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Solvatochromism of [Diamine-*N,N'*-polycarboxylato]chromium(III) and -cobalt(III) Complexes

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Visible absorption spectra of [diamine-*N,N'*-polycarboxylato]chromium(III) and -cobalt(III) complexes were measured in twelve different solvents. The diamine-*N,N'*-polycarboxylates used in this work were ethylenediamine-*N,N,N',N'*-tetraacetate ($edta^{4-}$), 1,2-cyclohexanediamine-*N,N,N',N'*-tetraacetate ($cydta^{4-}$), *N'*-(2-hydroxyethyl)ethylenediamine-*N,N,N'*-triacetate ($hedtra^{3-}$), and *N'*-methylethylenediamine-*N,N,N'*-triacetate ($medtra^{3-}$). The first d-d absorption maxima of these complexes depend considerably on the solvents. From the solvatochromic behaviors of these complexes, it was concluded that solid complexes, K[Co(edta)]·$2H_2O$, K[Co(cydta)]·$3H_2O$, [Co(hedtra)(H_2O)], [Co(medtra)(H_2O)]·$3H_2O$, Na[Cr(cydta)]·$4.5H_2O$, and probably K[Cr(edta)]·$2H_2O$, dissolve in the solvents while holding their first coordination sphere intact; in some solvents, however, [Cr(medtra)(H_2O)]·$1.5H_2O$ and [Cr(hedtra)(H_2O)]·$1.5H_2O$ undergo substitutions of the coordinated water molecule to form [Cr(medtra)(solvent)] and [Cr(hedtra)(solvent)], respectively.

It has been known that the metal to ligand or ligand to metal charge-transfer absorption bands of transition metal complexes are solvent-dependent.[1-3] The first d-d absorption bands of the octahedral cobalt(III) or chromium(III) complexes, on the other hand, are generally insensitive to the solvents, and there are only a few reports concerning solvent-dependent d-d absorptions.[4-7] Bjerrum et al. measured the electronic absorption spectra of amine complexes of chromium (III) and cobalt(III) in water, methanol, acetone, and nitromethane, and reported for the first time that the d-d absorption band maxima are practically independent of the solvents.[4] Later, Adamson investigated visible absorption spectra of K[$Cr(NCS)_4(NH_3)_2$] in eleven different solvents and found that the first ligand field band appears between 518 and 530 nm, depending on the solvents.[5] Nishimura et al. observed rather large solvatochromism for the d-d transition bands of [$CrCl_2(CH_3)$(tetrahydrofuran)$_3$].[6] Recently, Taura has reported that the peak position (λ_{max}) for the first d-d absorption band of K[Co(edta)]·$2H_2O$[7,8] changes with solvents and correlates with the acceptor numbers of the solvents which were proposed by Mayer, Gutmann, and Gerger.[9]

In the present paper, solvatochromism of the chromium(III) and cobalt(III) complexes containing diamine-*N,N'*-polycarboxylates was investigated. The ligand, L, used were classified into two types. One is tetraacetates ($edta^{4-}$ and $cydta^{4-}$) to form uninegatively charged complexes and the other is triacetates ($hedtra^{3-}$ and $medtra^{3-}$) to form neutral complexes.

As the Co(III) complexes are substitution inert,[10-12] the incorporation of a solvent molecule into the first coordination sphere does not occur. In fact, the Co(III)-L complexes did not show any spectral change with time in various solvents. Such inertness towards ligand substitution allowed us to measure the absorption spectra of $[Co(edta)]^-$, $[Co(cydta)]^-$, [Co(hedtra)(H_2O)], and [Co(medtra)(H_2O)] in various solvents without incorporating the solvent molecules into their first coordination spheres.

