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Elucidation of Solvatochromism for the Ligand Field Absorption Bands of Polyamine-*N*-polycarboxylato Cobaltate(III) and Chromate(III) Complexes of $[M(N)_2(O)_4]$ Type

Sumio Kaizaki,* Norio Koine,† and Narumi Sakagami††,§
Department of Chemistry, Faculty of Science, Osaka University,
Toyonaka, Osaka 560
† Department of Industrial Chemistry, Faculty of Engineering, Ehime University,
Bunkyou-chyo, Matsuyama 790
†† Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630

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The solvatochromism of the first ligand field absorption bands and/or the solvent dependence of ^{13}C and ^{59}Co NMR shifts for *trans*- and *cis*-$[M(N)_2(O)_4]$ type complexes of cobalt(III) or chromium(III) with various kinds of polyamine-*N*-polycarboxylato ligands was elucidated in terms of the angular overlap model (AOM) parametrization. On the basis of the difference in the solvent-dependence of spectroscopic data of the complexes studied in various solvents, it was found that the solvatochromism could result from variations of the metal-ligand σ and/or π bond interactions (expressed by the $e_\sigma(O)$, $e_\sigma(N)$, and anisotropic $e_\pi(O)$ AOM parameter values) due to the preferential solvation toward the oxygen p_π orbitals coplanar with the $M(O)_2$ coordinate planes.

There have been a few reports on the solvent dependence of the ligand field d–d transitions of inert complexes with the saturated coordination numbers in comparison with a number of investigations on remarkable solvatochromism in the charge transfer transitions of metal complexes.1) For Co(III) and Cr(III) complexes with ethylenediaminetetraacetate (edta) type ligands, the first d–d absorption band maxima were found to shift to the shorter wavelength with increasing acceptor numbers,2) which were defined as a quantitative empirical electron pair acceptor number for solvents by Gutmann et al.3) on the basis of the ^{31}P NMR chemical shifts of triethylphosphine oxide in various kinds of solvents. Nevertheless, there has been no systematic study on the elucidation for the solvent dependence of the ligand field bands of this type of complexes. Though Taura proposed the preferential solvation model toward the σ electrons of the carboxylato oxygens for *cis*-$[Co(ox)_2(NH_3)_2]^-$ in terms of EHMO calculations,2d) this approach could not necessarily account for the blue shift of the first ligand field band. For the higher symmetry complexes of *trans*-$[CrX_2(N)_4]$ type, on the other hand, it has recently been reported that the solvent dependent ligand field band and ^2H NMR shifts can be elucidated in terms of the ligand field or the angular overlap model (AOM) parametrization.4) A notable ligand field variability and the interligand cooperative effect due to the selective solvation toward electronegative ligating atoms has been revealed. These findings might make feasible to account for the solvatochromism of the edta type complexes with multiple (at most triple) d–d transition components due to much lower symmetry than tetragonal or octahedral, and could provide a basis for more plausible solvation models than Taura's one.2d)

In this article, we will examine the solvent-dependence of the ligand field absorption spectra for *trans*- and *cis*-$[M(N)_2(O)_4]$ type complexes of Co(III) and Cr(III) together with ^{13}C and ^{59}Co NMR spectra for the Co(III) complexes and analyze them on the basis of the AOM parametrization. Assuming that the polyamine-*N*-polycarboxylato ligands are nonlinear ligators with the anisotropic π interaction between metal d orbitals and ligating oxygen p_π orbitals perpendicular to the chelate plane, it has been revealed that preferential (additional) solvations toward a pair of two neighboring oxygen p_π orbitals coplanar with the $M(O)_2$ plane play an important role in the solvatochromism and that the solvatochromic behavior reflects the difference in the topological arrangements of the ligating oxygen p_π orbitals in the carboxylato groups.

Experimental

Materials. The complexes used in this study are given in Table 1 together with numbering (**1**—**37**) for short. The ligands' abbreviations are as follows: ida=iminodiacetate; mida=*N*-methyliminodiacetate; eida=*N*-ethyliminodiacetate; bida=*N*-butyliminodiacetate; nta=nitrilotriacetate; β-alada=β-alanine-*N*,*N*-diacetate; edta=ethylenediaminetetraacetate; (*S*)-pdta=(*S*)-1,2-propanediaminetetraacetate; 1,3-pdta=1,3-propanediaminetetraacetate; eddda=ethylenediamine-*N*,*N*′-diacetate-*N*,*N*′-dipropionate; (*S*,*S*)-edds=(*S*,*S*)-ethylenediamine-*N*,*N*′-disuccinate; edtp=ethylenediaminetatrapropionate; (*S*)-pdtp=(*S*)-1,2-propanediaminetetrapropionate; dmedda=*N*,*N*′-dimethylethylenediamine-*N*,*N*′-diacetate; edda=ethylenediamine-*N*,*N*′-diacetate; aeida=*N*-(2-aminoethyl)iminodiacetate or ethylenediamine-*N*,*N*-diacetate.

