BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (11), 3329—3330 (1976)

Preparation and Circular Dichroism of Cyanoamminebis[(R)-propylenediamine]cobalt(III) Complexes

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(Received June 7, 1976)

Synopsis. Three new complexes, *trans*-, *cis*-*Λ*-, and *cis*-*Δ*-$[Co(CN)(NH_3)(R\text{-}pn)_2]^{2+}$(pn = propylenediamine) were prepared. The geometrical structure was determined on the basis of ^1H NMR spectra. The optical isomers were characterized from the circular dichroism spectra.

The normal character of cyanide as a ligand has been reported in the splitting of the first and second absorption bands of cobalt(III) complexes.[1] A different case was reported [2] in which the splitting of the first absorption band in *trans*-$[Co(CN)_2(NH_3)_4]^+$ is small for the one expected from Yamatera's theory.[3] This indicates that more spectral data are necessary for cyanide complexes.

The circular dichroism (CD) spectra of dicyanobis(diamine)cobalt(III) complexes were discussed in a previous paper.[4] The CD spectra of $[Co(CN)(NH_3)(R\text{-}pn)_2]^{2+}$ complexes are discussed herewith.

Experimental

Preparation and Separation of the Isomers. $[Co(CN)(NH_3)_5]Cl_2$[5] (2g, 8.3mmol) was dissolved in a 50 cm^3 aqueous solution of R-pn(27mmol). The solution was kept at 60—70°C for 3 h with active charcoal (0.5 g). The orange red solution was filtered. The filtrate was cooled to room temperature and poured into a column (2.5 × 50 cm) of a Dowex 50W-X8 (200—400 mesh) ion exchange resin of sodium form. After the column had been washed with water, the adsorbed band was eluted with a 1M aqueous sodium chloride solution at a 15 cm^3/h rate. A small amount of the first light yellow eluate was found to be *cis*-$[Co(CN)_2(R\text{-}pn)_2]^+$ from the visible and ultraviolet absorption spectra.[4] The second orange yellow eluate was concentrated to a small volume at 40°C in a rotary evaporator under reduced pressure. Ethanol was added to the concentrate to precipitate sodium chloride. This was repeated several times in order to remove sodium chloride as far as possible. Finally, the filtrate was passed through a column (2.5×50 cm) of Sephadex LH-20 with an eluent of ethanol–water (4 : 1) for complete removal of the sodium choride. The eluate evaporated to dryness to afford an orange yellow product which was obtained in a *ca.* 100 mg yield. The product (FI) is very soluble in water, but not in organic solvents. Found : C, 22.99 ; H, 7.47 ; N, 24.00%. Calcd for $[Co(CN)(NH_3)(R\text{-}pn)_2]Cl_2\cdot 2H_2O$:C, 23.54; H, 7.62; N, 23.53%.

The third and fourth orange yellow eluates from the Dowex 50W-X8 column were treated in the same way as for the first eluate, orange yellow products FII and FIII, respectively, being obtained. The products are very soluble in water, but not in organic solvents. Yield, *ca.* 150 mg for FII and *ca.* 250 mg for FIII. Found for FII: C, 25.19; H, 7.60; N, 24.35%. Calcd for $[Co(CN)(NH_3)(R\text{-}pn)_2]Cl_2\cdot H_2O$: C, 24.79; H, 7.43; N, 24.78%. Found for FIII: C, 23.67; H, 7.47; N, 24.08%. Calcd for $[Co(CN)(NH_3)(R\text{-}pn)_2]Cl_2\cdot 2H_2O$: C, 23.54; H, 7.62; N, 23.53%.

Another orange band was observed near the top of the column, but was not characterized.

Measurements. The electronic absorption spectra were obtained with a Hitachi 323 recording spectrophotometer. The CD spectra were recorded on a Jasco Model ORD/UV-5 spectropolarimeter and the ^1H NMR spectra on a Varian A-60 spectrometer in deuterium oxide using sodium trimethylsilylpropanesulfonate (DSS) as an internal standard.

Results and Discussion

Three isomers, *trans*(CN-NH_3) and two *cis*(CN-NH_3), are possible for $[Co(CN)(NH_3)(R\text{-}pn)_2]^{2+}$ if the location of the methyl group in the pn chelate is not considered. They were isolated with a Dowex 50W-X8 ion exchange resin. No more isomers due to the location of the methyl group were obtained.

The ^1H NMR spectra of FI exhibits a doublet (J= 5.8 Hz) due to a CH_3 group of R-pn at 1.31 ppm. FII and FIII isomers showed two doublets with J=5.9 Hz and 6.3 Hz at 1.32 and 1.46 ppm, respectively. Thus, we have assigned FI to the *trans*(CN-NH_3) isomer and FII and FIII to the *cis*(CN-NH_3) isomer.

The visible and ultraviolet absorption spectra of FI, FII, and FIII are almost the same as each other and are very similar to the spectrum of $[Co(CN)(NH_3)_5]^{2+}$. The absorption data in the d-d transition region are shown in the Table together with the CD data.