The Cr(III)-L complexes, on the other hand, have variable reactivities towards ligand substitution. Although chromium(III) complexes have been known to be substitution inert, substitutions at the site of the coordinated water molecule in $[Cr(edta)(H_2O)]^-$ and [Cr(hedtra)(H_2O)] proceed very rapidly:[13]

$$[CrL(H_2O)]^{n-} + X^- \rightleftharpoons [CrXL]^{(n+1)-} + H_2O \qquad (1)$$

Ligand substitution reactions of [Cr(medtra)(H_2O)] are much slower than those of $[Cr(edta)(H_2O)]^-$ and [Cr(hedtra)(H_2O)], but are still considerably faster than the reactions of ordinary chromium(III) complexes.

An X-ray crystal structure analysis of K[Cr(edta)]·$2H_2O$ has shown that the complex contains sexidentate $edta^{4-}$ and does not contain a water molecule in the first coordination sphere.[14] Although we have formulated the Cr(III)-EDTA complex as $[Cr(edta)(H_2O)]^-$, there is a serious problem concerning the structure of the Cr(III)-EDTA complex in an aqueous solution: whether the $edta^{4-}$ ion acts as a quinquedentate ligand or as a sexidentate ligand.[15-17] Therefore, it is of interest to determine whether the Cr(III)-EDTA complex is present as $[Cr(edta)]^-$, $[Cr(edta)(H_2O)]^-$, or $[Cr(edta)(solvent)]^-$ in various solvents.

The differences in solution behaviors of Co(III)-L and Cr(III)-L complexes should be reflected in the solvatochromism of these complexes, which led us to make the present study.

Experimental

Materials. The chromium(III) and cobalt(III) complexes, K[Cr(edta)]·$2H_2O$,[18] Na[Cr(cydta)]·$4.5H_2O$,[19] [Cr(hedtra)(H_2O)]·$1.5H_2O$,[13] [Cr(medtra)(H_2O)]·$1.5H_2O$,[13] K[Co(edta)]·$2H_2O$,[20,21] K[Co(cydta)]·$3H_2O$,[22] [Co(hedtra)(H_2O)],[11] and [Co(medtra)(H_2O)]·$3H_2O$[23] were prepared by methods described in the literature. Methyltrioctylammonium chloride (Tokyo Kasei), Dicyclohexano-18-crown-6 (Nippon Soda Co.), and dibenzo-18-crown-6 (Aldlich) were used without further purification.

Solvents. Hexamethylphosphoric triamide (HMPA) was

Table 1. Linear Correlations between $\tilde{\nu}_{max}$ Values of the [Diamine-*N,N'*-polycarboxylato]cobalt(III) and -chromium(III) Complexes[a)]

Complex 1	Complex 2	Slope	Intercept 10^4 cm^{-1}	Correlation coefficient
$[Co(cydta)]^-$	$[Co(edta)]^-$	1.10	−0.197	0.96
$[Co(hedtra)(H_2O)]$	$[Co(edta)]^-$	0.671	0.572	0.86
$[Co(medtra)(H_2O)]$	$[Co(edta)]^-$	0.615	0.688	0.96
$[Co(hedtra)(H_2O)]$	$[Co(cydta)]^-$	0.581	0.746	0.84
$[Co(medtra)]H_2O)]$	$[Co(cydta)]^-$	0.538	0.838	0.95
$[Co(hedtra)(H_2O)]$	$[Co(medtra)(H_2O)]$	0.888	0.193	0.98
$[Cr(cydta)]^-$	$[Cr(edta)]^-$	1.03	−0.066	0.98
$[Cr(hedtra)(H_2O)]$	$[Cr(edta)]^-$			b)
$[Cr(medtra)(H_2O)]$	$[Cr(edta)]^-$			b)
$[Cr(hedtra)(H_2O)]$	$[Cr(medtra)(H_2O)]$	0.864	0.237	0.95
$[Cr(edta)]^-$	$[Co(edta)]^-$	1.78	−1.46	0.95
$[Cr(cydta)]^-$	$[Co(edta)]^-$	1.86	−1.62	0.95
$[Cr(edta)]^-$	$[Co(cydta)]^-$	1.53	−0.992	0.94
$[Cr(cydta)]^-$	$[Co(cydta)]^-$	1.58	−1.08	0.92

a) The values of the slope and intercept were calculated from the following equation: $\tilde{\nu}_{max}$(complex 1)= intercept+slope$\times\tilde{\nu}_{max}$ (complex 2).
b) Very scattered plots.

purified by distillation over calcium hydride. Other solvents, acetone (AC), acetonitrile (AN), formamide (FA), *N*-methylformamide (NMF), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), nitromethane (NM), methanol (MA), ethanol (EA), and toluene were of reagent grade, and were used as received.

