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# Raman Spectra of Cobalt(III) Complexes. II. Nitroammine Series of Cobalt(III) Complexes

Kan Kanamori,* Tsutomu Morikawa, and Kiyoyasu Kawai
*Department of Chemistry, Faculty of Science, Toyama University, Gofuku, Toyama 930*

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Solid and aqueous Raman spectra of the nitroammine series of cobalt(III) complexes, $[Co(NO_2)_n(NH_3)_{6-n}]^{(3-n)+}$ ($n$=1—6), have been measured for the region of 1500—100 $cm^{-1}$. The assignments of the Raman bands due to the skeletal vibrations of the complexes have been made on an empirical basis and compared with those of the infrared bands in the literature.

Infrared investigations[1-3] of the nitroammine series and the halogenoammine series of cobalt(III) complexes, including normal coordinate treatments by Nakagawa and Shimanouchi,[2,3] have offered interesting problems in the study of coordination bonds as well as in the stereoisomerism. The facial isomer of trinitrotriamminecobalt(III) was synthesized very recently,[4] though *cis*-tetranitrodiamminecobaltate(III) has not yet obtained.

Recently, the Raman spectra of the halogenoammine series have been measured by Swaddle *et al.*[5] and Loehr *et al.*[6] and the assignments of the infrared bands have been reexamined. Therefore, a detailed Raman study of the nitroammine series seems to be required for the full assignments of the skeletal vibrations of the complexes; brief communications for *trans*-$[Co(NO_2)_4(NH_3)_2]^-$ [7] and $[Co(NO_2)_6]^{3-}$ [8,9] have already appeared.

In the present work, we have measured the solid and the aqueous Raman spectra of the nitroammine series of cobalt(III) complexes and reinvestigated the assignments of the skeletal vibrations. We have also studied the intra-ligand vibrations of the *N*-deuterated complexes in $D_2O$, for which the overlapping of the bands due to the ammine and the nitro groups are eliminated.

## Experimental

*fac*-Trinitrotriamminecobalt (III) was prepared by the method of Siebert.[4] Potassium pentanitroamminecobaltate (III) was prepared by the method of Shibata *et al.*[10] All other complexes were prepared by standard means. All the complexes were identified by the visible and ultraviolet spectra and by elemental analysis. *mer*- and *fac*-trinitrotriamminecobalt (III) complexes were also identified by the $^1H$-NMR spectra.

The Raman spectra were recorded for the region lower than 1500 $cm^{-1}$ on a JASCO R-800 Raman spectrometer with a data processor, using a He–Ne (632.8 nm) laser as an excitation source. The spectra observed in the low frequency region are shown in Fig. 1. The infrared spectra were recorded on a JASCO A-3 and Hitachi FIS infrared spectrometer. The observed frequencies were calibrated by those of indene for the Raman spectra and those of polystylene film for the infrared spectra. The observed frequencies are accurate within ±2 $cm^{-1}$.

