable association complexes with chlorinated phenols in heptane.[7)] Such the association with the phenols may occur for other metal chelates, such as [Cr(acac)$_3$]. It is necessary to accumulate systematic data concerning the specific interaction in order to quantitatively discuss both the nature and characteristics of the specific interaction between metal chelates and proton donors.

In this paper, the effect of a series of chlorinated phenols on the partition of [Cr(acac)$_3$] between heptane and 0.1 mol dm^{-3} aqueous sodium perchlorate solutions was investigated in detail. The association constants of [Cr(acac)$_3$] with the phenols in heptane were determined by a partition-equilibrium analysis; they are discussed by comparing them with those of [Co(acac)$_3$].

Theoretical

The partition coefficient of [Cr(acac)$_3$] (P_0) in the absence of chlorinated phenols is defined as the ratio of the equilibrium molar concentration of the complex in the organic phase to that in the aqueous phase,

$$P_0 = [[\mathrm{Cr(acac)_3}]]_{\mathrm{org}} / [[\mathrm{Cr(acac)_3}]]_{\mathrm{aq}}, \tag{1}$$

where the subscripts aq and org denote the aqueous and organic phases, respectively.

When [Cr(acac)$_3$] and chlorinated phenols (HA) form association complexes ([Cr(acac)$_3$]$\cdot i$HA) in the organic phase, the apparent partition coefficient of [Cr(acac)$_3$] (P') in the presence of HA can be expressed as

$$P' = \frac{[[\mathrm{Cr(acac)_3}]]_{\mathrm{org}} + \sum_{i=1}^{n}[[\mathrm{Cr(acac)_3}]\cdot i\mathrm{HA}]_{\mathrm{org}}}{[[\mathrm{Cr(acac)_3}]]_{\mathrm{aq}}} \tag{2}$$

$$= P_0(1 + \sum_{i=1}^{n}\beta_{\mathrm{ass},i}[\mathrm{HA}]_{\mathrm{org}}^{\,i}), \tag{3}$$

where $\beta_{\mathrm{ass},i}$ is the association constant in the organic phase corresponding to the following equilibrium:

$$[\mathrm{Cr(acac)_3}]_{\mathrm{org}} + i\mathrm{HA}_{\mathrm{org}} \rightleftarrows [\mathrm{Cr(acac)_3}]\cdot i\mathrm{HA}_{\mathrm{org}},$$

$$\beta_{\mathrm{ass},i} = \frac{[[\mathrm{Cr(acac)_3}]\cdot i\mathrm{HA}]_{\mathrm{org}}}{[[\mathrm{Cr(acac)_3}]]_{\mathrm{org}}[\mathrm{HA}]_{\mathrm{org}}^{\,i}}. \tag{4}$$

Therefore, the following equation can be derived:

$$P'/P_0 = 1 + \sum_{i=1}^{n}\beta_{\mathrm{ass},i}[\mathrm{HA}]_{\mathrm{org}}^{\,i}. \tag{5}$$

An enhancement of the partition coefficient of

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[Cr(acac)$_3$] in the presence of HA is directly related to the association constant and the equilibrium concentration of HA in the organic phase by Eq. 5.

Experimental

Reagents. [Cr(acac)$_3$] was obtained from Dojin Chem. Lab., recrystallized from hexane, and dried in vacuo. The purity was checked by a melting-point measurement and elemental analysis: Mp, 214 °C (literature value, 216 °C[8]). Found: C, 52.36; H, 6.14%. Calcd for $C_{15}H_{21}O_6Cr$: C, 51.58; H, 6.06%. 3-Chlorophenol (3-CP), 2,3-dichlorophenol (2,3-DCP), 3,5-dichlorophenol (3,5-DCP), 2,3,5-trichlorophenol (2,3,5-TCP), 2,3,6-trichlorophenol (2,3,6-TCP), and 2,4,5-trichlorophenol (2,4,5-TCP), which were of more than 98% purity, were commercially obtained and further purified by recrystallization from hexane or vacuum sublimation. Pentachlorophenol (PCP) (Aldrich, more than 98% purity) was used as obtained. Heptane was purified by ordinary methods. Water was doubly distilled. Other reagents were of analytical reagent grade and used without further purification.

