# Raman Spectral Characteristics of [Co(ida)$_n$(dien)$_{2-n}$]-Type and Related Complexes

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The Raman spectra of [Co(ida)$_n$(dien)$_{2-n}$]$^{(3-2n)+}$($n$=0, 1, and 2), where ida and dien denote iminodiacetate and diethylenetriamine respectively, and related complexes in the skeletal vibration region were measured in order to deduce the relation between their spectra and their geometrical structures. The Raman bands could be classified into five vibration modes: Totally symmetric stretching vibration modes (polarized bands in the 510—625 cm$^{-1}$ region); Co-O and Co-N stretching vibration modes (depolarized bands in the 430—525 cm$^{-1}$ region); metal-ligand skeletal breathing vibration modes (polarized bands in the 360—480 cm$^{-1}$ region); skeletal bending deformation modes (depolarized bands in the 290—405 cm$^{-1}$ region), and chelate ring deformation modes (polarized bands in the 220—260 cm$^{-1}$ region). The polarized bands around 400 cm$^{-1}$ were regarded as characteristic of the mono and bis(terdentate)cobalt(III) complexes. The mer isomers of each complex gave Raman spectra clearly different from those of the fac isomers in the stretching vibration region.

It has been accepted[1] that vibrational spectra are one of the most useful means for investigating the stereochemistry of transition metal complexes. Especially, the Raman spectra of the complexes in the skeletal vibration region, which appear in the low frequency region, reflect their structural characteristics.

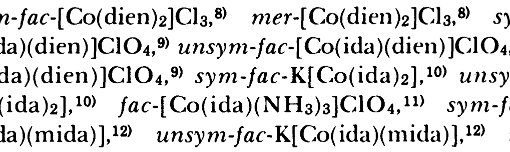
The Raman spectra in the skeletal vibration region of [Co(a)(b)(en)$_2$],[2] [Co(a)(b)(NH$_3$)$_4$],[3] [Co(a)(b)(tn)$_2$],[4] and [Co(a)$_2$(NH$_3$)$_2$(en)],[5] where a and b stand for unidentate ligands and where en and tn denote ethylenediamine and trimethylenediamine respectively, have been measured in order to find the vibrational criteria for differentiating their geometrical configurations. Recently, the Raman spectra of the nitroammine series[6] and the complete series of the [Co(gly)$_x$(ox)$_y$(en)$_z$]-type complexes ($x+y+z=3$),[7] where gly and ox denote glycinate and oxalate respectively, have been systematically investigated in order to establish the relation between the spectra and geometrical structures among their isomers. In particular, it has been concluded that the Raman bands of the [Co(gly)$_x$(ox)$_y$(en)$_z$]-type complexes could be treated in terms of the effective symmetry, which was mainly determined by the arrangement of coordinated atoms around the cobalt(III), and could be classified into several vibration modes.

The present investigation aims at finding more general information as to the relation between the geometrical structures and the Raman spectra in the skeletal vibration region of the cobalt(III) complexes. For this purpose, the Raman spectra of [Co(ida)$_n$(dien)$_{2-n}$]$^{(3-2n)+}$($n$=0, 1, and 2), [Co(NH$_3$)$_3$(dien)]$^{3+}$, and [Co(ida)(NH$_3$)$_3$]$^+$ were measured in the low frequency region (200—800 cm$^{-1}$) in an aqueous solution and were compared with those of the [Co(gly)$_x$(ox)$_y$(en)$_z$]-type complexes. Furthermore, the Raman spectra of [Co(ida)(mida)]$^-$, [Co(mida)$_2$]$^-$, and [Co(mida)(mdien)]$^+$, where mida and mdien denote *N*-methyliminodiacetate and *N,N*-bis(2-aminoethyl)methylamine respectively, were measured and compared with those of the [Co(ida)$_n$(dien)$_{2-n}$]-type complexes.

## Experimental

**Complexes.** The complexes were prepared and characterized according to the literature procedures except for [Co(NH$_3$)$_3$(dien)]Cl$_3$ (vide infra): *sym-fac*-[Co(dien)$_2$]Br$_3$,[8] *unsym-fac*-[Co(dien)$_2$]Cl$_3$,[8] *mer*-[Co(dien)$_2$]Cl$_3$,[8] *sym-fac*-[Co(ida)(dien)]ClO$_4$,[9] *unsym-fac*-[Co(ida)(dien)]ClO$_4$,[9] *mer*-[Co(ida)(dien)]ClO$_4$,[9] *sym-fac*-K[Co(ida)$_2$],[10] *unsym-fac*-K[Co(ida)$_2$],[10] *fac*-[Co(ida)(NH$_3$)$_3$]ClO$_4$,[11] *sym-fac*-Na[Co(ida)(mida)],[12] *unsym-fac*-K[Co(ida)(mida)],[12] *mer*-K[Co(ida)(mida)],[13] *sym-fac*-K[Co(mida)$_2$],[14] *unsym-fac*-K[Co(mida)$_2$],[14] *mer*-K[Co(mida)$_2$],[14] *sym-fac*-[Co(mida)(mdien)]Cl,[15] and *mer*-[Co(mida)(mdien)]Cl.[15]

