

Raman Spectra of Tris(bidentate)cobalt(III) Complexes Containing 1,3-Propanediamine and β -Alaninate

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The Raman spectra of the tris(bidentate)cobalt(III) complexes containing the six-membered tn and/or β -ala chelate ring, where tn and β -ala denote 1,3-propanediamine and β -alaninate respectively, were measured in order to investigate the relation between the Raman spectra and the structures of the complexes. The Raman bands can be classified into four vibration modes: A totally symmetric stretching vibration mode in the 440–640 cm^{-1} region, a stretching vibration mode excluding the totally symmetric one in the 380–480 cm^{-1} region, a metal-ligand skeletal bending deformation mode in the 260–400 cm^{-1} region, and a chelate ring deformation mode in the 220–290 cm^{-1} region. The present complexes characteristically exhibited more Raman bands than the complexes with the five-membered chelate rings in the totally symmetric stretching vibration mode. For the $[\text{Co}(\beta\text{-ala})_2(\text{tn})]^+$ complex, the three geometrical isomers, *trans*(O), *C*₂-*cis*(O), and *C*₁-*cis*(O), which were prepared for the first time, each exhibited characteristic Raman spectral features.

Recently, it has been recognized that the configurational structural characteristics of metal complexes are sensitively reflected on the skeletal vibrations rather than on the intra-ligand vibrations of the Raman spectra. For instance, the Raman spectra of the nitro-ammine series of the cobalt(III) complexes, $[\text{Co}(\text{NO}_2)_n(\text{NH}_3)_{6-n}]$ -type,¹⁾ have been studied in order to establish the assignments of the skeletal vibrations. Further, the Raman spectra in the skeletal vibration region have been applied successfully to the differentiation of the geometrical isomers of various sorts of cobalt(III) complexes with unidentate ligands and of mixed complexes with unidentate and bidentate ligands.^{2,3)} In our previous work, the Raman spectra of the $[\text{Co}(\text{gly})_x(\text{ox})_y(\text{en})_z]$ -type⁴⁾ and $[\text{Co}(\text{ida})_n(\text{dien})_{2-n}]$ -type complexes,⁵⁾ where gly, ox, en, ida, and dien denote glycinate, oxalate, 1,2-ethanediamine, iminodiacetate, and diethylenetriamine respectively, have been measured in order to find general information on the relation between the spectra and the structures of these complexes in the skeletal vibration region.

The present work was undertaken on the tris(bidentate)cobalt(III) complexes containing 1,3-propanediamine (tn) and/or β -alaninate (β -ala) in order to investigate the relation between the Raman spectral characteristics in the 200–700 cm^{-1} region and the structures of the complexes.

Experimental

Complexes. The complexes were prepared and characterized according to the literature procedures except for $[\text{Co}(\beta\text{-ala})_2(\text{tn})]\text{Cl}$ (vide infra): $[\text{Co}(\text{en})_2(\text{tn})]\text{Br}_3$,⁶⁾ $[\text{Co}(\text{en})(\text{tn})_2]\text{Br}_3$,⁶⁾ $[\text{Co}(\text{tn})_3]\text{Cl}_3$,⁷⁾ $[\text{Co}(\text{gly})(\text{tn})_2]\text{Cl}_2$,⁸⁾ $[\text{Co}(\beta\text{-ala})(\text{en})_2]\text{Cl}_2$,⁹⁾ *trans*(O)- $[\text{Co}(\beta\text{-ala})_2(\text{en})]\text{Cl}$,⁹⁾ *fac*(N)- $[\text{Co}(\beta\text{-ala})_3]$,¹⁰⁾ and *mer*(N)- $[\text{Co}(\beta\text{-ala})_3]$.¹⁰⁾

