Raman Spectral Characteristics of Cobalt(III) Complexes with Quadridentate Ligands

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The Raman spectra of cobalt(III) complexes with quadridentate ligands such as triethylenetetramine (trien), ethylenediamine-*N,N′*-diacetate (edda), tris(2-aminoethyl)amine (tren), and *N*-(2-aminoethyl)iminodiacetate (aeida), were measured for the skeletal vibration region of 200—700 cm^{-1} in order to obtain general information on the relation between the spectra and the structures of these complexes. The Raman bands can be classified into four vibration modes; a totally symmetric stretching vibration mode in the 420—670 cm^{-1} region, a stretching vibration mode excluding the totally symmetric one in the 390—450 cm^{-1} region, a metal-ligand skeletal bending deformation mode in the 300—420 cm^{-1} region, and the chelate ring deformation mode in the 240—290 cm^{-1} region. The skeletal vibrations of cis-α and cis-β isomers of the cobalt(III) complexes with linear quadridentate ligands correspond to those of the tris(bidentate)cobalt(III) and the mer isomers of bis(terdentate)cobalt(III) complexes, respectively. In addition, the skeletal vibrations of the cobalt(III) complexes with tripodlike quadridentate ligands also correspond to those of the mer isomers of bis(terdentate)cobalt(III) complexes. The Raman spectra of the present complexes depend primarily on the configuration of the quadridentate ligands and the effect due to the bidentate ligands is of secondary importance.

In the last few years, it has been recognized that Raman spectra in the skeletal vibration region can be applied successfully to the differentiation of geometrical isomers of cobalt(III) complexes.(1) The main interest has been focused on the low frequency region where the Raman bands for the skeletal vibrations appear. However, little systematic investigations had been reported at this time concerning the relation between the Raman spectra and the structural characteristics of the metal complexes.

In the previous papers, we reported the Raman spectral characteristics of the [Co(gly)$_x$(ox)$_y$(en)$_z$]-type complexes (gly, glycinate; ox, oxalate; and en, 1,2-ethanediamine),(2) the [Co(ida)$_n$(dien)$_{2-n}$]-type complexes (ida, iminodiacetate and dien, diethylenetriamine),(3) and the cobalt(III) complexes containing the six-membered chelate ring.(4) The Raman spectra of the [Co(gly)$_x$(ox)$_y$(en)$_z$]-type complexes have been treated in terms of the effective symmetry,(2) which was mainly specified by the arrangement of the coordinated atoms around the cobalt(III). It has been found that the striking differences in the Raman spectral characteristics of the mer and fac isomers of the [Co(ida)$_n$(dien)$_{2-n}$]-type complexes reflect the structural distortion in the isomeric pairs.

In this paper, the Raman spectra in the skeletal vibration region of the cobalt(III) complexes with quadridentate ligands, triethylenetetramine (trien), ethylenediamine-*N,N′*-diacetate (edda), tris(2-aminoethyl)amine (tren), and *N*-(2-aminoethyl)iminodiacetate (aeida), are measured and the relation between the stereochemical properties and Raman spectra of these complexes is discussed in relation to the Raman spectral characteristics of the tris(bidentate)- and bis(terdentate)cobalt(III) complexes.

Experimental

Complexes. The following complexes were prepared and characterized according to procedures in the literature *cis*-α-[Co(en)(trien)]I$_3$,(5) *cis*-β-[Co(en)(trien)]Cl$_3$,(5,6) *cis*-α-[Co(edda)(en)]ClO$_4$,(7) *cis*-β-[Co(edda)(en)]ClO$_4$,(7) *cis*-α-[Co(edda)(NH$_3$)$_2$]NO$_3$,(7) *cis*-α-[Co(edda)(gly)],(8) and *cis*-α-Na[Co(edda)(ox)].(9)

[Co(ox)(trien)]Cl. *cis*-α- and *cis*-β-[Co(ox)(trien)]I, which were prepared in the same way as has been reported,(10) were converted to the chloride by passing the solution through a column of Dowex 1-X8 anion-exchange resin in the chloride form. Found for the cis-α isomer: C, 28.27; H, 5.63; N, 16.47%. Calcd for [Co(ox)(trien)]Cl·1/2H$_2$O=CoC$_8$H$_{18}$N$_4$O$_4$Cl·1/2H$_2$O: C, 28.46; H, 5.67; N, 16.59%. Found for the cis-β isomer: C, 25.98; H, 5.92; N, 15.18%. Calcd for [Co(ox)(trien)]Cl·9/4H$_2$O: C, 26.03; H, 6.14; N, 15.18%.