**[Co(NH$_3$)$_3$(dien)]Cl$_3$.** Two grams of [CoCl$_3$(dien)] were dissolved in 50 cm$^3$ of 28% aqueous ammonia, and the solution was evaporated to dryness on a steam bath. The precipitate was then dissolved in a small amount of water and poured onto a column (40 mm$\phi$×600 mm) containing strong acid cation exchange resin (SP-Sephadex, C-25, Na$^+$ form). Having been swept with water, the band adsorbed on the column was eluted with a 0.3 mol dm$^{-3}$ aqueous sodium chloride solution. A yellow band of the desired complex was then eluted and fractionated. It was found, from the absorption spectra of the fractions, that the middle eluates contained [Co(NH$_3$)$_3$(dien)]$^{3+}$. Then the middle fractions were combined and concentrated to a small volume, and the Raman spectrum was measured. This



(a) (b) (c)

Fig. 1. Three geometrical isomers of [Co(terdentate-X,N,X)$_2$] (X=O or N). (a): sym-fac, (b): unsym-fac, (c): mer.

complex was characterized on the basis of the electronic absorption spectrum and elemental analysis.

**Measurements.** The Raman spectra were recorded on a JASCO Laser Raman Spectrometer, which had been constructed specially with a double monochromator, model CT-25, a He-Ne Laser, model NEC GLS-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.

## Results and Discussion

**General Aspect.** For the present bis(terdentate-X,N,X)cobalt(III)(X=O or N) complexes, these are three geometrical isomers, sym-fac, unsym-fac, and mer, as may be seen in Fig. 1.[8—15] Their Raman spectral data, obtained in the skeletal vibration region, are summarized in Table 1, together with those of such related complexes as $[Co(NH_3)_3(dien)]^{3+}$ and $[Co(ida)(NH_3)_3]^{+}$.

Figure 2 shows the Raman spectrum of *unsym-fac*-$[Co(dien)_2]^{3+}$ as a typical example of the bis(terdentate)cobalt(III) complexes, together with those of $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$;[7] these three complexes equally have $O_h$ symmetry for the coordinated atoms. Their Raman frequencies, intensities, and depolarization ratios indicate that *unsym-fac*-$[Co(dien)_2]^{3+}$ has the same spectral characteristics as $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ except for a polarized band at 409 cm$^{-1}$. That is, the Raman bands at 546, 430—485, and 321 cm$^{-1}$ of the unsym-fac isomer correspond to those at 495, 440, and 320 cm$^{-1}$ of $[Co(NH_3)_6]^{3+}$ and to those at 525, 440, and 378 cm$^{-1}$ of $[Co(en)_3]^{3+}$

Table 1. Observed Raman Bands and Their Assignments for $[Co(ida)_n(dien)_{2-n}]^{(3-2n)+}$ ($n$=0, 1, and 2) and Related Complexes

| No. | Complex | Raman frequency/cm$^{-1}$ a) | | | | |
|---|---|---|---|---|---|---|
| 1 | *sym-fac*-$[Co(dien)_2]^{3+}$ | 549 s(0) | 478 m(dp)<br>448 vw(—)<br>437 m(dp) | 401 m(0.36) | | 260 vw(—)<br>230 vw(—) |
| 2 | *unsym-fac*-$[Co(dien)_2]^{3+}$ | 546 s(0) | 485 m(dp)<br>444 m(dp)<br>434 m(dp) | 409 w(0) | 321 m(dp) | 255 vw(—) |
| 3 | *mer*-$[Co(dien)_2]^{3+}$ | 579 m(0)<br>546 vw(—)<br>514 s(0.15) | | 480 s(0)<br>442 s(0.37) | 402 m(dp)<br>381 vw(dp)<br>323 m(dp) | 222 m(0) |
| 4 | *sym-fac*-$[Co(ida)(dien)]^{+}$ | 609 m(0)<br>546 s(0) | 510 w(dp)<br>472 w(dp)<br>461 sh(dp) | 418 w(—)<br>387 s(0.22) | | 235 s(0) |
| 5 | *unsym-fac*-$[Co(ida)(dien)]^{+}$ | 610 m(0)<br>546 s(0) | 504 m(dp)<br>470 vw(dp)<br>453 vw(dp) | 410 m(0.27)<br>401 m(0.36) | 301 w(dp) | 235 w(0) |
| 6 | *mer*-$[Co(ida)(dien)]^{+}$ | 614 vw(0)<br>585 w(0)<br>524 s(0.12) | | 476 m(0.18)<br>451 s(0.31)<br>436 w(—)<br>390 s(0) | 346 w(dp)<br>302 vw(dp) | |
| 7 | *sym-fac*-$[Co(ida)_2]^{-}$ | 610 s(0)<br>569 m(0) | 522 vw(dp) | 394 w(—)<br>372 m(0.29) | | 229 m(0) |
| 8 | *unsym-fac*-$[Co(ida)_2]^{-}$ | 621 s(0)<br>562 m(0) | 446 vw(—) | 398 m(0.39)<br>382 vw(—) | 291 w(—) | |
| 9 | $[Co(NH_3)_3(dien)]^{3+}$ b) | 547 s(0) | 486 m(dp)<br>469 m(dp)<br>454 w(dp) | 422 s(0.39) | | |
| 10 | *fac*-$[Co(ida)(NH_3)_3]^{+}$ | 614 w(0)<br>514 m(0.24) | 505 sh(dp)<br>457 vw(dp) | 417 m(0.18)<br>403 m(0.27) | 339 vw(dp) | |
| 11 | *sym-fac*-$[Co(ida)(mida)]^{-}$ | 611 m(0)<br>546 m(0.23) | 497 w(dp)<br>450 w(—) | 407 w(—)<br>382 w(—)<br>361 w(—) | | 246 m(0) |
| 12 | *unsym-fac*-$[Co(ida)(mida)]^{-}$ | 622 w(0)<br>547 m(0.35) | 495 vw(—)<br>450 vw(—) | 409 w(0)<br>386 vw(—) | 354 vw(dp) | |