$[\text{Co}(\beta\text{-ala})_2(\text{tn})]\text{Cl}$. This complex was prepared by a procedure similar to that used for $[\text{Co}(\text{gly})_2(\text{en})]\text{Cl}$.¹¹⁾ A solution containing 1.7 cm^3 of 1,3-propanediamine and 3.6 g of β -alanine in 15 cm^3 of water was added to a solution

containing 5 g of cobalt(II) chloride hexahydrate in 10 cm^3 of water. The solution was oxidized over a steam bath by gradually adding 10 g of lead dioxide for 1 h. After it had then been cooled to room temperature, the mixture was filtered. The filtrate was poured onto a column of SP-Sephadex C-25 (Na^+ form, 3.5 $\text{cm} \times 60 \text{ cm}$). After the column had been swept with water, the adsorbed band was eluted with a 0.05 mol dm^{-3} aqueous solution of NaCl. Three colored bands, violet (A-1), pink (A-2), and red-violet (A-3), were eluted in this order; they were present in a ratio of about A-1:A-2:A-3=1.6:1.4:3.5. Each eluate was concentrated to a small volume by the use of a rotary evaporator below 30 °C, and the deposited NaCl was filtered off. The filtrate was passed through a column of Sephadex G-10 (3 $\text{cm} \times 50 \text{ cm}$) by means of elution with water. A small amount of ethanol was added to the eluate after its concentration again. The precipitate which appeared was collected by filtration. Found for A-1: C, 28.76; H, 6.51; N, 14.89%. Calcd for $[\text{Co}(\beta\text{-ala})_2(\text{tn})]\text{Cl} \cdot 5/4\text{H}_2\text{O} \cdot 1/7\text{NaCl} = \text{CoC}_9\text{H}_{22}\text{N}_4\text{O}_4\text{Cl} \cdot 5/4\text{H}_2\text{O} \cdot 1/7\text{NaCl}$: C, 28.78; H, 6.58; N, 14.92%. Found for A-2: C, 26.24; H, 6.17; N, 13.57%. Calcd for $[\text{Co}(\beta\text{-ala})_2(\text{tn})]\text{Cl} \cdot 3/2\text{H}_2\text{O} \cdot 5/8\text{NaCl}$: C, 26.48; H, 6.17; N, 13.72%. Found for A-3: C, 29.18; H, 6.45; N, 15.22%. Calcd for $[\text{Co}(\beta\text{-ala})_2(\text{tn})]\text{Cl} \cdot 1/2\text{H}_2\text{O} \cdot 1/4\text{NaCl}$: C, 29.35; H, 6.30; N, 15.21%. Absorp. max. $10^{-3}\sigma/\text{cm}^{-1}$ (log ϵ): A-1: 18.1 (2.17), 21.5sh (1.88), 27.3 (2.12); A-2: 19.9 (2.07), 27.6 (1.95); A-3: 19.3 (2.17), 27.4 (1.99). ¹³C NMR: A-2: δ =27.8, 36.0, 40.3, 40.7, 184.8; A-3: δ =28.0, 36.0, 36.2, 40.0, 40.4, 182.1, 185.2. On the basis of the absorption spectra of *trans*(O)-, *C*₂-*cis*(O)-, and *C*₁-*cis*(O)- $[\text{Co}(\text{gly})_2(\text{en})]^+$,¹¹⁾ it was found from their absorption spectra that the A-1 eluate contained the *trans*(O) isomer, and the A-2 and A-3 eluates, *cis*(O) isomers. Further, from the ¹³C NMR spectral measurements, it was found that A-2 and A-3 eluates contained *C*₂-*cis*(O) and *C*₁-*cis*(O) isomers respectively.

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 a JASCO UVIDEQ-1 spectrophotometer, and the ^1H 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 the internal reference.