[Co(en)(tren)]Cl$_3$. This complex was prepared by a procedure alternative to that described in the literature.(11) To a solution of [CoCl$_2$(tren)]Cl(12) (3.3 g) in 20 cm^3 of water on a steam bath was added 1,2-ethanediamine (0.6 g). Heating was continued for 30 min. After cooling, [Co(en)(tren)]Cl$_3$ was isolated by the column chromatographic method using SP-Sephadex C-25 (Na$^+$ form, 4 cm×20 cm) and a 0.2 mol dm^{-3} aqueous solution of NaCl as an eluent. Found: C, 23.47; H, 7.48; N, 20.50%. Calcd for [Co(en)(tren)]Cl$_3$·2H$_2$O=CoC$_8$H$_{26}$N$_6$Cl$_3$·2H$_2$O: C, 23.57; H, 7.42; N, 20.62%.

[Co(ox)(tren)]Cl. This complex was prepared by a procedure similar to that used for [Co(ox)(trien)]$^+$. A solution containing [CoCl$_2$(tren)]Cl (0.5 g) and oxalic acid (0.4 g) in 10 cm^3 of water was warmed on a steam bath for 30 min. After cooling, the resulting red solution was passed through a column of SP-Sephadex C-25 (Na$^+$ form, 3 cm×40 cm) with a 0.05 mol dm^{-3} aqueous solution of NaCl as an eluent. The red eluate was concentrated and then cooled in an ice bath in order to obtain [Co(ox)(tren)]Cl. Found: C, 27.69; H, 5.88; N, 16.23%. Calcd for [Co(ox)(tren)]Cl·H$_2$O=CoC$_8$H$_{18}$N$_4$O$_4$Cl·H$_2$O: C, 27.72; H, 5.82; N, 16.16%. Absorp. max. $10^{-3}\sigma/\mathrm{cm}^{-1}(\log \varepsilon/\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{cm}^{-1})$: 20.12 (2.13) and 28.17 (2.16).

$[Co(edda)(tn)]ClO_4$. The preparation procedure was identical with that of $[Co(edda)(en)]^{+}$[7] except that 1,3-propanediamine (tn) was used instead of en. The reaction mixture was poured onto a column of Dowex 50W-X8 (200—400 mesh, Na^+ form, 3 cm×60 cm) and the three main red bands were eluted. It was found that the second eluate was *cis-α*-$[Co(edda)(tn)]^+$ and the third one was *cis-β*-$[Co(edda)(tn)]^+$ from their absorption, ^1H NMR, and ^{13}C NMR spectra. Found for the cis-α isomer: C, 26.48; H, 4.87; N, 13.61%. Calcd for $[Co(edda)(tn)]ClO_4{=}CoC_9H_{20}N_4O_8Cl$: C, 26.58; H, 4.96; N, 13.78%. Found for the cis-β isomer: C, 25.43; H, 5.18; N, 13.00%. Calcd for $[Co(edda)(tn)]ClO_4\cdot H_2O$: C, 25.45; H, 5.22; N, 13.19%. Absorp. max. $10^{-3}\sigma/\mathrm{cm}^{-1}$ $(\log \varepsilon/\mathrm{mol}^{-1}\mathrm{dm}^3\mathrm{cm}^{-1})$: the cis-α isomer: 18.59 (2.00), 21.69sh (1.73), 27.55 (2.18) and the cis-β isomer: 19.92 (2.14), 27.86 (2.23).

