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Raman Spectra in the Skeletal Vibration Region of $[Co(gly)_x(ox)_y(en)_z]^{(3-x-2y)+}$ Complexes $(x+y+z=3)$

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The Raman spectra were measured for the complete series of cobalt(III) complexes, $[Co(gly)_x(ox)_y(en)_z]^{(3-x-2y)+}$, where gly, ox, and en denote glycinate, oxalate, and ethylenediamine, respectively, and $x+y+z$ is equal to 3, in aqueous solution in the skeletal vibration region to deduce their structure-spectra relation. The spectra could be classified into four categories: polarized bands in the 610—520 cm^{-1} region due to a totally symmetric stretching vibration mode, depolarized bands in the 520—400 cm^{-1} region due to Co-O and Co-N stretching vibration modes, depolarized bands in the 400—300 cm^{-1} region due to the metal-ligand skeletal bending deformation mode, and polarized bands in the 300—200 cm^{-1} region due to the chelate ring deformation mode. The depolarized bands due to the stretching vibration mode could be used for the differentiation of C_2-*cis* and C_1-*cis* isomers of $[Co(N)_4(O)_2]$ and $[Co(N)_2(O)_4]$ type complexes.

Elucidation of the spectra-structure relations of coordination compounds is of practical importance for the study of their stereochemistry. The Raman spectroscopy in the skeletal vibration region of cobalt(III) complexes has produced several studies on their spectral characteristics,[1—13] which were found to be available for differentiation of some of their geometrical isomers, such as *cis* and *trans* ones of $[Co(a)(b)(NH_3)_4]$,[12] $[Co(a)(b)(en)_2]$,[10] and $[Co(a)(b)(tn)_2]$[13] type complexes, where a and b stand for unidentate ligands and en and tn denote ethylenediamine and trimethylenediamine, respectively.

The present study was attempted to deduce more general information on the relation between geometrical structure and the Raman spectra in the skeletal vibration region of cobalt(III) complexes. A series of $[Co(gly)_x(ox)_y(en)_z]^{(3-x-2y)+}$ complexes, where gly and ox denote glycinate and oxalate and $x+y+z$ is equal to 3, were chosen as a typical example and their Raman spectra were measured in the 610—200 cm^{-1} region in aqueous solution in order to avoid contribution of lattice vibrations observed in the solid state.

Experimental

Complexes. The complete series of $[Co(gly)_x(ox)_y(en)_z]^{(3-x-2y)+}$ complexes were prepared and characterized according to standard literature procedures; $[Co(en)_3]Cl_3 \cdot 3H_2O$,[14] $[Co(gly)(en)_2]I_2 \cdot H_2O$,[15] $[Co(ox)(en)_2]Cl \cdot H_2O$,[16] C_1-*cis(O)*-$[Co(gly)_2(en)]Cl \cdot 3H_2O$,[17] C_2-*cis(O)*-$[Co(gly)_2(en)]Cl \cdot 0.5H_2O$,[17] *trans(O)*-$[Co(gly)_2(en)]Cl \cdot H_2O$,[18] *mer(N)*-$[Co(gly)(ox)(en)]$,[18] *mer(N)*-$[Co(gly)_3] \cdot 1.5H_2O$,[19] *fac(N)*-$[Co(gly)_3] \cdot H_2O$,[19] *fac(N)*-$[Co(gly)(ox)(en)]$,[18] *trans(N)*-$K[Co(gly)_2(ox)]$,[17] C_2-*cis(N)*-$Na[Co(gly)_2(ox)]$,[17] C_1-*cis(N)*-$Na[Co(gly)_2(ox)]$,[17] $Na[Co(ox)_2(en)] \cdot 2.5H_2O$,[16] $Na_2[Co(gly)(ox)_2] \cdot 2H_2O$,[20,21] and $K_3[Co(ox)_3] \cdot 2H_2O$.[22] $[Co(NH_3)_6]Cl_3$ was also prepared according to the literature procedure.[23]