Results and Discussion

The Raman spectral data in the skeletal vibration region of the tris(bidentate)cobalt(III) complexes containing the six-membered tn and/or β -ala chelate ring are summarized in Table 1, together with those of $[\text{Co}(\text{gly})_n(\text{en})_{3-n}]^{3-n+}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$. There is a significant distinction between the Raman spectral characteristics of the cobalt(III) complexes containing the six-membered chelate ring and those with the five-membered rings; on going from the latter to the former, the number of the Raman bands is increased, and the bands are shifted to lower frequencies (vide infra). For instance, the Raman spectrum of $[\text{Co}(\text{en})_3]^{3+}$ exhibits four major low frequency lines, which were assigned to the stretching and bending deformation modes ($A_{1g} + E_g + T_{2g}$ with the effective symmetry of O_h) and to the chelate ring deformation mode on the basis of a comparison with the skeletal vibrations of $[\text{Co}(\text{NH}_3)_6]^{3+}$,^{4,12} whereas the spectrum of $[\text{Co}(\text{tn})_3]^{3+}$ exhibits eight Raman bands. The increase in the number of Raman bands reflects the difference between tn and en chelate rings, and it is expected that the Raman bands of $[\text{Co}(\text{tn})_3]^{3+}$ can be treated in terms of a molecular symmetry slightly lower than the true one, $D_3(3A_1 + 5E)$, which is determined by the configuration of the chelate rings. Above all, the 451 cm^{-1} band (strong and polarized) and the 431 cm^{-1} band (shoulder and depolarized) can be assigned to A_1 (totally symmetric stretching mode) and E (stretching vibration mode excluding the totally symmetric one) respectively. An X-ray structure analysis¹³ and model consideration of $[\text{Co}(\text{tn})_3]^{3+}$ show that the six-membered rings are more flexible than the five-membered ones and that the distortion of the octahedral coordination¹³ makes the former more conformationally labile than the latter. In fact, the CD spectrum of Δ -(+)₅₈₉- $[\text{Co}(\text{tn})_3]^{3+}$ indicates a conformational equilibrium in solution between the tris skew-boat and tris chair forms.¹⁴ Accordingly, it may be inferred that the Raman spectrum of $[\text{Co}(\text{tn})_3]^{3+}$ reflects the conformational complexity of the six-membered chelate ring. Here, we should refer to the Raman spectra of the $[\text{Co}(\text{a})(\text{b})(\text{tn})_2]$ -type complexes, where a and b denote unidentate ligands, exhibiting also some Raman bands in the region of $400\text{--}550\text{ cm}^{-1}$.³ The very strong bands at ca. 450 cm^{-1} and the bands in the region of $480\text{--}550\text{ cm}^{-1}$ have been assigned to the Co-N(tn) stretching mode, $\nu(\text{Co-N}(\text{tn}))$, and the deformation vibration of the chelate ring, $\delta(\text{CNN})$, respectively, by considering the

Raman spectra of the $[\text{Co}(\text{a})(\text{b})(\text{en})_2]$ -type complexes and the $[\text{M}(\text{en})_2]^{2+}$ ($\text{M}=\text{Cu}$, Pd , and Pt) complexes based on the normal coordinate analysis. However, in the case of the $[\text{Co}(\text{tn})_3]^{3+}$ complex, it seems reasonable to consider that the bands in the region of $450\text{--}530\text{ cm}^{-1}$ can be assigned to the totally symmetric stretching vibration mode, because the bands at 451 and 530 cm^{-1} of $[\text{Co}(\text{tn})_3]^{3+}$ are shifted to lower frequencies (ca. 15 cm^{-1}) upon a deuteration of the amino protons of the 1,3-propanediamine ligand, as is to be expected for the bands due to the Co-N stretching vibration. On the basis of the above consideration and the Raman spectral characteristics summarized in Table 1, the Raman spectra of the cobalt(III) complexes containing the six-membered chelate ring can be classified into four vibration modes, like those with the five-membered chelate rings:⁴ The totally symmetric stretching vibration mode ($440\text{--}640\text{ cm}^{-1}$), the stretching vibration mode excluding the totally symmetric one ($380\text{--}480\text{ cm}^{-1}$), the metal-ligand skeletal bending deformation mode ($260\text{--}400\text{ cm}^{-1}$), and the chelate ring deformation mode ($220\text{--}290\text{ cm}^{-1}$) from the higher frequency region.

