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The Preparation and Spectral Properties of *trans*(*CN*)-[Co(CN)$_2$(tmdda)]$^-$ and -[Co(CN)$_2$(L-ala)$_2$]$^-$ Complexes

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(Received May 23, 1984)

All-*trans*- and *trans*(*CN*),*cis*(*N*)-[Co(CN)$_2$(L-ala)$_2$]$^-$ and *trans*(*CN*)-[Co(CN)$_2$(tmdda)]$^-$ were newly prepared; here, tmdda denotes trimethylenediamine-*N*,*N*′-diacetate. These complexes were characterized from their electronic absorption, NMR, and Raman spectra. The CD spectra of two *trans*(*CN*) isomers of the bis(L-alaninato)-complex are also presented.

There have been few reports on the preparation of *trans*(*CN*)-[Co(CN)$_2$(N)$_2$(O)$_2$]-type complexes, though many reports have appeared on *trans*(*CN*)-[Co(CN)$_2$-(N)$_4$]-type complexes, where (N)$_2$(O)$_2$ denotes diamine-*N*,*N*′-diacetate or bis(amino carboxylate) and (N)$_4$ tetraammine[1)] or bis(diamine).[2)] For instance, three *cis*-(*CN*)-[Co(CN)$_2$(am)$_2$]$^-$ isomers (am=amino carboxylate) have been reported for the glycinato complexes,[3,4)] but the *trans*(*CN*) isomer has not yet appeared. Recently, work on synthesizing cobalt(III) complexes with a linear quadridentate O–N–N–O ligand, tmdda, have been reported, and it was suggested that tmdda prefers the *unsym-cis* to the *sym-cis* geometry, when the ligand coordinates to the Co^{III} ion.[5,6)] This fact seems to reveal that the *trans*(*CN*) coordination is possibly formed in the preparation of the dicyano Co^{III} complex with tmdda.

The present work is concerned with the preparation of all-*trans*- and *trans*(*CN*),*cis*(*N*)-[Co(CN)$_2$(L-ala)$_2$]$^-$ and *trans*(*CN*)-[Co(CN)$_2$(tmdda)]$^-$, which are characterized by their electronic absorption, Raman, and NMR spectra. The CD spectra of the two isomers of [Co(CN)$_2$(L-ala)$_2$]$^-$ are also presented.

Experimental

Preparation. *1) Lithium* trans(CN)-*Dicyano(trimethylenediamine*-N,N′-*diacetato)cobaltate(III),* trans(CN)-*Li[Co(CN)$_2$(tmdda)].* To a solution of trimethylenediamine-*N*,*N*′-diacetic acid dihydrochloride[7)] (5.2 g; 0.02 mol) in 200 cm^3 of water we added 4.5 g (0.02 mol) of [CoCl(CN)(NH$_3$)$_4$]Cl.[8)] The mixture was adjusted to pH=8 with an aqueous NaOH solution, and then a small amount of activated charcoal was added. The mixture was stirred at 60 °C for 30 h. After removing the activated charcoal, the filtrate was adjusted to pH=7 with dilute acetic acid and diluted to 1 dm^3 with water. Then the charged compound was removed by passing it through a cation-exchange (Dowex 50W×8, Li$^+$ form) column and an anion-exchange (Dowex 1×8, Cl$^-$ form) column. The eluate was concentrated to dryness with a rotary evaporator. The residue was washed with ethanol and dried. This dark-red intermediate product, which was presumed to be [Co(CN)(tmdda)(NH$_3$)], was used in the next step without any purification. The intermediate product (4.5 g) and KCN (0.98 g; 0.015 mol) were kept at 60 °C in 200 cm^3 of dimethyl sulfoxide for 30 h. After the reaction solution has then been diluted to 2 dm^3 with water, a small amount of an insoluble material was filtered off. The filtrate was applied to an anion-exchange column (Dowex 1× 8, 200-400 mesh, Cl$^-$ form, 4×60 cm), and the adsorbed band was eluted with an aqueous LiCl solution (0.5 g/dm^3), separating into orange and orange-red bands. It was found from the spectral properties that the first, orange eluate contained the all-*cis*-[Co(CN)$_2$(tmdda)]$^-$ complex, with the second, orange red one contained the desired *trans*(*CN*)-[Co(CN)$_2$(tmdda)]$^-$ complex. The orange-red eluate was evaporated to dryness with a rotary evaporator, and the residue was washed with ethanol to remove the LiCl. The crude product was recrystallized from a small amount of water by adding methanol. Yield, 0.4 g. Found: C, 32.09; H, 4.52; N, 16.53%. Calcd for Li[Co(CN)$_2$(tmdda)]·1.75H$_2$O= LiCoC$_7$H$_{12}$N$_4$O$_4$·1.75H$_2$O: C, 32.05; H, 4.63; N, 16.61%.

