2362 © 1991 *The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***64***, *2362—2371 (1991)* [Vol. 64, No. 8

Spectrochemical Series for the Outersphere Coordination of Carboxylatocobaltate(III) Complexes with Solvent Molecules[1)]

Toshiaki Taura
Department of Chemistry, University of Aichi Prefecture, Takadacho 3-28, Mizuho-ku, Nagoya 467

(Received March 2, 1991)

The d–d transition spectra of $K[Co(edta)]\cdot 2H_2O$, $K[Co(mal)_2en]\cdot H_2O$, $K[Co(ox)_2en]\cdot 1.5H_2O$, $K_2[Co(ox)_2gly]\cdot 3H_2O$, and $K_3[Co(ox)_3]\cdot 3H_2O$ (edta=ethylenediaminetetraacetate, mal=malonate, en=ethylenediamine, ox=oxalate, and gly=glycinate) were measured in a variety of solvents: H_2O, $HOCH_2CH_2OH$, CH_3OH, $HCONH_2$, C_2H_5OH, i-C_3H_7OH, $CHCl_3$, CH_3NO_2, CH_2Cl_2, $(CH_3)_2SO$, CH_3CN, $HCON(CH_3)_2$, C_6H_5CN, $C_6H_5NO_2$, $CH_3CON(CH_3)_2$, $(CH_3)_2CO$, and $[(CH_3)_2N]_3PO$. The ^{59}Co NMR spectra of $K[Co(edta)]\cdot H_2O$ and $K_3[Co(ox)_3]\cdot 3H_2O$ were also recorded at 25 °C in these solvents. It was found that the peak positions (λ_{max}) of the first and second d–d transition bands were greatly influenced by solvent molecules; the peak positions (λ_{max}) of all the cobalt(III) complexes were linearly correlated to the electrophilic ability (Gutmann's acceptor number) of the solvent and those of $K[Co(edta)]\cdot 2H_2O$ and $K_3[Co(ox)_3]\cdot 3H_2O$ were linearly correlated to the ^{59}Co NMR chemical shifts in the corresponding solvents. This suggests that the d–d transition energy (ΔE) is influenced by solvent molecules as electron acceptors since ^{59}Co NMR chemical shifts are theoretically correlated linearly to the peak positions in the first d–d transition (A_{1g}–T_{1g}). The ^{13}C NMR measurements indicated that solvent molecules directly interact with the carboxyl groups of cobalt(III) complexes. Therefore, the influence of the solvent on the d–d transition energy of the carboxylatocobaltate(III) complex is due to the electron-withdrawing effect of solvent molecules on the carboxyl oxygens of the cobalt(III) complex. A spectrochemical series for the outersphere coordination of the cobalt(III) complex with solvent molecules is proposed.

It was reported that potassium ethylenediaminetetraacetatocobaltate(III) dihydrate, $K[Co(edta)]\cdot 2H_2O$, was solubilized by macrocyclic polyethers, crown ethers and cryptand 222, in a variety of organic solvents including low-polarity chloroform (dielectric constant=4.8).[2)] In the course of this work, it was discovered that the color of this cobalt(III) complex changed from reddish violet in water to bluish violet in acetone. This complex was quite stable and inert against ligand substitution or redox reaction in these solvents, and thus this color change has been due to the outersphere interaction of $[Co(edta)]^-$ with solvent molecules.

In a previous paper,[3)] it was suggested that the peak positions (λ_{max}) of the first d–d transition band (corresponding to the color of the complex) were linearly correlated with the acceptor numbers of solvents, which were proposed by Mayer, et al.[4)] as a measure of the electrophilic ability of solvents. The solvent influence on the peak position and the interaction between $[Co(edta)]^-$ and solvent molecules could then be quantitatively estimated by using the acceptor number of the solvent. Using this procedure, the solvent influence of some cobalt(III) or chromium(III) complexes has been studied.[1,5—7)]

The present work is an attempt to elucidate what kind of interaction between solvent molecules and $[Co(edta)]^-$ or some related carboxylatocobaltate(III) complexes plays an important role in the solvent influence on the d–d transition spectra. The solvent influence on the electronic and ^{59}Co NMR spectra of $K[Co(edta)]\cdot 2H_2O$, $K[Co(mal)_2en]\cdot H_2O$, $K[Co(ox)_2en]\cdot 1.5H_2O$, $K_2[Co(ox)_2gly]\cdot 3H_2O$, and $K_3[Co(ox)_3]\cdot 3H_2O$, where edta=ethylenediaminetetraacetate, mal=malonate, en=ethylenediamine, ox=oxalate, and gly=glycine, was investigated, and was compared with the influence of the solvent on the ^{13}C NMR spectra which has already been reported.[5)]

Experimental

Materials. The cobalt(III) complexes used in this work ($K[Co(edta)]\cdot 2H_2O$,[8)] $K[Co(mal)_2en]\cdot H_2O$,[9)] $K[Co(ox)_2en]\cdot 1.5H_2O$,[10)] $K_2[Co(ox)_2gly]\cdot 3H_2O$,[11)] $K_3[Co(ox)_3]\cdot 3H_2O$,[12)] $[Co(en)_3](ClO_4)_3$,[13)] and $[Co(NH_3)_6](ClO_4)_3$[14)]) were prepared by the usual methods. The anhydrous salt of $K[Co(edta)]\cdot 2H_2O$ was prepared by heating the complex at 110 °C in an oven. The purities of these complexes were checked by elemental analysis and spectroscopic methods. The organic solvents and cryptand 222 (Merck: Kryptofix 222) were of the purest commercial grade available and were used without further purification. The solvents used in this study were; water (H_2O), ethylene glycol (EG), methanol (CH_3OH), formamide (FA), ethanol (C_2H_5OH), 2-propanol (i-C_3H_7OH), chloroform ($CHCl_3$), nitromethane (CH_3NO_2), dichloromethane (CH_2Cl_2), dimethyl sulfoxide (Me_2SO), acetonitrile (CH_3CN), *N,N*-dimethylformamide (DMF), benzonitrile (C_6H_5CN), nitrobenzene ($C_6H_5NO_2$), *N,N*-dimethylacetamide (DMA), acetone (Me_2CO), and hexamethylphosphoric triamide (HMPA).

Measurements. Electronic Spectra: The electronic absorption spectra of the cobalt(III) complexes in solutions of appropriate concentrations (0.001—0.005 mol dm^{-3}) were measured at room temperature. The complex salts were dissolved in organic solvents by the addition of an excess of cryptand 222 (amounts 1.5 times larger than the concentration of the K^+ ion). The spectra were recorded on a Shimadzu UV-240 recording spectrophotometer. The spectra were not influenced by the addition of various amounts of cryptand 222, by a change in the concentration of the cobalt(III) complex, or by a change in the temperature. Water of crystallization in the complexes was not found to change the peak positions of the absorption spectra.[15)]

The reflection spectra of the cobalt(III) complexes and the anhydrous salt of K[Co(edta)] were measured on a JASCO UVIDEC-410 spectrophotometer with a TIS-241 reflectance attachment.