A comparison of the Raman spectra in the skeletal vibration region of the four $[\text{Co}(\text{en})_n(\text{tn})_{3-n}]^{3+}$ ($n=0\text{--}3$) complexes (Fig. 1 and Table 1) clearly demonstrates

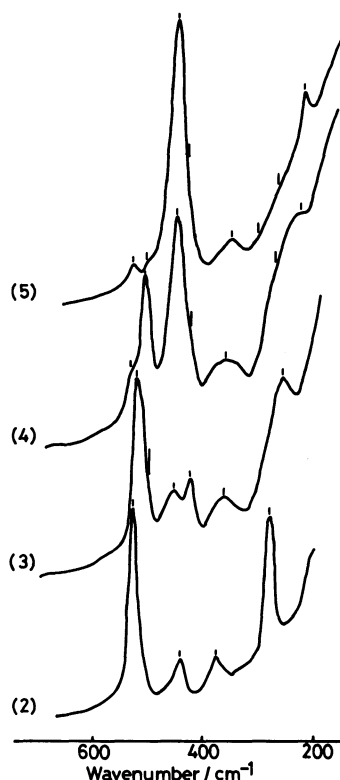


Fig. 1. Raman spectra of $[\text{Co}(\text{en})_n(\text{tn})_{3-n}]^{3+}$ ($n=0, 1, 2$, and 3). Numbers in parentheses correspond to those in Table 1.

Table 1. Raman Spectral Data of Tris(bidentate)cobalt(III) Complexes with Six-Membered Chelate Rings

No.	Complex	Raman frequency/cm ⁻¹ , a)			
1	[Co(NH ₃) ₆] ³⁺ b)	495 s (p)	440 m (dp)	320 w (dp)	
2	[Co(en) ₃] ³⁺ b)	525 s (p)	440 w (dp)	378 w (dp)	283 s (p)
3	[Co(en) ₂ (tn)] ³⁺	517 s (p)	423 m (dp)	364 m (dp)	254 m (p)
		502 sh (—)			
		449 m (p)			
4	[Co(en)(tn) ₂] ³⁺	534 vw (—)	423 sh (dp)	355 w (dp)	226 w (p)
		506 s (p)		271 vw (dp)	
		449 s (p)			
5	[Co(tn) ₃] ³⁺	530 w (p)	431 sh (dp)	352 m (dp)	222 m (p)
		502 vw (—)		307 vw (—)	
		451 s (p)		269 vw (dp)	
6	[Co(gly)(en) ₂] ³⁺ b)	584 w (p)	471 vw (dp)	374 w (dp)	279 s (p)
		521 s (p)	447 w (dp)		
7	[Co(gly)(tn) ₂] ³⁺	590 w (—)	380 m (dp)	342 w (dp)	221 w (p)
		534 vw (—)			
		482 m (p)			
		450 s (p)			
8	[Co(β -ala)(en) ₂] ²⁺	523 m (p)	439 vw (—)	440 vw (dp)	256 w (p)
9	C ₁ - <i>cis</i> (O)-[Co(gly) ₂ (en)] ⁺ b)	593 m (p)	494 w (dp)	358 w (dp)	276 s (p)
		526 m (p)	469 w (dp)		
			430 vw (dp)		
			422 vw (dp)		
10	C ₂ - <i>cis</i> (O)-[Co(gly) ₂ (en)] ⁺ b)	598 m (p)	486 w (dp)	360 w (dp)	276 s (p)
		538 s (p)	433 w (dp)		
11	<i>trans</i> (O)-[Co(gly) ₂ (en)] ⁺ b)	596 m (p)	504 sh (dp)	368 w (dp)	275 s (p)
		523 m (p)	458 w (dp)		
12	<i>trans</i> (O)-[Co(β -ala) ₂ (en)] ⁺	624 w (p)	421 vw (dp)	382 w (p)	
		510 m (p)			
		493 sh (—)			
13	C ₁ - <i>cis</i> (O)-[Co(β -ala) ₂ (tn)] ⁺	628 vw (p)	402 vw (—)	350 vw (dp)	
		534 w (p)			
		498 m (p)			
		454 s (p)			
14	C ₂ - <i>cis</i> (O)-[Co(β -ala) ₂ (tn)] ⁺	633 w (p)	466 sh (dp)	371 w (dp)	
		534 vw (p)	407 m (p)	362 w (dp)	
		486 s (p)			
15	<i>trans</i> (O)-[Co(β -ala) ₂ (tn)] ⁺	634 w (p)	479 sh (dp)		
		507 m (p)			
		465 s (p)			
16	<i>fac</i> (N)-[Co(gly) ₃] ^{b)}	603 s (p)	487 w (dp)	364 w (dp)	270 s (p)
			438 w (dp)		
17	<i>mer</i> (N)-[Co(gly) ₃] ^{b)}	602 s (p)	540 vw (dp)	356 w (dp)	272 s (p)
			496 w (dp)		
			440 vw (dp)		
18	<i>fac</i> (N)-[Co(β -ala) ₃]	616 vw (p)	405 w (p)	378 w (p)	288 vw (—)
		531 m (p)			
		503 w (p)			
19	<i>mer</i> (N)-[Co(β -ala) ₃]	632 vw (—)	409 vw (—)	381 vw (—)	
		534 w (—)			
		509 w (—)			
		485 w (—)			
Assignment ^{a)}		$\nu_{ts}(\text{Co-L})$	$\nu(\text{Co-L})$	$\delta_{sbd}(\text{L-Co-L})$	$\delta_{erd}(\text{Co-L-L})$