## Results and Discussion

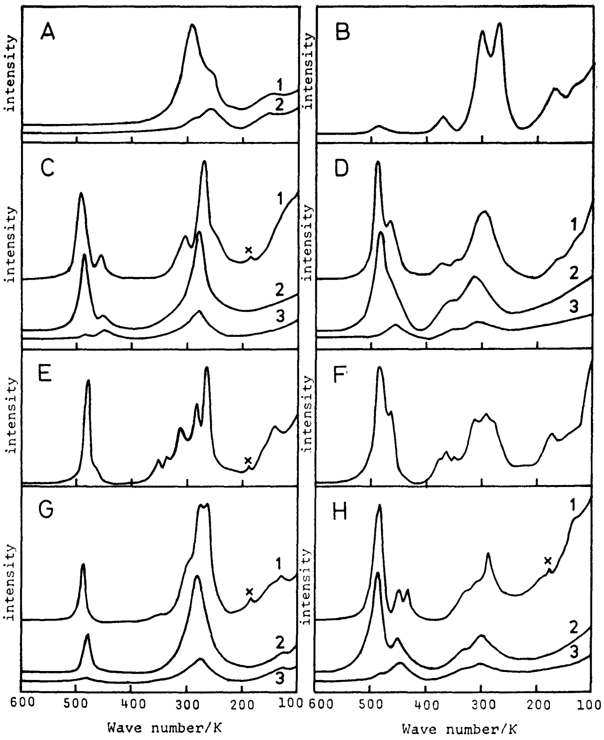


Fig. 1. Raman spectra of nitroammine cobalt (III) complexes. A: $Na_3[Co(NO_2)_6]$ in aqueous solution, //1, ⊥2. B: $K_2[Co(NO_2)_5(NH_3)]$ in solid state. C: *trans*-$[Co(NO_2)_2(NH_3)_4]NO_3$ in solid state, 1 and the fluoride in aqueous solution, //2, ⊥3. D: *cis*-$[Co(NO_2)_2(NH_3)_4]NO_3$ in solid state, 1 and the fluoride in aqueous solution, //2, ⊥3. E: *mer*-$[Co(NO_2)_3(NH_3)_3]$ in solid state. F: *fac*-$[Co(NO_2)_3(NH_3)_3]$ in solid state. G: *trans*-$NH_4[Co(NO_2)_4(NH_3)_2]$ in solid state, 1 and in aqueous solution, //2, ⊥3. H: $[Co(NO_2)(NH_3)_5]Br_2$ in solid state, 1 and the fluoride in aqueous solution, //2, ⊥3. x; no lasing line.

*Intra-ligand Vibrations.* The assignment of the vibrations due to ammine or nitro groups of coordination compounds has already established by many authors.[11] Table 1 summarizes the observed frequencies for the *N*-deuterated nitroammine cobalt(III) complexes in $D_2O$ and their approximate modes.

It is very interesting to compare the spectra of *trans* and *cis* isomers of $[Co(NO_2)_2(NH_3)_4]^+$ with a view toward differentiating between the geometric isomers. Faust and Quagliano[12] compared the solid infrared spectra of the isomeric pair. However, no essential difference was found between the spectra of the isomers, though the spectrum of the *cis* isomer is slightly more complicated than that of the *trans* isomer. The *cis* isomer of $[Co(NO_2)_2(NH_3)_4]^+$ shows two Raman bands

TABLE 1. OBSERVED FREQUENCIES ($cm^{-1}$) AND APPROXIMATE MODES OF THE INTRA-LIGAND VIBRATIONS OF *N*-DEUTERATED NITROAMMINE COBALT(III) COMPLEXES IN $D_2O$

| Complex | Method | $\nu(N\text{-}O)_{as}$ | $\nu(N\text{-}O)_s$ | $\delta(ND_3)_s$ | $\nu(NO_2)$ |
|---|---|---|---|---|---|
| $[Co(NO_2)(ND_3)_5]^{2+}$ | Raman | 1424 vw, p | 1333 m,p | 1055 m,p | 827 s,p |
| | | | | 1015 w,dp | |
| | IR | 1423 s | 1332 m | 1025 m | 827 w |
| *trans*-$[Co(NO_2)_2(ND_3)_4]^+$ | Raman | 1411 w,p | 1340 m,p | 1033 m,p | 824 s,p |
| | | | | 1003 w,dp | |
| | IR | 1422 m | 1324 s | 1016 m | 826 m |
| *cis*-$[Co(NO_2)_2(ND_3)_4]^+$ | Raman | 1417 vw | 1345 w,dp | 1037 w,p | 833 s,p |
| | | | 1317 m,p | 1010 w,dp | 827 w,dp |
| | IR | 1425 s | 1344 m | 1008 w | 827 w |
| | | | 1315 s | | |
| *trans*-$[Co(NO_2)_4(ND_3)_2]^-$ | Raman | 1408 vw,p | 1357 w,dp | 988 vw | 831 s,p |
| | | | 1308 m,p | | 821 m,dp |
| | IR | 1436 s | 1319 s | 982 vw | 828 w |

(one polarized and another depolarized) in both the $NO_2$ symmetric stretching and the $NO_2$ bending vibration regions; three of the four bands have counterparts in the infrared spectrum. On the other hand, the *trans* isomer shows only one band in each region of the Raman and infrared spectra; here the mutual exclusion is found.