Table 1. (Continued)

| No. | Complex | Raman frequency/cm$^{-1}$ a) | | | | |
|---|---|---|---|---|---|---|
| 13 | *mer*-[Co(ida)(mida)]$^-$ | 533 m(0) | 455 vw(—) | 407 m(0) | | |
| 14 | *sym-fac*-[Co(mida)$_2$]$^-$ | 541 vw(0) | 501 vw(dp) | | | |
| 15 | *unsym-fac*-[Co(mida)$_2$]$^-$ | 545 vw(—) | 506 vw(—) | | | |
| 16 | *mer*-[Co(mida)$_2$]$^-$ | 563 s(0.22) | 504 vw(dp)<br>465 w(dp) | 404 m(0.32) | | 259 vw(—) |
| 17 | *sym-fac*-[Co(mida)(mdien)]$^+$ | 531 s(0.05) | 505 w(0.67)<br>451 vw(—) | 405 w(0.15)<br>397 w(0.30)<br>370 w(0.25)<br>361 w(0.57) | | 224 m(—) |
| 18 | *mer*-[Co(mida)(mdien)]$^+$ | 546 sh(0.15)<br>535 s(0.14) | 487 w(—) | 440 m(0.24)<br>392 m(0.35)<br>377 sh(0.32) | | 254 vw(0) |
| 19 | [Co(NH$_3$)$_6$]$^{3+}$ c) | 495 s(p) | 440 m(dp) | | 320 w(dp) | |
| 20 | [Co(en)$_3$]$^{3+}$ c) | 525 s(p) | 440 m(dp) | | 378 w(dp) | 283 s(p) |
| | Assignment d) | $\nu_{\mathrm{ts}}$(Co–L) | $\nu$(Co–L) | $\nu_{\mathrm{br}}$ | $\delta_{\mathrm{sbd}}$(L–Co–L) | $\delta_{\mathrm{crd}}(\mathrm{Co}{<}^{\mathrm{L}}_{\mathrm{L}}))$ |

a) The following abbreviations are used: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; p, polarized; dp, depolarized. Numerals in the parentheses show the polarization ratio. b) This isomer seems to be facial, judging from the Raman spectral behavior. c) Ref. 7. d) $\nu_{\mathrm{ts}}$ denotes the totally symmetric stretching vibration mode; $\nu$, the stretching vibration mode excluding the totally symmetric one; $\nu_{\mathrm{br}}$, the skeletal breathing vibration mode; $\delta_{\mathrm{sbd}}$, the metal-ligand skeletal bending deformation mode; $\delta_{\mathrm{crd}}$, the chelate ring deformation mode, and L, the donor atom (N and/or O).