Preparation of Complexes. Most complexes except **11**, **12**, **16**, **32**, **33**, and **36** complexes in Table 1 were prepared by the literature methods; **1**,5) **2**,6) **3**,7) **4**,7) **5**,7), **6**,8) **7**,9) **8**,9) **9**,10) **10**,11) **13**,12) **14**,13) **15**,12) **17**,14) **18**,15) **19**,15) **20**,16) **21**,17) **22**,18a) **23**,19) **24**,20) **25**,19b) **26**,21) **27**,17) **28**,22) **29**,23) **30**,22) **31**,23) **34**,8) **35**,9) **37**.25) These complexes were identified by the absorption spectra.

***trans*(*N*)-K[Co(mal)(gly)$_2$]·2H$_2$O.** The reaction mixture was obtained by the same method as that for the corresponding oxalato complex10) by using potassium malonate instead of potassium oxalate. The separation of three isomers, *trans*(*N*),

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§ Present address: Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560.

Table 1. Solvatochromic Data of $[\mathrm{M(N)_2(O)_4}]$ Type Complexes

	Complexes	Absorption			^{59}Co NMR	
		Slope	Intercept	Correlation factor	Slope	Intercept
		$\mathrm{cm^{-1}}$	$10^3\ \mathrm{cm^{-1}}$		ppm	ppm
	trans(*N*) Type					
1	$[\mathrm{Co(ida)_2}]^-$	2.85	20.0	0.94	0.77	10552
2	$[\mathrm{Co(mida)_2}]^-$	1.11	19.0	0.91	−1.79	11011
3	$[\mathrm{Cr(mida)_2}]^-$	1.01	20.2	0.86		
4	$[\mathrm{Cr(eida)_2}]^-$	3.05	19.9	0.99		
5	$[\mathrm{Cr(bida)_2}]^-$	1.92	19.9	0.93		
6	$[\mathrm{Co(nta)(gly)}]^-$	2.72	19.5	0.86		
7	*sym*-$[\mathrm{Co(\beta\text{-}alada)(gly)}]^-$	3.80	19.2	0.88	−0.73	11091
8	*unsym*-$[\mathrm{Co(\beta\text{-}alada)(gly)}]^-$	3.09	19.2	0.88	0.29	10958
9	$[\mathrm{Co(ox)(gly)_2}]^-$	8.93	18.5	0.96		
10	$[\mathrm{Co(ox)(\beta\text{-}ala)_2}]^-$	5.20	18.5	0.93	−4.72	10833
11	$[\mathrm{Co(mal)(gly)_2}]^-$	8.37	18.5	0.99		
12	$[\mathrm{Co(mal)(\beta\text{-}ala)_2}]^-$	5.99	18.4	0.97		
	cis(*N*) Type					
13	$[\mathrm{Co(ox)_2(en)}]^-$	8.17	18.1	0.99	−3.46	10683
14	$[\mathrm{Cr(ox)_2(en)}]^-$	8.53	18.3	0.97		
15	$[\mathrm{Co(mal)_2(en)}]^-$	12.66	17.9	0.98	−5.70	11322
16	$[\mathrm{Cr(mal)_2(en)}]^-$	13.12	18.2	0.90		
17	$[\mathrm{Co(edta)}]^-$	9.46	18.2	0.97	−6.36	10626
18	$[\mathrm{Cr(edta)}]^-$	12.91	17.8	0.89		
19	$[\mathrm{Cr}\{(S)\text{-}\mathrm{pdta}\}]^-$	13.25	17.8	0.85		
20	$[\mathrm{Co(1,3\text{-}pdta)}]^-$	8.33	17.8	0.93		
21	$[\mathrm{Cr(1,3\text{-}pdta)}]^-$	11.09	19.1	0.79		
22	$[\mathrm{Co(eddda)}]^{-*}$	13.70	17.8	0.97	−8.80	11410
23	$[\mathrm{Cr(eddda)}]^{-*}$	22.36	17.8	0.97		
24	$[\mathrm{Co}\{(S,S)\text{-}\mathrm{edds}\}]^{-*}$	13.76	18.8	0.98		
25	$[\mathrm{Cr}\{(S,S)\text{-}\mathrm{edds}\}]^{-*}$	23.84	18.4	0.86		
26	$[\mathrm{Co(edtp)}]^-$	15.18	17.3	0.95	−8.61	11755
27	$[\mathrm{Cr}\{(S)\text{-}\mathrm{pdtp}\}]^-$	20.09	17.5	0.95		
28	*sym*-$[\mathrm{Co(edda)(ox)}]^-$	9.96	17.5	0.99		
29	*sym*-$[\mathrm{Cr(edda)(ox)}]^-$	12.57	18.1	0.92		
30	*sym*-$[\mathrm{Co(edda)(mal)}]^-$	9.35	17.4	0.98		
31	*sym*-$[\mathrm{Cr(edda)(mal)}]^-$	12.12	18.0	0.97		
32	*sym*-$[\mathrm{Co(dmedda)(ox)}]^-$	4.82	17.5	0.85		
33	*sym*-$[\mathrm{Co(dmedda)(mal)}]^-$	9.29	17.0	0.97	−5.50	11319
34	$[\mathrm{Co(nta)(gly)}]^-$	11.07	17.0	0.98		
35	*unsym*-$[\mathrm{Co(\beta\text{-}alada)(gly)}]^-$	9.97	17.1	0.88	−6.85	11475
36	*sym*-$[\mathrm{Co(aeida)(ox)}]^-$	6.91	17.6	0.86		
37	*unsym*-$[\mathrm{Co(aeida)(ox)}]^-$	9.57	18.5	0.97	−4.02	10519

The symbols, *sym*- and *unsym*-, denote symmetrical and unsymmetrical geometrical structures, respectively. The asterisked (*) complexes (**22**—**25**) take a *trans*-(O_5) geometrical structure in which the five-membered acetate rings occupy *trans*-axial sites while the propionate rings lie in the equatorial plane with two nitrogen atoms.