***cis*-α-[Co(edda)(β-ala)].** This complex has been prepared by Nakazawa et al.,[13] but the synthesis in the present work was carried out according to the procedure of the complex with the glycinate ligand,[8] except that β-alanine was used in place of glycine. Found: C, 32.02; H, 5.24; N, 12.67%. Calcd for $[Co(edda)(\beta\text{-ala})]\cdot 3/4H_2O{=}CoC_9H_{16}N_3O_6\cdot 3/4H_2O$: C, 32.30; H, 5.27; N, 12.56%. Absorp. max. $10^{-3}\sigma/\mathrm{cm}^{-1}$ $(\log \varepsilon/\mathrm{mol}^{-1}\mathrm{dm}^3\mathrm{cm}^{-1})$: 17.99sh (1.99), 19.69 (2.05), and 26.74 (2.09).

[Co(aeida)(en)]Cl. Two isomers were separated by an SP-Sephadex C-25 column chromatography using an aqueous solution of NaCl in place of that of $NaClO_4$ as an eluent given in literature.[14] Found for the trans(O) isomer: C, 25.00; H, 6.27; N, 14.70%. Calcd for $[Co(aeida)(en)]Cl\cdot 3H_2O{=}CoC_8H_{18}N_4O_4Cl\cdot 3H_2O$: C, 25.11; H, 6.32; N, 14.64%. Found for the cis(O) isomer: C, 26.27; H, 5.91; N, 15.29%. Calcd for $[Co(aeida)(en)]Cl\cdot 2H_2O$: C, 26.35; H, 6.08; N, 15.36%.

Measurements. The Raman spectra were recorded on a JASCO Laser Raman spectrometer, which was constructed specially with a double monochromator, model CT-25, a He-Ne laser, model NEC GLG-8500, and a data processor, model DP-500, as the main components. The sample solution was excited at 632.8 nm, and the Raman spectra were calibrated with indene. The electronic absorption spectra were recorded with JASCO UVIDEC-1 and -610 spectrophotometers, and the ^1H NMR and ^{13}C NMR spectra were recorded in deuterium oxide on a JEOL JNM-FX-100 NMR spectrometer at the probe temperature. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as internal reference.

Results and Discussion

General Aspect. [Co(quadridentate)(bidentate)]-type complexes used in this work for Raman spectral study are depicted in Fig. 1. The Raman spectral data in the skeletal vibration region of the cobalt(III) complexes with quadridentate ligands such as trien, tren, edda, and aeida, are summarized in Table 1, together with those of $[Co(NH_3)_6]^{3+}$,[2] $[Co(en)_3]^{3+}$,[2] *unsym-fac*-$[Co(dien)_2]^{3+}$,[3] and *trans*(O)-$[Co(gly)_2(en)]^{+}$[2] for comparison.

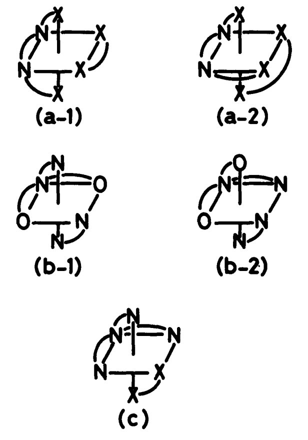

Fig. 1. Structures of [Co(quadridentate)(bidentate)]-type complexes. Cis-α (a-1) and cis-β (a-2) isomers of the complexes with trien (X=N) and edda (X=O), trans(O) (b-1) and cis(O) (b-2) isomers of $[Co(aeida)(en)]^+$, and the complexes with tren (c).

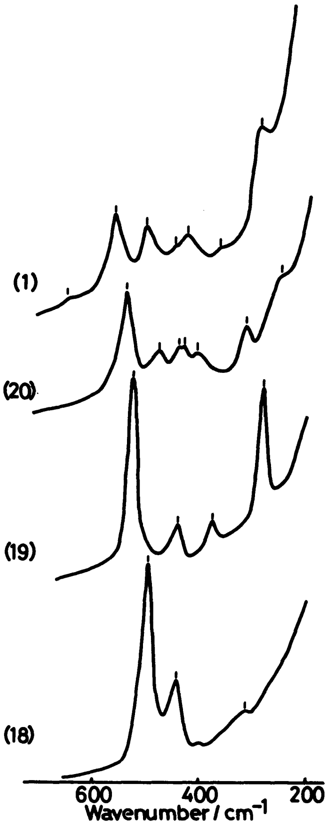

Fig. 2. Raman spectra of *cis-α*-$[Co(en)(trien)]^{3+}$, *unsyn-fac*-$[Co(dien)_2]^{3+}$ (Ref. 3), $[Co(en)_3]^{3+}$ (Ref. 2), and $[Co(NH_3)_6]^{3+}$ (Ref. 2). Numbers in parentheses correspond to those in Table 1.