Measurements. The Raman spectra were recorded on a JASCO Laser Raman Spectrometer, which was constructed specially from 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. Raman spectral data of $[Co(gly)_x(ox)_y(en)_z]^{(3-x-2y)+}$ complexes are summarized in Table 1. The Raman spectra of $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, and $[Co(ox)_3]^{3-}$ shown in Fig. 1 clearly demonstrate that $[Co(en)_3]^{3+}$ and $[Co(ox)_3]^{3-}$ give the same spectral characteristics; a polarized band in the 610—520 cm^{-1} region(depolarization ratio: ≈0), two

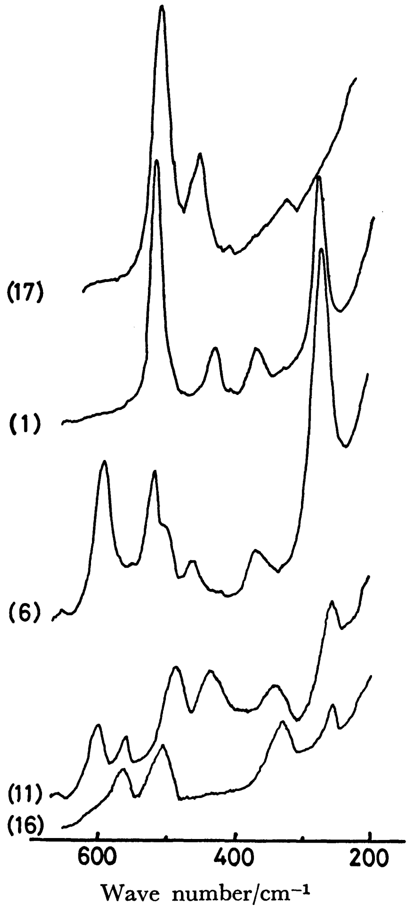

Fig. 1. Raman spectra of $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(ox)_3]^{3-}$, *trans(O)*-$[Co(gly)_2(en)]^+$, and *trans(N)*-$[Co(gly)_2(ox)]^-$. Numbers in parentheses correspond to those in Table 1.

TABLE 1. OBSERVED RAMAN BANDS AND THEIR ASSIGNMENTS FOR $[Co(gly)_x(ox)_y(en)_z]^{(3-x-2y)+}$ COMPLEXES ($x+y+z=3$)

