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Raman Spectral Characteristics of Bis(terdentate)cobalt(III) Complexes with N and O Donor Atoms

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The Raman spectra were measured for the bis and mixed type cobalt(III) complexes with ethylenediamine-*N*-acetate (edma) in an aqueous solution in the skeletal vibration region. The Raman bands could be classified into five vibration modes; a totally symmetric stretching vibration mode in the 510—650 cm^{-1} region, a stretching vibration mode excluding the totally symmetric one in the 410—540 cm^{-1} region, a skeletal breathing vibration mode in the 370—490 cm^{-1} region, a skeletal bending deformation mode in the 270—420 cm^{-1} region, and a chelate ring deformation mode in the 220—270 cm^{-1} region. Differences in the skeletal vibrations were observed between the fac and mer isomers for the chelate ring arrangement. Further, differences for the chelate ring arrangement between the Raman spectra of sym-fac and unsym-fac isomers were observed in the skeletal bending deformation mode. The cobalt(III) complexes with the terdentate ligands containing N-methyl group exhibited Raman bands shifted to a lower frequency than those of the corresponding cobalt(III) complexes containing no N-methyl group in the totally symmetric stretching vibration mode region.

The Raman spectral criteria in the skeletal vibration region have recently been established for differentiating the geometrical isomers of several cobalt(III) complexes.[1] Further, the nitro-ammine series of cobalt(III) complexes have also been studied in order to establish the assignments of the Raman bands.[2] In previous works, the Raman spectra of $[Co(gly)_x(ox)_y(en)_z]$-type complexes[3] (gly, glycinate; ox, oxalate; and en, 1,2-ethanediamine), of tris(bidentate)cobalt(III) complexes containing six-membered chelate rings,[4] and of cobalt(III) complexes with the quadridentate ligands[5] have been investigated in order to ascertain the relation between their Raman spectra in the skeletal vibration region and the structures of these complexes. Furthermore, the $[Co(ida)_n(dien)_{2-n}]$-type complexes (ida, iminodiacetate and dien, 3-azapentane-1,5-diamine) have been established to possess clearly different Raman spectral features between the fac and mer isomers.[6]

In this work, the Raman spectra of bis and mixed type cobalt(III) complexes with an asymmetrical linear terdentate ligand, ethylenediamine-*N*-acetate (edma), are measured in order to extend the investigation of the $[Co(ida)_n(dien)_{2-n}]$-type complexes and to find more general information on the relation between the stereochemical properties and the Raman spectra of the bis(terdentate)cobalt(III) complexes. The abbreviations used for the ligands are as follows: edma, ethylenediamine-*N*-acetate ($NH_2CH_2CH_2NHCH_2COO^-$); dien, 3-azapentane-1,5-diamine ($NH_2CH_2CH_2NHCH_2CH_2NH_2$); ida, iminodiacetate ($^-OOCCH_2NHCH_2COO^-$); mdien, 3-methyl-3-azapentane-1,5-diamine ($NH_2CH_2CH_2N(CH_3)CH_2CH_2NH_2$), and mida, *N*-methyliminodiacetate ($^-OOCCH_2N(CH_3)CH_2COO^-$). The prefixes sym-fac, unsym-fac, and mer represent the chelate ring arrangements, and the fac(N_t), mer(N_t), trans(N_t), cis(N_t), cis(N_t)trans(O), cis(N_t)cis(O), fac(N), and mer(N) abbreviations represent the coordinated atom arrangements. The N_t and N_c symbols stand for the terminal and central nitrogen atoms respectively of the linear terdentate ligands.

Experimental

Complexes. The complexes were prepared and characterized according to the literature procedures: *sym-fac*-$[Co(edma)(dien)]Cl_2$,[7] *unsym-fac-fac*(N_t)-$[Co(edma)(dien)]Cl_2$,[7] *unsym-fac-mer*(N_t)-$[Co(edma)(dien)]Cl_2$,[7] *mer*-$[Co(edma)(dien)]Cl_2$,[7] *sym-fac-trans*(N_t)-$[Co(edma)_2]Cl$,[8,9] *sym-fac-cis*(N_t)-$[Co(edma)_2]Br$,[8,9] *unsym-fac-cis*(N_t)*trans*(*O*)-$[Co(edma)_2]Cl$,[8,9] *unsym-fac-cis*(N_t)*cis*(*O*)-$[Co(edma)_2]Cl$,[8,9] *unsym-fac-trans*(N_t)-$[Co(edma)_2]Cl$,[8,9] *mer*-$[Co(edma)_2]Br$,[8,9] *sym-fac*-[Co(ida)(edma)],[10] *unsym-fac-mer*(*N*)-[Co(ida)(edma)],[10] *sym-fac*-$[Co(edma)(mdien)]SO_4$,[7] *unsym-fac-fac*(N_t)-$[Co(edma)(mdien)]Br_2$,[7] *unsym-fac-mer*(N_t)-$[Co(edma)(mdien)]SO_4$,[7] *mer*-$[Co(edma)(mdien)]SO_4$,[7] *sym-fac*-[Co(ida)(mdien)]Cl,[11] *unsym-fac*-[Co(ida)(mdien)]Cl,[11] *mer*-[Co(ida)(mdien)]Cl,[11] *sym-fac*-[Co(mida)(edma)],[12] and *unsym-fac-fac*(*N*)-[Co(mida)(edma)].[12]

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.