Figure 2 shows the Raman spectrum of *cis-α*-$[Co(en)(trien)]^{3+}$ as a typical example of the cobalt(III) complexes with quadridentate ligand, together with those of *unsym-fac*-$[Co(dien)_2]^{3+}$, $[Co(en)_3]^{3+}$, and $[Co(NH_3)_6]^{3+}$. These complexes all possess an O_h

Table 1. Raman Spectral Data of the Cobalt(III) Complexes with Quadridentate Ligands

No.	Complex	Raman frequency/cm^{-1} [a]			
1	*cis*-α-[Co(en)(trien)]$^{3+}$	646 vw(−) 555 s(p) 498 m(p)	446 w(−) 421 m(dp)	354 vw(−)	282 m(p)
2	*cis*-β-[Co(en)(trien)]$^{3+}$	575 m(p) 531 s(p) 507 s(p) 465 w(−) 433 s(p)		385 vw(−) 349 w(−) 318 vw(−)	
3	*cis*-α-[Co(ox)(trien)]$^{+}$	649 vw(−) 570 s(p) 510 w(p)	429 m(dp)		282 vw(−)
4	*cis*-β-[Co(ox)(trien)]$^{+}$	589 w(p) 539 s(p) 457 m(p)	428 m(dp)	370 vw(−) 342 w(−)	
5	[Co(en)(tren)]$^{3+}$	605 w(p) 531 s(p) 514 m(p)		442 m(p)[d] 419 w(−) 383 w(dp)	265 m(p)
6	[Co(ox)(tren)]$^{+}$	606 w(p) 542 s(p) 475 vw(−)		453 m(p)[d] 418 w(−) 370 w(dp)	242 w(−)
7	*cis*-α-[Co(edda)(en)]$^{+}$	617 m(p) 525 m(p) 461 m(p)	421 vw(dp)	349 w(−)	262 m(−)
8	*cis*-β-[Co(edda)(en)]$^{+}$	660 w(p) 594 vw(−) 530 m(p) 465 m(p)	438 w(−) 405 w(−)	346 vw(dp) 308 vw(−)	
9	*cis*-α-[Co(edda)(tn)]$^{+}$	613 m(p) 521 m(p) 478 sh(−) 448 m(p)	390 vw(−)	350 w(−)	
10	*cis*-β-[Co(edda)(tn)]$^{+}$	655 w(p) 556 vw(−) 530 w(−) 485 s(p) 425 m(p)		313 w(−)	
11	*cis*-α-[Co(edda)(NH$_3$)$_2$]$^{+}$	620 m(p) 522 m(p) 470 sh(−) 452 m(p)	398 vw(−)	349 m(−)	260 vw(−)
12	*cis*-α-[Co(edda)(gly)]	621 s(p) 537 m(p) 473 w(−)	429 w(−)	385 vw(−) 347 w(−)	265 m(−)
13	*cis*-α-[Co(edda)(β-ala)]	615 m(p) 529 w(p) 452 vw(−)		354 vw(−)	
14	*cis*-α-[Co(edda)(ox)]$^{-}$	618 m(p) 533 w(p)	417 w(−)	373 vw(−)	
15	*cis*-β-[Co(edda)(ox)]$^{-}$	662 vw(−) 570 vw(−)	425 vw(−)		

Table 1. (continued)