The mutual exclusion is also found for *trans*-$[Co(NO_2)_4(NH_3)_2]^-$. If it is assumed that this complex has a $D_{4h}$ molecular symmetry, the $NO_2$ symmetric stretching and the $NO_2$ bending vibrations transform as $(A_{1g}+B_{1g}+E_u)$. This complex shows two Raman bands but only one infrared band in the $NO_2$ symmetric stretching and in the $NO_2$ bending vibration regions. The infrared frequency in each region does not coincide with either of the two Raman frequencies; this is consistent with the molecular symmetry assumed for the complex. In conclusion, it seems to be useful for differentiation of stereoisomers of nitrocomplexes to study the aqueous Raman and infrared spectra in the $NO_2$ symmetric stretching and the $NO_2$ bending vibration regions.

No useful aqueous Raman and infrared spectra have been observed for *mer*- and *fac*-$[Co(NO_2)_3(NH_3)_3]$ because of the low solubilities of the complexes in $H_2O$ nor for $K_2[Co(NO_2)_5(NH_3)]$ because of the instability in water. No essential difference was found between the solid Raman spectra of the isomeric pair of $[Co(NO_2)_3(NH_3)_3]$. (see Table 2)

*Skeletal Vibrations.* Nakagawa and Shimanouchi[2)] have studied the solid infrared spectra of the nitroammine series of cobalt(III) complexes and have performed a normal coordinate analysis for $[Co(NO_2)_6]^{3-}$, $[Co(NO_2)(NH_3)_5]^{2+}$, and *trans*- and *cis*-$[Co(NO_2)_2(NH_3)_4]^+$ complexes.

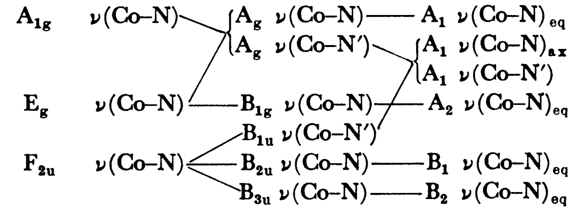
In order to assign the observed Raman bands in this region, we will use two qualitative band intensity criteria. One is concerned with deformation vibrations. The skeletal bending vibrations of $[Co(NH_3)_6]^{3+}$ and $[Co(NO_2)_6]^{3-}$ appear as very weak and diffused bands in the aqueous Raman spectra.[5,13)] Rocking vibrations of nitro groups of $[Co(NO_2)_6]^{3-}$ were not observed in the Raman spectrum.[9)] So we can expect similar band profiles and intensities for the skeletal bending and nitro rocking vibrations of the nitroammine complexes. Therefore, the strong bands near 300 $cm^{-1}$ in the aqueous Raman spectra of the nitroammine complexes will be confidently assigned to cobalt-nitro stretching vibrations, though skeletal bending and nitro rocking vibrations are expected to be in the same region.