Partition Measurements. An aqueous solution of 1.0×10^{-5}—7.7×10^{-4} (1 M=1 mol dm^{-3}) [Cr(acac)$_3$] was prepared by partitioning [Cr(acac)$_3$] from its heptane solution to water just before use, in order to minimize the dissociation of the complex in aqueous solution. The aqueous solution of [Cr(acac)$_3$] was mechanically shaken with pure heptane or a heptane solution of 3.5×10^{-4}—1.0×10^{-1} M chlorinated phenols for 5—60 min at 350 strokes per min in a thermostated room at 298.2±0.5 K. The two phases were separated by centrifugation at 3000 rpm. The absorbance of [Cr(acac)$_3$] in the aqueous phase before ($A_{i,aq}$) and after (A_{aq}) shaking was measured at 331 nm with a Hitachi U-3200 or JASCO Uvidec-2 spectrophotometer. The phenols had no absorption at this wavelength and did not affect the molar absorption coefficient of [Cr(acac)$_3$] in the aqueous phase. The partition coefficient of [Cr(acac)$_3$] in the absence (P_0) or presence (P') of chlorinated phenols was calculated using

$$P_0 \text{ or } P' = (A_{i,aq} - A_{aq})V_{aq}A_{aq}^{-1}V_{org}^{-1}, \qquad (6)$$

where V_{aq} and V_{org} are the volumes of aqueous and organic phases, respectively; the volume ratio V_{aq}/V_{org} was chosen to be 1—4 according to the magnitude of P' so as to minimize the absorbance-measurement error of the aqueous phase. The proton concentration of the aqueous phase was adjusted to 10^{-2}—10^{-3} M with perchloric acid to suppress any dissociation of the phenols. The ionic strength was adjusted to 0.10 M with sodium perchlorate.

Results

No dissociation of [Cr(acac)$_3$] in the partition experiment was confirmed as follows: The equilibrated aqueous phase was shaken with chloroform to remove [Cr(acac)$_3$] completely from the aqueous phase. Chloroform has a high partition coefficient for [Cr(acac)$_3$], 5.70×10^3.[3] No absorption due to dissociated complexes, such as [Cr(acac)]$^{2+}$, and [Cr(acac)$_2$]$^+$, was detected in the remaining aqueous phase. All partition equilibria of [Cr(acac)$_3$] were found to be established within 5-min shaking.

It was confirmed that the partition coefficient of [Cr(acac)$_3$] (P_0) in the absence of chlorinated phenols is independent of the [Cr(acac)$_3$] concentration within the range 1.3×10^{-5}—1.3×10^{-4} in the organic phase. The average and standard deviation of the P_0 value of [Cr(acac)$_3$] for 12 measurements were 0.370±0.018, which is in good agreement with a value from the literature, 0.351.[9]

The apparent partition coefficient of [Cr(acac)$_3$] (P') measured in the presence of a series of chlorinated phenols (HA) is shown in Fig. 1 as plots of $\log(P'/P_0)$ against the logarithmic value of the equilibrium concentration of the phenols in the organic phase, $\log[\mathrm{HA}]_{org}$. Here, $[\mathrm{HA}]_{org}$ is calculated from the initial concentration in the organic phase (C_{HA}) and the partition coefficient (P_{HA}) of those phenols as follows:

$$[\mathrm{HA}]_{org} = C_{HA}/(V_{aq}V_{org}^{-1}P_{HA}^{-1}+1), \qquad (7)$$

where the P_{HA} values were quoted from our previous study,[10] i.e., 0.534 for 3-CP, 21.5 for 2,3-DCP, 2.61 for 3,5-DCP, 89.8 for 2,3,5-TCP, 96.6 for 2,3,6-TCP, 62.9 for 2,4,5-TCP, and 980 for PCP. The $[\mathrm{HA}]_{org}$ calculated here should be approximately equal to the equilibrium concentration of HA free from association with [Cr(acac)$_3$], since the total concentration of [Cr(acac)$_3$] was always made to be smaller than 3% of C_{HA}. In all of the systems, the apparent partition coefficient of