a) The following abbreviations 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 one; δ_{sbd} , metal-ligand bending deformation mode; δ_{erd} , 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. The numerical data in the parentheses are the polarization ratios. b) Ref. 4.

that the number of bands increases with the substitution of the en ligand by the tn one and that the Raman bands of the chelate ring deformation mode are shifted to lower frequencies. Furthermore, $[\text{Co}(\text{en})_2(\text{tn})]^{3+}$ and $[\text{Co}(\text{en})(\text{tn})_2]^{3+}$ exhibit equally the bands due to the Co-N(en) and Co-N(tn) totally symmetric stretching vibration mode; the bands due to $\nu_{\text{ts}}(\text{Co-N(en)})$ and $\nu_{\text{ts}}(\text{Co-N(tn)})$ are observed in the region above 500 cm^{-1} and at ca. 450 cm^{-1} respectively. The shift of the Raman bands due to $\nu_{\text{ts}}(\text{Co-N(en)})$, 525 , 517 , and 506 cm^{-1} for the $[\text{Co}(\text{en})_n(\text{tn})_{3-n}]$ -type complexes may be attributed to the increased relaxation of the Co-N(en) bonds by stepwise substitution of the tn ligand for the en one. That is, there is no appreciable vibrational coupling between $\nu_{\text{ts}}(\text{Co-N(tn)})$ and $\nu_{\text{ts}}(\text{Co-N(en)})$. In addition, the intensities of the bands, $\nu_{\text{ts}}(\text{Co-N(tn)})$ and $\nu_{\text{ts}}(\text{Co-N(en)})$, of the mixed complexes are proportional to the number of the en ligand and the tn one. Here, it is worthy of note that the $\nu_{\text{ts}}(\text{Co-N})$ Raman shifts of $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{en})_3]^{3+}$, and $[\text{Co}(\text{tn})_3]^{3+}$ decrease in the following order; $\nu_{\text{ts}}(\text{Co-N(en)}) > \nu_{\text{ts}}(\text{Co-N}(\text{NH}_3)) > \nu_{\text{ts}}(\text{Co-N(tn)})$. This decreasing order is in line with that for the ${}^1\text{T}_{1g} \leftarrow {}^1\text{A}_{1g}(\text{O}_h)$ electronic transition energy of the $[\text{Co}(\text{N})_6]$ chromophore; $21.30 \times 10^3\text{ cm}^{-1}([\text{Co}(\text{en})_3]^{3+})^{15}) > 20.96 \times 10^3\text{ cm}^{-1}([\text{Co}(\text{NH}_3)_6]^{3+})^{16}) > 20.49 \times 10^3\text{ cm}^{-1}([\text{Co}(\text{tn})_3]^{3+})^{17})$. The spectral behavior caused by the substitution of the en ligand by the tn one is also observed for the $[\text{Co}(\text{gly})(\text{en})_2]^{2+}$ and $[\text{Co}(\text{gly})(\text{tn})_2]^{2+}$ complexes. That is, $[\text{Co}(\text{gly})(\text{tn})_2]^{2+}$ shows more Raman bands than does $[\text{Co}(\text{gly})(\text{en})_2]^{2+}$, as is to be expected from the results for the $[\text{Co}(\text{en})_n(\text{tn})_{3-n}]$ -type complexes (Fig. 2). The Raman band due to the chelate ring deformation mode of $[\text{Co}(\text{gly})(\text{tn})_2]^{2+}$ is