No.	Complex	Raman frequency/cm^{-1} [a]			
16	*trans*(O)-$[\text{Co(aeida)(en)}]^+$	546 w(p) 494 w(−) 449 vw(−)		400 m(p)[d]	
17	*cis*(O)-$[\text{Co(aeida)(en)}]^+$	550 m(p) 505 vw(−) 450 m(p)		409 m(−)[d]	245 vw(−)
18	$[\text{Co(NH}_3)_6]^{3+}$ [b]	495 s(p)	440 m(dp)	320 w(dp)	
19	$[\text{Co(en)}_3]^{3+}$ [b]	525 s(p)	440 w(dp)	378 w(dp)	283 s(p)
20	*unsym-fac*-$[\text{Co(dien)}_2]^{3+}$ [c]	546 s(p)	485 m(dp) 444 m(dp) 434 m(dp)	409 w(p)[d] 321 m(dp)	255 vw(−)
21	*trans*(O)-$[\text{Co(gly)}_2\text{(en)}]^+$ [b]	596 m(p) 523 m(p)	504 sh(dp) 458 w(dp)	368 w(dp)	275 s(p)
	Assignment[e]	ν_{ts}(Co–L)	ν(Co–L)	δ_{sbd}(L–Co–L)	$\delta_{\text{crd}}(\text{Co}<^{\text{L}}_{\text{L}})$

a) The following abbreviations are used: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; p, polarized; dp, depolarized. b) Ref. 2. c) Ref. 3. d) These bands correspond to the breathing vibration mode which is characteristic for the bis(terdentate)cobalt(III) complexes. e) ν_{ts} denotes the totally symmetric stretching vibration mode; ν, the stretching vibration mode excluding the totally symmetric one; δ_{sbd}, the metal-ligand skeletal bending deformation mode; δ_{crd}, the chelate ring deformation mode, and L, the donor atom (N and/or O).

symmetry with respect to the coordinated atoms. From their Raman frequencies and intensities, it seems that the Raman bands at 555, 420—500, 354, and 282 cm^{-1} of *cis*-α-$[\text{Co(en)(trien)}]^{3+}$ correspond to those at 546, 430—490, 321, and 255 cm^{-1} of *unsym-fac*-$[\text{Co(dien)}_2]^{3+}$ and to those at 525, 440, 378, and 283 cm^{-1} of $[\text{Co(en)}_3]^{3+}$, respectively. However, the depolarization ratio of the Raman band at 498 cm^{-1} of *cis*-α-$[\text{Co(en)(trien)}]^{3+}$ is different from that of the corresponding Raman bands of *unsym-fac*-$[\text{Co(dien)}_2]^{3+}$ (485 cm^{-1}), $[\text{Co(en)}_3]^{3+}$ (440 cm^{-1}), and $[\text{Co(NH}_3)_6]^{3+}$ (440 cm^{-1}) (Table 1, Fig. 2); the band at 498 cm^{-1} of *cia*-α-$[\text{Co(en)(trien)}]^{3+}$ is polarized, while the band at 485 cm^{-1} of *unsym-fac*-$[\text{Co(dien)}_2]^{3+}$ and the bands at 440 cm^{-1} of $[\text{Co(en)}_3]^{3+}$ and $[\text{Co(NH}_3)_6]^{3+}$ are depolarized. This spectral feature is unique for the cobalt(III) complexes with quadridentate ligands: The polarized Raman bands at 440—510 cm^{-1} are regarded as characteristic of the cobalt(III) complexes with quadridentate ligands, because they were not observed for bis(terdentate)- and tris(bidentate)cobalt(III) and related complexes.[2,3] On the contrary, the polarized Raman bands around 400 cm^{-1}, characteristic for the cobalt(III) complexes with terdentate ligands, could not be observed for the cobalt(III) complexes with quadridentate ligands.

It is evident from Fig. 2 and Table 1 that the Raman spectral characteristic of *cis*-α-$[\text{Co(en)(trien)}]^{3+}$ is similar to that of $[\text{Co(en)}_3]^{3+}$ rather than that of *unsym-fac*-$[\text{Co(dien)}_2]^{3+}$. Accordingly, the Raman spectrum of *cis*-α-$[\text{Co(en)(trien)}]^{3+}$ can be assigned on the basis of the Raman spectrum of $[\text{Co(en)}_3]^{3+}$ except for the Raman band at 498 cm^{-1}. This deduction is supported by comparison of *cis*-α-$[\text{Co(edda)(en)}]^+$ with *trans*(O)-$[\text{Co(gly)}_2\text{(en)}]^+$ which have a D_{4h} symmetry with respect to the coordinated atoms; that is, Table 1 shows that the Raman bands at 520—620, 420—470, 349, and 262 cm^{-1} of *cis*-α-$[\text{Co(edda)(en)}]^+$ correspond to those at 520—600, 450—510, 368, and 275 cm^{-1} of *trans*(O)-$[\text{Co(gly)}_2\text{(en)}]^+$, except for the difference in the depolarization ratio between the Raman band at 461 cm^{-1} of the former and that at 504 cm^{-1} of the latter. Furthermore, taking the Raman frequency and the depolarization ratio into account, it is considered that the polarized bands at 498 cm^{-1} of *cis*-α-$[\text{Co(en)(trien)}]^{3+}$ and at 461 cm^{-1} of *cis*-α-$[\text{Co(edda)(en)}]^+$ can be assigned to the totally symmetric vibration mode.