2) Lithium trans(CN)-*Dicyanobis(*L-*alaninato)cobaltate(III),* trans(CN)-*Li[Co(CN)$_2$(*L-*ala)$_2$].* The two isomers of *trans*-(*CN*)-[Co(CN)$_2$(L-ala)$_2$]$^-$ were obtained by a method similar to that in 1). That is, [CoCl(CN)(NH$_3$)$_4$]Cl (9.0 g; 0.04 mol), L-alanine (7.2 g; 0.08 mol), and NaOH (3.2 g; 0.08 mol) were dissolved in a mixture of 100 cm^3 of dimethyl sulfoxide and 100 cm^3 of water; then the solution was stirred at 60 °C for 30 h. The intermediate product, which was supposed to be [Co(CN)(L-ala)$_2$(NH$_3$)], was isolated by a manner similar to that used for [Co(CN)(tmdda)(NH$_3$)]. The intermediate product (5.6 g) and KCN (1.3 g; 0.02 mol) were kept at 60 °C in 200 cm^3 of dimethyl sulfoxide for 30 h. The reaction mixture was then diluted to 2 dm^3 with water and poured onto an anion-exchange column (Dowex 1×8, 200—400 mesh, Cl$^-$ form; 4×60 cm). Four colored bands, yellow, pinkish red, orange-red, and orange, were obtained, in this order, by eluting with an aqueous NH$_4$Cl solution (1 g/dm^3). The first two bands (yellow and pinkish red) partially overlapped, so the eluates were combined and evaporated to dryness under reduced pressure. The yellow isomer and NH$_4$Cl were extracted from the residue with ethanol, leaving the pinkish red isomer, which was insoluble in ethanol. The yellow isomer was found to be the *cis(CN), trans(N)* isomer by comparing its electronic absorption spectrum with that of *cis*(*CN*),*trans*(*N*)-[Co(CN)$_2$(gly)$_2$]$^-$.[4)] The pinkish red isomer was converted to lithium salt by rechromatography. The crude product was recrystallized by dissolving it in a small amount of water, and then adding methanol. It was found by spectral measurements to be described later that this isomer has the all-*trans* configuration. After these two bands were removed, the eluent was changed from an aqueous NH$_4$Cl solution to an aqueous LiCl solution (1 g/dm^3). The orange isomer was found to be the all-*cis* isomer by comparing its electronic absorption spectrum with that of all-*cis*-[Co(CN)$_2$(gly)$_2$]$^-$.[4)] The orange-red fraction was concentrated to dryness with a rotary evaporator, and the residue was washed with ethanol and recrystallized from a small amount of water by adding methanol. The orange-red isomer was assigned to have the *trans(CN)*, *cis(N)* configuration on the basis of the spectral properties to be described below. Yields, 0.5 g for the pinkish red isomer and 0.2 g for the orange-red isomer. Found for the pinkish red isomer: C, 28.62; H, 5.51; N, 15.56%. Calcd for Li[Co(CN)$_2$(L-ala)$_2$]·2.5H$_2$O·0.5CH$_3$OH=LiCoC$_8$H$_{12}$N$_4$O$_4$·2.5H$_2$O·0.5CH$_3$OH: C, 28.74; H, 5.39; N, 15.78%. The solvation of methanol was confirmed by the ^{1}H and ^{13}C NMR spectra. Found for the orange-red isomer: C, 27.82; H, 5.12; N, 16.10%. Calcd for Li[Co(CN)$_2$(L-ala)$_2$]·3H$_2$O=LiCoC$_8$H$_{12}$N$_4$O$_4$·3H$_2$O: C, 27.63; H, 5.22; N, 16.11%.