Results and Discussion

General Assignments of the Raman Spectra of $[Co(edma)(dien)]^{2+}$, $[Co(edma)_2]^+$, and [Co(ida)(edma)]. The possible geometrical isomers of $[Co(edma)(dien)]^{2+}$, $[Co(edma)_2]^+$, and [Co(ida)(edma)] are four, six, and four respectively, as is depicted in Figs. 1, 2, and 3.[7-10] The Raman spectral data in the skeletal vibration region of the isomers are summarized in

Table 1. Raman Spectral Data of Bis(terdetate)cobalt(III) Complexes with N and O Donor Atoms

No.	Complex	Raman frequency/cm^{-1}[a]				
1	*sym-fac*-[Co(edma)(dien)]$^{2+}$	641 w(p) 553 s(p)	509 w(dp) 456 w(dp)	401 m(p)		235 w(p)
2	*unsym-fac-fac*(N_t)-[Co(edma)(dien)]$^{2+}$	642 w(p) 558 s(p)	506 w(—) 473 vw(—) 447 vw(—)	421 m(p)	307 vw(—)	
3	*unsym-fac-mer*(N_t)-[Co(edma)(dien)]$^{2+}$	635 w(p) 547 s(p)	514 w(—) 453 m(dp)	411 m(p)	306 vw(—)	247 w(—)
4	*mer*-[Co(edma)(dien)]$^{2+}$	577 vw(—) 538 w(p) 518 vw(—)		481 vw(—) 445 m(p)	414 w(dp)	
5	*sym-fac-trans*(N_t)-[Co(edma)$_2$]$^+$	635 m(p) 549 s(p) 523 s(p)	459 w(dp)	407 m(p) 381 sh(—)		233 m(p)
6	*sym-fac-cis*(N_t)-[Co(edma)$_2$]$^+$	639 m(p) 577 s(p) 529 m(p)	486 w(dp)	394 s(p)		240 vw(p)
7	*unsym-fac-cis*(N_t)*trans*(O)-[Co(edma)$_2$]$^+$	649 m(p) 570 s(p) 522 s(p)	467 w(dp)	417 m(p)	305 w(—)	261 vw(—)
8	*unsym-fac-cis*(N_t)*cis*(O)-[Co(edma)$_2$]$^+$	645 m(p) 569 s(p) 526 s(p)	485 w(dp)	419 m(p) 400 sh(—)	299 vw(—)	243 w(p)
9	*unsym-fac-trans*(N_t)-[Co(edma)$_2$]$^+$	638 m(p) 552 s(p) 526 s(p)	470 w(dp)	415 m(p)	294 vw(—)	245 w(p)
10	*mer*-[Co(edma)$_2$]$^+$	634 w(p) 544 m(p) 510 w(p)	470 vw(—)[b] 461 vw(—)[b]	421 s(p)	379 w(dp)	
11	*sym-fac*-[Co(ida)(edma)]	618 w(—) 573 m(p)	533 w(—) 497 vw(—)	390 m(p)		229 vw(—)
12	*unsym-fac-mer*(N)-[Co(ida)(edma)]	645 w(—) 565 m(p)	529 w(—)	409 m(p) 401 m(p)	290 vw(—)	
13	*sym-fac*-[Co(edma)(mdien)]$^{2+}$	643 w(p) 554 sh(—) 529 s(p)	466 sh(—) 443 m(dp)	401 m(p)		235 s(p)
14	*unsym-fac-fac*(N_t)-[Co(edma)(mdien)]$^{2+}$	637 vw(—) 555 m(—) 527 s(p)	450 m(dp)	403 w(—)	346 m(—) 289 vw(—)	249 w(—)
15	*unsym-fac-mer*(N_t)-[Co(edma)(mdien)]$^{2+}$	636 w(p) 585 vw(—) 529 s(p)	450 w(dp) 417 vw(dp)	378 vw(—)		237 vw(—)
16	*mer*-[Co(edma)(mdien)]$^{2+}$	631 vw(—) 533 s(p)	503 sh(—)	442 s(p) 417 m(—)	373 vw(—) 326 vw(—) 279 sh(—)	
17	*sym-fac*-[Co(ida)(mdien)]$^+$	614 w(p) 529 s(p)	518 w(dp) 471 vw(—) 442 w(—)	390 m(p)		225 vw(p)
18	*unsym-fac*-[Co(ida)(mdien)]$^+$	617 w(p) 533 s(p)	517 w(dp) 450 w(—)	403 w(—)		237 vw(p)