also shifted to a lower frequency. Furthermore, a comparison of the Raman bands in the totally symmetric stretching vibration region of $[\text{Co}(\text{tn})_3]^{3+}$ (Fig. 1) and $[\text{Co}(\text{gly})(\text{tn})_2]^{2+}$ suggests that the band at 482 cm^{-1} of $[\text{Co}(\text{gly})(\text{tn})_2]^{2+}$ is the characteristic band of the coordinated gly ligand, similar to the spectral relation between $[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Co}(\text{gly})(\text{en})_2]^{2+}$.⁴⁾

The Raman spectra of $[\text{Co}(\beta\text{-ala})(\text{en})_2]^{2+}$ and $[\text{Co}(\text{en})_3]^{3+}$ reveal that the replacement of the en ligand in $[\text{Co}(\text{en})_3]^{3+}$ by the $\beta\text{-ala}$ one causes no changes in the intrinsic spectral features; the four bands of $[\text{Co}(\beta\text{-ala})(\text{en})_2]^{2+}$ can be correlated to those of $[\text{Co}(\text{en})_3]^{3+}$ (Fig. 3). This spectral behavior is quite in contrast to that resulting from the replacement of the en ligand by the gly one.⁴⁾ The good correlation of the Raman spectral features between $[\text{Co}(\beta\text{-ala})(\text{en})_2]^{2+}$ and $[\text{Co}(\text{en})_3]^{3+}$ may result from the fact that the skeletal vibration behavior of the former is determined by the two en chelate rings because of the conformational restriction due to the five-membered chelate ring and because of the proximity of the reduced mass of the donor atoms. The Raman spectra of $[\text{Co}(\beta\text{-ala})(\text{en})_2]^{2+}$ and $\text{trans}(\text{O})\text{-}[\text{Co}(\beta\text{-ala})_2(\text{en})]^+$ show that the Raman spectral features are no longer retained upon a structural change from the former to the latter (Fig. 3), whereas a comparison of the spectra of $[\text{Co}(\text{gly})(\text{en})_2]^{2+}$ and $\text{trans}(\text{O})\text{-}[\text{Co}(\text{gly})_2(\text{en})]^+$ reveals that the spectral features are well retained

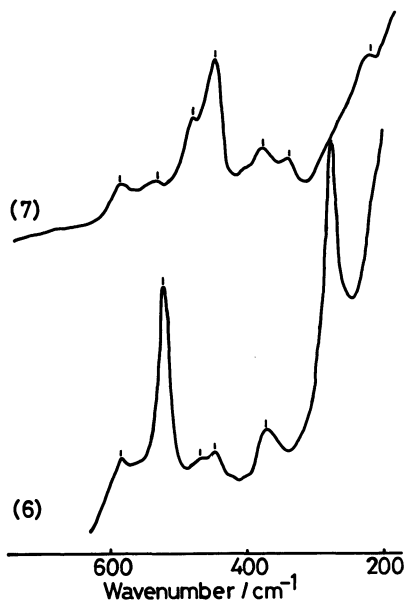


Fig. 2. Raman spectra of $[\text{Co}(\text{gly})(\text{tn})_2]^{2+}$ and $[\text{Co}(\text{gly})(\text{en})_2]^{2+}$. Numbers in parentheses correspond to those in Table 1.