Measurements. The electronic absorption spectra were recorded with a Hitachi 220 spectrophotometer and the CD spectra, with JASCO J-20 and J-500 spectrophotometers. Raman spectra were recorded on a JASCO R-800 Laser Raman spectrophotometer with an excitation of the He–Ne laser (632.8 nm, 50 mW) in water and a disk. The IR spectra were recorded on a JASCO IRA-3 spectrophotometer, and the samples were provided as nujol mulls. The NMR spectra were recorded on JEOL FX-100 and FX-90Q spectrometers in D$_2$O. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as the internal reference.

Results and Discussion

Structural Assignment. Figure 1 shows five geometrical isomers of [Co(CN)$_2$(N)$_2$(O)$_2$]-type complexes. All of them are possible for [Co(CN)$_2$(L-ala)$_2$]$^-$, while the possible isomers for [Co(CN)$_2$(tmdda)]$^-$ are reduced to three, *trans(CN)*, *cis(N)*, *cis(CN)*, *trans(O)*, and all-*cis*. Poznjac and Pawlowski[3)] reported the preparations and spectroscopic properties of three *cis(CN)* isomers of [Co(CN)$_2$(gly)$_2$]$^-$ and two *cis(CN)* isomers of [Co(CN)$_2$(edda)]$^-$. Figure 2 shows the absorption spectra of the orange-red isomer of [Co(CN)$_2$(tmdda)]$^-$ and the pinkish red and orange-red isomers of [Co(CN)$_2$(L-ala)$_2$]$^-$; their data are summarized in Table 1. As the absorption spectrum of the orange isomer of [Co(CN)$_2$(tmdda)]$^-$ is quite similar to that of all-*cis*-[Co(CN)$_2$(edda)]$^-$,[5)] it can be assigned to the all-*cis* one. On the other hand, the orange-red isomer of [Co(CN)$_2$(tmdda)]$^-$ can be assigned to the *trans(CN)* one, since the absorption spectrum differs distinctly from that of the *cis(CN)*,*trans(O)*-[Co(CN)$_2$(edda)]$^-$ (Table 1).

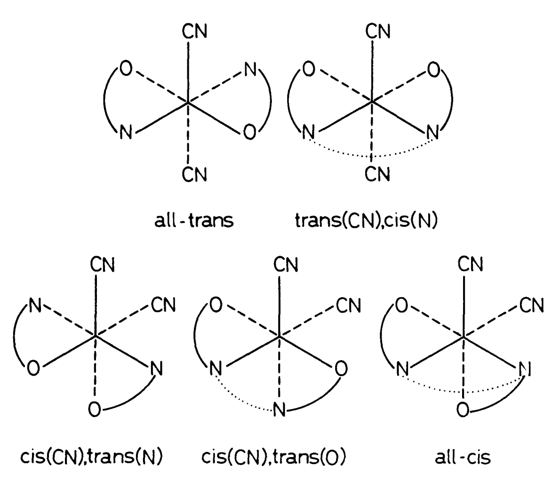

Fig. 1. Possible geometrical isomers of [Co(CN)$_2$(N)$_2$(O)$_2$]-type complex; (N)$_2$(O)$_2$=(tmdda) or (L-ala)$_2$.