Table 1. (Continued)

No.	Complex	Raman frequency/cm^{-1}[a]				
19	*mer*-$[\mathrm{Co(ida)(mdien)}]^{+}$	538 m(p)	499 vw(—)	442 m(p) 386 m(p)		
20	*sym-fac*-$[\mathrm{Co(mida)(edma)}]$	644 w(p) 569 sh(p) 537 s(p)	498 m(—) 458 vw(—)	406 m(p) 378 m(p)		
21	*unsym-fac-fac*(*N*)-$[\mathrm{Co(mida)(edma)}]$	642 vw(—) 534 m(p)	498 vw(—)	413 w(—)		
22	$[\mathrm{Co(gly)(en)_2}]^{2+}$[c]	584 w(p) 521 s(p)	471 vw(dp) 447 w(dp)		374 w(dp)	279 s(p)
23	*trans*(*O*)-$[\mathrm{Co(gly)_2(en)}]^{+}$[c]	596 m(p) 523 m(p)	504 sh(dp) 458 w(dp)		368 w(dp)	275 s(p)
24	*sym-fac*-$[\mathrm{Co(dien)_2}]^{3+}$[d]	549 s(p)	478 m(dp) 448 vw(—) 437 m(dp)	401 m(p)		260 vw(—) 230 vw(—)
25	*unsym-fac*-$[\mathrm{Co(dien)_2}]^{3+}$[d]	546 s(p)	485 m(dp) 444 m(dp) 434 m(dp)	409 w(p)	321 m(dp)	255 vw(—)
26	*sym-fac*-$[\mathrm{Co(ida)(dien)}]^{+}$[d]	609 m(p) 546 s(p)	510 w(dp) 472 w(dp) 461 sh(dp)	418 w(—) 387 s(p)		235 s(p)
27	*unsym-fac*-$[\mathrm{Co(ida)(dien)}]^{+}$[d]	610 m(p) 546 s(p)	504 m(dp) 470 vw(dp) 453 vw(dp)	410 m(p) 401 m(p)	301 w(dp)	235 w(p)
28	*sym-fac*-$[\mathrm{Co(ida)_2}]^{-}$[d]	610 s(p) 569 m(p)	522 vw(dp)	394 w(—) 372 m(p)		229 m(p)
29	*unsym-fac*-$[\mathrm{Co(ida)_2}]^{-}$[d]	621 s(p) 562 m(p)	446 vw(—)	398 m(p) 382 vw(—)	291 w(—)	
	Assignment[a]	ν_{ts}(Co–L)	ν(Co–L)	ν_{br}	δ_{sbd}(L–Co–L)	$\delta_{\mathrm{crd}}(\mathrm{Co}{<}^{\mathrm{L}}_{\mathrm{L}}))$

a) The following abbrevations are used: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; p, polarized; dp, depolarized; ν_{ts}, totally symmetric stretching vibration mode; ν, stretching vibration mode excluding the totally symmetric stretching character; ν_{br}, skeletal breathing vibration mode; δ_{sbd}, skeletal bending deformation mode; δ_{crd}, chelate ring deformation mode. The Raman band intensities (s, m, w, vw, and sh) are classified by a comparison of all the Raman bands among all the complexes. b) Consult the text. c) Ref. 3. d) Ref. 6.

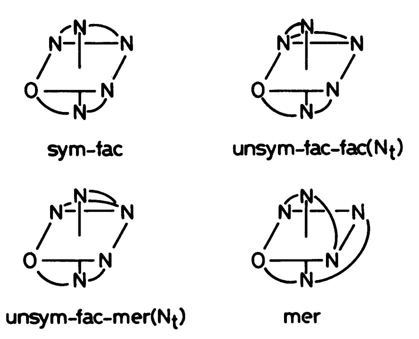
sym-fac　unsym-fac-fac(Nt)
unsym-fac-mer(Nt)　mer

Fig. 1. Four geometrical isomers of $[\mathrm{Co(edma)(dien)}]^{2+}$.

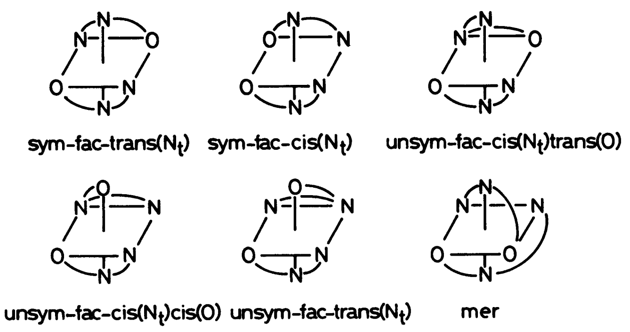
sym-fac-trans(Nt)　sym-fac-cis(Nt)　unsym-fac-cis(Nt)trans(O)
unsym-fac-cis(Nt)cis(O)　unsym-fac-trans(Nt)　mer

Fig. 2. Six geometrical isomers of $[\mathrm{Co(edma)_2}]^{+}$.