Another criteria is concerned with stretching vibrations. Table 3 shows symmetry correlations related to metal-ligand stretching vibrational modes among $[Co(NH_3)_6]^{3+}$ ($O_h$), *trans*-$[Co(NO_2)_2(NH_3)_4]^+$ ($D_{2h}$), and $[Co(NO_2)(NH_3)_5]^{2+}$ ($C_{2v}$). For instance, the $B_1$ and $B_2$ modes due to the four equatorial Co–$NH_3$ bonds in $C_{2v}$ symmetry, though formally Raman-allowed, correlate with the $B_{2u}$ and $B_{3u}$ modes in $D_{2h}$ symmetry, respectively, so we expect that they will be hardly

TABLE 2. OBSERVED FREQUENCIES ($cm^{-1}$) AND APPROXIMATE MODES OF THE INTRA-LIGAND VIBRATIONS OF *mer*- AND *fac*-$[Co(NO_2)_3(NH_3)_3]$

| Isomer | $\nu(N\text{-}O)_{as}$ | $\nu(N\text{-}O)_s$ $\delta(NH_3)_s$ | $\delta(NO_2)$ $\delta(NH_3)_r$ |
|---|---|---|---|
| *mer* | 1415 sh | 1359 w | 832 m |
| | 1400 w | 1320 sh | 817 vs |
| | | 1316 s | |
| | | 1285 m | |
| *fac* | 1430 sh | 1355 w | 834 s |
| | 1410 w | 1313 s | 824 s |
| | 1388 w | 1288 s | |

TABLE 3. SYMMETRY CORRELATIONS RELATED TO THE METAL-LIGAND STRETCHING VIBRATIONS OF $[Co(NH_3)]^{3+}$ ($O_h$), *trans*-$[Co(NO_2)_2(NH_3)_4]^+$ ($D_{2h}$), AND $[Co(NO_2)(NH_3)_5]^{2+}$ ($C_{2v}$)[a)]



a) N and N′ stand for $NH_3$ and $NO_2$ groups, respectively.

TABLE 4. OBSERVED FREQUENCIES ($cm^{-1}$) AND ASSIGNMENTS OF THE SKELETAL VIBRATIONS OF *trans*-$[Co(NO_2)_2(NH_3)_4]^+$ AND *trans*-$[Co(NO_2)_4(NH_3)_2]^-$

| *trans*-$[Co(NO_2)_2(NH_3)_4]^+$ | | | | *trans*-$[Co(NO_2)_4(NH_3)_2]^-$ | | |
|---|---|---|---|---|---|---|
| Solid[a] | Solution[b] | Assignment[c] | ($D_{2h}$) | Solution[b] | Assignment[c] | ($D_{4h}$) |
| 492 s | 485(453) s,p | ν(Co–N) | $A_g$ | 479(453) s,p | ν(Co–N) | $A_{1g}$ |
| 461 w | 453(419) w,dp | ν(Co–N) | $B_{1g}$ | | | |
| 308 m | | δ(N–Co–N) | $A_g$ | | | |
| 272 vs | 281(281) s,p | ν(Co–N′) | $A_g$ | 282(283)[d] vs,p | ν(Co–N′) | $A_{1g}$ |
| | | | | 276(276)[e] w,dp | ν(Co–N′) | $B_{1g}$ |
| 240 sh | | ν(N–Co–N′) | $B_{2g}$<br>$B_{3g}$ | | | |
| | | | | 128(129) w,dp | δ(N′–Co–N′) | $B_{2g}$ |
| 121 vw | | lattice vib. | | | | |

a) For nitrate. b) For *N*-deuterated compound in parenthesis. c) N and N′ stand for $NH_3$ and $NO_2$ groups, respectively. d) Peak frequency in the isotropic spectrum, e) Peak frequency in the anisotropic spectrum.

detectable in the Raman spectrum of $[Co(NO_2)(NH_3)_5]^{2+}$.

