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Circular Dichroism Spectra of Some Transition Metal Complexes with (1*R*,2*R*)-1,2-Cyclopentanediamine

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Bischelates, three isomers of dicyanocobalt(III), *trans*-dichlorocobalt(III), and copper(II), and a monochelate, tetracyanoferrate(II), of the title diamine were prepared, and their CD spectra were reported. Major positive components were found for I_a bands, as was to be expected for the preferred λ conformation, but minor positive components were observed for the I_b band with the *trans*-dianionocobalt(III) complexes. The configurational and the vicinal effects, as calculated from the CD spectra of the *cis*-dicyanocobalt(III) complexes, are shown to be different from those of (1*R*,2*R*)-1,2-cyclohexanediamine. The CD spectra of the Fe(II) and Cu(II) complexes are consistent with the conformational effect of the title diamine.

The optical activity of transition metal complexes has been studied with a variety of ligands. Among them, 1,2-diamines are most widely employed, and the results have been recognized as well established. However, the results have been obtained mostly with en, pn, and chxn as 1,2-diamines.[1,2] The CD spectra of metal chelates with these diamines are almost identical with their corresponding structures, and the proposed empirical rules of the optical activity are based on these results. However, two exceptions are known. Phenyl-substituted diamines, stien[3] and phenen,[4] yield cobalt(III) complexes which have CD spectra different from those of the other diamines mentioned above. Another is the tris cobalt(III) complexes of cptn. An earlier study of the complexes of cptn has been reported by Jaeger and Blumendal.[5] Saito *et al.* have reported that the CD spectrum of Λ-[Co(*S*-cptn)$_3$]Cl$_3$ is anomalous, even though the structure has been confirmed by X-ray crystallography to be similar to that of other corresponding tris(diamine)cobalt(III) complexes.[6] The CD spectra of Δ- and Λ-[Co(*R*-cptn)$_3$]$^{3+}$ have been reported by Toftlund and Pedersen.[7] The diamine, cptn, may be expected, because of its fused five-membered cyclopentane ring, to form a chelate with a rigid structure on coordination to a metal ion.

Tetragonal complexes, *trans*-dianionobis(diamine)cobalt(III), exhibit CD spectra which are free from any configurational contribution. The sector rule predicts that the signs of CD components corresponding to the $^1A_{1g}\rightarrow{}^1E_g{}^a$ and $^1A_{1g}{}^a\rightarrow{}^1A_{2g}$ transitions (D_{4h}) are positive and negative respectively with 1,2-diamines which form chelate rings of the λ conformation upon coordination.[2] Anomalous CD spectra can be expected for the tetragonal complexes with resolved cptn if the vicinal effect of this diamine differs from those of other 1,2-diamines.

This paper will deal with the syntheses and CD spectra of *trans*-dichloro and three isomers of dicyanocobalt(III) complexes, the tetracyanoferrate(II) complex, and the biscopper(II) complex with *R*-cptn as the diamine.

Experimental

Materials. The cyclopentanone (Merck, Synthetic Grade) was used without further purification. The pyridine,[8] methanol,[9] and sulfolane[10] were purified according to the known methods. The other chemicals were used as purchased.

*Preparation of (1*R*,2*R*)-1,2-Cyclopentanediamine. 1,2-Cyclopentanedione*: This was prepared by a modification of the method for preparing 1,2-cyclohexanedione.[11] A 3-dm^3 round-bottomed flask containing 1.5 dm^3 of cyclopentanone and fitted with a stirrer and a dropping funnel was placed in a water bath. The contents were warmed to 30 °C, and then a solution containing 361 g (3.25 mol) of selenium dioxide, 420 cm^3 of dioxane, and 155 cm^3 of water was added dropwise into the cyclopentanone over a period of 24 h with stirring. Stirring was continued for further 18 h at 35 °C. The red selenium thus separated was filtered off on a Buchner funnel. The selenium was returned to the reaction flask and extracted with 500 cm^3 of boiling ethanol for 3 h. The solution obtained by filtration was combined with the above filtrate. The combined filtrate was distilled using a 60-cm Vigreau column at 2700 Pa, and the lower-boiling portion (35—90 °C) was removed. The remaining portion was distilled at 1300 Pa until a thick brown residue formed in the distilling flask, thus preventing further distillation. The higher-boiling fraction was redistilled at 2100 Pa, and a fraction which distilled at 86—88 °C was collected. Yield, 74 g (23% based on SeO$_2$).

The 1,2-cyclopentanedione dioxime and *trans*-1,2-cyclopentanediamine were prepared successively from 1,2-cyclopentanedione according to the method of Jaeger and Blumendal.[5] The optical resolution of the diamine was carried out according to the method of Toftlund and Pedersen[7] to isolate the (1*R*,2*R*)-isomer using (+)-tartaric acid as the resolving agent. The (1*S*,2*S*)-isomer was obtained by employing (−)-tartaric acid as the resolving agent after the recovery of the free base from the remainder of the (1*R*,2*R*)-isomer.