Table 1, together with those of the related complexes of primary concern.

Figure 4 shows the Raman spectra of *unsym-fac-mer*(N_t)-[Co(edma)(dien)]$^{2+}$, [Co(gly)(en)$_2$]$^{2+}$, *unsym-fac-cis*(N_t)*trans*(O)-[Co(edma)$_2$]$^+$, and *trans*(O)-[Co(gly)$_2$(en)]$^+$, chosen as representative for a general spectral consideration. In a previous paper,⁶⁾ the Raman bands of *unsym-fac*-[Co(dien)$_2$]$^{3+}$ and *unsym-fac*-[Co(ida)(dien)]$^+$ have all been correlated to those of [Co(en)$_3$]$^{3+}$ and C_2-*cis*(O)-[Co(gly)$_2$(en)]$^+$ respectively except for one, which was assigned to the skeletal breathing vibration mode. The Raman bands at 547—635, 453—514, 306, and 247 cm^{-1} of *unsym-fac-mer*(N_t)-[Co(edma)(dien)]$^{2+}$ correspond to those at 521—584, 447—471, 374, and 279 cm^{-1} of [Co(gly)(en)$_2$]$^{2+}$ respectively, and the Raman bands at 570—649, 467—522, 305, and 261 cm^{-1} of *unsym-fac-cis*(N_t)*trans*(O)-[Co(edma)$_2$]$^+$ correspond to those at 523—596, 458—504, 368, and 275 cm^{-1} of *trans*(O)-[Co(gly)$_2$(en)]$^+$ respectively. Thus, a comparison of these spectra demonstrates that the cobalt(III) complexes with the edma ligand give the same spectral patterns as the tris(bidentate)cobalt(III) complexes³⁾ with the same donor atom arrangement, except for the Raman bands at ca. 400 cm^{-1}; this is characteristic of [Co(ida)$_n$(dien)$_{2-n}$]-type complexes.⁶⁾ In addition, as is shown in Fig. 5, the Raman spectral patterns of *cis*(O)-[Co(edma)$_2$]$^+$ and *cis*(O)-[Co(ida)(dien)]$^+$ are similar to each other throughout the spectral regions except for the somewhat high frequency shift in the Raman bands of [Co(edma)$_2$]$^+$ in comparison with those of [Co(ida)(dien)]$^+$ and the difference in degree of the depolarization ratios of the Raman bands at ca. 500—530 cm^{-1}. On the basis of these observations and the Raman spectral characteristics summarized in Table 1, the Raman spectra of the present edma complexes can be classified into five vibration modes as in the case of the [Co(ida)$_n$(dien)$_{2-n}$]-type complexes;⁶⁾ that is, the polarized bands in the 510—650 cm^{-1} region, depolarized ones in the 410—540 cm^{-1} region, polar-

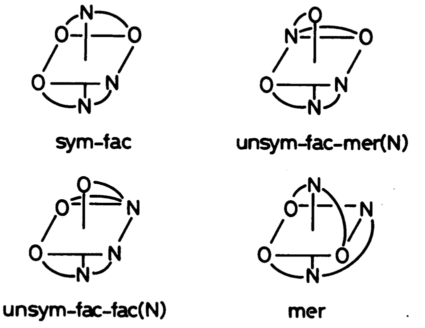

Fig. 3. Four geometical isomers of [Co(ida)(edma)].

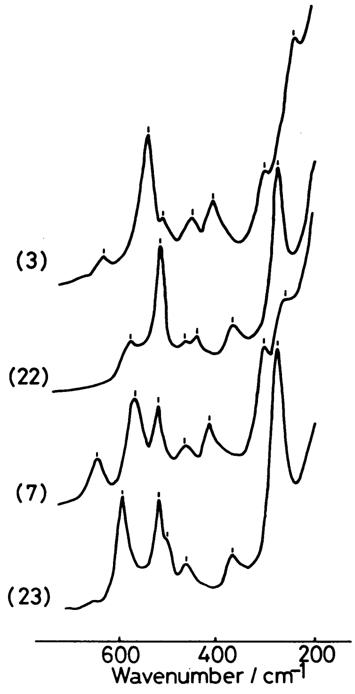

Fig. 4. Raman spectra of *unsym-fac-mer*(N_t)-[Co(edma)(dien)]$^{2+}$, [Co(gly)(en)$_2$]$^{2+}$, *unsym-fac-cis*(N_t)*trans*(O)-[Co(edma)$_2$]$^+$, and *trans*(O)-[Co(gly)$_2$(en)]$^+$. Numbers in parentheses correspond to those in Table 1.