On the basis of the above discussion and the Raman spectral characteristics summarized in Table 1, it can be concluded that the Raman spectra of the cobalt(III) complexes with quadridentate ligands can be classified into four categories similar to those of tris(bidentate)cobalt(III) complexes;[2] polarized bands in the 420—670 cm^{-1} region, depolarized ones in the 390—450 cm^{-1} region, depolarized ones in the 300—420 cm^{-1} region, and polarized ones in the 240—290 cm^{-1} region. These can be assigned to the totally symmetric stretching vibration mode, the stretching vibration mode excluding the totally symmetric one, the metal-ligand skeletal bending deformation mode, and the chelate ring deformation mode, respectively.

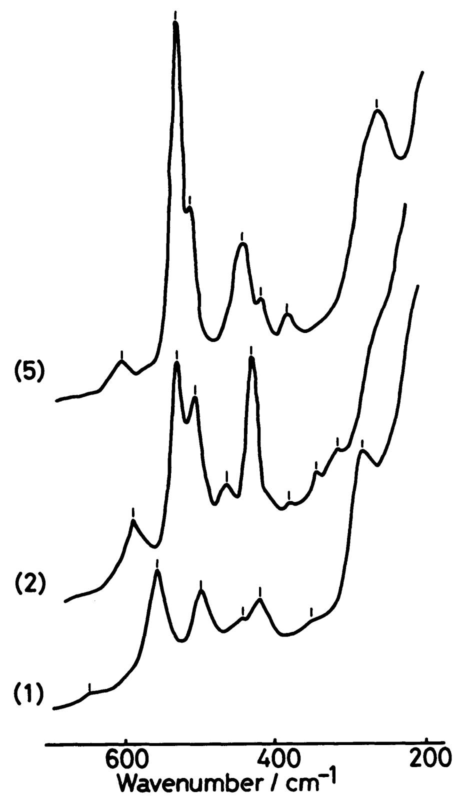

Fig. 3 Raman spectra of *cis-α-* and *cis-β-*[Co(en)(trien)]$^{3+}$ and [Co(en)(tren)]$^{3+}$. Numbers in parentheses correspond to those in Table 1.

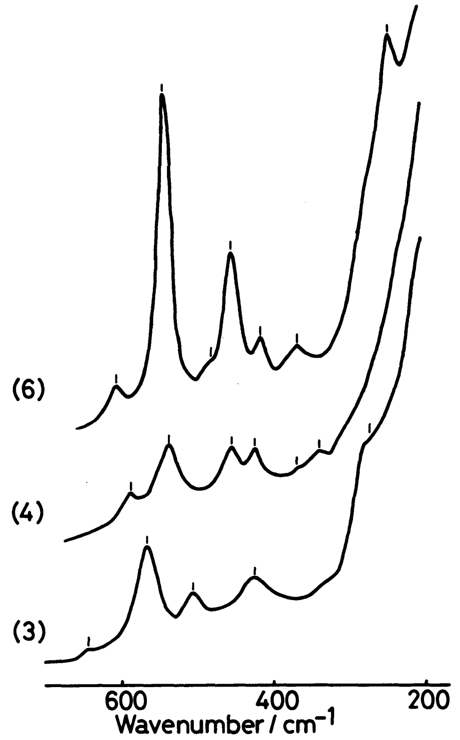

Fig. 4. Raman spectra of *cis-α-* and *cis-β-*[Co(ox)(trien)]$^+$ and [Co(ox)(tren)]$^+$. Numbers in parentheses correspond to those in Table 1.