No.	Complex	Raman frequency/cm^{-1} [a,b]						
1	$[Co(en)_3]^{3+}$			525(501) s, p 526($A_{1g}(O_h)$)[9]		440(422) w, dp 444($E_g(O_h)$)[9]	378(350) w, dp 376($T_{2g}(O_h)$)[9]	283(274) s, p 280(δ_{crd})[9]
2	$[Co(gly)(en)_2]^{2+}$	584(583) w, p		521(493) s, p	471(439) vw, dp	447(427) w, dp	374(344) w, dp	279(265) s, p
3	$[Co(ox)(en)_2]^{+}$		565(555) m, p	528(496) s, p	480(454) vw, dp	456(430) w, dp	374 (344) w, dp 358 (344) vw, dp	278(265) s, p
4	C_1-*cis*(*O*)-$[Co(gly)_2(en)]^{+}$	593(577) m, p		526(495) m, p	494(466) w, dp 469(449) w, dp	430(422) vw, dp 422(409) vw, dp	358(343) w, dp	276(269) s, p
5	C_2-*cis*(*O*)-$[Co(gly)_2(en)]^{+}$	598(580) m, p		538(506) s, p	486(458) w, dp	433(425) w, dp	360(340) w, dp	276(269) s, p
6	*trans*(*O*)-$[Co(gly)_2(en)]^{+}$	596(571) m, p		523(486) m, p	504(486) w(sh), dp	458(442) w, dp	368(347) w, dp	275(264) s, p
7	*mer*(*N*)-$[Co(gly)(ox)(en)]$	602 w, p	567 m, p	532 m, p	498 vw, dp[c] 466 w, dp[c]	436 vw, dp[c]	362 w, dp	275 s, p
8	*mer*(*N*)-$[Co(gly)_3]$	602 s, p			540 vw, dp[c] 496 w, dp[c]	440 vw, dp[c]	356 w, dp	272 s, p
9	*fac*(*N*)-$[Co(gly)_3]$	603 s, p			487 w, dp	438 w, dp	364 w, dp	270 s, p
10	*fac*(*N*)-$[Co(gly)(ox)(en)]$	603 m, p	566 m, p	531 s, p	488 w, dp	426 w, dp	358 w, dp	270 s, p
11	*trans*(*N*)-$[Co(gly)_2(ox)]^{-}$	608 vw, p	565 vw, p		494 w, dp	440 w, dp	348 w, dp	260 w, p
12	C_2-*cis*(*N*)-$[Co(gly)_2(ox)]^{-}$	602 m, p	564 m, p		510 w, dp	432 w, dp	348 w, dp	260 s, p
13	C_1-*cis*(*N*)-$[Co(gly)_2(ox)]^{-}$	604 m, p	564 m, p		512 w, dp 504 w, dp	432 w, dp 419 w, dp	342 w, dp	262 s, p
14	$[Co(ox)_2(en)]^{-}$		567 s, p	542 m, p	492 w, dp	432 w, dp	354 w, dp 340 vw, dp	268 s, p
15	$[Co(gly)(ox)_2]^{2-}$	605 w, p	567 w, p		505 w, dp	446 w, dp	340 w, dp	260 w, p
16	$[Co(ox)_3]^{3-}$		570 w, p		506 w, dp		335 w, dp	257 w, p
17	$[Co(NH_3)_6]^{3+}$			495 s, p 495($A_{1g}(O_h)$)[3] 490($A_{1g}(O_h)$)[4] 494($A_{1g}(O_h)$)[6]		440 m, dp 440($E_g(O_h)$)[3] 440($E_g(O_h)$)[4] 442($E_g(O_h)$)[6]	320 w, dp — 317($T_{2g}(O_h)$)[4] 322($T_{2g}(O_h)$)[6]	—
	Assignment[b]	ν_{ts}(Co–L) for gly	ν_{ts}(Co–L) for ox	ν_{ts}(Co–L) for en	ν(Co–O)	ν(Co–N)	δ_{sbd}(L–Co–L)	$\delta_{crd}(Co\langle^{L}_{L})$

a) Numerical data in the parentheses are for the N-deuterated complexes. b) The following abbreviations were 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 skeletal bending deformation mode; δ_{crd}, chelate ring deformation mode; and L, donor atom(N and/or O). c) Consult the text.

depolarized bands in the 520—400 cm^{-1} and 400—300 cm^{-1} regions(depolarization ratio: $\approx$0.75), and a polarized one in the 300—200 cm^{-1} region(depolarization ratio: 0.12—0.16). Furthermore, it is evident that the Raman bands of $[Co(en)_3]^{3+}$ can well be correlated to those of $[Co(NH_3)_6]^{3+}$ having an O_h symmetry[9] except the polarized one in the 300—200 cm^{-1} region, which relates to the en chelate ring.