Spectral Measurements. The visible absorption spectra were recorded on a Hitachi 330 or a Union-Giken SM 401 recording spectrophotometer. Most of the measurements were made at room temperature. Solutions of the complexes were prepared by simply dissolving a complex in solvents. Some anionic complexes with low solubility were dissolved with dibenzo-18-crown-6 or dicyclohexano-18-crown-6. Dissolution rate of the complexes varied depending on the complex and the solvent. In order to achieve sufficient concentrations of the complexes in solution, it was necessary, in some cases, that the mixtures of the complexes and the solvents were shaken vigorously or sonicated for 3—4 h before the spectral measurements. Among the complexes investigated in this study, $[Cr(medtra)(H_2O)]$ and $[Cr(eedtra)(H_2O)]$ revealed spectral changes with times over 1—2 h after dissolution into various solvents. The spectral data for these complexes were those taken after spectral changes came to an end. No spectral changes with time were observed for other complexes examined in this study. Lists of the $\tilde{\nu}_{max}$ values for the complexes measured in this study are deposited at the office of the Chemical Society of Japan (Document No. 8726).

Results and Discussion

Solvatochromism of the Cobalt(III) Complexes Containing Diamine-*N,N'*-polycarboxylate. It is well-established that the $edta^{4-}$ and $cydta^{4-}$ ions act as sexidentate ligands in $[Co(edta)]^-$ and $[Co(cydta)]^-$, respectively.[11,24,25] When the $\tilde{\nu}_{max}$ values for $[Co(cydta)]^-$ in various solvents are plotted against those of the $\tilde{\nu}_{max}$ values for $[Co(edta)]^-$, a linear relation is obtained

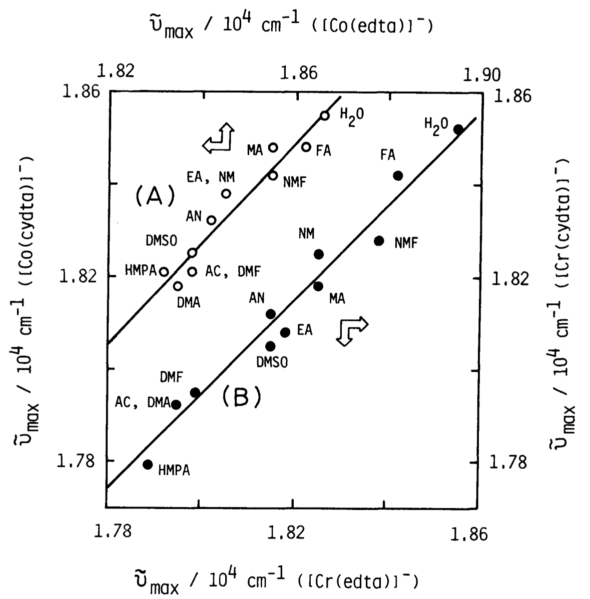

Fig. 1. Linear relationships between $\tilde{\nu}_{max}([Co(cydta)]^-)$ and $\tilde{\nu}_{max}([Co(edta)]^-)$ (A), and between $\tilde{\nu}_{max}([Cr(cydta)]^-)$ and $\tilde{\nu}_{max}([Cr(edta)]^-)$ (B).

as shown in Fig. 1. The slopes of the plots are close to unity (Table 1). Therefore, the solvatochromism of both $[Co(cydta)]^-$ and $[Co(edta)]^-$ arises from common effect(s) which is(are) induced by the solvent molecules surrounding the first coordination sphere.