Preparation of Metal Complexes. trans-[*CoCl*$_2$(R-*cptn*)$_2$]*Cl·0.5H*$_2$*O*: To 100 cm^3 of an aqueous solution of CoCl$_2$·6H$_2$O (4.76 g, 0.02 mol), *R*-cptn (3.00 g, 0.03 mol) was added, after which, the mixture was aerated for 3 h. To the resultant brown solution, 30 cm^3 of concentrated hydrochloric acid was added. The mixture was then concentrated on a steam bath to near dryness. The separated crystals were collected on a filter and washed thoroughly with acetone until the filtrate showed no blue color. The crystals were then added to 40 cm^3 of methanol. The mixture was refluxed for 2 h and filtered. The filtrate was allowed to stand in a refrigerator overnight; the green crystals thus separated were collected on a filter and washed thoroughly with acetone. Yield, 1.7 g (23%).

Perchlorates: To the filtrate, a large excess of lithium perchlorate was added. The green crystals thus separated were

Table 1. Analytical data of complexes prepared

Complex	Found, %			Calcd, %		
	C	H	N	C	H	N
trans-[CoCl$_2$(*R*-cptn)$_2$]ClO$_4$	28.02	5.36	13.44	27.96	5.63	13.04
trans-[CoCl$_2$(R-cptn)$_2$]Cl·0.5H$_2$O	32.17	6.68	15.19	31.31	6.83	14.60
trans-[Co(CN)$_2$(*S*-cptn)$_2$]ClO$_4$·H$_2$O	33.61	6.11	19.60	33.93	6.12	19.30
cis-Δ-[Co(CN)$_2$(*S*-cptn)$_2$]ClO$_4$·0.5NaClO$_4$	30.62	5.03	17.66	30.47	5.12	17.77
cis-Λ-[Co(CN)$_2$(*S*-cptn)$_2$]ClO$_4$·0.5H$_2$O	34.31	5.48	19.89	34.33	6.00	20.02
Na$_2$[Fe(CN)$_4$(*R*-cptn)]0.5NaClO$_4$·0.5H$_2$O	28.87	3.97	21.86	28.65	3.46	22.27
[Cu(*S*-cptn)$_2$]SO$_4$·0.5H$_2$O	32.79	6.54	15.21	32.55	6.82	15.19

collected on a filter and washed with ethanol and ether. The analytical data are listed in Table 1, along with those for other complexes.

*Preparation and Isolation of the Isomers of Dicyanobis(*S*-cptn)cobalt(III) Perchlorates*: Potassium cyanide (460 mg) was dissolved in 80 cm^3 of dimethyl sulfoxide (DMSO) at 60 °C. Into this solution was added 940 mg of *trans*-[CoCl$_2$(*S*-cptn)$_2$]Cl·0.5H$_2$O in portions with stirring. The color of the solution turned from green to orange. The solution was allowed to stand at 60 °C for 30 min, cooled to room temperature, and then poured into a column (10 cm × 3 cm) packed with an SP-Sephadex C-25 ion exchanger. The absorbed resin was washed with water to remove the DMSO and mounted on the top of another SP-Sephadex C-25 exchanger (120 cm × 3 cm). When the absorbed band was eluted with a 0.05 mol dm^{-3} aqueous sodium perchlorate at a rate of 500 cm^3 d^{-1}, one orange and then two light yellow bands were separated. The first, orange elute was evaporated to dryness at 40 °C with a rotatory evaporator under reduced pressure. Twenty cm^3 of acetone was added to remove the sodium perchlorate, leaving an orange residue, which was subsequently dissolved in a minimum amount of hot water and then filtered. The filtrate was allowed to stand in a refrigerator overnight to obtain orange plates. Yield, 100 mg (9%).

The second and the third, light yellow elutes were evaporated at 40 °C with rotatory evaporators to dryness. Ethanol was added to extract light yellow precipitates, and the ethanol solutions were evaporated again to dryness. The residues were dissolved in minimum amounts of hot water, and the solutions were cooled in refrigerators. Separated crystals were collected on filters. Yields, 23 mg and 57 mg for the second and the third fractions respectively.

*Na$_2$[Fe(CN)$_4$(*R*-cptn)]0.5NaClO$_4$·0.5H$_2$O*: In a 200-cm^3 three-necked round-bottomed flask equipped with a mechanical stirrer and a dropping funnel, iron(II) perchlorate hexahydrate (6.55 g, 18.2 mmol) was placed under nitrogen, and then a 40-cm^3 portion of methanol flushed with nitrogen was added through a serum cap with a syringe. The flask was immersed in an ice–water bath. With stirring, a solution of *R*-cptn (3.63 g, 36 mmol) in 25 cm^3 of methanol was then added in small portions. White precipitates were formed. To the mixture, a solution of sodium cyanide (3.56 g, 72 mmol) in 8 cm^3 of water was added from the dropping funnel with vigorous stirring. The mixture turned into a dark brown solution and was concentrated with a rotatory evaporator, yielding a viscous liquid. Ethanol (200 cm^3) was added, and the mixture was allowed to stand in a refrigerator overnight. The yellow precipitates thus separated were collected on a filter and washed with ethanol and then with ether.