The orange-red isomer of [Co(CN)$_2$(L-ala)$_2$]$^-$ is also assignable to the *trans(CN)*,*cis(N)* one, since the d-d spectrum is quite similar to that of *trans(CN)*-[Co(CN)$_2$(tmdda)]$^-$, as may be seen in Fig. 2. The d-d spectrum of the pinkish red isomer differs remarkably from that of *trans(CN)*,*cis(N)*-[Co(CN)$_2$(L-ala)$_2$]$^-$ and those of the three *cis(CN)* isomers of [Co(CN)$_2$(gly)$_2$]$^-$[4)] (Fig. 2 and Table 1). Consequently, the pinkish red isomer of [Co(CN)$_2$(L-ala)$_2$]$^-$ can be assigned to the all-*trans* one.

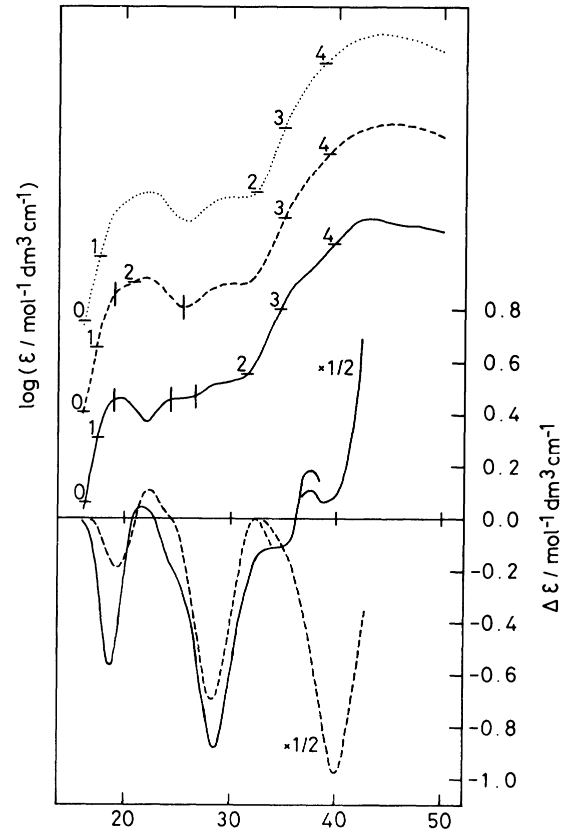

Fig. 2. Electronic absorption and CD spectra of *trans(CN)*-[Co(CN)$_2$(tmdda)]$^-$, (······), *trans(CN)*,*cis(N)*-[Co(CN)$_2$(L-ala)$_2$]$^-$, (----), and all-*trans*-[Co(CN)$_2$(L-ala)$_2$]$^-$, (——). Short vertical lines show the predicted positions of the first d-d absorption band.

Table 1. Absorption and CD data of $[\mathrm{Co(CN)_2(N)_2(O)_2}]$-type complexes (Wave numbers are given in $10^3\ \mathrm{cm^{-1}}$ and $\log \varepsilon$ and $\Delta\varepsilon$ (in parentheses) $\mathrm{mol^{-1}\ dm^3\ cm^{-1}}$)