Good linear correlations between the $\tilde{\nu}_{max}$ values for $[Co(edta)]^-$ (or $[Co(cydta)]^-$) and those for the neutral complexes, $[Co(hedtra)(H_2O)]$ and $[Co(medtra)(H_2O)]$, could also be observed (Fig. 2 and Table 1). These show that the factor(s) governing the solvatochromism of the $[Co(edta)]^-$ and $[Co(cydta)]^-$ complexes is also effective to the solvatochromism of the neutral com-

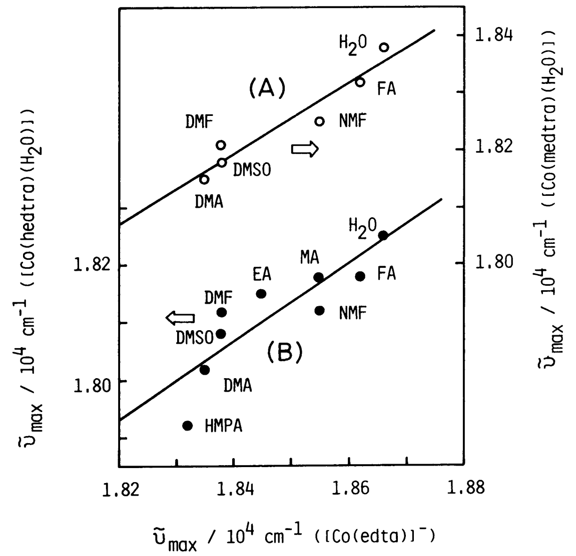

Fig. 2. Plots of $\tilde{\nu}_{max}$([Co(medtra)(H_2O)]) against $\tilde{\nu}_{max}$([Co(edta)]$^-$) (A), and the plots of $\tilde{\nu}_{max}$([Co(hedtra)(H_2O)]) against $\tilde{\nu}_{max}$([Co(edta)]$^-$) (B).

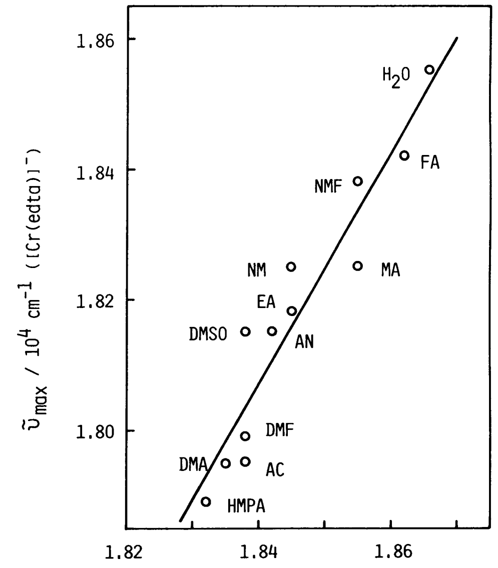

Fig. 3. Plots of $\tilde{\nu}_{max}$([Cr(edta)]$^-$) against $\tilde{\nu}_{max}$([Co(edta)]$^-$).

plexes. However, the degree of the solvent effect is smaller for the neutral complexes than for the [Co(edta)]$^-$ or [Co(cydta)]$^-$: The slopes of the plots in Fig. 2 are only about 0.6.

Solvatochromism of the Chromium(III) Complexes Containing Diamine-*N,N'*-polycarboxylate. The structure of [Cr(edta)]$^-$ in a crystal of K[Cr(edta)]·$2H_2O$ has been determined to be an octahedral coordination with the sexidentate edta^{4-}.[14] Similarly, Na[Cr(cydta)]·$4.5H_2O$ contains the sexidentate cydta^{4-}.[17] However, there have been controversial discussions concerning the structure of the Cr(III)-EDTA complex in an aqueous solution, as to whether it contains a quinquedentate edta^{4-} or a sexidentate one.[15–17] A similar problem may arise when the complex is dissolved in a solvent other than water. If