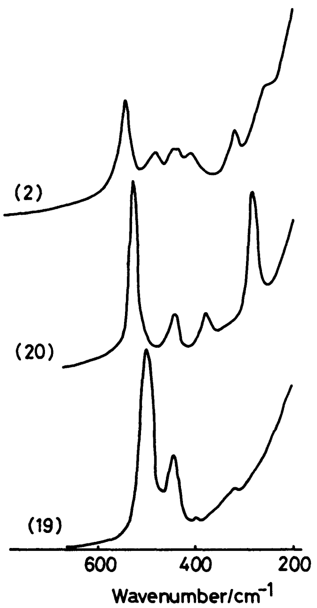


Fig. 2. Raman spectra of *unsym-fac*-[Co(dien)$_2$]$^{3+}$, [Co(en)$_3$]$^{3+}$, and [Co(NH$_3$)$_6$]$^{3+}$ (Ref. 7). Numbers in parentheses correspond to those in Table 1.

respectively, while the Raman band at 255 cm$^{-1}$ of the unsym-fac isomer corresponds to that at 283 cm$^{-1}$ of [Co(en)$_3$]$^{3+}$. Hence, the polarized band at 546 cm$^{-1}$, the depolarized bands in the 430—485 cm$^{-1}$ region, the depolarized band at 321 cm$^{-1}$, and the polarized band at 255 cm$^{-1}$ of *unsym-fac*-[Co(dien)$_2$]$^{3+}$ can be assigned to the totally symmetric metal-ligand stretching, the Co–N stretching, the metal-ligand skeletal bending deformation, and the chelate ring deformation modes respectively. The polarized band at 409 cm$^{-1}$ of *unsym-fac*-[Co(dien)$_2$]$^{3+}$ is regarded as a band characteristic of the bis(terdentate)cobalt(III) complexes, for we could not find the corresponding band in the spectra of [Co(NH$_3$)$_6$]$^{3+}$ and [Co(en)$_3$]$^{3+}$, but could find it uniquely in the spectra of the [Co(ida)$_n$(dien)$_{2-n}$]-type complexes (Table 1). On the basis of the Raman frequency and polarization characteristics, the polarized band at 409 cm$^{-1}$ of *unsym-fac*-[Co(dien)$_2$]$^{3+}$ is tentatively assigned to the breathing mode, which corresponds to the symmetric vibration of the overall structure of the complexes, i.e., the coupled vibration of the totally symmetric metal-ligand stretching and the chelate ring deformation. Furthermore, the good correlation between the vibration modes of *unsym-fac*-[Co(dien)$_2$]$^{3+}$ ($C_2$ symmetry) with those of [Co(NH$_3$)$_6$]$^{3+}$ ($O_{\mathrm{h}}$ symmetry) and [Co(en)$_3$]$^{3+}$ ($D_3$ symmetry)[7] suggests that the Raman spectra of the bis(terdentate)cobalt(III) complexes with linked five-membered chelate rings can be treated as a first approximation on the basis of the effective symmetry, which is mainly determined by the arrangement of the coordinated atoms around the central metal ion, as in the case of the tris(bidentate)cobalt(III) complexes with the five-membered chelate rings.[7]

Figure 3 shows the Raman spectra of the three geometrical isomers of [Co(dien)$_2$]$^{3+}$ and [Co(ida)-

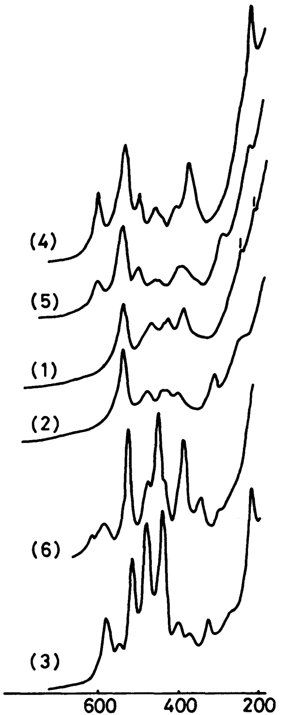


Fig. 3. Raman spectra of three geometrical isomers of $[Co(ida)(dien)]^+$ and $[Co(dien)_2]^{3+}$. Numbers in parentheses correspond to those in Table 1.