It has been pointed out that, based on the depolarization characteristics and the comparison with $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$ has an effective symmetry[9] of O_h for the skeletal vibrations. This simplified treatment can be supported by two depolarized bands in the 520—400 cm^{-1} region of *trans(O)*-$[Co(gly)_2(en)]^+$ and of *trans(N)*-$[Co(gly)_2(ox)]^-$ (*cf.* Fig. 1) having the effective symmetry of D_{4h}(Co–O and Co–N stretching vibration modes(except totally symmetric one): $A_{1g}+B_{1g}$) rather than the true symmetry of C_2. (Polarized bands in the 610—520 cm^{-1} region show a peculiar aspect(*cf.* Table 1) and will be treated separately.) Hence we may expect that, so far as the skeletal vibrations of the octahedral tris(bidentate)cobalt(III) complexes with five-membered chelate rings are concerned, the Raman spectra are treated in terms of the effective symmetry which is mainly specified by arrangement of coordinated atoms around the central metal atom. Accordingly, the polarized band in the 610—520 cm^{-1} region, the depolarized bands in the 520—400 cm^{-1} region, and the depolarized band in the 400—300 cm^{-1} region can be assigned to totally symmetric metal-ligand stretching, Co–O and Co–N stretching, and metal-ligand skeletal bending deformation modes,[1–4,6,8,9] respectively. The polarized band in the 300—200 cm^{-1} region with the depolarization ratio of 0.12—0.16 can be assigned to the chelate ring deformation mode which is totally symmetric.[9,10] The contribution of the totally symmetric stretching character of the metal-ligand to this has been pointed out by Flint and Matthews[24] based on vibronic spectra in the d-d transition region($^1A_{1g}$—$^1T_{1g}(O_h)$) of $[Co(en)_3]^{3+}$.

It is interesting to note that the intensities of the polarized bands of $[Co(ox)_3]^{3-}$, $[Co(gly)(ox)_2]^{2-}$, and *trans(N)*-$[Co(gly)_2(ox)]^-$ decreased when the first absorption band($^1A_{1g}$—$^1T_{1g}(O_h)$) of the complexes is in the proximity of the excitation wavelength (632.8 nm) (*cf.* Table 1). This de-enhancement of the Raman intensities may be due to a sort of anti-resonance Raman effect.[9]

Polarized Bands in the 610—520 cm^{-1} Region. Figure 2 depicts the spectra-structure relation of $[Co(gly)_x(ox)_y(en)_z]^{(3-x-2y)+}$ complexes in the totally symmetric stretching vibration region. It is noteworthy that *mer(N)*- and *fac(N)*-$[Co(gly)_3]$ show only one Raman band and that the Raman bands of $[Co(en)_3]^{3+}$ and $[Co(ox)_3]^{3-}$ as well as *mer(N)*- and *fac(N)*-$[Co(gly)_3]$ become doublets for $[Co(gly)_x(ox)_y]^{(3-x-2y)+}$, $[Co(gly)_x(en)_z]^{(3-x)+}$, and $[Co(ox)_x(en)_z]^{(3-2y)+}$ and triplets for [Co(gly)(ox)(en)] irrespective of the geometry. These splittings of the Raman bands may be caused by relaxation of the selection rule with respect to the effective symmetry of the complexes. It is evident from Table 1 that the coordinated en, ox, and gly ligands have characteristic bands in the regions 542—521 cm^{-1}, 570—564 cm^{-1}, and 608—584 cm^{-1}, respectively. Inconsistency in metal-coordinated atom bond strengths and totally symmetric stretching frequencies of coordinated en relative to gly and ox reflects the contribution of rigidity of the framework of the chelate ring. These results demonstrate that the coordinated bidentate ligands with five-membered chelate rings behave, for the totally symmetric stretching vibration, as a unit, owing to restrictions by the chelate rings. The Raman bands in this region are characteristic of coordinated ligands for the tris(bidentate)cobalt(III) complexes with five-membered chelate rings.