^{59}Co NMR. The ^{59}Co NMR spectra of K[Co(edta)]·2H_2O and K_3[Co(ox)$_3$]·3H_2O were measured at 25 °C in solutions of the complex anion for water, and for organic solvents containing cryptand 222 (amounts 1.5 times larger than the concentration of the K^+ ion). The ^{59}Co chemical shift is influenced by the concentration of the complex. Therefore, measurements were carried out in solutions of various concentrations. A JEOL JNM-GX400 NMR spectrometer was operated in Fourier transform mode at 95.856 MHz for K[Co(edta)]·2H_2O and 96.095 MHz for K_3[Co(ox)$_3$]·3H_2O. The 10-mm NMR tube used here contained a sample solution of 2.5 ml; D_2O in a 2-mm tube was fixed inside a sample 10-mm tube during spectra accumulation. The reference was not used, but the signal of the complex appeared quite broad and the peak position in water was set at 0 ppm before the other ^{59}Co NMR measurements were taken. The position of the signal in water did not change after the measurements of the other samples. The spectra were recorded after 256—4096 accumulations of 0.1 s pulse intervals.

Results and Discussion

Electronic Spectra in a Variety of Solvents. The electronic spectra of K[Co(edta)]·2H_2O and K[Co(mal)$_2$en]·H_2O in water, methanol, ethanol, and chloroform are shown in Fig. 1. The spectral bands in the longer wavelength region correspond to the first d–d transition[16] of the cobalt(III) center. The second d–d transition bands appear in the shorter wavelength region. It is clear that the peak positions of the first and second d–d transition bands appear in the shorter wavelength regions in water, and shift to longer wavelengths in the other solvents.[17] As the [Co(edta)]$^-$ and [Co(mal)$_2$en]$^-$ anions are inert and stable in these solvents under the conditions of the measurements, the differences in the peak positions are due to the outersphere interaction between the complex anion and solvent molecules.

As for the other complex anions, the peak positions also appear in the shorter wavelength regions in water and shift to longer wavelengths in the other solvents. The data of the observed peak positions (λ_{max} : λ_1 and λ_2) of the first and second d–d transition bands are presented in Table 1 for the solvents listed in the Experimental section. This table also includes some solvent parameters: Gutmann's acceptor number (*AN*) and Kosower's parameter (*Z*).[18]

Correlation between the Peak Positions in the d–d Transition Spectrum and the Acceptor Numbers of Solvents. As the solvent influence should be generated by the outersphere interaction between the complex anion and solvent molecules, we have considered the solvent influence on the peak position (λ_{max}) on the basis of the acceptor numbers (*AN*) which were proposed by Mayer, Gutmann, and Gerger as a measure of estimating the electrophilic ability of solvents.[4] The *AN* values of the solvents were determined on the basis of ^{31}P NMR chemical shifts of triethylphosphine oxide ((C_2H_5)$_3$P=O) in the solvents. A large acceptor number indicates that a solvent is a good electron acceptor. Therefore, solvent molecules could interact strongly with an anion like [Co(edta)]$^-$ if the solvent has a large acceptor number.

In Fig. 2, the λ_{max} (λ_1) values of the first d–d transition bands of the complex anions are plotted versus the acceptor numbers of the solvents: H_2O, CH_3OH, FA,

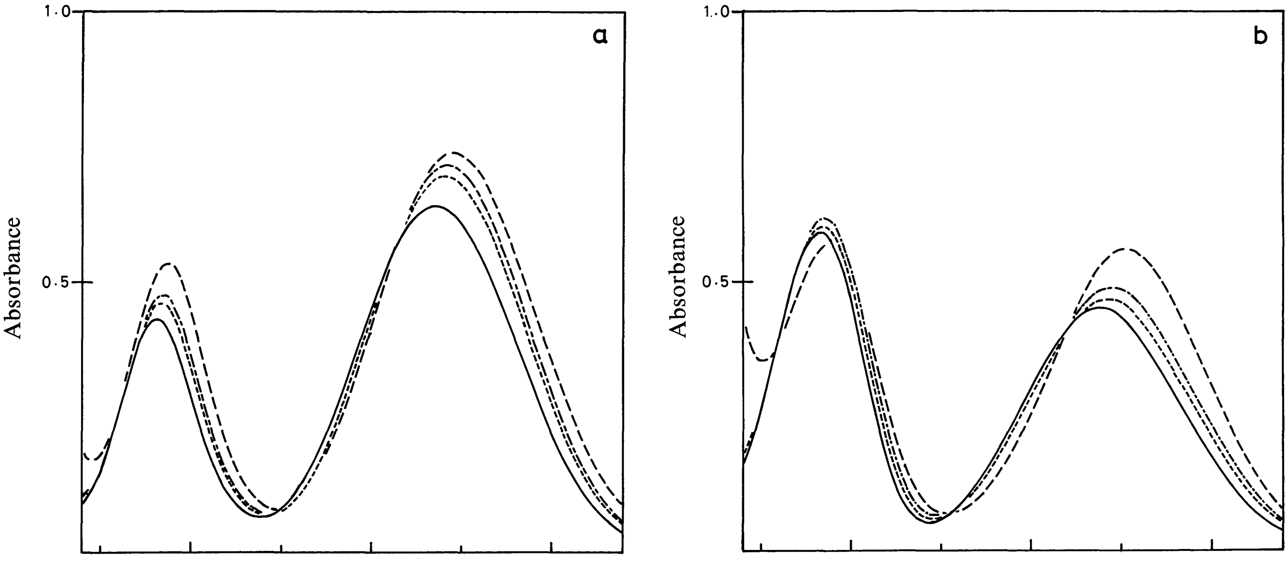


Fig. 1. The electronic absorption spectra of K[Co(edta)]·2H_2O (0.002 mol dm^{-3}) (a) and K[Co(mal)$_2$en]·H_2O (0.005 mol dm^{-3}) (b) in water (——), methanol (------), ethanol (— — —), and chloroform (——).