$(dien)]^+$. It is evident from Fig. 3 and Table 1 that the unsym-fac and sym-fac isomers of $[Co(dien)_2]^{3+}$ of the $[Co(N)_6]$-type have the same spectral characteristics except for minor differences in the low frequency region. The same thing is observed for the unsym-fac and sym-fac isomers of $[Co(ida)(dien)]^+$ of the $[Co(N)_4(O)_2]$-type (Fig. 3 and Table 1) and $[Co(ida)_2]^-$ of the $[Co(N)_2(O)_4]$-type (Table 1). Hence, we may expect that, so far as the skeletal vibrations of the fac isomers for the bis(terdentate)cobalt(III) complexes with the two linked five-membered chelate rings are concerned, the Raman spectral characteristics are predominantly determined by the arrangement of the coordinated atoms. The predominant contribution of the arrangement of the coordinated atoms to the Raman spectral characteristics is further supported by the Raman spectral characteristics of *unsym-fac*-$[Co(ida)_2]^-$ and *C*$_2$-*cis(N)*-$[Co(gly)_2(ox)]^-$ and of *unsym-fac*-$[Co(ida)(dien)]^+$ and *C*$_2$-*cis(O)*-$[Co(gly)_2(en)]^+$ (Fig. 4). Figure 4 and Table 1 show that the Raman bands at 560—625, 446, and 291 cm$^{-1}$ of *unsym-fac*-$[Co(ida)_2]^-$ correspond to those at 560—605, 430—510, and 348 cm$^{-1}$ of *C*$_2$-*cis(N)*-$[Co(gly)_2(ox)]^-$, while the Raman bands at 545—610, 450—505, 301, and 235 cm$^{-1}$ of *unsym-fac*-$[Co(ida)(dien)]^+$ correspond to those of 535—600, 430—490, 360, and 276 cm$^{-1}$ of *C*$_2$-*cis(O)*-$[Co(gly)_2(en)]^+$ respectively, irrespective of the chelate ring structure. On the other hand, the mer isomer shows Raman spectral characteristics quite different from those of the fac isomers. Figure 3 and Table 1 demonstrate that the Raman spectra of the mer isomers of $[Co(dien)_2]^{3+}$ and $[Co(ida)(dien)]^+$ exhibit several polarized bands, but no depolarized bands, in the 390—615 cm$^{-1}$ region, while those of the fac isomers of $[Co(dien)_2]^{3+}$ and $[Co(ida)(dien)]^+$ exhibit both polarized and depolarized bands in this region. This striking difference in the Raman spectral characteristics in the stretching vibration region can be ascribed to the difference in the stretching vibration mode depending on the coordination mode whether the linked two five-membered chelate rings take the mer coordination or the fac one.

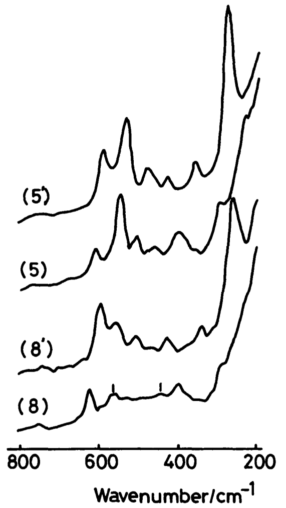


Fig. 4. Raman spectra of *unsym-fac*-$[Co(ida)(dien)]^+$ and $[Co(ida)_2]^-$. Raman spectra of *C*$_2$-*cis(O)*-$[Co(gly)_2(en)]^+$(5′) and *C*$_2$-*cis(N)*-$[Co(gly)_2(ox)]^-$(8′) were also shown (Ref. 7).

On the basis of the above discussion and the Raman spectral characteristics summarized in Table 1, the Raman spectra of the bis(terdentate)cobalt(III) complexes can be classified into five categories: Polarized bands in the 510—625 cm$^{-1}$ region, depolarized ones in the 430—525 cm$^{-1}$ region, polarized ones in the 360—480 cm$^{-1}$ region, depolarized ones in the 290—405 cm$^{-1}$ region, and polarized ones in the 220—260 cm$^{-1}$ region which can be assigned to the totally symmetric metal-ligand stretching, the Co–N and Co–O stretching except for the totally symmetric stretching character, the metal-ligand skeletal breathing, the skeletal bending deformation, and chelate ring deformation modes respectively.

Figure 5 shows the Raman spectra of the triamminecobalt(III)-type complexes, $[Co(NH_3)_3(dien)]^{3+}$ and $[Co(ida)(NH_3)_3]^+$, together with those of related complexes. The Raman spectrum of $[Co(NH_3)_3(dien)]^{3+}$ can be better correlated to that of *sym-fac*-$[Co(dien)_2]^{3+}$ than to that of $[Co(NH_3)_6]^{3+}$. That is, the character of the linked chelate rings appears similarly in the spectra of the mono(terdentate)cobalt(III)-type complexes. Further, Fig. 5 and Table 1 demonstrate that the Raman spectral characteristics of *fac*-$[Co(ida)(NH_3)_3]^+$

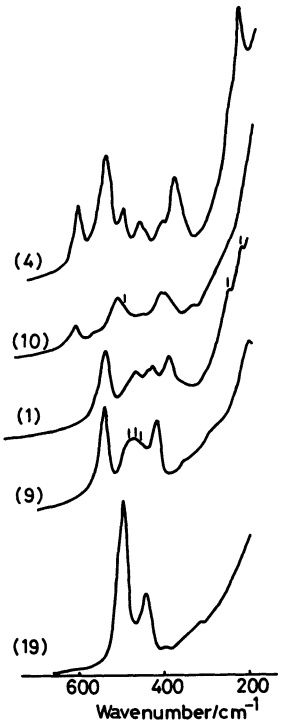


Fig. 5. Raman spectra of *sym-fac*-$[Co(ida)(dien)]^+$, *fac*-$[Co(ida)(NH_3)_3]^+$, *sym-fac*-$[Co(dien)_2]^{3+}$, $[Co(NH_3)_3(dien)]^{3+}$, and $[Co(NH_3)_6]^{3+}$ (Ref. 7). Numbers in parentheses correspond to those in Table 1.