Complex		First band	Second band	CT band
trans(CN)-$[\mathrm{Co(CN]_2(tmdda)}]^-$		*ca.* 19 sh (1.7)	29.8 (1.91)	43.7 (4.39)
		21.5 (1.98)		
trans(CN),cis(N)-$[\mathrm{Co(CN)_2(}$L-ala$\mathrm{)_2}]^-$		*ca.* 19 sh (1.8)	*ca.* 30 sh (2.0)	*ca.* 37 (3.6)
		22.0 (2.05)		45.9 (4.41)
	CD	19.3 (−0.19)	28.2 (−0.69)	39.5 (−1.95)
		22.2 (+0.11)		
all-*trans*-$[\mathrm{Co(CN)_2(}$L-ala$\mathrm{)_2}]^-$		19.5 (1.60)	*ca.* 29 sh (1.8)	*ca.* 37 (3.5)
		ca. 24 sh (1.5)		43.3 (4.35)
	CD	18.7 (−0.56)	28.2 (−0.88)	37.9 (+0.22)
		21.5 (+0.04)		
		ca. 24 sh (−0.2)		
cis(CN),trans(N)-$[\mathrm{Co(CN)_2(gly)_2}]^-$ a)		23.3 (2.34)	30.9 (2.13)	
cis(CN),trans(O)-$[\mathrm{Co(CN)_2(gly)_2}]^-$ a)		19.2 (1.84)	30.7 (2.14)	
		ca. 26 sh (1.9)		
all-*cis*-$[\mathrm{Co(CN)_2(gly)_2}]^-$ a)		21.1 (2.04)	30.5 (2.16)	
		24.4 (2.05)		
cis(CN),trans(O)-$[\mathrm{Co(CN)_2(edda)}]^-$ b)		19.4 (1.87)	30.5 (2.16)	
		ca. 26 sh (1.8)		
all-*cis*-$[\mathrm{Co(CN)_2(edda)}]^-$ b)		21.2 (2.08)	30.6 (2.06)	
		24.4 (1.95)		

a) Ref. 4. b) Values estimated from the figure in Ref. 3.

The ^{1}H and ^{13}C NMR spectra of the cobalt(III) complexes with tmdda have also been investigated.[5,6] The ^{13}C NMR spectrum of *trans*(*CN*)-$[\mathrm{Co(CN)_2(tmdda)}]^-$ exhibits four resonance lines (at δ 28.88, 53.09, 60.08, and 183.60), corresponding to the four different carbon atoms; these lines are assignable to the resonances of $-\mathrm{CH_2\underline{C}H_2CH_2}-$, $-\mathrm{NH\underline{C}H_2CH_2}-$, $-\mathrm{NH\underline{C}H_2COO}-$, and $-\mathrm{CH_2\underline{C}OO}-$ respectively, following the assignment of Gailey *et al.*[5] This observation indicates that the two glycinate moieties of the coordinated tmdda are equivalent, being consistent with the *trans(CN)* configuration. The six-membered backbone chelate ring of *trans*(*CN*)-$[\mathrm{Co(CN)_2(tmdda)}]^-$ would take either the skew-boat or chair form. The middle methylene protons of the backbone trimethylenediamine ring would be in different magnetic environments to each other in the chair form, whereas they would be equivalent in the skew-boat form. In order to determine the conformation of the backbone chelate ring, the ^{1}H NMR spectra of *trans*(*CN*)-$[\mathrm{Co(CN)_2(tmdda)}]^-$ were measured. Figure 3-A shows its ^{1}H NMR spectrum in $\mathrm{D_2O}$ acidified with $\mathrm{D_2SO_4}$ (pD≈2), and Figure 3-B, that in $\mathrm{D_2O}$. The proton-exchange rate of imino groups would be slow enough to give the observable signals in an acidified solution. In contrast, imino protons are expected to be quickly exchanged with deuterons in $\mathrm{D_2O}$. From a comparison of Fig. 3-A with Fig. 3-B, the broad band at δ 5.8, which was observed only in the acidified $\mathrm{D_2O}$, can be assigned to the imino protons. The doublet (at δ 3.35 and 3.27) and the multiplet (at *ca.* δ 2.5) in Fig. 3-A, which are transformed into a singlet and a simpler multiplet in $\mathrm{D_2O}$ (Fig. 3-B), can be assigned to the methylene protons adjacent to the imino groups. Two multiplets (at *ca.* δ 2.1 and