C_1-*cis*(*N*), C_2-*cis*(*N*), was chromatographically performed by a method similar to that for the oxalato complex. The *trans*(*N*) isomer was first eluted and was isolated as crystals from its eluate. The geometrical structure of the *trans*(*N*) isomer was determined on the basis of the presence of a shoulder at the lower energy region in the first absorption band as found for the corresponding oxalato complex.[10] Found: C, 22.02; H, 3.76; N, 7.21%. Calcd for $\mathrm{K[Co(mal)(gly)_2]\cdot 2H_2O}$: C, 21.88; H, 3.67; N, 7.29%.

***trans*(*N*)-$\mathbf{K[Co(mal)(\beta\text{-}ala)_2]\cdot 2.5H_2O\cdot KCl}$.** This complex was prepared and characterized by a similar method to that for the corresponding glycinato complex. Found: C, 22.10; H, 3.80; N, 5.68%. Calcd for $\mathrm{K[Co(mal)(\beta\text{-}ala)_2]\cdot 2.5H_2O\cdot KCl}$: C, 21.80; H, 3.86; N, 5.65%.

$\mathbf{Na[Cr(mal)_2(en)]\cdot 0.5H_2O}$. Five grams of *cis*-$\mathrm{Na[Cr(mal)_2(H_2O)_2]\cdot 3H_2O}$ was dissolved in 400 $\mathrm{cm^3}$ of hot *N*,*N*-dimethylformamide (DMF) at 90 °C. To the resulting dark blue solution was added 1.2 g of ethylenediamine in 25 $\mathrm{cm^3}$ of DMF. The color of the mixture changed to be light violet. After this solution was allowed to stand for a while at 90 °C, it was cooled to room temperature. By the addition of a large amount of ether to the reaction solution, red precipitate was obtained. The aqueous solution of this precipitate was poured onto a QAE-Sephadex C-25 anion-exchange column (ϕ 3.5×40 cm). After washing the column with water, the chromatography was carried out by eluting with 0.04 M (1 M=1 mol $\mathrm{dm^{-3}}$) aqueous NaCl solution. The column gave three bands. The first eluate was collected and evaporated to dryness. By the repetition of the extraction of the red complex with methanol, sodium chloride was removed. This was recrystallized from water and acetone. Calcd for $\mathrm{Na[Cr(mal)_2(en)]\cdot 0.5H_2O}$: C, 27.58; H, 3.73; N, 8.04%. Found: C, 27.59; H, 3.55; N, 7.95%.

***sym-cis*-$\mathbf{K[Co(dmedda)(ox)]\cdot 0.5H_2O}$.** This complex was prepared according to the literature method for the corresponding sodium salt[24] by using potassium oxalate instead of sodium oxalate. Found: C, 30.20; H, 3.69; N, 7.14%. Calcd for $K[Co(ox)(dmedda)]\cdot 0.5H_2O$: C, 30.23; H, 3.44; N, 7.05%.

***sym-cis*-$K[Co(dmedda)(mal)]\cdot 1.5H_2O$.** This complex was prepared by the same method as that for the corresponding oxalato complex by using potassium malonate instead of potassium oxalate. Found: C, 30.90; H, 4.35; N, 6.54%. Calcd for $K[Co(dmedda)(mal)]\cdot 1.5H_2O$: C, 30.78; H, 4.46; N, 6.53%. The *sym-cis* structure with a C_2 symmetry was confirmed by the ^{13}C NMR spectroscopy.

***sym*-K[Co(aeida)(ox)].** This complex could be prepared using *unsym*-$K[Co(NO_2)_2(aeida)]\cdot H_2O$ as a starting material. Potassium salt of the dinitro complex was prepared according to the literature method for the corresponding sodium salt[26] by using potassium nitrite instead of sodium nitrite. Found: C, 18.95; H, 3.24; N, 14.45%. Calcd for $K[Co(NO_2)_2(aeida)]\cdot H_2O$: C, 18.85; H, 3.16; N, 14.65%.

To a solution containing 5 g of the dinitro complex and 5.32 g of potassium oxalate in 50 cm^3 of water was added 0.3 g of activated charcoal. The mixture was stirred at 60 °C for 1 h. Then, the dinitro complex was almost quantitatively converted to a mixture of the *sym* and *unsym* isomers of the oxalato complex. After the charcoal was removed, the *unsym* and *sym* isomers were separately obtained by means of fractional crystallization; the former complex being less soluble than the latter one. Found: C, 26.65; H, 2.90; N, 7.75%. Calcd for *sym*-K[Co(aeida)(ox)]: C, 26.68; H, 2.80; N, 7.78%.