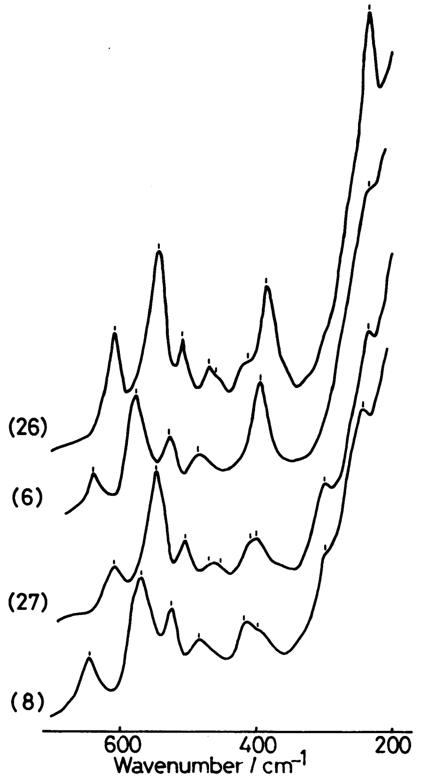

Fig. 5. Raman spectra of *sym-fac*-[Co(ida)(dien)]$^+$, *sym-fac-cis*(N_t)-[Co(edma)$_2$]$^+$, *unsym-fac*-[Co(ida)(dien)]$^+$, and *unsym-fac-cis*(N_t)*cis*(O)-[Co(edma)$_2$]$^+$. Numbers in parentheses correspond to those in Table 1.

ized ones in the 370—490 cm^{-1} region, depolarized ones in the 270—420 cm^{-1} region, and polarized ones in the 220—270 cm^{-1} region can be assigned to the totally symmetric stretching vibration, the stretching vibration excluding the totally symmetric stretching character, the skeletal breathing vibration, the skeletal bending deformation, and the chelate ring deformation modes respectively. Furthermore, the skeletal breathing vibration mode can be regarded as the key bands for the bis(terdentate)cobalt(III) complexes with linear terdentate ligands.

Raman Spectral Characteristics of the Geometrical Isomers of [Co(edma)(dien)]$^{2+}$, [Co(edma)$_2$]$^+$, and [Co(ida)(edma)]. The *fac*- and *mer*-[Co(edma)(dien)]$^{2+}$ isomers exhibit a striking difference in the chelate ring arrangements on their Raman spectra (Fig. 6). Similar spectral behavior has also been substantiated for the *fac*- and *mer*-[Co(edma)$_2$]$^+$ isomers (Fig. 7). This spectral behavior corresponds well to that of the [Co(ida)$_n$(dien)$_{2-n}$]-type complexes.⁶⁾ That is, in the skeletal breathing vibration mode, the mer isomers exhibit sharp Raman bands at higher frequencies than the fac isomers; the Raman bands caused by the skeletal bending deformation of the mer isomers also appear at higher frequencies. Furthermore, the mer isomers have no bands in the chelate ring deformation mode region, as in the case of [Co(ida)(dien)].⁶⁾ These features can be ascribed to the difference in strain energy in the vibrational motion between the ligand of the meridional arrangement and that of the facial one. It has been reported in the previous paper⁶⁾ that the mer isomers of [Co(ida)(dien)]$^+$ and [Co(dien)$_2$]$^{3+}$ exhibit the polarized character in the stretching vibration region, while the fac isomers give depolarized Raman bands. A close inspection of the Raman frequencies, intensities, and depolarization ratios of *mer*-[Co(edma)(dien)]$^{2+}$ reveals a retention of the polarized character of the mer isomers of [Co(ida)(dien)]$^+$ and [Co(dien)$_2$]$^{3+}$. This polarized character, however, was found to be obscured in *mer*-[Co(edma)$_2$]$^+$; (an attempt at a reliable estimation of the Raman bands at 470 and 461 cm^{-1} relative to the polarized Raman bands was unsuccessful because they were too weak for their depolarization ratios to be measured precisely; rather, they were tentatively classified as depolarized ones based on the profiles of the polarized and depolarized Raman spectra in this region). The obscurity of the polarized character in *mer*-[Co(edma)$_2$]$^+$ may, in part, be attributed to the disturbance of the overall harmonic stretching vibrational motion by different terminal donor atoms and force constants.