$$[\mathrm{Cr(edta)}]^- + \text{solvent} \rightleftharpoons [\mathrm{Cr(edta)(solvent)}]^- \quad (2)$$

takes place in various solvents, the correlation between $\tilde{\nu}_{max}$ values of [Cr(edta)]$^-$ and [Co(edta)]$^-$ is expected to be poor, since the [Co(edta)]$^-$ maintains its strucure in solution. However, plots of the $\tilde{\nu}_{max}$ values of [Cr(edta)]$^-$ against those of [Co(edta)]$^-$ show a good linear relation (Fig. 3 and Table 1). This indicates that [Cr(edta)]$^-$ in K[Cr(edta)]·$2H_2O$ retains its original strucure in most solvents, i.e. octahedral coordination with sexidentate edta^{4-}.[26]

In connection with this, interesting phenomena were found: The Cr(III)-EDTA complex can be extracted from an aqueous solution of K[Cr(edta)]·$2H_2O$ to toluene in the presence of a phase-transfer catalyst, methyltrioctylammonium chloride. The extracted species is reddish violet in a toluene layer and shows visible absorption maximum at 544 nm (only 5 nm longer than the absorption maximum of the aqueous solution (λ_{max}=539 nm)). When solid K[Cr(edta)]·$2H_2O$ is dissolved directly into toluene with methyltrioctylammonium chloride, a bluish violet solution (λ_{max}=554 nm) is obtained, which may indicate that [CrCl(edta)]$^{2-}$ is formed. In the toluene extract from the aqueous solution of K[Cr(edta)]·$2H_2O$, the complex may be present as [Cr(edta)]$^-$ or [Cr(edta)(H_2O)]$^-$. A similar phenomenon was also observed for [Cr(hedtra)(H_2O)].

There is a tendency that the metal complexes containing sexidentate cydta^{4-} are much more stable than corresponding complexes containing both quinquedentate cydta^{4-} and a unidentate ligand: There is no spectral change when an acetate buffer solution is added (up to 1 mol dm^{-3}) to an aqueous solution of Na[Cr(cydta)]·$4.5H_2O$, suggesting that the acetate ions do not coordinate to Cr(III)-CyDTA complex.[27] Although there have been moderately stable cobalt(III) complexes, [CoX(edta)]$^{2-}$ (X=Cl^-, Br^-, NO_2^-, OH^-, NCS^-, SCN^-)[28–30] and [Co(edta)(H_2O)]$^-$,[31] no cydta^{4-} analogue of this type has been known except [CoCl(cydta)]$^{2-}$.[22] Moreover, [CoCl(cydta)]$^{2-}$ is quite unstable and quickly changes to [Co(cydta)]$^-$ in an aqueous solution. These findings and some other facts[11,19,32] suggest that a Cr(III)-CyDTA complex contains a sexidentate cydta^{4-} ligand in aqueous solution.

The $\tilde{\nu}_{max}$ values of [Cr(cydta)]$^-$ in various solvents correlate linearly well with those of [Cr(edta)]$^-$ and [Co(cydta)]$^-$ as shown in Fig. 1 and Table 1. These facts may indicate that K[Cr(edta)]·$2H_2O$ and Na[Cr(cydta)]·$4.5H_2O$ dissolve in various solvents to form [CrL]$^-$ ions which contain sexidentate L^{4-} without the coordinated solvent molecule. The solvatochromic shifts of [Cr(cydta)]$^-$ and [Cr(edta)]$^-$ observed in this study are larger than those of [Co(edta)]$^-$.