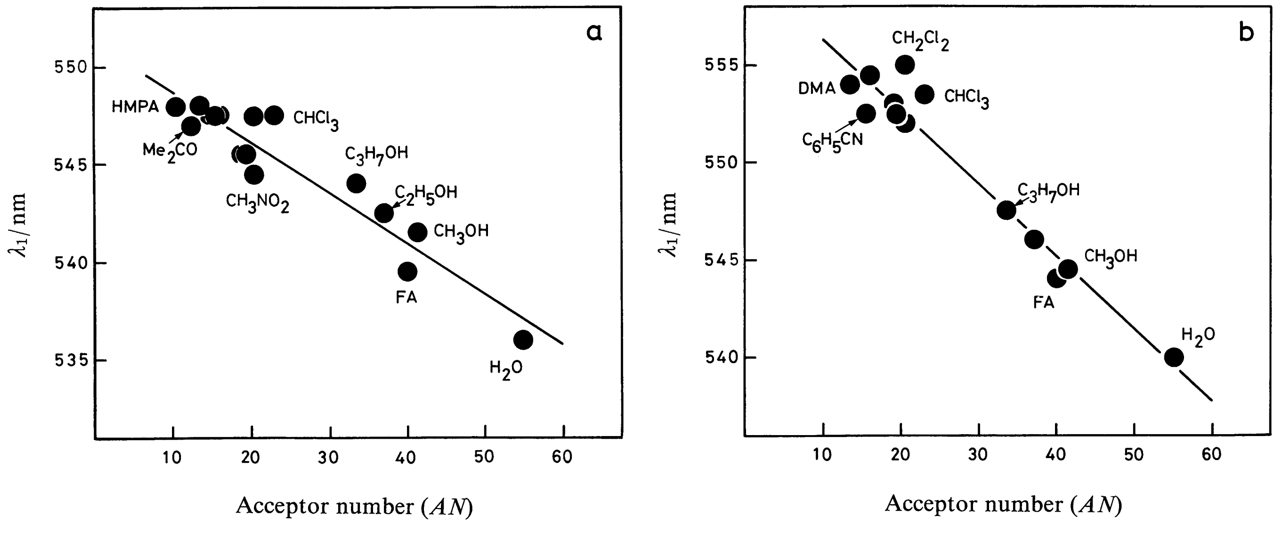
Table 1. The Peak Positions (λ_1 and λ_2) of the First and Second d–d Transition Bands of the Carboxylatocobaltate(III) Complexes in a Variety of Solvents

Solvent	AN[a]	Z[a]	$K[Co(edta)]\cdot 2H_2O$		$K[Co(mal)_2en]\cdot H_2O$		$K[Co(ox)_2en]\cdot 1.5H_2O$		$K_2[Co(ox)_2gly]\cdot 3H_2O$		$K_3[Co(ox)_3]\cdot 3H_2O$	
			λ_1/nm	λ_2/nm	λ_1/nm	λ_2/nm	λ_1/nm	λ_2/nm	λ_1/nm	λ_2/nm	λ_1/nm	λ_2/nm
1 H_2O	54.8	94.6	536.0	381.5	540.0	384.0	540.5	382.5	566.5	403.5	602.0	424.0
2 EG		85.1	540.5	382.5	543.0	385.5	543.0	384.5	568.5	405.5	603.0	425.0
3 CH_3OH	41.3	83.6	541.5	383.5	544.5	385.5	544.5	386.0	569.5	405.5	603.5	425.0
4 FA	39.8	83.3	539.5	383.0	544.0	387.0	543.0	385.0	568.5	405.0	603.5	424.5
5 C_2H_5OH	37.1	79.6	542.5	384.0	546.0	386.0	546.0	387.0	572.0	407.0	603.0	425.0
6 i-C_3H_7OH	33.5	76.3	544.0	385.0	547.5	386.5	548.5				606.5	427.0
7 $CHCl_3$	23.1	63.2	547.5	388.0	553.5	388.5			577.0	409.5	609.0	427.0
8 CH_3NO_2	20.5	71.2	544.5		552.0		549.5		574.0		606.0	424.5
9 CH_2Cl_2	20.4	64.7	547.5	388.0	555.0	389.5			577.0	410.0	609.0	427.0
10 Me_2SO	19.3	71.1	545.5	387.0	552.5	390.0	549.5	390.5	576.0	409.0	609.0	427.0
11 CH_3CN	18.9	71.3	545.5	386.5	553.0	389.0			574.0	408.5	606.0	426.5
12 DMF	16.0	68.5	547.5	388.0	554.5	391.0			576.5	410.0	607.0	427.5
13 C_6H_5CN	15.5	65.0	547.5	387.5	552.5	388.0					607.5	427.0
14 $C_6H_5NO_2$	14.8		547.5									
15 DMA	13.6	66.9	548.0	387.5	554.0	389.5					609.5	428.5
16 Me_2CO	12.5	65.5	547.0	388.0							609.5	428.5
17 HMPA	10.6	62.8	548.0	387.0								
		A[b] =	551.3	390.0	560.1	391.9	555.2	394.9	581.0	412.7	610.9	428.5
			±0.6	±0.5	±0.8	±0.6	±1.6	±1.0	±1.2	±0.6	±0.8	±0.6
		B[b] =	0.259	0.154	0.373	0.146	0.264	0.226	0.271	0.171	0.171	0.086
			±0.023	±0.016	±0.028	±0.020	±0.043	±0.025	±0.038	±0.019	±0.029	±0.019
		r[b] =	−0.947	−0.941	−0.970	−0.918	−0.940	−0.982	−0.931	−0.961	−0.865	−0.794

a) AN and Z refer to the acceptor number of the solvent and Kosower's solvent parameter, respectively. b) A, B, and r refer to the intercept, the slope, and the correlation coefficient in Eq. 2, respectively.

C_2H_5OH, i-C_3H_7OH, $CHCl_3$, CH_3NO_2, CH_2Cl_2, Me_2SO, CH_3CN, DMF, C_6H_5CN, $C_6H_5NO_2$ DMA, Me_2CO, and HMPA. The λ_1 value shifts to the longer wavelength regions as the acceptor number becomes smaller. For example, the λ_1 value (Fig. 2a, Table 1) for $K[Co(edta)]\cdot 2H_2O$ is 536 nm in water (AN=54.8) and shifts to 547 nm in acetone (AN=12.5) (the color changes from reddish violet in water to bluish violet in acetone). According to the literature,[19] protic solvents such as ethanol, methanol, and water having large AN values can strongly solvate the anion through hydrogen bonding, while dipolar aprotic solvents such as acetone, dimethyl sulfoxide, and acetonitrile having small AN values solvate the anion weakly. Therefore, the λ_1 values in aprotic solvents correspond to those of weakly solvated $[Co(edta)]^-$ anions and the values in protic solvents seem to be greatly influenced by solvating molecules as outersphere ligands.