The crude product was dissolved in 12 cm^3 of water, while the undissolved materials were removed by centrifugation. A methanol solution of sodium perchlorate (16 g/100 cm^3) was added to the supernatant liquid, and then 200 cm^3 of ethanol. The mixture was allowed to stand in a refrigerator overnight. Separated yellow crystals were collected on a filter and were washed with ethanol and ether subsequently. Yield, 1.6 g (23%).

*[Cu(*S*-cptn)$_2$]SO$_4$·0.5H$_2$O*: To a solution of copper(II) sulfate pentahydrate (500 mg) in 30 cm^3 of water, *S*-cptn (0.4 g) was added. The solution turned blue. The solution was warmed, and ethanol (40 cm^3) was added. The hot mixture was filtered, and the filtrate was allowed to stand in a refrigerator. Separated blue needles were collected on a filter and washed with ethanol. Yield, 250 mg.

Physical Measurements. The electronic spectra were recorded with a Shimadzu UV-200 spectrophotometer. The CD spectra were measured with a JASCO J-40 recording polarimeter using aqueous solutions, unless otherwise stated. The infrared spectra were measured with a JASCO IRA-2 spectrophotometer using KBr disks. The ^{1}H-NMR spectra were measured with a JEOL JNM-MH-100 spectrometer using D$_2$O solutions and with sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as the internal standard.

Results and Discussion

The synthesis of *R*-cptn was carried out with cyclopentanone as the starting material. Generally, the yields of 1,2-diketones from ketones with selenium dioxide are affected by the structures of the ketones, and the yield of cyclopentanedione has been reported to be low.[12] The use of cyclopentanone as a solvent improved the yield to 23% based on the SeO$_2$ but the yield is still low compared to the yield of 60% for 1,2-cyclohexanedione from cyclohexanone. The successive reactions and optical resolution were carried out according to the known methods.[5,7]

The origins of the optical activities of metal chelates have been classified as: (i) configurational, (ii) conformational, and (iii) vicinal effects. The latter two effects correlate with the absolute configuration of a coordinated diamine. The absolute configuration of (−)-cptn was determined by Saito *et al.* as (1*R*,2*R*)-.[6] The absorption and CD spectra of solutions of cobalt(III) complexes of *R*-pn, *R*-bn, and *R*-chxn are similar to each other for the corresponding structures because of their preferred λ conformation, in which alkyl group (s) adopt an equatorial position in a five-membered chelate ring.[6] The diamines, *R*-cptn and *R*-chxn, have the same absolute configuration and are expected to coordinate to metal ions exclusively in a λ conformation by virtue of their fused ring structures. Therefore, the electronic and CD spectra of complexes of *R*-cptn are compared with those of *R*-chxn in this report.

trans-*Dichlorocobalt(III) Complex.* Aeration of a mixture of cobalt(II) chloride and *R*-cptn, followed by the addition of concentrated hydrochloric acid, afforded *trans*-dichlorobis((1*R*,2*R*)-1,2-cyclopentanediamine)cobalt(III) chloride. The electronic and CD spectra of this chelate in methanol are shown in Fig. 1, along with the CD spectrum of *trans*-$[CoCl_2(R\text{-chxn})_2]^+$; the latter has been reported by Treptow.[13] The numerical data are listed in Table 2 and compared with those of other complexes. The absorption maximum of the I_a band of the *R*-cptn complex appears at the same energy as the corresponding maximum of the *R*-chxn complex. However, the absorption maximum of the I_b band moved to an energy lower by 1600 cm^{-1} for the *R*-cptn complex. In the CD spectra, the I_a components are almost the same for both complexes. However, the CD spectra for the I_b components are different. A positive component is observed for the *R*-cptn complex. The CD spectra of *trans*-$[CoCl_2(R\text{-cptn})_2]Cl$ were measured in three solvents—pyridine, methanol, and sulfolane. The magnitudes of the major positive CD bands were little affected, but the magnitudes of the minor CD components were changed as follows in $\Delta\varepsilon$: pyridine, +0.67; methanol, +0.24; sulfolane, +0.19.

*Dicyanobis(*R*-cptn)cobalt(III) Isomers.* Three isomers of $[Co(CN)_2(S\text{-cptn})_2]^+$ were isolated from a reaction mixture of the *trans*-dichloro complex with KCN, followed by column chromatography with SP-Sephadex C-25 resin. The fraction eluted first with a 0.05 mol dm^{-3} $NaClO_4$ was orange in color and exhibited a large splitting in the first absorption band. This was assigned to the *trans*-isomer. The second and third fractions were yellow in color, had similar