The difference in the chelate ring arrangement between the sym-fac and unsym-fac isomers is noticeable in the skeletal bending deformation mode (Figs. 6 and 7). Each unsym-fac isomer has a

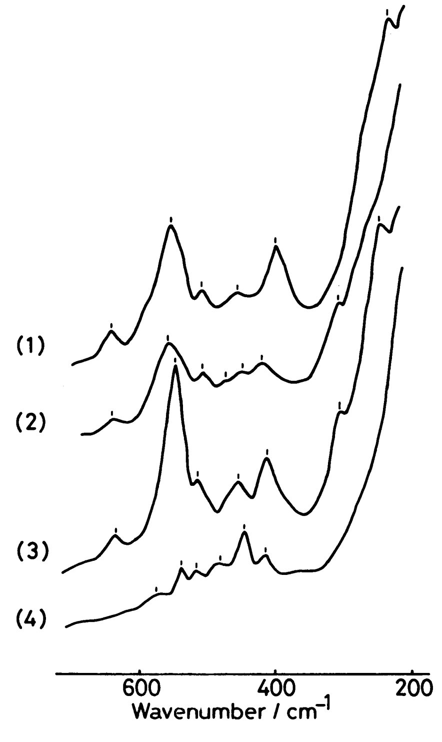

Fig. 6. Raman spectra of four geometrical isomers of [Co(edma)(dien)]$^{2+}$. Numbers in parentheses correspond to those in Table 1.

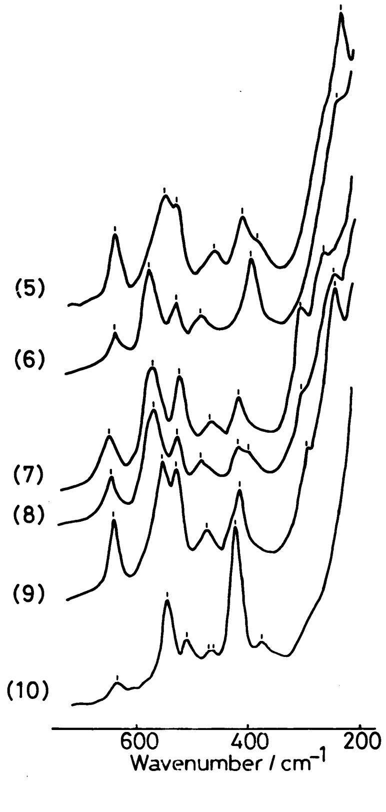

Fig. 7. Raman spectra of six geometrical isomers of [Co(edma)$_2$]$^+$. Numbers in parentheses correspond to those in Table 1.

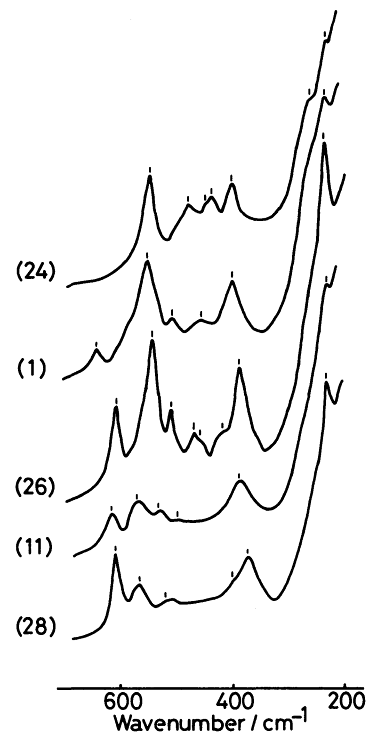

Fig. 8. Raman spectra of sym-fac isomers for chelate ring arrangement of $[Co(dien)_2]^{3+}$, $[Co(edma)(dien)]^{2+}$, $[Co(ida)(dien)]^+$, $[Co(ida)(edma)]$, $[Co(ida)_2]^-$. Numbers in parentheses correspond to those in Table 1.

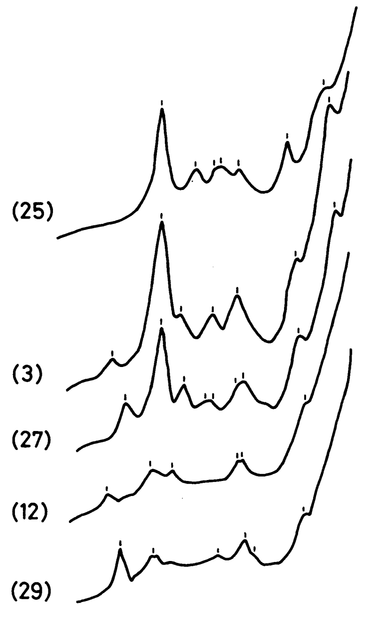

Fig. 9. Raman spectra of unsym-fac isomers for chelate ring arrangement of $[Co(dien)_2]^{3+}$, $[Co(edma)(dien)]^{2+}$, $[Co(ida)(dien)]^+$, $[Co(ida)(edma)]$, $[Co(ida)_2]^-$. Numbers in parentheses correspond to those in Table 1.