Therefore, the colors (corresponding to the λ_1 values) of the $[Co(edta)]^-$ anions are caused by the ligands (edta) and the solvating molecules. A plot of the λ_1 values in Table 1 versus the acceptor numbers of the



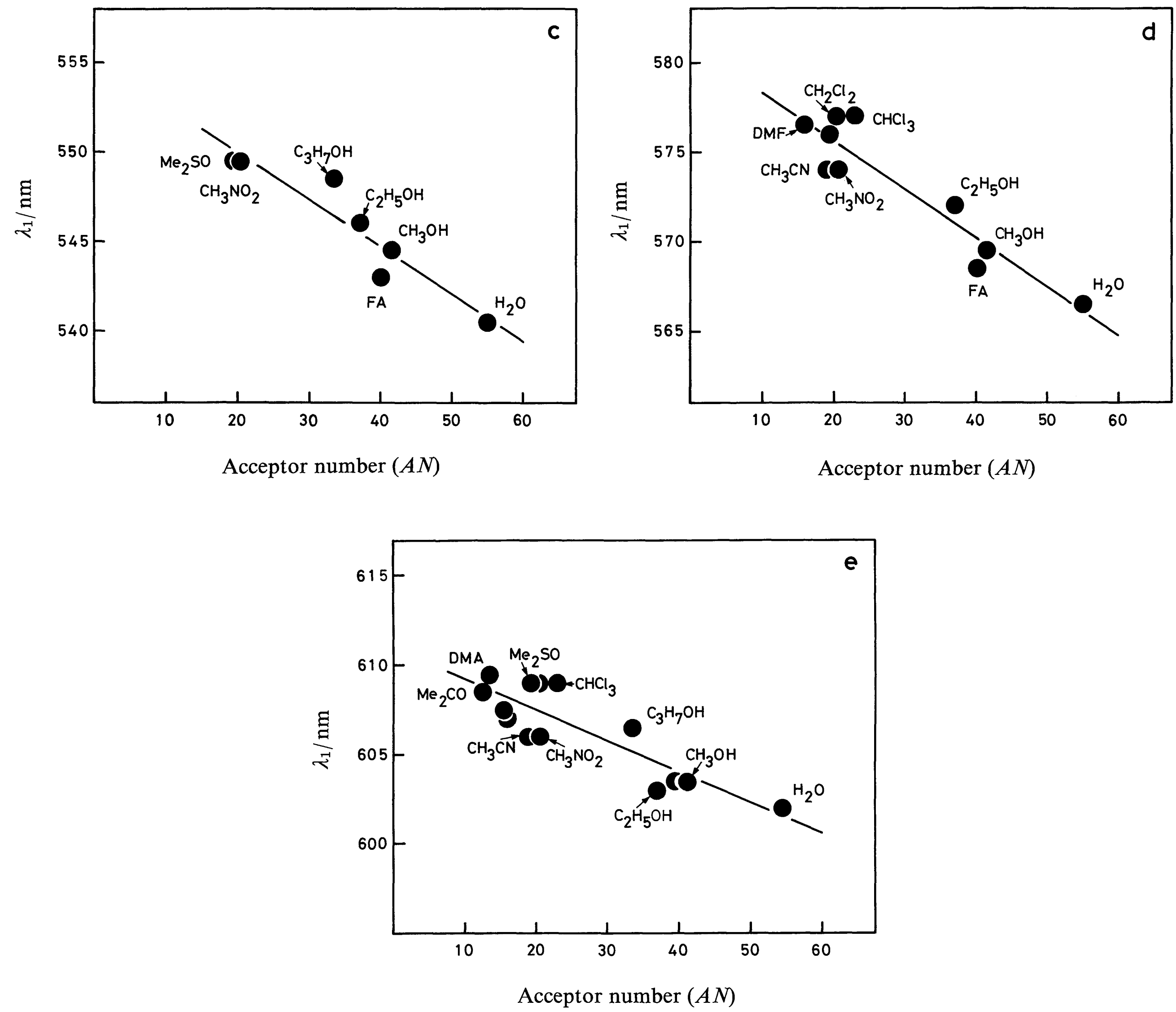


Fig. 2. The correlation between the peak positions (λ_1 in Table 1) of the first d–d transition bands of K[Co(edta)]·2H$_2$O (a), K[Co(mal)$_2$en]·H$_2$O (b), K[Co(ox)$_2$en]·1.5 H$_2$O (c), K$_2$[Co(ox)$_2$gly]·3H$_2$O (d), and K$_3$[Co(ox)$_3$]·3H$_2$O (e) and the acceptor numbers (*AN*) of the solvents.

solvents gives a straight line as shown in Fig. 2a.[20] The linearity of the line suggests that the contribution of the solvent molecules to the peak position is linearly correlated to the *AN* values of the solvents. The peak position in the solvent is calculated by the following equation (error bars are one standard deviation):

$$\lambda_1 = \lambda_1^\circ - (0.259 \pm 0.023) \times AN \qquad (1)$$

where λ_1° refers to the peak position ($\lambda_1^\circ = 551.3 \pm 0.6$ nm determined by a least-squares analysis) in hexane as a standard solvent ($AN = 0$), and *AN* is the acceptor number of the solvent. The first term in this equation corresponds to the inherent peak position of the [Co(edta)]$^-$ anion which is not solvated and the second term to the outersphere-ligand effect which is caused by solvating molecules.

We have concluded that the color (or λ_1) of the cobalt(III) complex is changed by the outersphere coordination of solvent molecules and that this color (or λ_1) change can be predicted by using the acceptor number of the solvent.

The linear correlation[20] between the peak positions and the acceptor numbers was observed for the other anionic cobalt(III) complexes: K[Co(mal)$_2$en]·H$_2$O (Fig. 2b), K[Co(ox)$_2$en]·1.5H$_2$O (Fig. 2c), K$_2$[Co(ox)$_2$gly]·3H$_2$O (Fig. 2d), and K$_3$[Co(ox)$_3$]·3H$_2$O (Fig. 2e). The correlation is generally represented by the following equation:

$$\lambda_1 = A - B \times AN \qquad (2)$$

The intercepts (*A*) and slopes (*B*), which refer to the inherent peak positions and the contribution of the solvent molecules, respectively, were also obtained by least-squares calculations, and are listed in Table 1.

The slopes (B) were slightly different from each other, but were independent of the charge of the complex anion (−, 2−, or 3−). The highly-charged anion could generally be strongly solvated by the solvent molecules. Therefore, this slight difference in the slopes (B) is attributed to an other factor; for example, the probability of the d–d transition for the 1 : 1 solvation of the anion and solvent molecules. The magnitude of the slope is smaller for $K_3[Co(ox)_3]\cdot 3H_2O$ than for $K_3[Co(CN)_6]$, which has already been obtained.[6] Therefore, the magnitude of the solvent influence depends on the ligand which is coordinated with the cobalt(III) ion.