TABLE 2. COMPARISON OF ELECTRONIC AND CD SPECTRA OF *R*-cptn AND *R*-chxn COMPLEXES

Complex	*R*-cptn				*R*-chxn			
	ν_{max}[a]	(ε_{max})	ν_{max}^{CD}[a]	($\Delta\varepsilon_{max}$)	ν_{max}[a]	(ε_{max})	ν_{max}^{CD}[a]	($\Delta\varepsilon_{max}$)
trans-$[CoCl_2L_2]^+$	16.2	(42.5)	16.2	(+1.32)	16.3	(39.2)[b]	16.4	(+0.93)[b]
	20.3	(27.0)	20.3	(+0.29)	21.9	(31.6)	21.4	(−0.10)
	24.9	(77.6)	24.5	(−0.16)	25.6	(53.7)	23.7	(−0.05)
							27.3	(+0.21)
	31.0	(2040)	29.9	(+1.78)	32.4	(1530)	30.5	(+1.12)
			32.7	(−0.12)			35.0	(−3.90)
	39.2	(26600)	37.7	(+9.94)	39.8	(29000)	40.0	(+12)
			43	(+2.5)				
trans-$[Co(CN)_2L_2]^+$	20.6	(sh)	20.0	(+0.20)	22	(sh)[c]	20.9	(−0.28)[c]
	23.7	(75.4)	23.7	(+1.97)	24.4	(67.6)	24.5	(+2.28)
			29.0	(−0.02)	32.0	(69.2)	30.6	(−0.36)
	37.0	(sh, 3760)	37.8	(+9.80)				
	44.0	(19000)	42.7	(+15.2)	46.1	(13800)	44.0	(+16.5)
	47.2	(22500)	47.8	(−7.3)			50.0	(−3.6)
cis-*Λ*-$[Co(CN)_2L_2]^+$	23.2	(86)	25.4	(+1.88)	24.8	(93.3)[c]	25.5	(+2.24)[c]
	24.8	(91.6)						
	31.0	(sh, 100)	31.9	(−0.15)	32.3	(100)	32.4	(−0.20)
	38.0	(sh, 6000)	37.7	(+9.30)			39.8	(+2.10)
			42.6	(−34.9)			44.4	(−24.1)
	45.9	(21200)	48.0	(+45.5)			49.5	(+41.2)
cis-*Δ*-$[Co(CN)_2L_2]^+$	23.2	(83)	23.1	(+1.72)	24.9	(100)[c]	21.6	(−0.38)[c]
	25.0	(88)	27.8	(−0.23)			24.3	(+1.06)
							28.6	(−0.14)
	31.0	(sh, 120)	32.0	(+0.22)	32.3	(98)	32.6	(+0.06)
	38.0	(sh, 4800)	42.6	(+60.8)			44.2	(+48.6)
	46.2	(19100)	48.5	(−45.9)			49.5	(−37.1)
$[Fe(CN)_4L]^{2-}$	25.3	(438)	25.2	(+0.69)	25.5	(407)[d]	22.2	(−0.18)[d]
							26.0	(+0.51)
	31.8	(410)	30.1	(−0.36)	32.0	(457)	30.3	(−0.16)
	36.0	(sh, 1200)	37.0	(sh, +1.00)			37.0	(+0.6)
	42.9	(10500)	41.9	(+2.55)	44.8	(9770)	42.0	(+2.8)
	45.0	(10000)						
$[CuL_2]^{2+}$	17.2	(70)	17.8	(+0.38)	18.5	(83)	16.0	(+0.055)
							19.6	(+0.37)
	35.6	(1800)	35.6	(+3.25)				
	42.9	(6200)	42.6	(+2.70)	41.8	(8300)	41.0	(+3.8)

a) In 10^3 cm^{-1}. b) From Ref. 13. c) From Ref. 14. d) From Ref. 16.

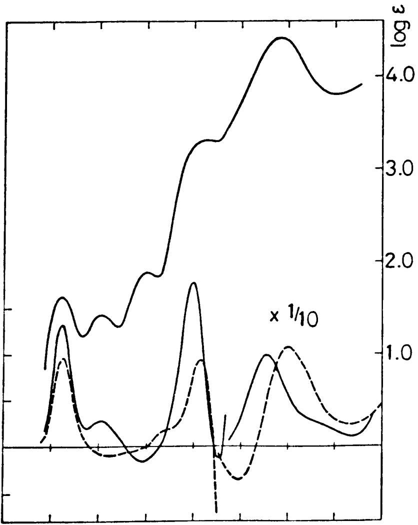

Fig. 1. Electronic and CD spectra of *trans*-$[CoCl_2(diamine)_2]ClO_4$ in methanol. Diamine: *R*-cptn, ——; *R*-chxn, — — —.

absorption spectra, and were assigned to *cis*-isomers.

The second fraction was assigned to *cis*-Δ-$[Co(CN)_2(S\text{-cptn})_2]^+$, and the third, to *cis*-Λ-$[Co(CN)_2(S\text{-cptn})_2]^+$, by comparing the CD spectra in the region between 40000 and 50000 cm^{-1} with those of the corresponding *R*-chxn complexes.[14] The yield of the *cis*-Δ-isomer was about one half of that of the *cis*-Λ-isomer. The C≡N stretching appeared at 2122 and 2128 for the *trans*-, at 2127 for the *cis*-Δ-, and at 2118 cm^{-1} for the *cis*-Λ-isomer. The two *cis*-isomers have very similar infrared spectra except for the N–H stretching region. The *cis*-Δ-isomer has three absorptions, at 3400, 3200, and 3080 cm^{-1}, while the *cis*-Λ-isomer has six absorptions in this region.