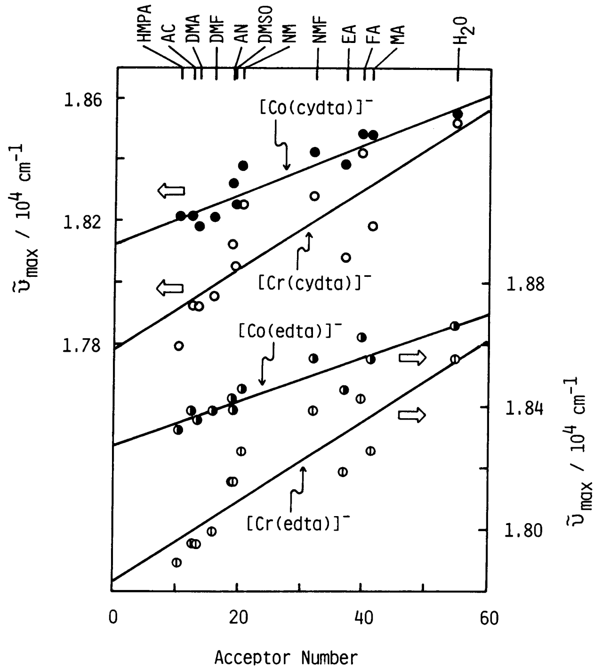

Fig. 4. Relationships between the $\tilde{\nu}_{max}$ values of $[ML]^-$ (M=Cr, Co; L=$edta^{4-}$, $cydta^{4-}$) and the acceptor numbers of the solvents. ●: $[Co(cydta)]^-$, ○: $[Cr(cydta)]^-$, ◑: $[Co(edta)]^-$, ⦶: $[Cr(edta)]^-$.

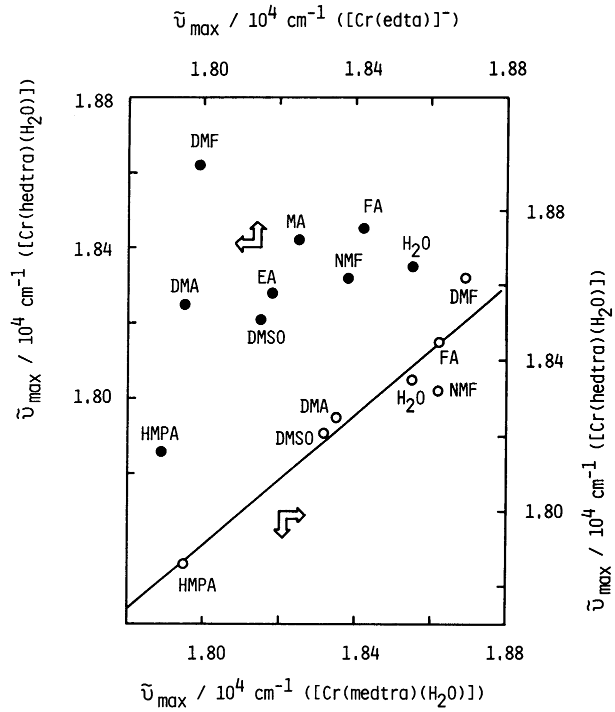

Fig. 5. Plots of $\tilde{\nu}_{max}([Cr(hedtra)(H_2O)])$ against $\tilde{\nu}_{max}([Cr(edta)]^-)$ (●), and linear relationship between $\tilde{\nu}_{max}([Cr(hedtra)(H_2O)])$ and $\tilde{\nu}_{max}([Cr(medtra)(H_2O)])$ (○).

Taura reported that a linear relation could be obtained between the plots of the λ_{max} values of $[Co(edta)]^-$ and the acceptor numbers of the solvents.[7] On the basis of the more extensive measurements in this study, Taura's observation was confirmed, as shown in Fig. 4.[33] It is also shown in Fig. 4 that a linear relation exists between the $\tilde{\nu}_{max}$ values of $[Co(cydta)]^-$, $[Cr(edta)]^-$, or $[Cr(cydta)]^-$ and the accepter numbers. This is quite natural since linear relations exist mutually among the $\tilde{\nu}_{max}$ values of $[Co(edta)]^-$, $[Co(cydta)]^-$, $[Cr(edta)]^-$, and $[Cr(cydta)]^-$ as shown in Figs. 1 and 3 and Table 1.