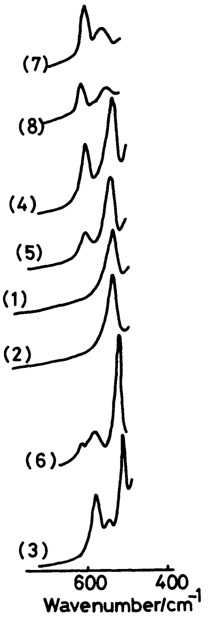


Fig. 6. Raman spectra of $[Co(ida)_n(dien)_{2-n}]^{(3-2n)+}$ ($n$= 0, 1, and 2) in the totally symmetric stretching vibration region. Numbers in parentheses correspond to those in Table 1.

are superimposed on those of the sym-fac and unsym-fac isomers of $[Co(ida)(dien)]^+$. It is interesting to note in Table 1 that the Raman spectral characteristics of $[Co(NH_3)_3(dien)]^{3+}$ can be correlated to those of the fac isomers of $[Co(dien)_2]^{3+}$ rather than to those of the mer isomer. Hence, we can expect that the dien in $[Co(NH_3)_3(dien)]^{3+}$ takes the facial coordination.

Finally, it should be noted that *sym-fac*-$[Co(dien)_2]^{3+}$ has more Raman bands than those expected from $C_{2h}$ symmetry ($4A_g+2B_g$) because of the splitting of the chelate ring deformation mode. In crystal, *sym-fac*-$[Co(dien)_2]Br_3$ has been reported to have an "approximate" $C_{2h}$ symmetry as a result of X-ray crystal structure analysis.[8,16] This Raman spectrum evidence implies that the sym-fac isomer is somewhat distorted structurally from $C_{2h}$ molecular symmetry in an aqueous solution so far as the skeletal vibration characteristics are concerned.

**Polarized Bands in the 510—625 cm$^{-1}$ Region.** Figure 6 shows the Raman spectra in the totally symmetric stretching vibration region. The mer isomers of $[Co(ida)_n(dien)_{2-n}]$-type complexes exhibit characteristic Raman spectra in this region. That is, each of the mer isomers of $[Co(dien)_2]^{3+}$ and $[Co(ida)(dien)]^+$ exhibits three polarized bands and no depolarized bands in the vibration region of lower frequencies. This is in contrast to the fac isomers, which exhibit both polarized and depolarized bands in the vibration region. The change of the depolarized bands to the polarized ones, together with the shift to the higher frequency region on going from the fac isomers to the mer ones, can be explained in terms of the strengthening of the harmonic stretching vibration characteristic of the totally symmetric stretching mode because of the diagonally connected chelate rings; in fact, the mer isomers are distorted from the regular octahedral structure, for the Co–N(imino nitrogen) bond in the mer isomers is appreciably stronger than the others.[8,17] Hence, the Raman spectral characteristics in this region can be used for the differentiation of the fac and mer isomers.

In the fac isomers, $[Co(dien)_2]^{3+}$ exhibits only one Raman band, whereas $[Co(ida)(dien)]^+$ and $[Co(ida)_2]^-$ give doublets. It is evident from the Raman frequencies of the cobalt(III) complexes with the fac coodination (Table 1) that the Raman bands can be classified into two categories: Those above 605 cm$^{-1}$ and those below 570 cm$^{-1}$, and that the former can be assigned to the $\nu_{ts}$(Co–O) mode, and the latter, to the $\nu_{ts}$(Co–N) mode. This assignment was supported by the isotopic shift; the polarized bands near 545 cm$^{-1}$ of the fac isomers of $[Co(ida)(dien)]^+$ and $[Co(dien)_2]^{3+}$ exhibited a shift to a lower frequency upon the deuteration of the amino protons.

**Depolarized Bands in the 430—525 cm$^{-1}$ Region.** In this region, the Raman spectra exhibit from one to three depolarized bands, except for *mer*-$[Co(dien)_2]^{3+}$ and $[Co(ida)(dien)]^+$, which give no depolarized bands at all (Fig. 7). These Raman bands can be assigned to the stretching mode, excluding the totally symmetric one, by comparison with the Raman spectra of the tris(bidentate)cobalt(III) complexes.[7] Furthermore,

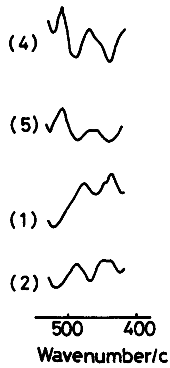


Fig. 7. Raman spectra of the fac isomers of [Co(ida)(dien)]$^+$ and [Co(dien)$_2$]$^{3+}$ in the stretching vibration region excluding the totally symmetric one. Numbers in parentheses correspond to those in Table 1.