*$[Co(NO_2)_6]^{3-}$*: The Raman spectra of $[Co(NO_2)_6]^{3-}$ have been studied for the potassium salt by Nakagawa[9] and for the sodium salt and the aqueous solution by Krasser.[8] Krasser[8] has reported the Raman bands at 410, 300, 245, 175, and 150 $cm^{-1}$ for the complex in aqueous solution. We have observed only three bands in this region of the aqueous spectrum (see Fig. 1A). The most intense and polarized band at 292 $cm^{-1}$, the somewhat intense and depolarized band at 262 $cm^{-1}$, and the weak and depolarized band at 158 $cm^{-1}$ are assigned, respectively, to the ν($Co-NO_2$) $A_g$, the ν($Co-NO_2$) $E_g$, and the δ($NO_2-Co-NO_2$) $F_g$ modes; this assignment is consistent with the assignment of the solid spectrum by Nakagawa.[9] The weak shoulder near 230 $cm^{-1}$ is attributed to a degradation product, since the relative intensity of the shoulder increased with time.

trans- *and* cis-*$[Co(NO_2)_2(NH_3)_4]^+$ and* trans-*$[Co(NO_2)_4(NH_3)_2]^-$*: The observed frequencies and assignments of the skeletal vibrations for *trans*-$[Co(NO_2)_2(NH_3)_4]^+$ and *trans*-$[Co(NO_2)_4(NH_3)_2]^-$ are summarized in Table 4 and those for *cis*-$[Co(NO_2)_2(NH_3)_4]^+$ in Table 5.

The X-ray study[14] for *trans*-$[Co(NO_2)_2(NH_3)_4]NO_3\cdot H_2O$ shows that this complex has approximately $D_{2h}$ symmetry, with the first mirror containing the two nitro groups, the second containing the four nitrogens of the ammine groups and the last perpendicular to the other mirrors.

There appears to be no previous Raman study of this complex. If it is assumed that this complex possesses an idealized $D_{2h}$ molecular symmetry, the metal-ligand stretching vibrations transform as shown in Table 3, with the g modes being Raman active and the u modes being infrared active. The aqueous Raman spectrum has a very simple shape (see Fig. 1C) and can be easily assigned on the basis of polarization measurements and comparison with the assignments of $[Co(NH_3)_6]^{3+}$ and $[Co(NO_2)_6]^{3-}$.

The X-ray study[15] for *cis*-$[Co(NO_2)_2(NH_3)_4]NO_3$ shows that this complex actually has a lower symmetry than $C_{2v}$. However, if it is assumed that this complex possesses an idealized $C_{2v}$ symmetry, the cobalt-ligand stretching vibrations transform as ($2A_1+B_1+B_2$ for ν($Co-NH_3$)), and ($A_1+B_1$ for ν($Co-NO_2$)), all of which are Raman and infrared active. According to the normal coordinate analysis[2] based on the $C_{2v}$ symmetry of this complex, the frequency order of the four ν($Co-NH_3$) is $B_2>A_1>B_1>A_1$. The most strong and polarized band at 483 $cm^{-1}$ is assigned to the $A_1$ mode

TABLE 5. OBSERVED FREQUENCIES ($cm^{-1}$) AND ASSIGNMENT OF *cis*-$[Co(NO_2)_2(NH_3)_4]^+$

| Raman | | | IR[d] | Assignment[e] | ($C_{2v}$) |
|---|---|---|---|---|---|
| Solid[a] | Solid[b] | Solution[c] | | | |
| | | | 519 m | ν(Co–N) | $B_2$ |
| 483 vs | 485 vs | 483(449) vs,p | 486 m | ν(Co–N) | $A_1$ |
| 464 m | 464 m | 459(425)[g] sh,dp | 463 s | ν(Co–N) | $B_1$ |
| | 445 sh | | 447 m | ν(Co–N) | $A_1$ ? |
| 370 w | | | 380 w | skel. def. | |
| 350 w | 358 m | 357(350) w,p | 358 w | skel. def. | |
| 310 sh | 320 sh | 310(317)[f] w,dp | 318 vs | ν(Co–N′) | $A_1$ |
| 298 s | 303 s | 303(310)[g] w,dp | 296 vs | ν(Co–N′) | $B_1$ |
| | | (268) w,dp | | skel. def. | |
| | | | 153 s | lattice vib. | |
| 128 vw | 133 vw | | 120 m | lattice vib. | |

a) For nitrate. b) For chloride. c) For *N*-deuterated compound in parenthesis. d) For chloride. e) N and N′ stand for $NH_3$ and $NO_2$ groups, respectively. f) Peak frequency in the isotropic spectrum. g) Peak frequency in the anisotropic spectrum.