On the other hand, Fig. 3 presents the correlation between the peak positions of the first d–d transition of $K[Co(edta)]\cdot 2H_2O$ (λ_1) and Kosower's solvent parameters (Z).[18] This plot also gives a straight line. The linearity of the plot is higher than that of the plot versus the acceptor number (AN): the correlation coefficient (−0.980) is greater in the plot versus Z than in the plot versus AN (Table 1: −0.947). For other carboxylato complexes described here, the linearity is also higher in the plots versus Z than the plots versus AN, though the data are not presented in this paper. Kosower's parameters were determined on the basis of the peak positions in the UV absorption spectra (CT: charge transfer) of 1-ethylpyridium iodide in the solvents.[18] Therefore, the influence of the solvent on the d–d transition seems to be correlated more with the parameter from the CT transition than that from the NMR chemical shifts.[21]

In order to confirm that the blue shift of the peak position of $[Co(edta)]^-$ in H_2O was due to the interaction between the complex anion and solvent molecules, the reflection spectra of solid $K[Co(edta)]\cdot 2H_2O$ and $K[Co(edta)]$ were obtained. It was found that the peak positions of solid $K[Co(edta)]\cdot 2H_2O$ were 552 nm for the first d–d transition and 387 nm for the second d–d transition, and its anhydrous salt showed peaks at 556 nm and 387 nm for the first and second d–d transitions, respectively. If, in the solid state, the $[Co(edta)]^-$ anion does not interact with H_2O, these peak positions can be seen to be quite similar to the hypothetical positions (551 nm and 390 nm) in hexane in which the complex does not interact with solvent molecules. In contrast to the edta complexes, the λ_{max} values of other hydrates: $K[Co(mal)_2en]\cdot H_2O$, $K[Co(ox)_2en]\cdot 1.5H_2O$, $K_2[Co(ox)_2gly]\cdot 3H_2O$, and $K_3[Co(ox)_3]\cdot 3H_2O$ are 535, 541, 561, and 596 nm for the first d–d transition and 385, 384, 402, and 423 nm for the second d–d transition, respectively. These values are similar to those in water (540.5, 540.0, 566.5, and 602.0 nm for the first transition and 382.5, 384.0, 403.5, and 424.0 nm for the second transition). An interaction such as hydrogen bonding may exist in those complexes in the solid state, though it could not be confirmed by X-ray analysis.

Spectrochemical Parameter Δ and Interelectronic Repulsion Parameter B. The λ_{max} (λ_2) values of the second d–d transition are also correlated linearly to the AN values of the solvents, as shown in Fig. 4. Therefore, the spectrochemical parameter Δ and Racah parameter B can be evaluated by the λ_1 and λ_2 values of the first and second d–d transition bands. We have used these two parameters to clarify the mechanism of the change in the d–d transition spectra. The parameters Δ and B are approximately calculated by the equations of Schäffer.[22]

$$\Delta = 1/\lambda_1 + (1/\lambda_2 - 1/\lambda_1)[0.1824(\lambda_1/\lambda_2)^2 - 0.5531(\lambda_1/\lambda_2) + 0.6165], \tag{3}$$

$$B = (1/\lambda_2 - 1/\lambda_1)[4.077\times 10^{-2}(\lambda_1/\lambda_2)^2 - 7.090\times 10^{-2}(\lambda_1/\lambda_2) + 9.352\times 10^{-2}]. \tag{4}$$

The peak positions of the first and second d–d transition

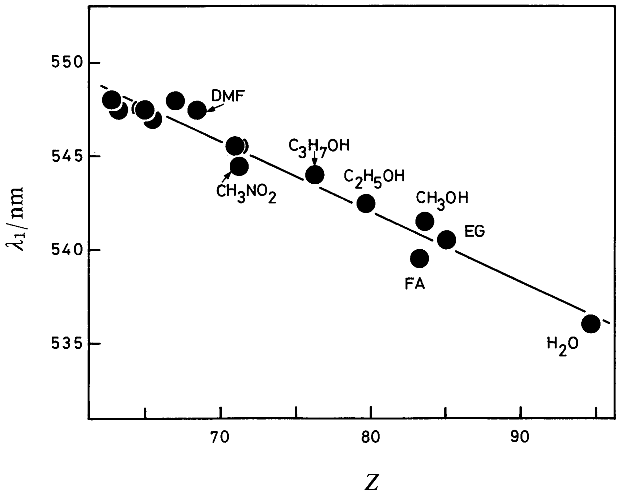


Fig. 3. The correlation between the peak positions (λ_1 in Table 1) of $K[Co(edta)]\cdot 2H_2O$ and Kosower's solvent parameters (Z).

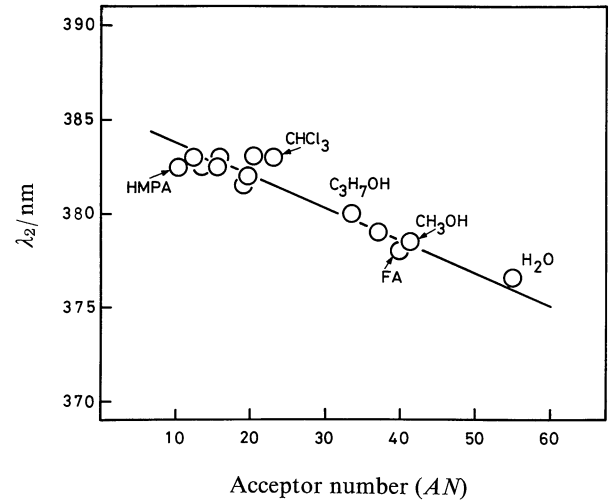


Fig. 4. The correlation between the peak positions (λ_2 in Table 1) of the second d–d transition band of $K[Co(edta)]\cdot 2H_2O$ and the acceptor numbers (AN).

Table 2. The Spectrochemical Parameters (Δ) and the Interelectronic Repulsion Parameters (B) of the Carboxylatocobaltate(III) Complexes in a Variety of Solvents

Solvent[a)]	$K[Co(edta)]\cdot 2H_2O$		$K[Co(mal)_2en]\cdot H_2O$		$K[Co(ox)_2en]\cdot 1.5H_2O$		$K_2[Co(ox)_2gly]\cdot 3H_2O$		$K_3[Co(ox)_3]\cdot 3H_2O$	
	Δ	B	Δ	B	Δ	B	Δ	B	Δ	B
1	20116	561.5	20020	559.7	20021	571.0	19072	530.1	17996	523.0
2	20021	571.0	19919	560.5	19932	570.0	19001	525.0	17962	521.3
3	19986	568.4	19878	565.5	19872	562.7	18976	528.0	17954	522.4
4	20049	564.2	19868	555.2	19924	563.2	19007	528.0	17960	525.2
5	19946	568.7	19831	567.7	19818	561.2	18894	527.6	17962	521.3
6	19892	567.2	19774	570.0					17868	520.2
7	19756	560.7	19594	577.2			18743	528.7	17811	527.3
8									17902	532.4
9	19756	560.7	19540	575.7			18737	525.9	17811	527.4
10	19827	560.2	19601	564.7	19677	551.9	18773	528.5	17811	527.4
11	19832	563.0	19597	573.3			18828	525.3	17882	522.0
12	19756	560.7	19532	566.2			18754	523.9	17846	519.4
13	19755	565.4	19624	576.9					17844	523.2
14										
15	19755	565.4	19565	572.6					17788	520.8
16	19773	558.7							17813	523.5
17	19755	565.4								

a) The number of the solvent corresponds to the number assigned in Table 1.

bands shifted to shorter wavelengths as the acceptor number became larger. The spectrochemical parameter Δ, the energy splitting of d orbitals in the O_h field, also became larger as the acceptor number increased (Table 2). Therefore, we have concluded that the solvent influence on the electronic absorption spectra is attributed to an influence on the d–d transition energy (the energy splitting of the d orbital).