depolarized band, while the sym-fac isomers have none. This spectral feature has also been found in the $[Co(ida)_n(dien)_{2-n}]$-type complexes.[6] Furthermore, the *sym-fac-trans*(N_t)- and *unsym-fac-cis*(N_t)*cis*(*O*)-$[Co(edma)_2]^+$ with lower symmetries, C_i and C_1 respectively, give a doublet in the skeletal breathing mode, whereas *sym-fac-cis*(N_t)-, *unsym-fac-cis*(N_t)*trans*(*O*)-, and *unsym-fac-trans*(N_t)-$[Co(edma)_2]^+$, having a higher symmetry, C_2, give only one Raman band in this region. By contrast, the Raman spectral difference between the trans(O) and cis(O) isomers of $[Co(edma)_2]^+$ is of no intrinsic importance. Accordingly, these findings suggest that, so far as the bis(terdentate)cobalt(III) complexes with equal numbers of coordinated nitrogen and oxygen atoms are concerned, the Raman spectral characteristics depend mainly on the arrangement of the chelate ring around the central metal atom.

Role of Coordinated Atoms on Raman Spectral Characteristics. Figures 8 and 9 show the Raman spectra of the sym-fac and unsym-fac isomers with different numbers of coordinated nitrogen and oxygen atoms. The Raman bands above 600 cm^{-1} of the sym-fac and unsym-fac isomers are intensified with an increase in the number of coordinated oxygen atoms, whereas those at ca. 460 and 550 cm^{-1} become weaker with a decrease in the number of coordinated nitrogen atoms. Accordingly, the former bands may have a largely Co–O stretching character, and the latter ones, a Co–N stretching character. Furthermore, it is observed that the number of Raman bands in the skeletal breathing mode increases with an increase in the number of coordinated oxygen atoms.

The Raman spectra of the isomers of $[Co(ida)(dien)]^+$ can be regarded as a superposition of those of $[Co(dien)_2]^{3+}$ and $[Co(ida)_2]^-$.[6] Moreover, as is shown in Fig. 5, the Raman spectra of the isomers of $[Co(edma)_2]^+$ can also be correlated to those of $[Co(ida)(dien)]^+$. It is not surprising that $[Co(edma)_2]^+$ can be considered to have both of the spectral features of the corresponding isomers of $[Co(dien)_2]^{3+}$ and $[Co(ida)_2]^-$, because the Raman spectral characteristics of the bis(terdentate)cobalt(III) complexes with equal numbers of coordinated nitrogen and oxygen atoms depend mainly on the arrangement of the chelate ring around the central metal atom.

In conclusion, the empirical rule derived from bis(terdentate)cobalt(III) complexes with symmetrical linear terdentate ligands holds also for those with asymmetrical linear terdentate ligands.

Raman Spectra of $[Co(edma)(mdien)]^{2+}$, $[Co(ida)(mdien)]^+$, and $[Co(mida)(edma)]$. The Raman spectra of $[Co(edma)(mdien)]^{2+}$ and $[Co(ida)(mdien)]^+$ are shown in Figs. 10 and 11 respectively. The Raman bands in the skeletal bending deformation mode region, which were observed on the unsym-fac isomers

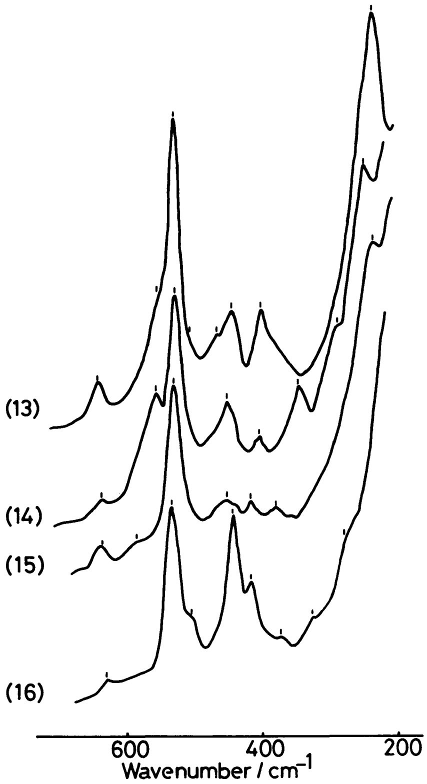

Fig. 10. Raman spectra of four geometrical isomers of [Co(edma)(mdien)]$^{2+}$. Numbers in parentheses correspond to those in Table 1.