The following discussion will be argued, for the sake of brevity, using three complexes, *trans*-$[Co(CN)_2(R\text{-cptn})_2]^+$, *cis*-$\Lambda$-$[Co(CN)_2(R\text{-cptn})_2]^+$, and *cis*-$\Delta$-$[Co(CN)_2(S\text{-cptn})_2]^+$, which should have CD spectra with signs the reverse of those of the enantiomers, *trans*-$[Co(CN)_2(S\text{-cptn})_2]^+$, *cis*-$\Delta$-$[Co(CN)_2(S\text{-cptn})_2]^+$, and *cis*-$\Lambda$-$[Co(CN)_2(S\text{-cptn})_2]^+$ respectively.

The electronic and CD spectra of *trans*-$[Co(CN)_2(R\text{-cptn})_2]^+$ are shown in Fig. 2. The data for the isomers of the *R*-chxn complexes were provided by Kashiwabara.[14] The first absorption band appears at an energy lower by 700 cm^{-1} for the *R*-cptn complex than that for the *R*-chxn complex. The second absorption band of the *R*-chxn complex appears clearly, but that of the *R*-cptn complex is obscured by intense charge-transfer absorptions. In the CD spectra, the first absorption band contains two CD bands of opposite signs for the *R*-chxn complex, while the CD spectrum of the *R*-cptn complex shows two positive components. Another feature of the CD spectrum of the *R*-cptn complex is a positive CD component which appears at 37800 cm^{-1}. The positive CD component, which has a maximum at 42700 cm^{-1} for the *R*-chxn complex, is not symmetric, but has tails on the longer-wavelength side.

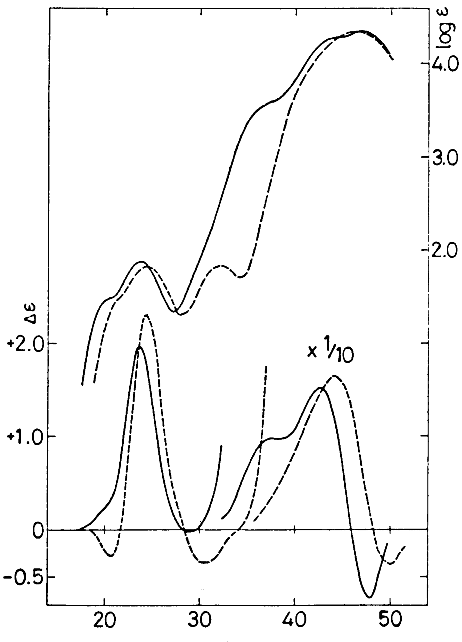

Fig. 2. Electronic and CD spectra of *trans*-$[Co(CN)_2(diamine)_2]^+$ in water. Diamine: *R*-cptn, ——; *R*-chxn, — — —. Data of *R*-chxn are reproduced from Ref. 16.

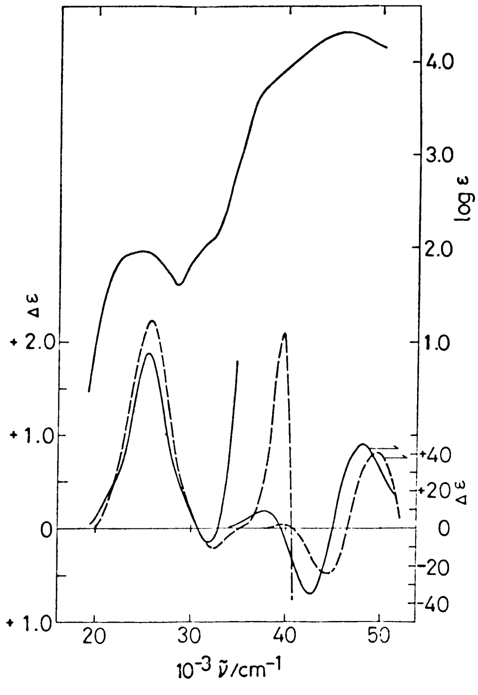

Fig. 3. Electronic and CD spectra of *cis*-Λ-$[Co(CN)_2(diamine)_2]^+$ in water. Diamine: *R*-cptn, ——; *R*-chxn, — — —. Data of *R*-chxn are reproduced from Ref. 16.