Table 2 indicates that the Racah parameter B of $K[Co(mal)_2en]\cdot H_2O$ in a variety of solvents becomes small as the electrophilic ability (AN value) of the solvents (outersphere ligand) becomes larger. It is well known that a decrease of the B value indicates a decrease in the interelectronic repulsion, and is generated by the expansion of the d electron cloud. This expansion of the d electron cloud is due to the electron-withdrawing effect of solvent molecules on the d electrons of $[Co(mal)_2en]^-$ through the ligand atoms (oxygen and carbon). This cloud expanding (nephelauxetic) effect roughly corresponds to the electrophilic ability of the solvents. The expansion of d electron clouds is known to be due to the increase of the covalency of the Co–L bond. We suggest that the solvent influence on the d–d transition energy of $[Co(mal)_2en]^-$ is based on the change of the covalency between the cobalt ion and the innersphere ligand, though the parameter B is similar in a variety of solvents for the other complexes. The spectrochemical series and the nephelauxetic series of outersphere coordination with solvent molecules could be proposed: for the spectrochemical series of $[Co(mal)_2en]^-$,

H_2O, EG, CH_3OH~FA, C_2H_5OH, i-C_3H_7OH, $CHCl_3$~Me_2SO~CH_3CN~C_6H_5CN, DMA, CH_2Cl_2~DMF,

and for the nephelauxetic series of $[Co(mal)_2en]^-$,

FA, H_2O, EG, Me_2SO, CH_3OH, DMF, C_2H_5OH, i-C_3H_7OH, DMA, CH_3CN, CH_2Cl_2, C_6H_5CN, $CHCl_3$.

Correlation between the Peak Positions in the Electronic Spectra and the Chemical Shifts in the ^{59}Co NMR Spectra. If the energy of the d–d electronic transition of the cobalt(III) ion could be changed by the interaction between the solvent molecules and this complex anion, the ^{59}Co NMR chemical shifts should also vary according to changes in the electronic spectrum. This is because the chemical shift of ^{59}Co NMR is correlated to the peak position in the electronic spectrum, as shown in the following equation (which is abbreviated):[23)]

$$\delta(^{59}\mathrm{Co}) \propto 1/\Delta E \tag{5}$$

where $\delta(^{59}Co)$ and ΔE are the ^{59}Co chemical shift and the energy difference for the first d–d transition band of the cobalt(III) complex, respectively.

Figure 5 shows the ^{59}Co NMR spectra of $K[Co(edta)]\cdot 2H_2O$ and $K_3[Co(ox)_3]\cdot 3H_2O$ in H_2O,

Table 3. The Chemical Shifts of the ^{59}Co NMR Spectra of $K[Co(edta)]\cdot 2H_2O$ and $K_3[Co(ox)_3]\cdot 3H_2O$ in a Variety of Solvents

Solvent	$K[Co(edta)]\cdot 2H_2O$ $\delta(^{59}Co)$/ppm	$K_3[Co(ox)_3]\cdot 3H_2O$ $\delta(^{59}Co)$/ppm
H_2O	0	0
CH_3OH	146	71
C_2H_5OH	197	127
CH_3NO_2	190	98
CH_2Cl_2	230	114
Me_2SO	221	134
CH_3CN	219	122
DMF	262	184
C_6H_5CN	252	141
DMA	274	204

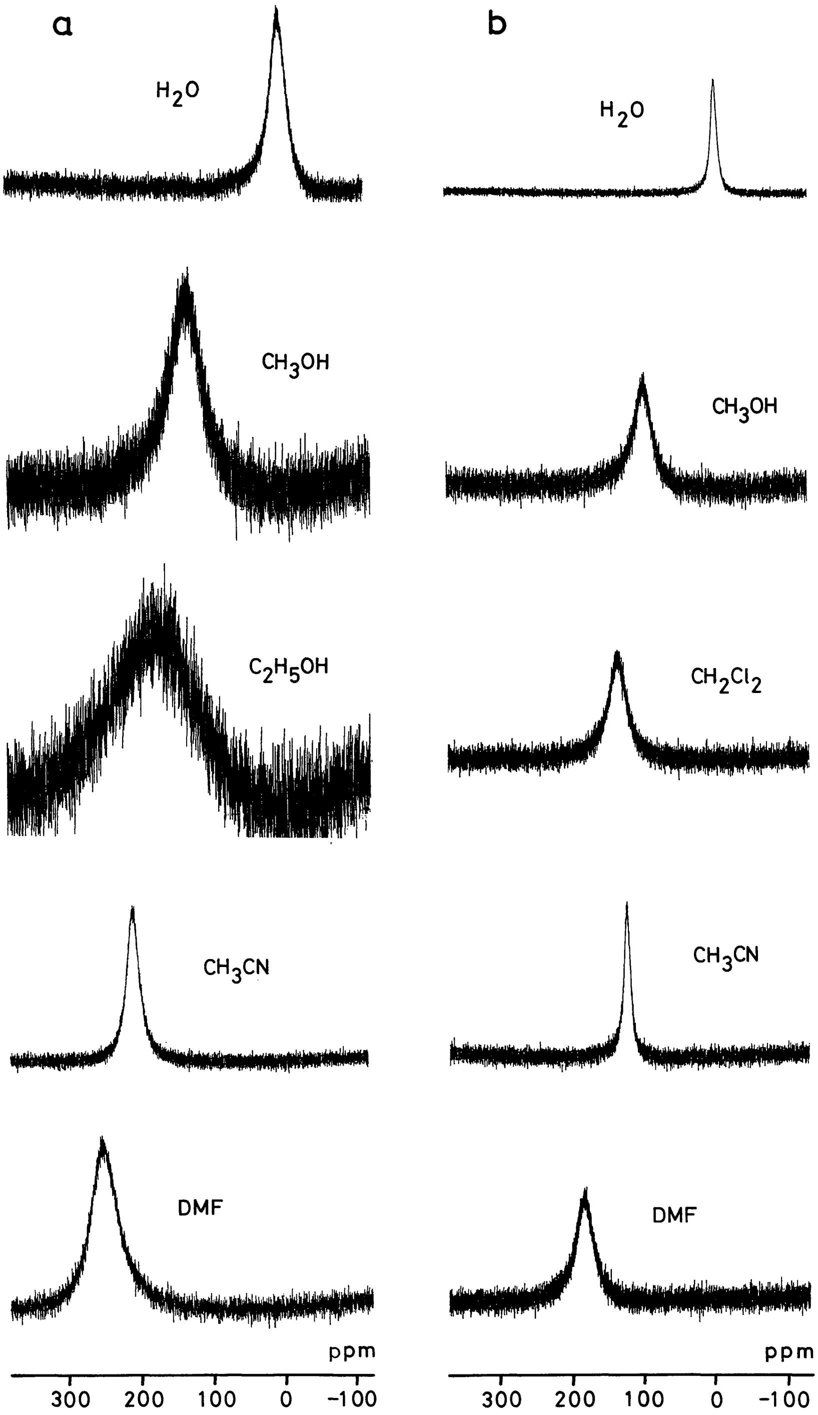


Fig. 5. ^{59}Co NMR spectra of K[Co(edta)]·2H_2O (a) and K_3[Co(ox)$_3$]·3H_2O (b) in a variety of solvents (0.1 mol dm^{-3}).