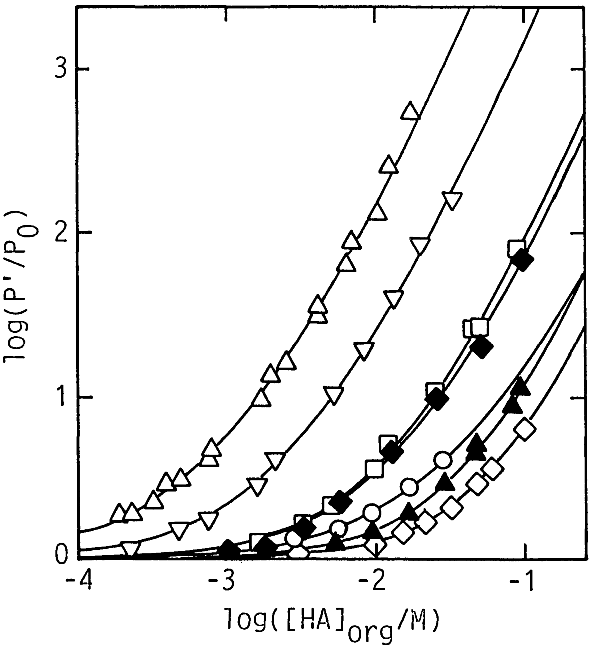

Fig. 1. Enhancement of the partition coefficient of [Cr(acac)$_3$] as a function of the equilibrium concentration of chlorinated phenols (HA) in the organic phase. The solid lines indicate the regression curves by the nonlinear least-squares procedure based on Eq. 5.
▽, 3-CP; ▲, 2,3-PCP; △, 3,5-DCP; ◆, 2,3,5-TCP; ◇, 2,3,6-TCP; □, 2,4,5-TCP; ○, PCP.

[Cr(acac)$_3$] rapidly increases with an increase in the phenol concentration in the organic phase. The largest effect is found in the 3,5-DCP system: the partition coefficient of [Cr(acac)$_3$] rises by about 1000-fold in the presence of 0.02 M 3,5-DCP. This enhancement effect is remarkably different among the phenols, and increases according to the following order: 2,3,6-TCP<2,3-DCP<PCP<2,3,5-TCP≈2,4,5-TCP<3-CP<3,5-DCP.

Discussion

The enhancement of the apparent partition coefficient of [Cr(acac)$_3$] in the presence of the chlorinated phenols can be ascribed to an association of [Cr(acac)$_3$] with the phenols in the organic phase. According to Eq. 5, the slope of the plot of $\log(P'/P_0)$ vs. $\log[\mathrm{HA}]_{\mathrm{org}}$ is equal to the mean number of HA molecule associating with one molecule of [Cr(acac)$_3$]. The plots in Fig. 1 for 3-CP, 3,5-DCP, 2,3,5-DCP, and 2,4,5-TCP, which give especially great enhancement of the partition coefficient of [Cr(acac)$_3$], are close to straight lines with a slope of 2 in the higher concentration region of the phenols. In the case of 2,3-DCP and 2,3,6-TCP, although no such limiting slope can be observed, the slopes of the plots increase to higher than unity at high concentrations of the phenols. These results mean that the maximum association number of the chlorinated phenols is two under these experimental conditions. From the plots given in Fig. 1, the association constants, $\beta_{\mathrm{ass},1}$ and $\beta_{\mathrm{ass},2}$ were computed by a nonlinear least-squares procedure (SALS program, The University of Tokyo) based on Eq. 5, and listed in Table 1. In the case of PCP, the P' measurement was only possible for a limited concentration range of PCP due to its low solubility (ca. 0.03 M in heptane); the slope of the plot is nearly unity, even at higher concentrations. In accordance with the results for other chlorinated phenols, however, the association constants were computed by assuming the formation of 1 : 1 and 1 : 2 association complexes. Hence, the $\beta_{\mathrm{ass},2}$ value of PCP may involve a fairly large error. The solid lines in Fig. 1 indicate regression curves by the obtained association constants; they are well fitted to the experimental plots. The largest values of the association constants are found in the 3,5-DCP system. All of these values for the chlorinated phenols are very large compared with the very few data concerning the association constants of [Cr(acac)$_3$] with other proton donors reported so far, e.g., the $\log\beta_{\mathrm{ass},1}$ values with chloroform and methanol in carbon tetrachloride at 298 K are −0.52 and 0.11, respectively.[5]