The electronic and CD spectra of the *cis*-Λ- and *cis*-Δ-$[Co(CN)_2(R\text{-cptn})_2]^+$ isomers are shown in Figs. 3 and 4 respectively, along with those of the corresponding isomers of the *R*-chxn complexes. For the *R*-cptn complexes, the first absorption bands are not symmetric, and the second absorption bands are obscured by a partial superposition of intense charge-transfer bands. Their absolute configurations are determined from the CD components between 40000 and 50000 cm^{-1}, which closely resemble those of the *R*-chxn complexes. The absolute configurations of the chxn complexes have been determined[14] from the signs of these components on the basis of the empirical rule presented by Ogino *et al.*[15] In the first absorption bands, both *R*-cptn and *R*-chxn complexes show a positive CD band at 25500 cm^{-1} for *cis*-Λ-isomers, but the *R*-chxn complex exhibits a negative CD component at 21600 cm^{-1} in addition to the two components, which are found as a positive component and a negative component in the CD spectra of both complexes for *cis*-Δ-isomers.

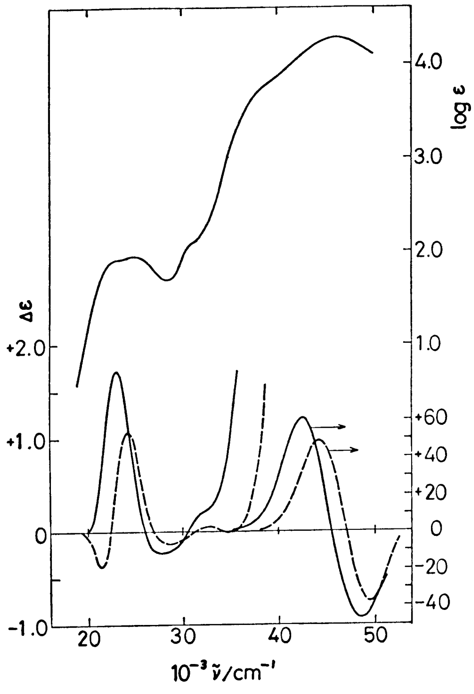

Fig. 4. Electronic and CD spectra of *cis*-Δ-[Co(CN)$_2$-(diamine)$_2$]$^+$ in water. Diamine: *R*-cptn, ——; *R*-chxn, — — —. Data of *R*-chxn are reproduced from Ref. 16.

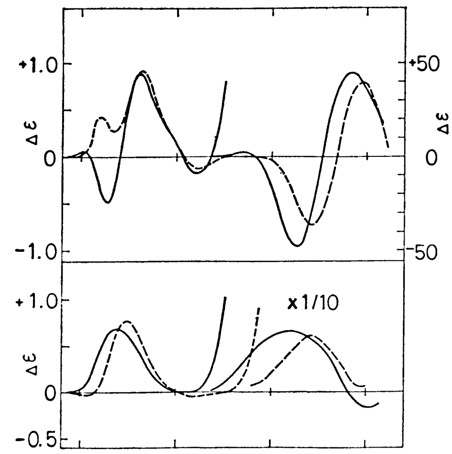

Fig. 5. Calculated configurational (upper, Λ) and conformational (bottom, *R*) curves of *cis*-[Co(CN)$_2$-(diamine)$_2$]$^+$. Diamine: *R*-cptn, ——; *R*-chxn, — — —. Calcd by $\Delta\varepsilon(\Lambda)=1/2[\Delta\varepsilon(\Lambda_{2R})-\Delta\varepsilon(\Delta_{2R})]$ and $\Delta\varepsilon(R)=1/4[\Delta\varepsilon(\Lambda_{2R})+\Delta\varepsilon(\Delta_{2R})]$. Data of *R*-chxn are reproduced from Ref. 16.

The configurational and vicinal curves of *cis*-[Co(CN)$_2$(*R*-cptn)$_2$]$^+$ are shown in Fig. 5, together with those of *cis*-[Co(CN)$_2$(*R*-chxn)$_2$]$^+$.[14] They were derived from the observed curves by the use of the following relations;

$$\Delta\varepsilon(R) = 1/4\{\Delta\varepsilon(\Lambda_{2R}) + \Delta\varepsilon(\Delta_{2R})\}$$
$$\Delta\varepsilon(\Lambda) = 1/2\{\Delta\varepsilon(\Lambda_{2R}) - \Delta\varepsilon(\Delta_{2R})\}$$

where $\Delta\varepsilon(\Lambda_{2R})$ and $\Delta\varepsilon(\Delta_{2R})$ are the observed CD for the Λ and Δ diastereoisomers of the *cis*-[Co(CN)$_2$-(diamine)$_2$]$^+$ complexes respectively, and where $\Delta\varepsilon(\Lambda)$ and $\Delta\varepsilon(R)$ are the configurational and the vicinal CD for the complexes.

*Tetracyano(*R*-cptn)ferrate(II) Complex.* Diamagnetic sodium tetracyano(*R*-cptn)ferrate(II) was prepared according to a method similar to that used earlier for preparing this class of compounds.[16] The complex showed absorptions which were almost the same as those of [Fe(CN)$_4$(*R*-chxn)]$^{2-}$, as is shown in Table 2. The infrared spectrum showed intense C≡N stretching at 2030 cm^{-1}. The ^{1}H-NMR spectrum showed four types of protons, which resonate at 1.22(2), 1.70(2), 1.86(2), and 2.86(2) ppm, the relative integrated signal areas are indicated in parentheses. The protons corresponding to the signal at 2.86 ppm are the axial protons of methine. The corresponding protons in [Fe(CN)$_4$(*R*-chxn)]$^{2-}$ appear at 2.05 ppm.[16] This down-field shift of the axial protons of cyclopentane ring occurs partly because of a decrease in anisotropy from the C–C bond due to the flatness of the cyclopentane ring.