of higher frequency. Nakagawa and Shimanouchi[2] have assigned the infrared band at 385 cm$^{-1}$ to another $A_1$ mode. This frequency seems to be rather low for $\nu$(Co–NH$_3$) and we have observed no distinct Raman band near 385 cm$^{-1}$. This $A_1$ mode may be assigned to the shoulder near 445 cm$^{-1}$ observed in the solid Raman spectrum of *cis*-[Co(NO$_2$)$_2$(NH$_3$)$_4$]Cl; this would be consistent with the assignment for the Raman spectrum of *cis*-[CoCl$_2$(NH$_3$)$_4$]Cl,[5] where the band at 435 cm$^{-1}$ has been assigned to the corresponding mode. The $B_2$ mode has been assigned to the infrared band at 518 cm$^{-1}$,[2] but no distinct Raman band has been observed at the frequency. The Raman intensity of this mode is expected to be rather weak, because this mode corresponds to an antisymmetric cobalt-ammine stretching vibration of the linear NH$_3$–Co–NH$_3$ moiety.

The peak frequency of the band near 310 cm$^{-1}$ in the isotropic spectrum of *cis*-[Co(NO$_2$)$_2$(NH$_3$)$_4$]$^+$ is 7 cm$^{-1}$ higher than that in the anisotropic one. This discrepancy of the band maxima suggests that the band near 310 cm$^{-1}$ consists of two components. The polarized component at 310 cm$^{-1}$ and the depolarized component at 303 cm$^{-1}$ are assigned to the $\nu$(Co–NO$_2$) $A_1$ and $B_1$ modes, respectively.

It is interesting to compare the Raman and infrared spectra of *trans*- and *cis*-[Co(NO$_2$)$_2$(NH$_3$)$_4$]$^+$. The coincidence of the Raman frequencies with the infrared ones has not been found in the *trans* isomer, but in the *cis* isomer (see Table 5). The relative intensity of the Raman band due to $\nu$(Co–NO$_2$) is stronger in the *trans* isomer than in the *cis* isomer (see Figs. 1C and D). A similar intensity difference of $\nu$(Co–NO$_2$) between isomeric pairs is also found in *mer*- and *fac*-[Co(NO$_2$)$_3$(NH$_3$)$_3$].

The X-ray study[16] for *trans*-NH$_4$[Co(NO$_2$)$_4$(NH$_3$)$_2$] shows that the four nitro groups are tilted 56°, 42°, 48°, and 86° to the square plane and actually this complex has no center of symmetry. This lowering of the molecular symmetry in solid state is reflected in the complexity of the spectral features. The observed data are listed in an Appendix. On the other hand, in aqueous solution this complex can be assumed to possess a $D_{4h}$ symmetry as stated above, and so one can expect that there will appear two bands (one polarized and another depolarized) due to the $\nu$(Co–NO$_2$) and one polarized band due to the $\nu$(Co–NH$_3$) in the Raman spectrum. The aqueous Raman spectrum exhibits two bands which can be attributed to the $\nu$(Co–NO$_2$) and the $\nu$(Co–NH$_3$), respectively. However, the discrepancy between the peak frequencies of the $\nu$(Co–NO$_2$) of the isotropic and the anisotropic spectra suggests that two Raman bands are overlapped. The polarized component at 282 cm$^{-1}$ and the depolarized component at 276 cm$^{-1}$ are assigned to the $\nu$(Co–NO$_2$) $A_g$ and $B_{1g}$ modes, respectively. The polarized band at 479 cm$^{-1}$ is unambiguously assigned to the $\nu$(Co–NH$_3$) $A_g$ mode. Accordingly, the aqueous Raman spectrum of *trans*-[Co(NO$_2$)$_4$(NH$_3$)$_2$]$^-$ is explained reasonably in terms of $D_{4h}$ symmetry in the skeletal vibration as well as in the intra-ligand vibration regions.