Table 1. Association Constants of [Cr(acac)$_3$] with Chlorinated Phenols (HA) in Heptane at 298.2 K

No.	HA	$\log(\beta_{\mathrm{ass},1}/\mathrm{M}^{-1})$	$\log(\beta_{\mathrm{ass},2}/\mathrm{M}^{-2})$
1	3-CP	3.02 (0.03)	5.13 (0.03)
2	2,3-DCP	1.63 (0.03)	2.83 (0.03)
3	3,5-DCP	3.56 (0.02)	6.04 (0.03)
4	2,3,5-TCP	2.26 (0.05)	3.72 (0.06)
5	2,3,6-TCP	1.39 (0.03)	2.49 (0.04)
6	2,4,5-TCP	2.27 (0.03)	3.87 (0.03)
7	PCP	1.97 (0.01)	2.71 (0.08)

Numerals in parentheses show the standard deviations calculated by SALS program.

The possibility of a direct coordination of the phenols to the inner sphere of [Cr(acac)$_3$] was completely denied by the fact that the absorption band at 560 nm of [Cr(acac)$_3$] in heptane, assigned to the d-d transition,[11] did not change in the presence of 0.05 M 3,5-DCP. If the association is caused by hydrogen bonding, the association constant is expected to correlate with the acid-dissociation constant of the chlorinated phenols.[12] Figure 2 shows the association constant of [Cr(acac)$_3$]·HA ($\log\beta_{\mathrm{ass},1}$) as a function of the acid-dissociation constant of the chlorinated phenols ($\log K_{\mathrm{a}}=-\mathrm{p}K_{\mathrm{a}}$); the p$K_{\mathrm{a}}$ values are cited from the literature, i.e., 8.97 for 3-CP, 7.71 for 2,3-DCP, 8.25 for 3,5-DCP, 6.43 for 2,3,5-TCP, 5.80 for 2,3,6-TCP, 6.72 for 2,4,5-TCP, and 4.74 for PCP.[13] Good correlations are found for three families of phenols with the same combination of substituents at the 2,6-positions: (1) 3-CP and 3,5-DCP, (2) 2,3-DCP, 2,3,5-TCP, and 2,4,5-TCP, and (3) 2,3,6-TCP and PCP. In each family, the association constant increases with an increase in the acid-dissociation constant of the phenols; such relations indicate that the association of [Cr(acac)$_3$] with the chlorinated phenols is due to hydrogen bonding of the hydroxyl hydrogen atom of the phenols to [Cr(acac)$_3$]. In addition, these three families lie at different regions in Fig. 2, and the