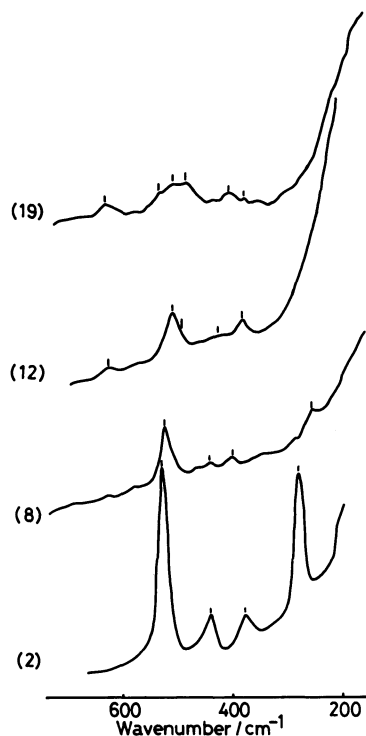


Fig. 3. Raman spectra of $\text{mer}(\text{N})\text{-}[\text{Co}(\beta\text{-ala})_3]$, $\text{trans}(\text{O})\text{-}[\text{Co}(\beta\text{-ala})_2(\text{en})]^+$, $[\text{Co}(\beta\text{-ala})(\text{en})_2]^{2+}$, and $[\text{Co}(\text{en})_3]^{3+}$. Numbers in parentheses correspond to those in Table 1.

even after the structural change.⁴⁾ This Raman spectral evidence clearly demonstrates that the six-membered β -ala chelate ring is more flexible than the five-membered gly chelate ring, as in the case of the tn and en chelate rings (vide supra).

A conspicuous difference was found in the Raman spectra in the totally symmetric stretching vibration mode of the geometrical isomers, *fac*(N)- and *mer*(N)-[Co(β -ala)₃], as is shown in Fig. 4; the *mer*(N) isomer exhibits a more complicated Raman spectrum than does the *fac*(N) one. An analogous tendency has been observed for the spectra of *fac*(N)- and *mer*(N)-[Co(gly)₃].⁴⁾ However, it is interesting that the Raman spectral differences among the geometrical isomers of the cobalt(III) complexes with the six-membered chelate rings are noticed in the totally symmetric stretching vibration mode, whereas those of the complexes with the five-membered chelate rings appear in the stretching vibration mode excluding the totally symmetric one.

As is shown in Fig. 5, the Raman spectral features of the three geometrical isomers, *trans*(O)-, *C*₂-*cis*(O)-, and *C*₁-*cis*(O)-[Co(β -ala)₂(tn)]⁺, which have been prepared for the first time in this work are, in a first approximation, similar to each other, as in the case of the geometrical isomers, *trans*(O)-, *C*₂-*cis*(O)-, and *C*₁-*cis*(O)-[Co(gly)₂(en)]⁺.⁴⁾ On a closer inspection,

however, we can find some differences among the Raman spectral features of the three geometrical isomers of [Co(β -ala)₂(tn)]⁺. Firstly, the difference between the *trans*(O) isomer and the two *cis*(O) ones can be observed in the skeletal bending deformation region; the *trans*(O) isomer has no Raman band, but the *cis*(O) isomers have a few Raman bands.

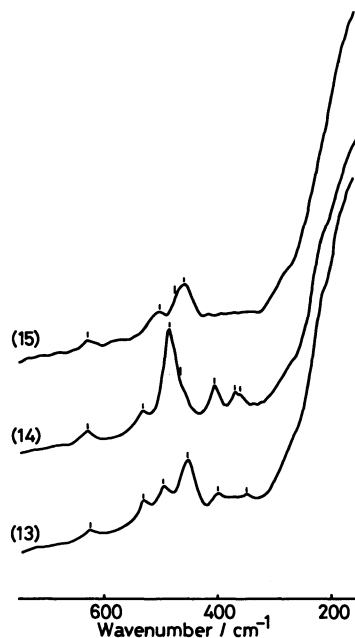


Fig. 5. Raman spectra of three geometrical isomers of [Co(β -ala)₂(tn)]⁺. Numbers in parentheses correspond to those in Table 1.