Figure 1 shows the CD spectra of *trans*-$[Co(CN)(NH_3)(R\text{-}pn)_2]^{2+}$ and *trans*-$[Co(CN)_2(R\text{-}pn)_2]^+$ in water. If the electronic state in the complex *trans*-$[Co(CN)(NH_3)(R\text{-}pn)_2]^{2+}$ can be approximated to the C_{4v} form, the two CD peaks in the first absorption band might be assigned to the A_2 and E components. The apparent energy difference of these two peaks (2.9×10^3 cm^{-1}) is smaller than that (3.7×10^3 cm^{-1}) of *trans*-

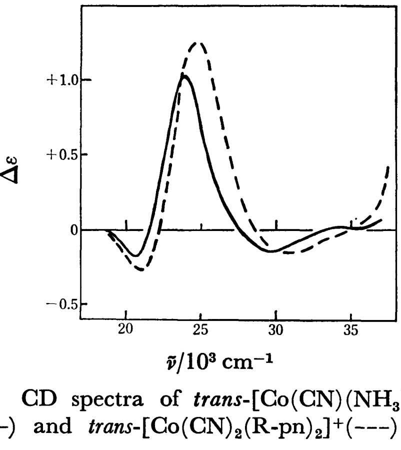

Fig. 1. CD spectra of *trans*-$[Co(CN)(NH_3)(R\text{-}pn)_2]^{2+}$ (——) and *trans*-$[Co(CN)_2(R\text{-}pn)_2]^+$(---) in water.

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TABLE 1. ABSORPTION AND CD SPECTRAL DATA FOR $[Co(CN)(NH_3)(R\text{-}pn)_2]^{2+}$ ($\tilde{\nu}$ in 10^3 cm^{-1})

Complex	I Band		II Band	
	$\tilde{\nu}_{max}$ (log ε)	$\tilde{\nu}^{cd}_{ext}$ ($\Delta\varepsilon_{ext}$)	$\tilde{\nu}_{max}$ (log ε)	$\tilde{\nu}^{cd}_{ext}$ ($\Delta\varepsilon_{ext}$)
FI	23.09(1.88)	20.62(−0.19) 23.53(+1.05)	31.10(1.90)	29.41(−0.14)
FII	23.04(1.88)	22.99(+1.11)	30.91(1.90)	29.50(−0.08)
FIII	22.94(1.94)	20.83(−0.67) 23.64(+0.69)	30.77(1.97)	30.30(−0.11)

$[Co(CN)_2(R\text{-}pn)_2]^+$ as expected from Yamatera's theory.

Figure 2 shows the CD spectra of FII and FIII. The CD spectrum of FII gives a very strong positive band in the first absorption band region, suggesting a *Λ* configuration on the basis of the empirical rule.[6] FIII can be assigned to *Δ* isomer although the spectrum shows a negative and a positive band, since the CD spectral patterns of *cis*-$[Co(CN)(NH_3)(R\text{-}pn)_2]^{2+}$ correspond to those of *cis*-*Δ*-$[Co(CN)_2(R\text{-}pn)_2]^+$.[4]

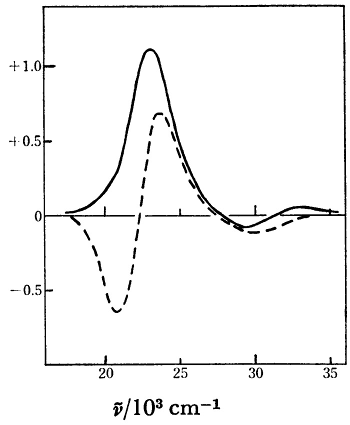

Fig. 2 CD spectra of *cis*-$[Co(CN)(NH_3)(R\text{-}pn)_2]^{2+}$ in water, FII (——) and FIII(- - - -).

Figure 3 shows the configurational and vicinal curves of *cis*-$[Co(CN)(NH_3)(R\text{-}pn)_2]^{2+}$ which were derived by the method reported previously.[4] The pattern of the derived vicinal CD curves is similar to the observed CD spectrum of FI. The configurational CD curve of FII confirms a *Λ* configuration for the isomer. The spectral pattern of the configurational effect is similar to that of *cis*-$[Co(CN)(NH_3)(en)_2]Br_2$,[7] indicating the validity of the additivity of CD to these complexes.

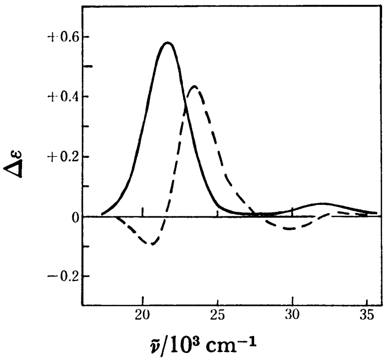

Fig. 3 Calculated configurational (——) and vicinal (- - - -) CD curves of *cis*-$[Co(CN)(NH_3)(R\text{-}pn)_2]^{2+}$.

The encouragement and helpful discussions of Professor Kazuo Saito are gratefully acknowledged.

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