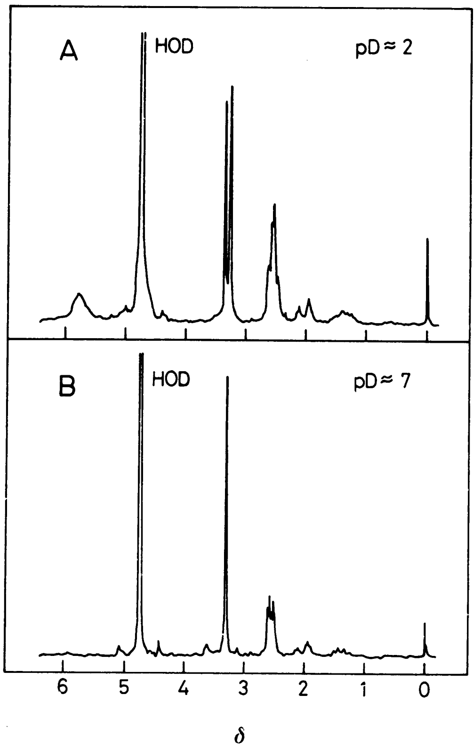

Fig. 3. ^{1}H NMR spectra of *trans*(*CN*)-$[\mathrm{Co(CN)_2(tmdda)}]^-$ in $\mathrm{D_2O}$ acidified with $\mathrm{D_2SO_4}$ (A) and $\mathrm{D_2O}$ (B). (Resonance lines around δ 1.4 are due to a contaminant in DSS.)

ca. 1.9), which remained unchanged by the deuteration of the imino groups, can be assigned to the middle methylene protons, though the integrated intensity was somewhat weaker than expected (the overall intensity of the two multiplets was about three-tenths of that of the multiplet at δ 2.5). This assignment is consistent with that of the middle methylene protons of a series of Co^{III}-tn complexes,[9] for which the middle methylene protons were assigned to the resonance lines near δ 2. The spacing of the two multiplets (δ 0.15) can not be explained on the basis of the spin-spin coupling between the middle methylene and the terminal methylene protons, since the spacing of the resonance lines due to the terminal methylene protons is much narrower than δ 0.15. Therefore, these two multiplets can be regarded as resonances of different protons in different magnetic environments. This fact suggests that the six-membered backbone chelate ring in the complex takes the chair form; in other words, the complex takes the *meso* form with respect to the coordinated nitrogen atoms.

The Raman spectrum gives useful information concerning the structural elucidation of Co^{III} complexes;[10,11] for instance, the Raman spectra in the skeletal stretching region were successfully applied to the differentiation of the isomers of [Co(gly)$_2$(AA)]-type complexes, where AA denotes en or ox.[11] The all-*trans* isomer can be regarded as having a C_{2h} symmetry, and then the Co–N and Co–O stretching vibrations are reduced to $2A_g+2B_u$, of which the A_g modes are Raman-active. On the other hand, the *trans*(*CN*),*cis*(*N*) isomer can be regarded as having a C_{2v} symmetry and the Co–N and Co–O stretching vibrations are reduced to $2A_1+2B_1$, of which all modes are Raman-active. The aqueous Raman spectra of the all-*trans*- and *trans*(*CN*),*cis*(*N*)-[Co(CN)$_2$(L-ala)$_2$]$^-$ complexes in the 650—450 cm^{-1} region are shown in Fig. 4 and correspond to those in the solid state well. The all-*trans* isomer exhibits two bands (581 and 537 cm^{-1}) in the Co–N and Co–O stretching vibration region, as expected from the symmetry. In contrast to the all-*trans* isomer, the *trans*(*CN*),*cis*(*N*) isomer exhibits three bands (595, 537, and 495 cm^{-1}) in the corresponding region. The fourth Raman-active band would be weak and concealed by the strong band at 595 cm^{-1}. The IR band at 577 cm^{-1} may be the counterpart of the concealed Raman band. These results confirm the assignment of the two isomers of [Co(CN)$_2$(L-ala)$_2$]$^-$ based on the absorption spectral behavior.