Measurements. The ligand field absorption spectra were obtained by a Shimadzu UV-240 spectrophotometer at room temperature. ^{13}C and ^{59}Co NMR spectra were measured by a JEOL GX-270 FT-NMR spectrometer at 20 °C and 25 °C, respectively, at Nara Women's University. ^{13}C NMR shifts were determined by using dioxane (66.6 ppm) as an external standard, whereas $[Co(edta)]^-$, *fac*-$[Co(\beta\text{-ala})_3]$, *cis*(*N*)-$[Co(nta)(gly)]^-$, and $[Co(ox)_3]^{3-}$ were taken as the external standards for ^{59}Co NMR shifts according to the chemical shift range of the complexes with the down field positive convention. The chemical shifts of the complexes were converted as $\delta(Co)=10300$ ppm for the edta complex relative to external aqueous $[Co(CN)_6]^{3-}$ ($\delta(Co)=0$). In order to obtain the sufficient concentrations for these spectroscopic measurements (0.001—0.01 M, 0.2 M, and 0.005—0.02 M for absorption, ^{13}C and ^{59}Co NMR, respectively) in aprotic solvents, cryptand 222 was used as a solubilizing agent.

The solvents used for the measurements were of spectrograde or reagent grade. The abbreviations for the solvents in parentheses and their acceptor numbers in square brackets as found in the literature[3] are as follows: *N*,*N*-dimethylacetamide (DMA) [13.6]; *N*,*N*-dimethylformamide (DMF) [16.0]; dimethyl sulfoxide (DMSO) [19.3]; *N*-methylformamide (NMF) [31.0]; formamide (FA) [39.8]; methanol (MeOH) [41.3]; H_2O [54.8].

Results and Discussion

Since the present complexes are so stable or inert to be isolated from aqueous solutions as described in the Experimental section, it is unlikely that the solvatochromism is associated with the ligand dissociation. There exists to be fairly good linear correlation between the ligand field band maxima and the solvents' acceptor numbers for the present complexes including those bearing the N-H protons. This fact indicates that the solvatochromism is accompanied by the acceptor properties of the solvents, but not by the donor properties. In view of the extent of the solvatochromism and/or the solvation sites, the trans and cis type complexes are classified into two and three groups, respectively, as below.

***trans*-$[M(N)_2(O)_4]$ Type Complexes.** In general, *trans*-$[Co(N)_2(O)_4]$ type complexes give two components in the first ligand field absorption band region. These components are assigned to the holohedrized tetragonal (D_4) $^1A_2$ and ^1E state in the $^1T_1\leftarrow{}^1A_1$ transition region from the longer wavelength side. As found for $[Co(edta)]^-$ and the analogous complexes,[2] the absorption band maxima corresponding to the transition $^1E\leftarrow{}^1A_1$ of the trans type complexes also give linear correlations with Gutmann's acceptor numbers[3] as

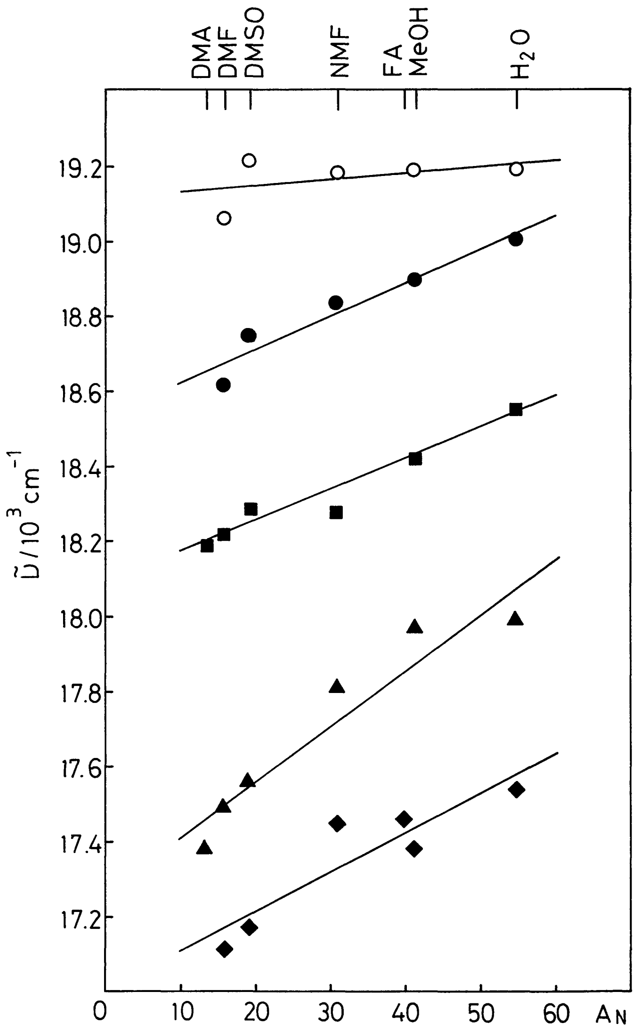

Fig. 1. Plots of the absorption band maxima ($\nu/10^3$ cm^{-1}) vs. the acceptor numbers (AN): ○ *trans*(*N*)-$[Co(mida)_2]^-$ (A group); ● *trans*(*N*)-$[Co(ox)(gly)_2]^-$ (B group); ■ $[Co(ox)_2(en)]^-$ (C group); ▲ $[Co(edtp)]^-$ (D group); ◆ *cis*(*N*)-$[Co(nta)(gly)]^-$ (E group).