The CD spectra of [Fe(CN)$_4$(*R*-cptn)]$^{2-}$ and [Fe(CN)$_4$(*R*-chxn)]$^{2-}$ are shown in Fig. 6. The CD spectra differ in the first absorption region. The signs of CD components for the same electronic transitions have been shown not to change in the d^6 diamagnetic isoelectronic and isostructural complexes on the basis of a comparison of the CD spectrum of [Fe(CN)$_4$(*R*-chxn)]$^{2-}$ with that of [Co(CN)$_4$(*R*-chxn)]$^-$.[16] The CD components of [Fe(CN)$_4$(*R*-pn)]$^{2-}$ and [Fe(CN)$_4$(*R*-chxn)]$^{2-}$ appear as two components with opposite signs in the first absorption region and are attributed to the conformational effects of *R*-pn and *R*-chxn.[16] The CD spectrum of [Fe(CN)$_4$(*R*-cptn)]$^{2-}$ shows a

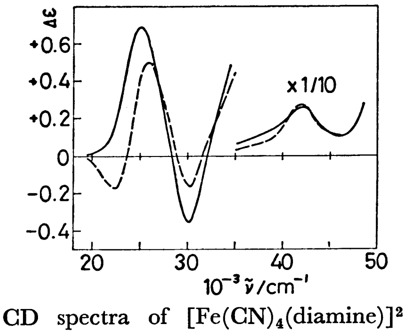

Fig. 6. CD spectra of [Fe(CN)$_4$(diamine)]$^{2-}$. Diamine: *R*-cptn, ——; *R*-chxn, — — —.

positive component in this region. We attempted to isolate the corresponding tetracyanocobaltate(III) complex, but did not succeed in doing so; however, the difference in the CD spectra between the *R*-cptn and the *R*-chxn complexes is attributable to the difference in the conformational effects of the diamines.

CD Spectra of d^6 Metal Complexes with R-*cptn.* The CD spectra of *trans*-$[CoX_2(R\text{-diamine})_2]^+$ have two components in the region of the first absorption band. The component corresponding to $^1A_{1g}\rightarrow{}^1E_{1g}{}^a$ has a positive sign with a large magnitude and changes in energy depending on the order in the spectrochemical series of the aniono group. The CD components of *trans*-$[CoX_2(R\text{-cptn})_2]^+$ have positive signs as expected for 1,2-diamines of *R*-configurations,[2] and the magnitudes are almost the same as those of the *R*-chxn complexes, as are shown in Figs. 1 and 2. A close relationship holds between the preferred conformation of the coordinated diamines and the sign of this CD component. The other component, corresponding to $^1A_{1g}\rightarrow{}^1A_{2g}$, remains approximately the same in energy as the parent $^1A_{1g}\rightarrow{}^1T_{1g}$ band of $CoN_6{}^{3+}$ ions and has an indefinite sign of a smaller magnitude which depends on the structure of the *R*-diamine and on the solvent. In methanol, the signs of these components of *trans*-dichloro complexes of *R*-pn,[17] *R*-bn,[18] and *R*-chxn[13,18] are negative, while those of phenen[4] and stien[3] are positive, but the signs of these components as well as their magnitudes change as the solvent is varied.[8,18] A good relationship has been found between the donor-power order of the solvent and the change in the CD spectrum for this region.[8] These components of *trans*-$[CoX_2(R\text{-cptn})_2]^+$ were small and positive. The CD component of *trans*-$[CoCl_2(R\text{-cptn})_2]^+$ increased in magnitude in pyridine and decreased in sulfolane, but did not change in sign in the latter solvent. The sign and the magnitude of this CD band suggest that the effect of *R*-cptn on the $^1A_{2g}$ band lies between those of phenyl-substituted diamines and of other alkyl-substituted diamines.

The vicinal curve of the *R*-cptn complexes calculated from *cis*-$[Co(CN)_2(R\text{-cptn})_2]^+$ isomers has positive components and lacks the negative component which appears in the vicinal curve for the *R*-chxn complexes, as is shown in Fig. 5. The vicinal curves of both complexes have features similar to those in the CD spectra of the corresponding *trans*-dicyano complexes in the first absorption region: the *R*-cptn complex exhibits only positive component, while the *R*-chxn complex shows a minor negative and a major positive component.