the depolarized bands of *sym-fac*-[Co(dien)$_2$]$^{3+}$ are assigned to $\nu$(Co–N), because the bands exhibit a large spectral shift (about 15 cm$^{-1}$) upon deuteration. As a whole, the Raman bands of *fac*-[Co(ida)(dien)]$^+$ and [Co(ida)$_2$]$^-$ are observed at higher frequencies (445—525 cm$^{-1}$) than those of *fac*-[Co(dien)$_2$]$^{3+}$ (430—485 cm$^{-1}$). This result implies that the Raman bands of [Co(ida)(dien)]$^+$ and [Co(ida)$_2$]$^-$ may be greatly influenced by the Co–O stretching vibration mode, for the Raman spectra of the tris(bidentate)cobalt(III) complexes have shown that the Raman bands of the $\nu$(Co–O) mode appear at a higher frequency than those of the $\nu$(Co–N) mode.[7]

**Polarized Bands in the 360—480 cm$^{-1}$ Region.** The Raman spectra of the [Co(ida)$_n$(dien)$_{2-n}$]-type complexes in this region exhibit some unique polarized bands, as is shown in Table 1. These sorts of polarized bands have not been found in the Raman spectra of the tris(bidentate)cobalt(III) complexes;[7] they may be characteristic of the octahedral mono and bis(terdentate)cobalt(III) complexes. As has been mentioned before, these bands can be assigned to the skeletal breathing mode in the sense of the totally symmetric stretching, to which the chelate ring deformation is coupled, because the Raman bands in this region have totally symmetric vibration characteristics.

**Depolarized Bands in the 290—405 cm$^{-1}$ Region.** From a comparison with the data of the tris(bidentate)cobalt(III) complexes,[7] the Raman bands in this region have been assigned to the metal-ligand skeletal bending deformation mode. Figure 8 shows the relation between the Raman spectra of the sym-fac and unsym-fac isomers of [Co(dien)$_2$]$^{3+}$, [Co(ida)(dien)]$^+$, and [Co(ida)$_2$]$^-$ and their geometrical structures. The Raman spectra reflect the chelate ring structure (Fig. 8 and Table 1): The unsym-fac isomers have a depolarized band, the sym-fac isomers have no bands, and the mer isomers have a few bands. That is, it can be said that the combination of the chelate rings changes the metal-ligand skeletal bending deformation characteristics. This result is quite unlike that for the [Co(gly)$_x$(ox)$_y$(en)$_z$]-type complexes, each of which gives a Raman band, irrespective of the chelate ring structure, except for the [Co(ox)$_y$(en)$_z$]-type complexes, which have a major band accompanied by a very weak one.[7]

Fig. 8. Raman spectra of [Co(ida)$_n$(dien)$_{2-n}$]$^{(3-2n)+}$ ($n$=0, 1, and 2) in the skeletal bending deformation and the chelate ring deformation regions. Numbers in parentheses correspond to those in Table 1.

It seems to indicate that tha Raman bands in this region can be used for the differentiation of the sym-fac and unsym-fac isomers of the [Co(ida)$_n$(dien)$_{2-n}$]-type complexes.

**Polarized Bands in the 220—260 cm$^{-1}$ Region.** Polarized Raman bands of the [Co(ida)$_n$(dien)$_{2-n}$]-type complexes in this region have been assigned to the chelate ring deformation mode of the coordinated terdentate ligands, because they correspond well to a sharp band near 270 cm$^{-1}$ of the [Co(a)(b)(en)$_2$]-type complexes.[2] Unlike those in the 290—405 cm$^{-1}$ region, the Raman bands of the [Co(ida)$_n$(dien)$_{2-n}$]-type complexes in this region do not reflect the chelate ring structure (Table 1 and Fig. 8). Rather, they belong to the same skeletal vibration modes as those of the tris(bidentate)cobalt(III) complexes with the five-membered chelate rings. A shift to the lower frequency side was noticed for the polarized band by the linkage of the chelate rings (Table 1[7]).

No polarized bands were observed on the Raman spectra of [Co(ida)(NH$_3$)$_3$]$^+$ and [Co(NH$_3$)$_3$(dien)]$^{3+}$, both of which have one linked chelate ring.

**Raman Spectra of [Co(ida)$_n$(mida)$_{2-n}$]$^-$($n$=0 and 1)**

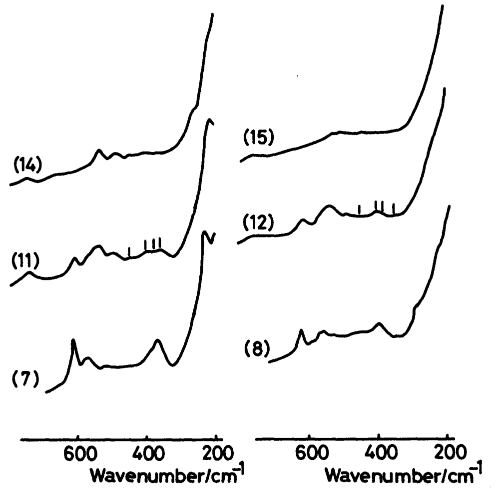


Fig. 9. Raman spectra of the fac isomers of $[\mathrm{Co(ida)}_n(\mathrm{mida})_{2-n}]^-$ ($n$=0, 1, and 2). Numbers in parentheses correspond to those in Table 1.