shown in Fig. 1. However, the extent of the solvent-dependence varies from one group of the complexes to the other. That is, for *trans*(*N*)-$[\mathrm{Co(ida)_2}]^-$ type complexes which are classified as the A group (**1**—**8**), the slopes of the plots of the shorter wavelength absorption band maxima (the $^1\mathrm{E}$ component near 20000 $\mathrm{cm^{-1}}$) with the acceptor numbers are smaller by about one half than those for *trans*(*N*)-$[\mathrm{Co(ox)(gly)_2}]^-$ type complexes which are classified as the B group (**9**—**12**) as shown in Fig. 1 and Table 1. In other words, the former A group complexes show negligible solvent-dependence, whereas the latter B group complexes exhibit considerable solvatochromism. Such solvatochromic behavior of the $^1\mathrm{E}$ component together with that for the $^1\mathrm{A}_2$ one is also substantiated by the ^{59}Co NMR shifts as in Table 1. The A group complexes give little dependence of the ^{59}Co NMR shifts on the acceptor numbers, whereas the ^{59}Co NMR shifts of the B group complexes are more dependent on the acceptor number. These ^{59}Co NMR shifts behave in a manner similar to the solvatochromism for the $^1\mathrm{E}$ component and reflect the solvent change of both the tetragonal split components in the first band region more directly than the solvatochromism, since the ^{59}Co NMR shifts are related with the sum of the reciprocal of the transition energy of each split component in the $^1\mathrm{T}_1 \leftarrow {}^1\mathrm{A}_1$ transition.[27] Such a remarkable difference in the solvatochromism can be accounted for by considering the AOM parametrization including the anisotropic π interaction between metal d orbitals and the ligating oxygen p_π orbitals perpendicular to the chelate planes rather than the isotropic one as in Fig. 2. The transition energies of the first ligand field band components for two groups of *trans*-$[\mathrm{Co(N)_2(O)_4}]$ type complexes with holohedrized tetragonal (D_4) symmetry are given in terms of the AOM parameters on the assumption of the orthoaxial coordination by taking account of only the anisotropic π metal–oxygen p_π interaction perpendicular to the chelate planes for the carboxylato groups as follows:

$$E(^1\mathrm{E}) = 3/2e_\sigma(\mathrm{N}) + 3/2e_\sigma(\mathrm{O}) + 4B \tag{1}$$

$$E(^1\mathrm{A}_2) = 3e_\sigma(\mathrm{O}) - 4e_\pi(\mathrm{O}) + 4B \tag{2}$$

for *trans*(*N*)-$[\mathrm{Co(ida)_2}]^-$ type complexes of the A group. The same formulations of the transition energies are given for *trans*(*N*)-$[\mathrm{Co(nta)(gly)}]^-$ type complexes assuming the identical topological arrangements of the ligating oxygen p_π orbitals of the carboxylato groups unless three kinds of the ligating oxygen atoms of the different carboxylato groups were discriminated.

$$E(^1\mathrm{E}) = 3/2e_\sigma(\mathrm{N}) + 3/4e_\sigma(\mathrm{O}) + 3/4e_\sigma(\mathrm{O'}) - e_\pi(\mathrm{O'}) + 4B \tag{3}$$

$$E(^1\mathrm{A}_2) = 3/2e_\sigma(\mathrm{O}) + 3/2e_\sigma(\mathrm{O'}) - 2e_\pi(\mathrm{O}) + 4B \tag{4}$$