CH_3OH, C_2H_5OH, (or CH_2Cl_2), CH_3CN, and DMF. In all solvents, the signal appeared quite broad, but the chemical shifts of the ^{59}Co NMR were fairly solvent-dependent. The chemical shifts obtained are shown in Table 3; the solvents used were H_2O, CH_3OH, C_2H_5OH, CH_3NO_2, CH_2Cl_2, Me_2SO, CH_3CN, DMF, C_6H_5CN, and DMA. The chemical shifts also changed as the concentration of the complex decreased. This may have been due to the ion association between the complex anion and K^+ with cryptand 222. The chemical shifts, which were obtained by extrapolation to be the concentration zero, should be the value without any influence of the counter cation. Therefore, the extrapolated values are listed in Table 3 instead of the observed values.

It seemed that the ^{59}Co chemical shifts were linearly correlated to the λ_1 values listed in Table 1. In order to confirm this correlation, the chemical shifts (δ(^{59}Co))

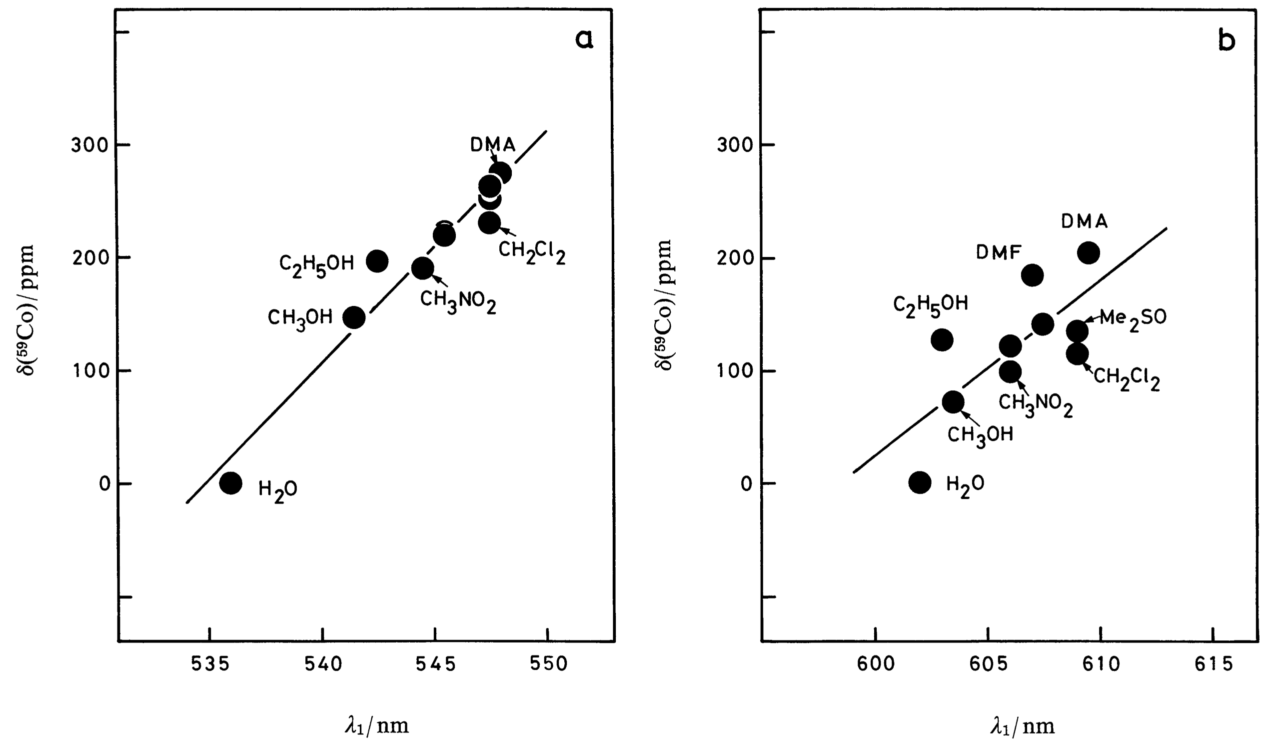


Fig. 6. The correlation between the ^{59}Co chemical shifts ($\delta(^{59}\mathrm{Co})$ in Table 3) and the peak positions (λ_1 in Table 1) of $\mathrm{K[Co(edta)]\cdot 2H_2O}$ (a) and $\mathrm{K_3[Co(ox)_3]\cdot 3H_2O}$ (b).

were plotted versus the λ_1 values of the first d–d transition band (A_{1g}—T_{1g}) in the corresponding solvents: H_2O, CH_3OH, C_2H_5OH, CH_3NO_2, CH_2Cl_2, Me_2SO, CH_3CN, DMF, C_6H_5CN, and DMA (Fig. 6a and 6b). It was clear that the $\delta(^{59}\mathrm{Co})$ values were linearly correlated to the λ_1 value (the intercepts were −11002.68 ppm for $\mathrm{[Co(edta)]^-}$ and −9299.24 ppm for $\mathrm{[Co(ox)_3]^{3-}}$, and the slopes were 20.57 for $\mathrm{[Co(edta)]^-}$ and 15.54 for $\mathrm{[Co(ox)_3]^{3-}}$).[24] This result indicated that the d–d transition energy (ΔE in Eq. 5) was influenced by the solvent molecules, and this influence changed the electronic spectrum and the ^{59}Co NMR of the cobalt(III) complex anion. The intercepts for $\mathrm{[Co(edta)]^-}$, $\mathrm{[Co(ox)_3]^{3-}}$, and $\mathrm{[Co(CN)_6]^{3-}}$ (−9968.75 ppm: obtained in the previous study[6]) were similar to each other, but the slopes for $\mathrm{[Co(edta)]^-}$, $\mathrm{[Co(ox)_3]^{3-}}$, and $\mathrm{[Co(CN)_6]^{3-}}$ (32.01[6]) were quite different. Thus, the solvent influence depended on the nature of the coordinated ligand atoms.