**and $[\mathrm{Co(mida)(mdien)}]^+$ Complexes.** The Raman spectra of the $[\mathrm{Co(ida)}_n(\mathrm{mida})_{2-n}]^-$($n$=0 and 1) and $[\mathrm{Co(mida)(mdien)}]^+$ complexes were measured in the skeletal vibration region as an extension of the $[\mathrm{Co(ida)}_n(\mathrm{dien})_{2-n}]$-type complexes; those spectral data are also summarized in Table 1. The coordinated mida and mdien ligands are characteristic in that their conformations are somewhat restricted by the methyl group on imino nitrogen.

The Raman bands of the $[\mathrm{Co(ida)}_n(\mathrm{mida})_{2-n}]$-type and $[\mathrm{Co(mida)(mdien)}]^+$ complexes can be classified into five vibration modes as in the case of the $[\mathrm{Co(ida)}_n(\mathrm{dien})_{2-n}]$-type ones.

Figure 9 shows the Raman spectra of the $[\mathrm{Co(ida)}_n(\mathrm{mida})_{2-n}]$-type complexes. The replacement of a hydrogen on the imino nitrogen by a methyl group causes a marked change in the Raman spectral characteristics rather than the spectral shift anticipated in the case of the deuteration of the amino protons. At the same time, the Raman spectra become less well defined with an increase in the numbers of the methyl group in the complexes.

The Raman spectra of the sym-fac and mer isomers of the $[\mathrm{Co(ida)}_n(\mathrm{mida})_{2-n}]$-type and $[\mathrm{Co(mida)(mdien)}]^+$ complexes are shown in Fig. 10, together with those of the $[\mathrm{Co(ida)}_n(\mathrm{dien})_{2-n}]$-type complexes. The Raman spectra in the stretching vibration region of the mer isomers for $[\mathrm{Co(ida)(mida)}]^-$, $[\mathrm{Co(mida)}_2]^-$, and $[\mathrm{Co(mida)(mdien)}]^+$ exhibit depolarized bands. These spectral characteristics differ somewhat from the Raman spectra of the mer isomers for the $[\mathrm{Co(ida)}_n(\mathrm{dien})_{2-n}]$-type complexes, which give only polarized bands. These findings suggest that the skeletal vibration characteristics of the mer isomers for the mida or mdien cobalt(III) complexes are mainly regulated by the linked chelate rings, which are folded by the restriction imposed by the methyl group on the imino nitrogen.

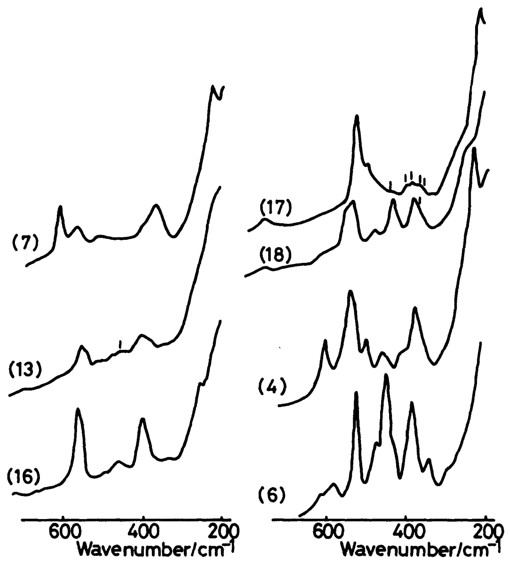


Fig. 10. Raman spectra of *sym-fac*-$[\mathrm{Co(ida)}_2]^-$, *mer*-$[\mathrm{Co(ida)(mida)}]^-$, *mer*-$[\mathrm{Co(mida)}_2]^-$, *sym-fac*-$[\mathrm{Co(mida)(mdien)}]^+$, *mer*-$[\mathrm{Co(mida)(mdien)}]^+$, *sym-fac*-$[\mathrm{Co(ida)(dien)}]^+$, and *mer*-$[\mathrm{Co(ida)(dien)}]^+$. Numbers in parentheses correspond to those in Table 1.

Finally, it should be pointed out that the two fac isomers of $[\mathrm{Co(mida)}_2]^-$ exhibit no intense bands around 400 cm$^{-1}$. This may be due to the two methyl groups on the imino nitrogen atoms, which change the normal vibrations of the fac isomers by means of the fixed conformation of all of the chelate rings.

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