for *trans*-$[\mathrm{Co(ox)(gly)_2}]^-$ type complexes of the B group

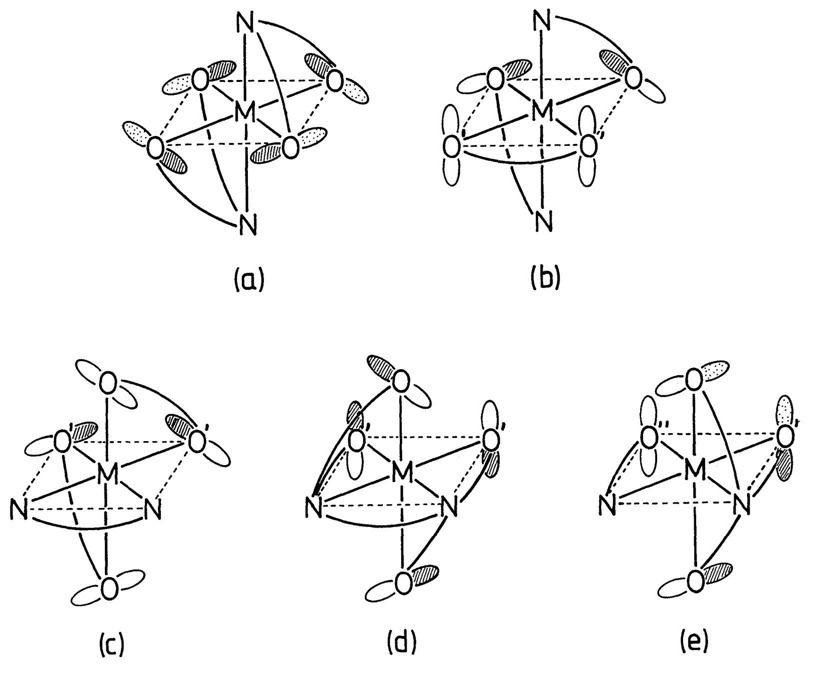

Fig. 2. Topological arrangements of the ligating oxygen p_π orbitals for which a pair of the shaded and/or dotted lobes at the octahedral edge is directed toward the solvents; implying the preferential (additional) solvation for the following types of complexes: (a) *trans*(*N*)-$[\mathrm{M(ida)_2}]$; (b) *trans*(*N*)-$[\mathrm{M(ox)(gly)_2}]$; (c) $[\mathrm{M(ox)_2(en)}]$; (d) $[\mathrm{M(edta)}]$; (e) *cis*(*N*)-$[\mathrm{M(nta)(gly)}]$.

where O and O′ denote the coordinated oxygen atoms of the amino acidato and oxalato ligands, respectively, as in Fig. 2(b). The last term B in Eqs. 1—4 is the Racah interelectronic repulsion parameter. It is plausible that this parameter is almost solvent independent as mentioned previously.[4)]

Although the absorption bands and ^{59}Co NMR shifts of the A group complexes are little altered with variation of the solvents' acceptor numbers as in Fig. 1 and Table 1, ^{13}C NMR signals of the carboxylato carbons shift to the lower field with increasing the acceptor numbers; the slope of the plots with the acceptor numbers is +0.1. This suggests the solvation toward the ligating oxygens of the carboxylato groups as claimed from the ^{13}C NMR behavior of $[Co(edta)]^-$ by Taura,[28)] leading to the change of the AOM parameter values in each energy term in Eqs. 1 and 2. It is likely that the highly preferential (additional) solvation occurs toward pairs of the ligating oxygen p_π orbitals coplanar with the $M(O)_4$ plane of the A group complexes as shown in Fig. 2(a). This may give the decrease in the AOM $e_\pi(O)$ parameters. As a result, both the AOM $e_\pi(O)$ and $e_\sigma(O)$ values decrease with increasing the acceptor numbers. This variation in the AOM parameter values results in the negligible change of the $^1A_2$ transition energy; the term $3e_\sigma(O)-4e_\pi(O)$ keeping almost constant with change of the solvents as found for $3e_\sigma(F)-4e_\pi(F)$ of *trans*-$[CrF_2(3.2.3\text{-tet})]^+$ complex.[4)] On the other hand, the $e_\sigma(N)$ value increases with increasing the acceptor numbers due to a cis electronic effect, followed by the decrease in the $e_\sigma(O)$ or $e_\pi(O)$ value as revealed for *trans*-$[CrF_2(3.2.3\text{-tet})]^+$ complex.[4)] The solvent dependent ^{13}C NMR shifts of the methyl carbons in *trans*(*N*)-$[Co(mida)_2]^-$ lend support to the solvent variation of the $e_\sigma(N)$ values, since the slope (−0.025) of the plots of these shifts with the acceptor numbers is opposite to that (+0.1) of the carboxylato carbons. Thus, the ^{1}E transition energy is little affected by the solvents' acceptor properties owing to the cancellation between the $e_\sigma(N)$ and $e_\sigma(O)$ values within the energy terms, whereas the parallel change of the $e_\sigma(O)$ and $e_\pi(O)$ values gives a small alternation of the $^1A_2$ transition energy. This is the finding for the solvatochromism of the A group complexes (**1**—**8**), though the solvatochromism cannot clearly be seen for the latter $^1A_2$ component of most *trans*(*N*) type complexes, because this component is usually observed only as the shoulders or poorly defined band maxima at the longer wavelength side of the ^{1}E component.

For *trans*(*N*)-$[Co(ox)(gly)_2]^-$ (the B group), however, ^{13}C NMR chemical shifts of the carboxylato carbons for the glycinato ligands is more largely solvent dependent than that for the oxalato ones; the slopes of the plots for ^{13}C NMR shifts with the acceptor numbers of the solvents are +0.12 and +0.065 for the carboxylato carbons of the glycinato and oxalato ligands, respectively. This suggests the preferential (additional) solvation toward a pair of the p_π orbitals of the glycinato oxygens coplanar with the $M(O)_4$ plane in support of the proposed solvation mode for the A group complexes as shown in Fig. 2(b). In this case, the observed solvatochromism may be explained by grouping the AOM parameters into the braces in the following equations for the transition energies (Eqs. 3 and 4) of each component:

$$E(^1E) = 3/4e_\sigma(N) + 3/4\{e_\sigma(N) + e_\sigma(O)\} + 1/4\{3e_\sigma(O') - 4e_\pi(O')\} + 4B \quad (5)$$