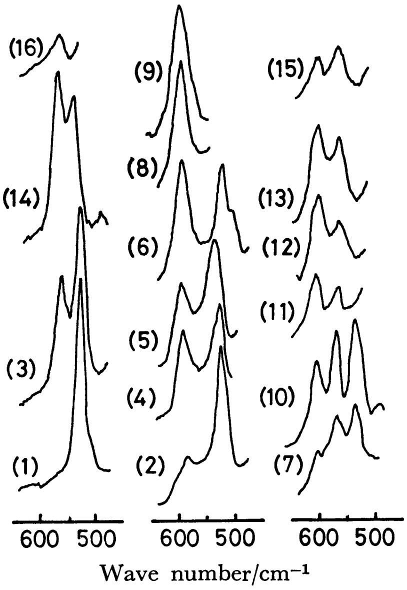

Fig. 2. Raman spectra of $[Co(gly)_x(ox)_y(en)_z]^{(3-x-2y)+}$ complexes in the totally symmetric stretching vibration region. Numbers in parentheses correspond to those in Table 1.

Depolarized Bands in the 520—400 cm^{-1} Region. Unlike those in the 610—520 cm^{-1} region, the Raman bands in this region show some unique aspects: the Co–N stretching mode lies as a general rule in the region below 460 cm^{-1} and the Co–O stretching mode above 470 cm^{-1}, respectively,[25] and numbers of the Raman bands reflect the effective symmetry of $[Co(gly)_x(ox)_y(en)_z]^{(3-x-2y)+}$ complexes. $[Co(N)_6]$ and $[Co(O)_6]$ type complexes with the effective symmetry of O_h give only one band, which becomes a doublet for *trans(O)*-$[Co(N)_4(O)_2]$ and *trans(N)*-$[Co(N)_2(O)_4]$ complexes with that of D_{4h}. The doublet for $[Co(N)_5(O)]$ and $[Co(N)(O)_5]$ type complexes, $[Co(gly)(en)_2]^{2+}$ and $[Co(gly)(ox)_2]^{2-}$, with that of C_{4v}(Co–O and Co–N stretching vibration modes(except totally symmetric one): A_1+B_1+E) may be explained by correlation of the E mode to the Raman inactive E_u mode of the D_{4h} symmetry, whereas the A_1 and B_1 modes of the former correspond to the A_{1g} and B_{1g} modes of the latter, respectively. Thus the E mode may be almost undetectable[12] in the Raman spectra of the complexes with the effective symmetry of C_{4v}.

Figures 3 and 4 show the spectra-structure relations of $[Co(N)_4(O)_2]$ and $[Co(N)_2(O)_4]$ type complexes and

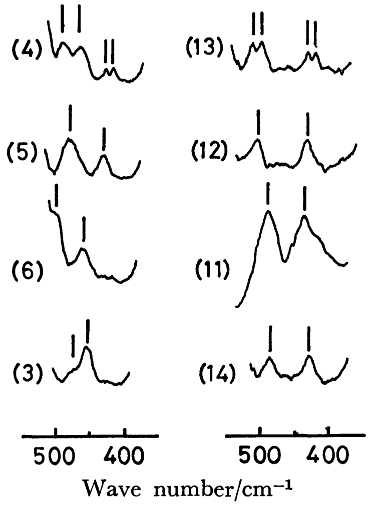

Fig. 3. Raman spectra of *trans*, C_2-*cis*, and C_1-*cis* isomers of $[Co(gly)_2(en)]^+$ and $[Co(gly)_2(ox)]^-$ and of $[Co(ox)(en)_2]^+$ and $[Co(ox)_2(en)]^-$ in the Co–O and Co–N stretching vibration region. Numbers in parentheses correspond to those in Table 1.

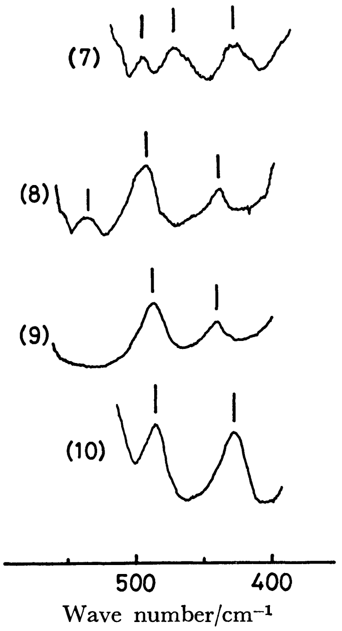

Fig. 4. Raman spectra of *mer* and *fac* isomers of $[Co(gly)_3]$ and $[Co(gly)(ox)(en)]$ in the Co–O and Co–N stretching vibration region. Numbers in parentheses correspond to those in Table 1.