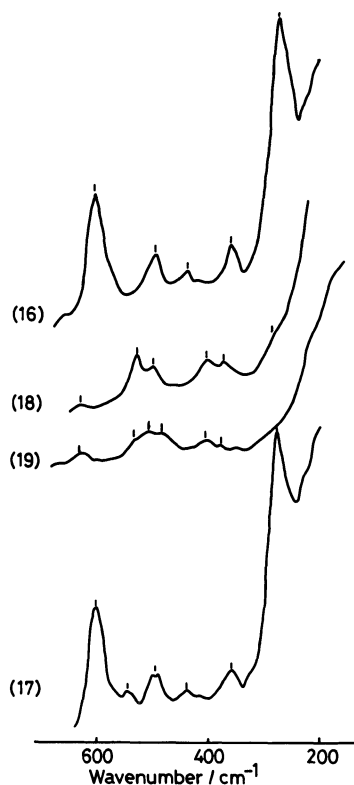


Fig. 4. Raman spectra of *mer*(N) and *fac*(N) isomers of [Co(gly)₃] and [Co(β -ala)₃]. Numbers in parentheses correspond to those in Table 1.

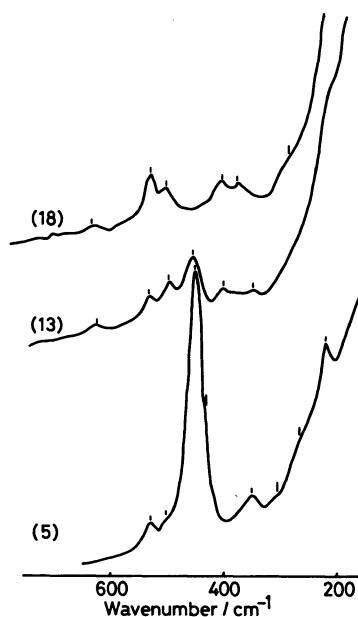


Fig. 6. Raman spectra of *fac*(N)-[Co(β -ala)₃], *C*₁-*cis*(O)-[Co(β -ala)₂(tn)]⁺, and [Co(tn)₃]³⁺. Numbers in parentheses correspond to those in Table 1.

Incidentally, the *trans*(O) isomer exhibits the strong and polarized band (465 cm^{-1}) at a slightly lower frequency than the depolarized one (479 cm^{-1}). Secondly, a difference between the C_2 -*cis*(O) isomer and the C_1 -*cis*(O) one can be observed in the totally symmetric stretching vibration region; the C_2 -*cis*(O) isomer with a higher symmetry exhibits three Raman bands, but the C_1 -*cis*(O) isomer splits into a quartet. This sort of spectral difference has also been observed for the two *cis*(O) isomers of $[\text{Co}(\text{gly})_2(\text{en})]^+$ with five-membered chelate rings⁴⁾ in the stretching vibration mode excluding the totally symmetric one ($400\text{--}520\text{ cm}^{-1}$). Finally, it should be pointed out that the characteristic feature of the Raman spectrum of C_1 -*cis*(O)- $[\text{Co}(\beta\text{-ala})_2(\text{tn})]^+$ is considered to be an overlapping with those of *fac*(N)- $[\text{Co}(\beta\text{-ala})_3]$ and $[\text{Co}(\text{tn})_3]^{3+}$ as is shown in Fig. 6. That is, we can say that the strong and polarized band at 454 cm^{-1} of C_1 -*cis*(O)- $[\text{Co}(\beta\text{-ala})_2(\text{tn})]^+$ corresponds to the totally symmetric stretching vibration mode, $\nu_{\text{ts}}(\text{Co-N}(\text{tn}))$, and also that the polarized bands in the region above 490 cm^{-1} are principally related to the β -ala ligand. Incidentally, the complexes containing more than one β -ala ligand exhibit their highest frequency polarized bands around 630 cm^{-1} , somewhat higher than those for the complexes containing the gly ligand. It is not certain at present what has brought about this interesting feature, but we can say that it reflects the skeletal vibrational characteristics of the cobalt(III) complexes with six-membered aminocarboxylate chelate rings.

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