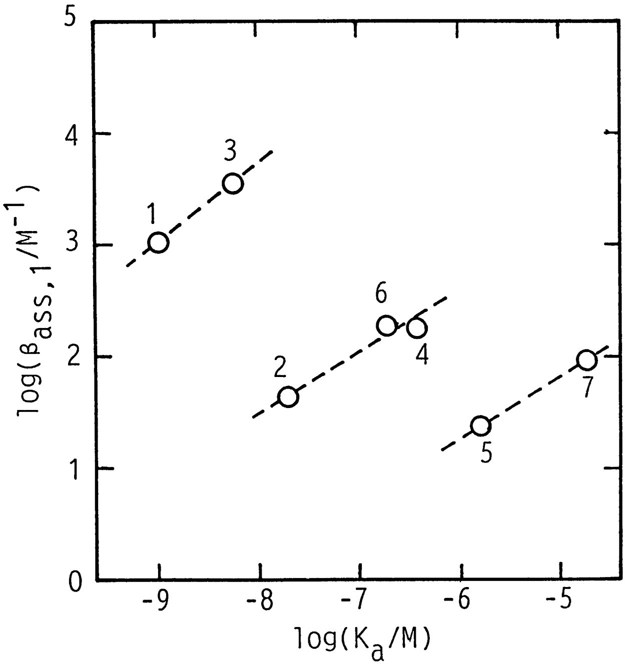

Fig. 2. Correlation between the logarithmic values of the association constant ($\beta_{\mathrm{ass},1}$) and the acid-dissociation constant (K_{a}) of chlorinated phenols. The numbers in figure correspond to those in Table 1.

association constants decrease as family(1)>family(2)>family(3). This difference among the families can be mainly interpreted in terms of the formation of an intramolecular hydrogen bond between the hydroxyl hydrogen atom and the chlorine atoms at the 2,6-positions, which should reduce the intermolecular association with $[Cr(acac)_3]$.[12] The intermolecular association may also be hindered sterically by bulky chlorine atoms at the 2,6-positions. Consequently, 3,5-DCP has the highest association ability among the investigated phenols, since this phenol has no chlorine atoms at the 2,6-positions and its acidity is relatively strong due to the electron-withdrawing nature of chlorine atoms at the 3,5-positions.

The association reaction of $[Cr(acac)_3]$ was compared with that of the same type of tris(acetylacetonato) complex, $[Co(acac)_3]$, which also forms 1 : 1 and 1 : 2 association complexes with the chlorinated phenols.[7] Figure 3 shows the correlation between the logarithmic value of the association constant of $[Cr(acac)_3]$ ($\beta_{ass,i}(Cr)$) with the chlorinated phenols and that of $[Co(acac)_3]$ ($\beta_{ass,i}(Co)$) with the corresponding phenols. The same and good linear free-energy relationships are found with respect to both $\beta_{ass,1}$ and $\beta_{ass,2}$:

$$\log(\beta_{ass,i}(Cr)/M^{-i}) = 0.90 \log(\beta_{ass,i}(Co)/M^{-i}) + 0.04, \quad (8)$$

with a correlation coefficient of r=0.998. This reveals that these association reactions for $[Cr(acac)_3]$ and $[Co(acac)_3]$ are the same regarding type. As shown by the slope of 0.90, the association constants of $[Cr(acac)_3]$ are always somewhat smaller than those of $[Co(acac)_3]$. That is to say, the proton-acceptor ability of $[Cr(acac)_3]$ is a little inferior to that of $[Co(acac)_3]$. In order to discuss the reason for this difference between $[Cr(acac)_3]$ and $[Co(acac)_3]$ in detail, further investigations concerning other metal acetylacetonates may be necessary.