*[Co(NO$_2$)(NH$_3$)$_5$]$^{2+}$ and [Co(NO$_2$)$_5$(NH$_3$)]$^{2-}$*: The X-ray study[17] for [Co(NO$_2$)(NH$_3$)$_5$]Br$_2$ shows that the virtual symmetry of this complex is very close to $C_{2v}$, with one of the mirrors containing the NO$_2$ group and bisecting the NH$_3$–Co–NH$_3$ angle. On the basis of $C_{2v}$ symmetry for this complex, the metal-ligand stretching vibrations transform as shown in Table 3, with all modes being Raman active and all but the $A_2$ mode being infrared active. However, we can hardly expect the Raman bands corresponding to the $B_1$ and $B_2$ modes due to the stretching vibrations of the equatorial ammine groups, according to the qualitative band intensity criteria discussed above.

The observed frequencies and the assignment of [Co(NO$_2$)(NH$_3$)$_5$]$^{2+}$ are summarized in Table 6 along with the infrared data. The somewhat intense band near 450 cm$^{-1}$ is unambiguously assigned to the $\nu$(Co–NH$_3$)$_{eq}$ $A_2$ mode since this band is depolarized and has no counterpart in the infrared spectrum. The most intense band near 490 cm$^{-1}$ is assigned to the $\nu$(Co–NH$_3$)$_{eq}$ $A_1$ mode on the basis of the correlation with the $\nu$(Co–NH$_3$) $A_{1g}$ mode of *trans*-[Co(NO$_2$)$_2$(NH$_3$)$_4$]$^+$, though the corresponding infrared band has been assigned to the $\nu$(Co–NH$_3$)$_{ax}$.[2] Our assignment is consistent with that for the $\nu$(Co–NH$_3$)$_{eq}$ of [CoCl(NH$_3$)$_5$]$^{2+}$ proposed by Swaddle *et al.*[5] and Loehr *et al.*[6] These authors have assigned the $\nu$(Co–NH$_3$)$_{ax}$ $A_1$ mode of [CoCl(NH$_3$)$_5$]$^{2+}$ to the medium band at 463 cm$^{-1}$. By the comparison

Table 6. Observed frequencies (cm$^{-1}$) and assignment of [Co(NO$_2$)(NH$_3$)$_5$]$^{2+}$

| Raman | | | IR[d] | Assignment[e] | ($C_{2v}$) |
|---|---|---|---|---|---|
| Solid[a] | Solid[b] | Solution[c] | | | |
| | | | 496 m | $\nu$(Co–N)$_{eq}$ | $B_1$,$B_2$ |
| 482 vs | 487 vs | 485(453) vs,p | 486 sh | $\nu$(Co–N)$_{eq}$ | $A_1$ |
| | 460 sh | | 460 w | $\nu$(Co–N)$_{ax}$ | $A_1$ ? |
| 448 w | 446 m | 448(416) m,dp | | $\nu$(Co–N)$_{eq}$ | $A_2$ |
| 429 w | | | | | |
| | | | 359 sh | skel. def. | |
| 330 sh | 340 sh | 342(326) w,p | 336 m | skel. def. | |
| 310 sh | | | | skel. def. | |
| 287 m | 299 m | 303(285) m,p | 294 s | $\nu$(Co–N′) | $A_1$ |
| 132 vw | 130 vw | | 140 s | lattice vib. | |

a) For bromide. b) For nitrate. c) For *N*-deuterated compound in parenthesis. d)For nitrate. e) N and N′ stand for NH$_3$ and NO$_2$ groups, respectively.