Raman Spectra of [Co(trien)(bidentate)]- and [Co(tren)(bidentate)]-type Complexes. It can be seen from Fig. 3 and Table 1 that *cis-α-* and *cis-β-*[Co(en)(trien)]$^{3+}$ show different Raman spectral feature in each skeletal vibration region; the Raman spectrum of *cis-β-*[Co(en)(trien)]$^{3+}$ is similar to that of [Co(en)(tren)]$^{3+}$ rather than that of the cis-α isomer. The significant aspect in structures of *cis-β-*[Co(en)(trien)]$^{3+}$ and [Co(en)(tren)]$^{3+}$ is that the coordinated N-N-N portion of the quadridentate ligands (trien and tren) have equally meridional configuration toward the central metal atom. It is obvious that this meridional configuration greatly influences the normal vibration modes in the skeletal vibration region of the Raman spectra of *cis-β-*[Co(en)(trien)]$^{3+}$ and [Co(en)(tren)]$^{3+}$, because the mer isomers of the bis(terdentate)cobalt(III) complexes have shown the Raman spectral feature quite different from that of the fac isomers.[3] This type of Raman spectral feature can also be observed for the two geometrical isomers of [Co(ox)(trien)]$^+$ and [Co(ox)(tren)]$^+$; the Raman spectrum of *cis-β-*[Co(ox)(trien)]$^+$ can not be correlated to that of cis-α isomer, but, that of [Co(ox)(tren)]$^+$ (Fig. 4).

As shown in Figs. 3 and 4, the cobalt(III) complexes with quadridentate ligands, *cis-β-*[Co(en)(trien)]$^{3+}$, *cis-β-*[Co(ox)(trien)]$^+$, [Co(en)(tren)]$^{3+}$, and [Co(ox)(tren)]$^+$, which have equally meridional configuration with respect to the coordinated N–N–N portion in the quadridentate ligands, exhibit multiple polarized bands in the stretching vibration region, which is characteristic for the mer isomers of bis(terdentate)cobalt(III) complexes.[3] These findings suggest that their Raman spectra are mainly regulated by the normal vibrational modes of the meridional configuration of the quadridentate ligands. Especially, the polarized Raman bands around 450 cm^{-1} are regarded as characteristic for cis-β isomers of the [Co(trien)(bidentate)]- and [Co(tren)(bidentate)]-type complexes since the corresponding bands could not be observed in the spectra of the tris(bidentate)cobalt(III) complexes and the fac isomers of the bis(terdentate)cobalt(III) complexes.

Hence, in the cobalt(III) complexes with trien and tren ligands, so far as skeletal vibrations are concerned, the Raman spectra of the cis-α isomers can be correlated with those of the tris(bidentate)cobalt(III) complexes, and those of the cis-β isomers and the complexes with the tripodlike quadridentate ligands can be correlated with those of the mer isomers of the bis(terdentate)cobalt(III) complexes, respectively.

Raman Spectra of [Co(edda)(bidentate)]-type and [Co(aeida)(en)]$^+$ Complexes. Figure 5 shows the Raman spectra of cis-α and cis-β isomers of [Co(edda)(en)]$^+$ and [Co(edda)(tn)]$^+$. In view of the Raman spectra of the tris(bidentate)cobalt(III)[2] and

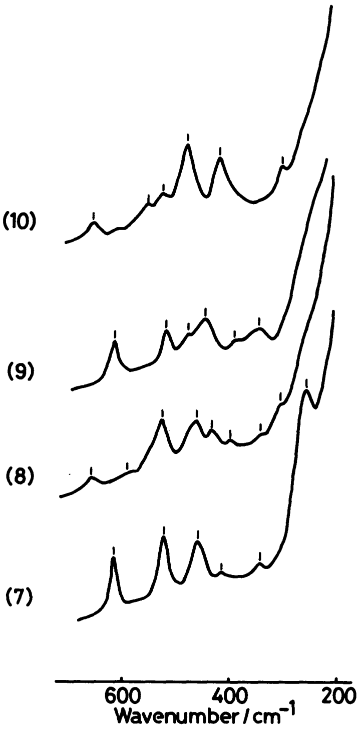

Fig. 5. Raman spectra of cis-α and cis-β isomers of $[Co(edda)(en)]^+$ and of $[Co(edda)(tn)]^+$. Numbers in parentheses correspond to those in Table 1.