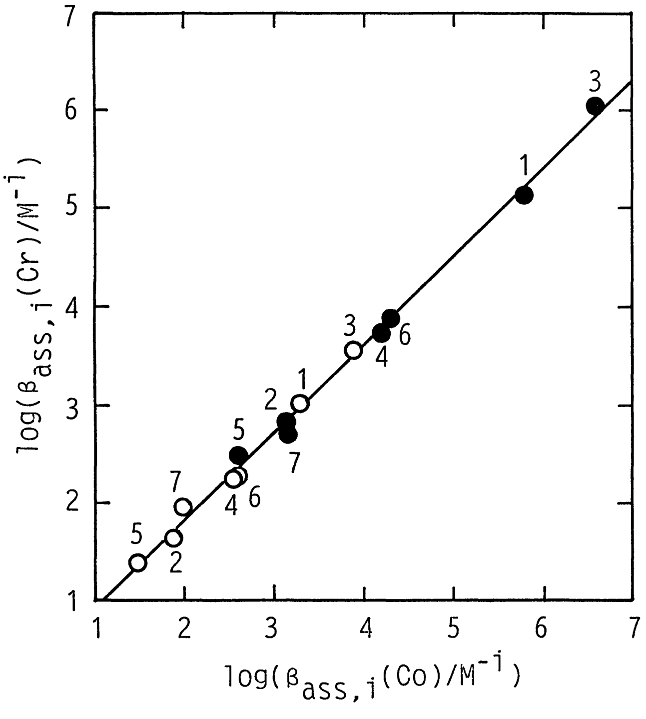

Fig. 3. Correlation between the logarithmic values of the association constants of $[Cr(acac)_3]$ ($\beta_{ass,i}(Cr)$) and $[Co(acac)_3]$ ($\beta_{ass,i}(Co)$) with chlorinated phenols in heptane. The solid line indicates the regression line by the linear least-squares procedure (Eq. 8). The numbers in figure correspond to those in Table 1. ○, i=1; ●, i=2.

The structure of the association complex may be estimated from the maximum association number of the phenols observed for both tris(acetylacetonato) complexes. The tris(acetylacetonato) complex has an octahedral configration with the ligand oxygen atoms about the central metal atom.[14] In the eight octahedral faces, two faces perpendicular to the C_3 axis of the tris-complex, each of which comprises three closely positioned oxygen atoms from three acetylacetonato ligands, are relatively open to the approach of phenols. The hydroxyl hydrogen of the phenol probably interacts with equal probability with the three oxygens on each of these two faces and, consequently, one molecule of the complex can associate with two molecules of the phenols.

In conclusion, it was found that $[Cr(acac)_3]$ forms highly stable 1 : 1 and 1 : 2 association complexes with chlorinated phenols by hydrogen bonding in heptane. This association reaction causes a great enhancement of the partition of the metal acetylacetonate between heptane and aqueous solutions in the presence of the chlorinated phenols. Many other metal chelates can probably associate with the chlorinated phenols and, from an analytical viewpoint, the addition of the chlorinated phenols can be expected to provide a great enhancement for the solvent extraction of various metal chelates or to strongly affect the retention behavior of metal chelates in liquid chromatography.

References

1) H. Imura and N. Suzuki, *J. Radioanal. Nucl. Chem.*, **88**, 63 (1985).

2) H. Imura and N. Suzuki, *Talanta*, **32**, 785 (1985).

3) H. Imura, J. Kodera, and N. Suzuki, 8th Symposium on Solution Chemistry, Kanazawa, October 1985, Abstr., p. 72.

4) N. Suzuki, S. Matsumora, and H. Imura, *Polyhedron*, **6**, 497 (1987).

5) V. M. Nekipelov and K. I. Zamaraev, *Coord. Chem. Rev.*, **61**, 185 (1985), and the references cited therein.

6) P. L. Wang, J. H. Lee, and L. P. Hwang, *J. Phys. Chem.*, **91**, 4856 (1987).

7) H. Imura, S. Katsuta, and N. Suzuki, *Polyhedron*, in press.

8) W. C. Fernelius and J. E. Blanch, *Inorg. Synth.*, **5**, 130 (1957).

9) H. Awano, H. Watarai, and N. Suzuki, *J. Inorg. Nucl. Chem.*, **41**, 124 (1979).

10) S. Katsuta, M. Sc. Thesis, Tohoku University, Sendai, 1989.

11) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).

12) M. M. Davis, "Brønsted Acid-Base Behavior in "Inert" Organic Solvents," in "The Chemistry of Nonaqueous Solvents," ed by J. J. Lagowski , Academic Press, New York (1970), Vol. 3, Chap. 1.

13) J. Drahonovsky and Z. Vacek, *Collect. Czech. Chem. Commun.*, **36**, 3431 (1971).

14) P. K. Hon and C. E. Pfluger, *J. Coord. Chem.*, **3**, 67 (1973).