$$E(^1A_2) = 3/2e_\sigma(O') + 1/2\{3e_\sigma(O) - 4e_\pi(O)\} + 4B \quad (6)$$

The terms $\{e_\sigma(N)+e_\sigma(O)\}$ and $\{3e_\sigma(O)-4e_\pi(O))\}$ and/or $\{(3e_\sigma(O')-4e_\pi(O')\}$ are almost solvent independent as revealed for the A group complexes, whereas the remaining $e_\sigma(N)$ and $e_\sigma(O)$ parameters may be more susceptible to the solvent dependence as revealed from the following consideration. The preferential solvation toward a pair of the p_π orbitals for two glycinato coordinated oxygens (O in Fig. 2(b)) causes shortening both the Cr–N and Cr–O′ bond or increasing both the $e_\sigma(N)$ and $e_\sigma(O')$ values, followed by the lengthening of the Cr–O bonds or the decrease in the $e_\sigma(O)$ or $e_\pi(O)$ owing to a cis electronic effect or the electroneutrality principle. Accordingly, it is plausible that the band maxima of two components in the first band region shift to the higher frequency side with increasing the acceptor numbers. This indeed accounts for the fact that the solvatochromism for the B group complexes is significantly larger than that for the A group complexes.

For the corresponding Cr(III) complexes, the transition energies of two tetragonal split components in the $^4T_2 \leftarrow {}^4A_2$ transition are given by the same AOM parametrization as for the Co(III) complexes except for the use of the irreducible representation $^4B_2$ instead of the $^1A_2$ and the exclusion of the Racah parameter B. Therefore, it is expected that the solvatochromism for *trans*(*N*)-$[Cr(mida)_2]^-$, -$[Cr(eida)_2]^-$, and -$[Cr(bida)_2]^-$ complexes occurs as similarly to the corresponding cobalt(III) complexes. This is the finding as in Table 1.

***cis*-$[M(N)_2(O)_4]$ Type Complexes.** On the basis of the AOM parametrization, the cis type complexes are also classified into three groups. That is, the C group is represented by $[M(ox)_2(en)]$ type complexes (**13**—**16**) and the others D and E are the edta type (**17**—**33**) and the *cis*(*N*)-(nta)(gly) type complexes (**34**—**37**), respectively.

The transition energies of each tetragonal split component in the first ligand field transition of the C and D group complexes of Co(III) are given by the AOM parameters as follows:

$$E(^1A_2) = 3/2e_\sigma(N) + 3/2e_\sigma(O') - 2e_\pi(O') + 4B \quad (7)$$

$$E(^1E) = 3/4e_\sigma(N) + 3/4e_\sigma(O') + 3/2e_\sigma(O) - e_\pi(O) + 4B \quad (8)$$

for the C group complexes, and

$$E(^1A_2) = 3/2e_\sigma(N) + 3/2e_\sigma(O') + 4B \tag{9}$$

$$E(^1E) = 3/4e_\sigma(N) + 3/2e_\sigma(O) - e_\pi(O) + 3/4e_\sigma(O') - e_\pi(O') + 4B \tag{10}$$

for the D group complexes. For both cases, the O and O′ denote the carboxylato ligating oxygens cis and trans to the amine nitrogens, respectively, as shown in Fig. 2. The same situation of the AOM parameters is encountered with Cr(III) complexes where the Racah parameter is excluded. The absorption band maxima of both the Co(III) and Cr(III) complexes and ^{59}Co NMR chemical shifts of the Co(III) complexes are linearly correlated with the acceptor numbers as shown in Table 1.

For the C group complexes, the preferential solvation is expected to occur toward a pair of two oxygen p_π orbitals on the $M(N)_2(O)_2$ plane (Fig. 2(c)), as in the cases of the A and B group complexes. Then, the Co–N and Co–O bond distances become shorter or the $e_\sigma(N)$ and $e_\sigma(O)$ values increase, followed by the decrease in the $e_\sigma(O')$ and $e_\pi(O')$ values or the lengthening of the Co–O′ bonds. On the other hand, the transition energies in terms of the AOM parameters (Eqs. 7 and 8) are reformulated by grouping almost solvent-independent terms into the braces in Eqs. 11 and 12.

$$E(^1A_2) = 3/2e_\sigma(N) + 1/2\{3e_\sigma(O') - 4e_\pi(O')\} + 4B \tag{11}$$

$$E(^1E) = 3/4e_\sigma(N) + 3/4\{e_\sigma(O) + e_\sigma(O')\} + 1/4\{3e_\sigma(O) - 4e_\pi(O)\} + 4B \tag{12}$$

The first terms $3/2e_\sigma(N)$ and $3/4e_\sigma(N)$ for the $^1A_2$ and ^1E components are solvent dependent, respectively. Thus, the $e_\sigma(N)$ values or both the tetragonal split components are predicted to increase the transition energies or to shift to the higher frequency side with increasing the acceptor numbers. This predicted tendency is in accordance with the finding for the C group complexes (**13**—**16**) as in Fig. 1 and Table 1, although the observed band maxima correspond to the position of either one of the split components or the weighted average of two components.