of $[Co(N)_3(O)_3]$ type complexes, respectively. C_2-*cis(O)* and C_2-*cis(N)* isomers of $[Co(gly)_2(en)]^+$ and $[Co(gly)_2(ox)]^-$ give doublets, which however split into quartets on going from the C_2-*cis* to C_1-*cis* isomers. Here, the configuration of the chelate rings comes to play a role in the effective symmetry because both of the isomers belong to C_{2v} symmetry for the arrangement of the coordinated atoms. $[Co(ox)(en)_2]^+$ and $[Co(ox)_2(en)]^-$ with the effective symmetry of C_{2v} also give doublet in this region. Analogously, the *fac* isomers of $[Co(gly)_3]$ and $[Co(gly)(ox)(en)]$ with the higher effective symmetry give doublets, whereas the *mer* isomers with the lower symmetry give triplets. In the latter isomers, the middle bands of 476 cm^{-1} for *mer(N)*-$[Co(gly)(ox)(en)]$ and 496 cm^{-1} for *mer(N)*-$[Co(gly)_3]$ (*cf.* Table 1) may have a largely Co–O stretching character.

These results, together with considerations on numbers of the Raman active stretching vibrations for $[Co(a)_{6-n}(b)_n]$ and $[Co(AB)_3]$ type complexes, reveal that the effective symmetry of the $[Co(gly)_x(ox)_y(en)_z]^{(3-x-2y)+}$ complexes is higher than the true symmetry. In fact, the *fac(N)* isomers of $[Co(gly)_3]$ and $[Co(gly)(ox)(en)]$ can be treated uniformly as *fac(N)*-$[Co(N)_3(O)_3]$ type with the effective symmetry of C_{3v} and likewise the *mer(N)* isomers can be treated as having C_{2v}-type effective symmetry.

In summary, the Raman bands in this region are characteristic of the geometry of the $[Co(N)_4(O)_2]$ and $[Co(N)_2(O)_4]$ type complexes and of $[Co(N)_3(O)_3]$ type complexes. They can be used for the differentiation of the *fac* and *mer* isomers of the latter and of the C_2-*cis* and C_1-*cis* isomers of the former. This is considered to be of practical importance, although the differentiation by comparison of the d-d transition energies and the molar absorptivities in the first ($^1A_{1g}$—$^1T_{1g}$(O_h)) and the second absorption band($^1A_{1g}$—$^2T_{1g}$(O_h)) may also be possible.[17)]

Depolarized Bands in the 400—300 cm^{-1} Region. The Raman spectra in the metal-ligand skeletal bending deformation region show only one band, except for $[Co(ox)_x(en)_z]^{(3-2y)+}$, which gives a major band accompanied with a very weak one in its lower wavelength side. Numbers of the Raman bands depend neither on the composition nor on the geometry of the complexes, indicating that N–Co–N, N–Co–O, and O–Co–O bending deformation modes are mostly degenerate. However, correlation was noticed between an increase in the Raman shift and an increase in the d-d transition energies in the first and the second absorption bands, as is readily deduced from Table 1. This means that the bending deformation mode reflects coordinate bond strength.

Polarized Bands in the 300—200 cm^{-1} Region. A polarized Raman band is observed in this region for $[Co(en)_3]^{3+}$, $[Co(ox)_3]^{3-}$, and $[Co(gly)_3]$, and for all the mixed-ligand complexes as well. Hence, the totally symmetric chelate ring deformation modes of en, ox, and gly are considered to be degenerate. The same correlation as that found in the skeletal bending deformation was noticed for the chelate ring deformation.

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