Absorption and CD Spectra. It has been suggested that, in the first absorption band of the *trans(CN)*-[Co(CN)$_2$(N)$_4$]-type complex ((N)$_4$=tetraammine or bis(diamine)), the position of the lower-energy component agrees with the one predicted from the semiempirical calculation,[12] whereas the position of the absorption component at a higher energy deviates from the one predicted.[1] This behavior in the first-absorption-band region is also realized in the present *trans(CN),cis(N)* isomer. The short vertical lines in Fig. 2 show the positions of the absorption components of the first absorption band, estimated in terms of the parameters, δ^1(CN)=32050 from [Co(CN)$_6$]$^{3-}$, δ^1(N)=21300 from [Co(en)$_3$]$^{3+}$, and δ^1(O)=16600 cm^{-1} from [Co(ox)$_3$]$^{3-}$. The splitting pattern of the first absorption band for the *trans*(*CN*),*cis*(*N*)-[Co(CN)$_2$(L-ala)$_2$]$^-$ isomer is similar to that of *trans*(*CN*)-[Co(CN)$_2$(NH$_3$)$_4$]$^+$;[1] namely, the higher energy component deviates remarkably from the one predicted. In the first absorption band of the all-*trans*-[Co(CN)$_2$(L-ala)$_2$]$^-$ isomer, however, the observed components agree fairly well with the predicted ones. This fact seems to deny that only *trans(CN)* arrangement is responsible for the deviation.

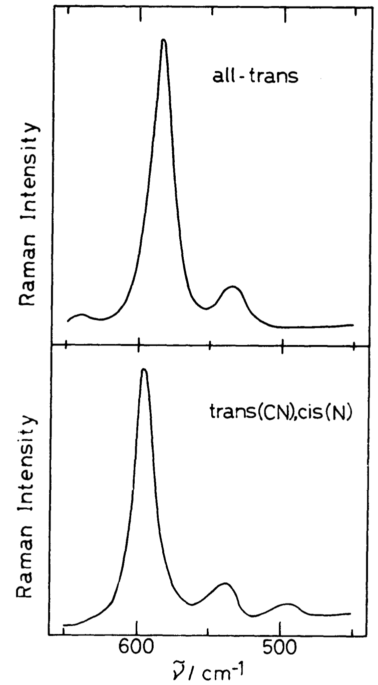

Fig. 4. Aqueous Raman spectra of the two isomers of *trans*(*CN*)-[Co(CN)$_2$(L-ala)$_2$]$^-$.

The CD spectra of *trans(CN),cis(N)*- and all-*trans*-[Co(CN)$_2$(L-ala)$_2$]$^-$ are mainly contributed by the *S*(C)-configuration of the L-alaninate ligand. In the d-d absorption-band region, the two isomers show similar CD patterns, though the CD spectrum of the all-*trans* isomer is somewhat stronger in intensity than that of the *trans*(*CN*),*cis*(*N*) isomer. Their CD bands in the second-absorption-band region are comparatively intense (Fig. 2 and Table 1). In contrast to the d-d absorption-band region, their CD spectra in the charge-transfer region (*ca.* 35—42×10^3 cm^{-1}) differ significantly from one another. It is apparent that the positive CD band (at 37.9×10^3 cm^{-1}) of the all-*trans* isomer corresponds to the absorption shoulder at *ca.* 37×10^3 cm^{-1}, and the negative CD band (at 39.5×10^3 cm^{-1}) of the *trans*(*CN*),*cis*(*N*) one, to the absorption shoulder at *ca.* $37\times10^3\,\mathrm{cm}^{-1}$. However, more data will be needed in order to discuss this CD spectral behavior in relation to the structural difference between the two geometrical isomers.

The authors wish to express their thanks to Professor Yoichi Shimura of Osaka University for his fruitful discussion.

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