with the assignment, the shoulder near 460 cm$^{-1}$, which is observed in the solid Raman spectrum of [Co(NO$_2$)(NH$_3$)$_5$](NO$_3$)$_2$, may be assigned to the $\nu$(Co–NH$_3$)$_{ax}$ A$_1$ mode. The band at 429 cm$^{-1}$ of the solid Raman spectrum of nitropentaamminecobalt(III) bromide or chloride has not been observed for the aqueous solution nor for the nitrate, though the corresponding band has been observed for the infrared spectrum.[2] This band is rather low in the frequency for $\nu$(Co–NH$_3$) and may not be a fundamental vibration.

No X-ray study has been done for K$_2$[Co(NO$_2$)$_5$(NH$_3$)]. The observed frequencies of the solid Raman spectrum are listed in the Appendix. The band at 488 cm$^{-1}$ is confidently assigned to the $\nu$(Co–NH$_3$). However, a detailed assignment of other bands is difficult, since a useful aqueous Raman spectrum could not be obtained because of the fast decomposition in water. In the aqueous Raman spectrum, the band at 488 cm$^{-1}$ disappears and a new band appers at 467 cm$^{-1}$.

TABLE 7. OBSERVED FREQUENCIES (cm$^{-1}$) AND APPROXIMATE MODE OF *mer* AND *fac* ISOMERS OF [Co(NO$_2$)$_3$(NH$_3$)$_3$]

| *mer*(C$_{2v}$) | | *fac*(C$_{3v}$) | | Assignment[b] |
|---|---|---|---|---|
| Solid | Solution[a] | Solid | Solution[a] | |
| 482 vs | 481 vs,p | 489 vs | 480 vs,p | $\nu$(Co–N) A$_1$ |
| 470 sh | 470 sh,dp | 468 m | 472 m,dp | $\nu$(Co–N) B$_1$ for *fac.*<br>$\nu$(Co–N) E for *mer.* |
| | | 381 vw | | skel. def. and $\nu$(Co–N′) |
| 352 m | | 363 m | | |
| 340 vw | | 347 w | | |
| 320 m | | 315 m | | |
| 285 s | | 291 m | | |
| 266 vs | | 271 m | | |
| | | 179 m | | lattice vib. |
| 137 m | | 125 vw | | |

a) For DMSO solution. b) N and N′ stand for NH$_3$ and NO$_2$ groups, respectively.

mer- *and* fac-[*Co*(*NO*$_2$)$_3$(*NH*$_3$)$_3$]: The X-ray study[18] for the *mer* isomer shows that this complex has a lower symmetry than C$_{2v}$. No X-ray study has been reported for the *fac* isomer. We have observed the Raman spectrum of dimethylsulfoxide solution of each isomer because of the low solubility of these complexes in water. The observed frequencies and the tentative assignments are summarized in Table 7. As explained for the relative intensities of $\nu$(Co–NO$_2$) of *trans*- and *cis*-[Co(NO$_2$)$_2$(NH$_3$)$_4$]$^+$, the *mer* isomer, which contains *trans* nitro groups, exhibits a very strong band due to $\nu$(Co–NO$_2$), while the *fac* isomer, which contains *cis* nitro groups only, exhibit medium or weak bands (see Figs. 1E and F).

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## Appendix

The solid Raman data of K$_2$[Co(NO$_2$)$_5$(NH$_3$)]: 1400 vw, 1317 s, 836 s, 821 vs, 488 w, 383 sh, 373 w, 304 s, 273 s, 171 m, 133 w (cm$^{-1}$); of NH$_4$[Co(NO$_2$)$_4$(NH$_3$)$_2$]: *ca.* 1400 sh, 1360 w, 1307 s, *ca.* 1290 sh, 828 s, 817 s, 485 s, 349 w, 299 m, 277 s, 264 s, 176 w, 157 w, 128 w (cm$^{-1}$).

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