For the D group complexes including the *sym-cis*-[M(edda)(ox)] type, each transition energy of two tetragonal components contains only almost solvent independent terms in the braces as in Eqs. 13 and 14.

$$E(^1A_2) = 3/2\{e_\sigma(N) + e_\sigma(O')\} + 4B \tag{13}$$

$$E(^1E) = 3/4\{e_\sigma(N) + e_\sigma(O)\} + 1/4\{3e_\sigma(O) - 4e_\pi(O)\} + 1/4\{3e_\sigma(O') - 4e_\pi(O')\} + 4B \tag{14}$$

In contrast with the C group complexes, there are two preferential solvation sites for the D group complexes as in Fig. 2(d). It is assumed that the extent of the bond length variation due to the solvation per one solvation site does not change so much on going from the C group complexes with one solvation site to the D group complexes with two solvation sites in view of the similarity of the slopes of the plots for the ^{13}C NMR shifts of the carboxylato carbons with the acceptor numbers; +0.083 for $[Co(edta)]^-$ [28] and +0.08 for $[Co(mal)_2(en)]^-$. This situation is analogous to the case for ruthenium(III) ammine complexes where the correlation of the donor solvent dependent solvatochromism with the numbers of the ammine protons has been claimed.[29] Thus, the increase in the $e_\sigma(N)$ value due to the solvation for the D group complexes may be about twice as large as that for the C group complexes and the decrease in the $e_\sigma(O')$ and $e_\sigma(O)$ values owing to the electroneutrality principle. As a result, $3/2\{e_\sigma(N)+e_\sigma(O')\}$ and $3/2\{e_\sigma(N)+e_\sigma(O)\}$ terms in Eqs. 13 and 14 are not necessarily solvent independent as for the A, B, and C group complexes, but are expected to change in a similar manner to the variation of the $e_\sigma(N)$ which increase with increasing the acceptor numbers. Since the other remaining terms are almost solvent independent, the transition energies of two components increase with increasing the acceptor numbers. This is the finding for the D group complexes (**17**—**33**) as in Fig. 1 and Table 1.

For the E type complexes exemplified by *cis*(*N*)-$[Co(nta)(gly)]^-$ with two solvation sites, three components in the holohedrized D_2 field of the $^1T_1 \leftarrow {}^1A_1$ transition are different in energy from each other. The following transition energies for *cis*(*N*)-$[Co(nta)(gly)]^-$ are given in terms of the AOM parameters.

$$E(^1A_2) = 3/4e_\sigma(N) + 3/2e_\sigma(O) + 3/4e_\sigma(O'') - e_\pi(O'') + 4B \tag{15}$$

$$E(^1B_1) = 3/4e_\sigma(N) + 3/2e_\sigma(O) + 3/4e_\sigma(O') - e_\pi(O') - 2e_\pi(O) + 4B \tag{16}$$

$$E(^1B_2) = 3/2e_\sigma(N) + 3/4e_\sigma(O') + 3/4e_\sigma(O'') + 4B \tag{17}$$

where O, O′, and O″ denote two equivalent in-plane carboxylato oxygens (O), one out-of-plane carboxylato oxygen (O′) of the nta, and glycinato oxygen (O″), respectively, as in Fig. 2(e). For *sym*- and *unsym*-$[Co(aeida)(ox)]^-$, the same expressions for the transition energies are given by disregarding the difference in the carboxylato oxygens in view of the identical topological arrangements of the ligating oxygen p_π orbitals in the carboxylato groups. By grouping $3e_\sigma(X)-4e_\pi(X)$ (X=O, O′, and O″) and comparing the increasing $e_\sigma(N)$ and $e_\sigma(O'')$ values with the decreasing $e_\lambda(X)$ values($\lambda=\sigma$ and π; X=O and O′) as a result of the preferential solvation toward the O and O′ ligating oxygens, three components for the E group complexes are expected to shift to the higher frequency side with increasing the acceptor numbers, assuming that $e_\sigma(N)$ and $e_\sigma(O'')$ variation due to the solvation is about twice as large as the $e_\sigma(\mathrm{O})$ and $e_\sigma(\mathrm{O'})$ ones as in the case of the D group complexes with two solvation sites. This is the finding for the E group complexes (**34**—**37**) as in Table 1.

These elucidations of the solvatochromism seem to be in accordance with the difference in the observed solvent dependence of the absorption band maxima from complex to complex, depending on the topological arrangements of the ligating oxygen p_π orbitals perpendicular to the chelate plane. The slopes of the plots of the absorption band maxima with the solvents' acceptor numbers for the C and D group complexes with six-membered malonato or amino acidato chelates are larger than those with five-membered ones as shown in Table 1. This behavior may arise from the difference in the displacement from the regular octahedral vertices; i.e., the ligating oxygens of the six-membered chelate rings are in general located closer to the regular octahedral vertices (90°) than those of the five-membered ones. Such a displacement may result in the mismatch of the coordinated oxygen p_π orbitals with the donor sites of the solvents. This appears to be responsible for the difference in the extent of the solvent dependence between the complexes with five- and six-membered rings.

In the edta type complexes of the D group, the solvent dependence is larger by more than 30% for the chromium(III) complexes than for the cobalt(III) complexes with the identical ligands as shown in Table 1 (**17**—**31**). Thus, the ligand field for the chromium(III) complexes may be more susceptible with variation of solvents than that for the cobalt(III) complexes; suggesting the more ligand field variability or the higher electronegativity of the coordinated oxygen in the chromium(III) complexes than in the cobalt(III) complexes as claimed from a comparison of the solvatochromism for *trans*-$[\mathrm{CrX_2(3.2.3\text{-}tet)}]^+$ complexes with various halide ligands.[4)]

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