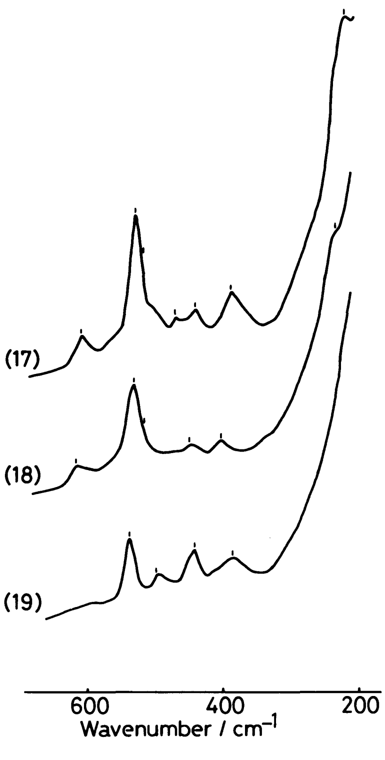

Fig. 11. Raman spectra of three geometrical isomers of [Co(ida)(mdien)]$^{+}$. Numbers in parentheses correspond to those in Table 1.

of [Co(edma)(dien)]$^{2+}$, [Co(ida)(dien)]$^{+}$, and [Co(ida)(edma)] (Figs. 6 and 9 and Ref. 6), are no longer present in the Raman spectra of *unsym-fac-mer*(N_t)-[Co(edma)(mdien)]$^{2+}$, *unsym-fac*-[Co(ida)(mdien)]$^{+}$, and *unsym-fac-fac*(N)-[Co(mida)(edma)] (Table 1). By contrast, two Raman bands are observed in the skeletal bending deformation mode region for the unsym-fac-fac(N_t) isomer of [Co(edma)(mdien)]$^{2+}$. This may be related to the change in the O–Co–N_c angles caused by the steric interaction between the methyl group of the mdien ligand and the methylene group of the edma ligand.7) With all these differences, the cobalt(III) complexes with the terdentate ligands, mdien and mida, exhibit Raman spectral features corresponding to those of the cobalt(III) complexes with terdentate ligands, dien, edma, and ida. Accordingly, the Raman bands of the cobalt(III) complexes containing an N-methyl group can also be classified into the five vibrational modes. Especially, the Raman bands above 600 cm^{-1}, those appearing at ca. 615 cm^{-1} for the ida complexes and at ca. 640 cm^{-1} for the edma complexes, can be used as vibrational criterion for differentiating complexes containing either ida or edma, except for [Co(ida)(edma)], which shows the Raman bands at 618 cm^{-1} characteristic of the sym-fac isomer and at 645 cm^{-1} characteristic of the unsym-fac-mer(N) isomer because of the intensification of the one at the sacrifice of the other.

The cobalt(III) complexes containing an N-methyl group also show some characteristic Raman spectral behavior. First, the strongest Raman bands attributable to the totally symmetric stretching vibration of the cobalt(III) complexes containing an N-methyl group, except for *mer*-[Co(ida)(mdien)]$^{+}$, appear at a lower frequency region compared with the Raman spectra of the corresponding cobalt(III) complexes containing no N-methyl group. This fact suggests the existence of a mass effect in the totally symmetric stretching vibration mode as a result of the replacement of a hydrogen atom on the imino nitrogen by a methyl group, similar to the isotope shifts, and/or the difference in the central metal–donor atom bond strength, which can be related to the ligand field strength. In fact, the first and the second absorption maxima shift to the lower energy side when the methyl group is introduced on the central donor atom of the terdentate ligands. However, the shift to the lower frequency region in the Raman bands of the cobalt(III) complexes containing an N-methyl group could not be found in other vibrational modes. The replacement of a hydrogen atom on the imino nitrogen by a methyl group is responsible for concomitant changes in the spectra depending on the geometrical structure of the complexes. Second, the cobalt(III) complexes with the mida ligand ([Co(mida)(mdien)]$^{+}$,6) [Co(mida)(edma)], and [Co(ida)(mida)]$^{-}$6)) exhibit several Raman bands in the skeletal breathing vibration mode region. This feature may be correlated with the increase in the number of coordinated oxygen atoms, as in the case of the cobalt(III) complexes containing no N-methyl group. Third, the mer isomers of the cobalt(III) complexes containing an N-methyl group also exhibit spectral features appreciably different from those of the fac isomers. That is, the mer isomers have sharp Raman bands in a higher frequency region in the skeletal breathing vibration mode and have no Raman bands in the chelate ring deformation mode, except for *mer*-[Co(mida)$_2$]$^-$ and *mer*-[Co(mida)(mdien)]$^+$, which have two terdentate ligands containing an N-methyl group.[6] The fact that *mer*-[Co(mida)$_2$]$^-$ and *mer*-[Co(mida)(mdien)]$^+$ have Raman bands in the chelate ring deformation mode may be related to the high stability of these complexes; for example, *mer*-[Co(mida)$_2$]$^-$ has been found more stable than *mer*-[Co(ida)(mida)]$^-$ even in a weakly basic aqueous solution.[13] However, these features are in line with the general characteristics of the Raman spectra of the cobalt(III) complexes containing no N-methyl group.

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