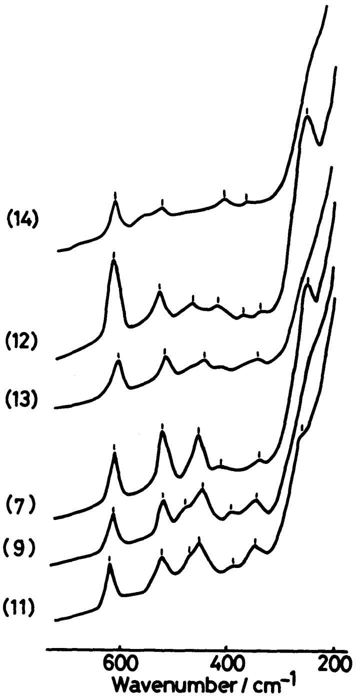

Fig. 6. Raman spectra of cis-α isomers of $[Co(edda)(ox)]^-$, $[Co(edda)(gly)]$, $[Co(edda)(\beta\text{-ala})]$, $[Co(edda)(en)]^+$, $[Co(edda)(tn)]^+$, and $[Co(edda)(NH_3)_2]^+$. Numbers in parentheses correspond to those in Table 1.

bis(terdentate)cobalt(III)[3] complexes, the Raman band at 617 cm⁻¹ of the cis-α isomer of $[Co(edda)(en)]^+$ and that at 660 cm⁻¹ of the cis-β isomer are closely associated with the coordinated oxygen atom. Furthermore, the shift of these bands is most prominent for the Raman spectra of *cis-α-* and *cis-β*-$[Co(edda)(en)]^+$ and is useful for differentiation between the cis-α and cis-β isomers. A similar feature is also observed for the Raman spectra of the cis-α and cis-β isomeric pairs of $[Co(edda)(tn)]^+$ (Fig. 5) and $[Co(edda)(ox)]^-$ (Table 1).

The Raman spectra of *trans*(O)- and *cis*(O)-$[Co(aeida)(en)]^+$ exhibit unique differences around 400 cm⁻¹ from the Raman spectrum of *cis-β*-$[Co(edda)(en)]^+$ with the different chelate ring structure (Table 1). The trans(O) and cis(O) isomers of $[Co(aeida)(en)]^+$ show polarized bands at 400 and 409 cm⁻¹, respectively, but the cis-β isomer of $[Co(edda)(en)]^+$ shows no polarized band in the corresponding region. These polarized bands around 400 cm⁻¹ can be assigned to the skeletal breathing mode on the basis of the Raman spectral characteristics of the mer isomers of $[Co(ida)(dien)]^+$, $[Co(mida)(mdien)]^+$, $[Co(ida)(mida)]^-$, and $[Co(mida)_2]^-$,[3] where mida and mdien denote *N*-methyliminodiacetate and *N,N*-bis(2-aminoethyl)methylamine, respectively. The skeletal breathing mode of the cobalt(III) complexes with a tripodlike quadridentate ligand, $[Co(en)(tren)]^{3+}$ and $[Co(ox)(tren)]^+$, are also detectable at 442 and 453 cm⁻¹ by comparison with the mer isomers of $[Co(dien)_2]^{3+}$, $[Co(ida)(dien)]^+$, and $[Co(mida)(mdien)]^+$.[3]

Role of Bidentate Ligands. It can be seen by comparison of Figs. 3 and 4 that *cis-α*-$[Co(en)(trien)]^{3+}$ and $[Co(en)(tren)]^{3+}$ exhibit Raman spectral characteristics similar to *cis-α*-$[Co(ox)(trien)]^+$ and $[Co(ox)(tren)]^+$, respectively. Furthermore, the Raman spectral behavior of the same geometrical isomers of the cobalt(III) complexes with edda ligand in the higher frequency region resemble each other as shown in Figs. 5 and 6. Accordingly, it is evident that the Raman spectra of the [Co(quadridentate)(bidentate)]-type complexes depend mainly on the configuration of the quadridentate ligands and the role of the bidentate ligands is of minor importance.

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