The influence of the solvent on the d–d transition energy (ΔE) has been speculatively interpreted as a change in the contribution of the empty π-orbital of the ligand oxygen to a complex that is composed of σ- and π-bonding between Co and the ligand.[6,25] If the contribution of the π-orbital in this case increases, the orbital split should become great, leading to blue shifts in hydrogen-bonding solvents. This model was preliminarily tested by EHMO calculation of the $\mathrm{[Co(ox)_2(NH_3)_2]^-}$ and H_2O system. The result of the calculation showed that H_2O interacts with carboxyl oxygens along the direction of the angle ranging from about 40 °C to −40 ° for the σ-electron lobes, and not only with the π-electron lobes.[26]

Solvation Site. We now consider the correlation between the solvent influence on the d–d absorption spectrum and the solvation site. Prior to the work described here, we found that $\mathrm{[Co(en)_3]^{3+}}$ and $\mathrm{[Co(NH_3)_6]^{3+}}$, which have no carboxyl groups, did not show a solvent influence on the d–d transition spectra: for $\mathrm{[Co(en)_3]^{3+}}$, λ_1=466.5, 466.5, 467.5, 467.0, 468.0, 468.0, 467.0, 467.0, and 468.0 nm and λ_2=338.0, 338.5, 339.0, 338.5, 339.0, 339.0, 339.0, 338.5, and no peak (in H_2O, EG, CH_3OH, FA, Me_2SO, CH_3CN, DMF, DMA, and Me_2CO, respectively); for $\mathrm{[Co(NH_3)_6]^{3+}}$, λ_1=474.0, 474.0, 475.0, 475.0, and 475.5 nm and λ_2=339.0, 339.0, 340.0, 340.0, and 340.0 (in H_2O, FA, Me_2SO, DMF, and DMA, respectively). Therefore, the interaction between solvent molecules and carboxyl groups of complex anions could play an important role in the solvent influence on the d–d transition spectra. In a previous paper,[5] we reported that the ^{13}C NMR chemical shifts of the $\mathrm{[Co(edta)]^-}$ anion were correlated to the electrophilic ability of the solvents (Gutmann's acceptor number). In order to elucidate the solvent influence on the d–d absorption, the peak positions (λ_1) in the first d–d transition were plotted versus the ^{13}C NMR chemical shifts of this complex anion in several solvents (Fig. 7). It is clear that the peak positions (λ_1) of the first d–d transition bands of the $\mathrm{[Co(edta)]^-}$ anion were correlated linearly with the ^{13}C NMR chemical shifts (δ values) of the carboxyl carbon. The downfield shift of

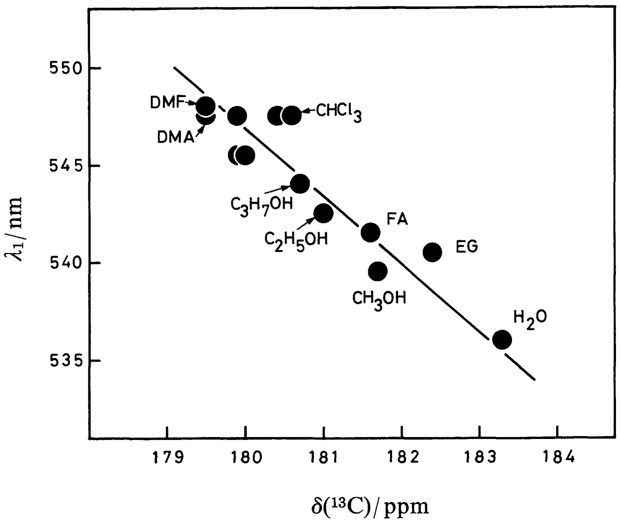


Fig. 7. The correlation between the peak positions (λ_1 in Table 1) and the ^{13}C chemical shifts (Ref. 5) of $K[Co(edta)]\cdot 2H_2O$.

carboxylate ^{13}C signals was due to the electron-withdrawing effect of solvent molecules on the carboxyl groups (specially, perhaps, the carboxyl oxygens) of the cobalt(III) complexes,[27] and thus this effect produced a change in the electronic state for the d–d transition band of the $[Co(edta)]^-$ anion.

We attempted to measure the ^{17}O NMR spectrum of $[Co(edta)]^-$ in the solvents, but no signals were detected. Therefore, we can not confirm the exact site of the interaction of solvation. However, the EHMO calculation of the solvation model, $[Co(ox)_2(NH_3)_2]^-$-H_2O, shows that H_2O interacts with carboxyl oxygens along the direction of the angle ranging from about 40° to −40° for the σ-electron lobes. A detailed examination of the correlation between the solvation mode and the change of the d–d transition state of the complex anion is now being carried out by ab initio calculations.

Conclusions

The color of the $[Co(edta)]^-$ anion was changed by the outersphere coordination of solvent molecules. This color change could be predicted by using the acceptor number of the solvent. The ^{59}Co NMR chemical shifts and the peak positions in the electronic spectra suggested that the color change was due to the change in the d–d transition energy of the cobalt(III) center. From a comparison with the solvent influence on the ^{13}C NMR, it was found that the $[Co(edta)]^-$ anion interacts with protic solvents through an interaction such as hydrogen bonding between solvent hydrogens and carboxyl oxygens of the cobalt(III) complex anion, and this interaction caused the color change of this complex anion in a variety of solvents. In this work, we have established the method by which the solvent influence on the UV, ^{59}Co NMR, and ^{13}C NMR spectra and the interaction between some carboxylatocobaltate(III) complex anions and solvent molecules can be quantitatively estimated by using the acceptor number of the solvent.

The author thanks the Instrument Center, Institute for Molecular Science, for the use of the NMR spectrometer (JEOL Model JNM-GX400). The author also thanks Dr. Y. Ihara for the measurements of reflection spectra in Kanazawa University. This work was partially supported by a Grant-in-Aid for Scientific Research No. 60740337 from the Ministry of Education, Science and Culture.

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did not change, though 1 vol% H_2O was added to the sample solution. As the volume of included water in the solution measured was less than that of the added water, there could be no influence of water of crystallization.

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$$\delta(^{59}\mathrm{Co}) = \delta(^{59}\mathrm{Co})^{\circ} - (5.33 \pm 0.77) \times AN,$$

where $\delta(^{59}\mathrm{Co})^{\circ} = 336 \pm 22$ ppm (the correlation coefficient was −0.924) for $K[Co(edta)] \cdot 2H_2O$, and

$$\delta(^{59}\mathrm{Co}) = \delta(^{59}\mathrm{Co})^{\circ} - (3.51 \pm 0.77) \times AN,$$

where $\delta(^{59}\mathrm{Co})^{\circ} = 210 \pm 22$ ppm (the correlation coefficient was −0.848) for $K_3[Co(ox)_3] \cdot 3H_2O$.

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