There is no correlation between $\tilde{\nu}_{max}$ values of $[Cr(hedtra)(H_2O)]$ or $[Cr(medtra)(H_2O)]$ and those of $[Cr(edta)]^-$ or $[Cr(cydta)]^-$ as exemplified in Fig. 5. This is contrasted to the cases of the corresponding cobalt(III) complexes (Fig. 2). A poor correlation (Fig. 5) may be best explained by the occurence of reaction 3, at least in some solvents:

$$[CrL(H_2O)] + \text{solvent} \rightleftharpoons [CrL(\text{solvent})] + H_2O \quad (3)$$
$$(L = hedtra^{3-}, medtra^{3-})$$

where the coordinated water molecule is replaced by a solvent molecule.

If the occurrence of reaction 3 is the case, a spectral change with time should be observed in the time scale corresponding to the ligand substitution rates of those chromium(III) complexes. When an aqueous solution of $[Cr(medtra)(H_2O)]$ was mixed with DMF or DMSO, a slow spectral change was observed. The initial λ_{max} value (539 nm) in an aqueous solution shifts to a shorter wavelength in a reaction with DMF, and to a longer wavelength in a reaction with DMSO; the rate of the spectral change is reasonable in view of the kinetic data of the ligand substitution reactions of $[Cr(medtra)(H_2O)]$.[34] When an aqueous solution of $[Cr(eedtra)(H_2O)]$ was mixed with DMF or DMSO, a spectral change similar to the case of $[Cr(medtra)(H_2O)]$ system was observed. These findings are consistent with the occurence of reaction 3. Therefore, the solvatochromism of those complexes such as $[Cr(medtra)(H_2O)]$ contains two factors: The change in chromophore introduced by the formation of [CrL(solvent)], and the solvation at the outer coordination sphere.

The scattered plots in Fig. 5 suggest that $[Cr(hedtra)(H_2O)]$ also undergoes reaction 3. The substitution reaction of the water molecule in $[Cr(hedtra)(H_2O)]$ with a solvent molecule is expected to occur in the stopped-flow time scale.[13,34] However, the stopped-flow experiments were hampered by heat evolving upon mixing, incomplete mixing, and/or cavitation. These unfavorable phenomena are often encountered upon the mixing of different solvents. Therefore, it is impossible to determine whether reaction 3 is completed within the time of mixing or does not take place: in other words, whether the complex exists in the solvents as [Cr(hedtra)(solvent)] or $[Cr(hedtra)(H_2O)]$. However, the $\tilde{\nu}_{max}$ values of $[Cr(hedtra)(H_2O)]$ correlates linearly with those of $[Cr(medtra)(H_2O)]$, as shown in Fig. 5 and Table 1. This may indicate that

[Cr(hedtra)(H_2O)] also undergoes reaction 3.

The formation of [Cr(hedtra)(solvent)] in some solvents raises a question why $[Cr(edta)]^-$ does not accomodate a solvent molecule into the first coordination sphere in most of the solvents, but [Cr(hedtra)(H_2O)] does. The formation of $[Cr(edta)(solvent)]^-$ would be less favorable than that of [Cr(hedtra)(solvent)], since the formation constants of the mixed ligand complexes, $[CrX(edta)]^{2-}$ ($X=OAc^-$, N_3^-, NCS^-), in aqueous solutions have been known to be 17—28 times smaller than those of the corresponding $[CrX(hedtra)]^-$.[13,34]

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8) Abbreviations used in this paper: $edta^{4-}$, ethylenediamine-*N,N,N′,N′*-tetraacetate; $cydta^{4-}$, 1,2-cyclohexanediamine-*N,N,N′,N′*-tetraacetate; $hedtra^{3-}$, *N′*-(2-hydroxyethyl)-ethylenediamine-*N,N,N′*-triacetate; $edtra^{3-}$, ethylenediamine-*N,N,N′*-triacetate; $medtra^{3-}$, *N′*-methylethylenediamine-*N,N,N′*-triacetate; $eedtra^{3-}$, *N′*-ethylethylenediamine-*N,N,N′*-triacetate; OAc^-, acetate.

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