The CD spectra of $[Fe(CN)_4(R\text{-cptn})]^{2-}$ and $[Fe(CN)_4(R\text{-chxn})]^{2-}$ differ in the first absorption region, as is shown in Fig. 6. The latter CD spectrum shows a minor negative and a major positive component at 22200 and 26000 cm^{-1} respectively, those components are recognized as arising from the $^1A_{2g}$ and $^1E_{1g}{}^a$ transitions of D_{4h} symmetry, *i.e.*, the conformational effect of *R*-chxn.[16] An analogous interpretation is applicable to the positive CD component of $[Fe(CN)_4(R\text{-cptn})]^{2-}$, which lacks a negative component in the first absorption region: the conformational effect intrinsic to the *R*-cptn gives positive CD components in the first absorption band.

The tris complex, Λ-$[Co(S\text{-cptn})_3]Cl_3\cdot4H_2O$, has shown a significantly different CD spectrum in an aqueous solution from those of Λ-$[Co(en)_3]^{3+}$, Λ-$[Co(S\text{-pn})_3]^{3+}$, and Λ-$[Co(S\text{-chxn})_3]^{3+}$.[6,7] The CD spectrum has a large negative component at 21100 cm^{-1} which is assigned to the $^1A_{1g}\rightarrow{}^1A_{2g}$ component on measurement with a single crystal.[7,19] Therefore, the signs of the D_3 components are the same among these tris complexes. The ratio of the rotatory strength of A_2 to that of the E bands exceeds unity for the cptn complex, but the ratios for the other complexes have values below 0.3.[6]

The calculated configurational curve for the Λ-configuration of *cis*-$[Co(CN)_2(R\text{-cptn})_2]^+$ is composed of two components with opposite signs. The corresponding curve of *cis*-$[Co(CN)_2(R\text{-chxn})_2]^+$ and the CD spectrum of $(+)_D$-$[Co(CN)_2(en)_2]^+$, the absolute configuration of which has been determined to be Λ by Matsumoto *et al.*,[20] are composed of components with the same sign, although the intensity of the component at 26200 cm^{-1} is stronger in the *R*-chxn complex than in the en complex.[14,21] McCaffery *et al.* have assigned the low- and high-energy portions under effective C_2 symmetry to a composite of E_g and A_2 transitions and to a E_g transition under D_3 symmetry respectively, and have stated that two positive CD components appear in this region for $(+)_D$-*cis*-$[Co(CN)_2(en)_2]^+$, since the rotational strength of E_g is greater than that of A_2.[21] The reversal of sign for the CD component at 22600 cm^{-1} for the Λ-configurational curve of the *R*-cptn complexes indicates that the ratio of the rotational strength of A_2 to that of E exceeds unity. This reversed ratio agrees with the ratio for the solution spectrum of Λ-$[Co(S\text{-cptn})_3]^{3+}$. The exceptional CD spectrum of the tris complex arises from the configurational effect intrinsic to cptn as well as from the conformational effect. The solution spectra of Λ- and Δ-$[Co(R\text{-cptn})_3]^{3+}$ also indicate

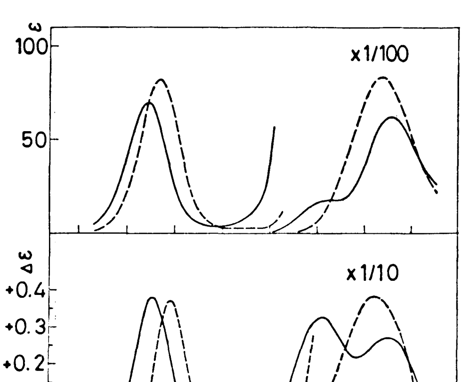

Fig. 7. Electronic and CD spectra of $[Cu(diamine)_2]^{2+}$ in water. Diamine: *R*-cptn, ——; *R*-chxn, – – –.

that the configurational effect for the *Λ*-configuration causes a marked enhancement of the negative CD component[7] and is almost opposite in sign to the configurational effect calculated from the pairs of the tris cobalt(III) complexes of en, *R*-pn, and *R*-chxn.[2]

*Bis(*R*-cptn)copper(II).* The CD and electronic spectra of $[Cu(R\text{-cptn})_2]SO_4\cdot 0.5H_2O$ are shown in Fig. 7, along with those of $[Cu(R\text{-chxn})_2]SO_4\cdot 3.5H_2O$. The d-d transitions of a Cu(II) complex of tetragonal symmetry may be expected to appear as three absorptions in the visible region. These are $^2B_{1g}\to {}^2A_{1g}$ $(d_{z^2}\to d_{x^2-y^2})$, $\to {}^2B_{2g}(d_{xy}\to d_{x^2-y^2})$, and $\to {}^2E_g(d_{xz}, d_{yz}\to d_{x^2-y^2})$, where single-electron excitations are shown in parentheses. Hathaway assigned these to: (i) 12200—16800, (ii) 16200—18000, and (iii) 17900—20300 cm^{-1} absorptions respectively.[22] If the sign of the CD component corresponding to each single-electron excitation does not change with an alteration in the electronic configuration from d^6 to d^9, two positive CD components may be expected for $[Cu(R\text{-cptn})_2]^{2+}$, while one negative and one positive components may be expected for $[Cu(R\text{-chxn})_2]^{2+}$ in the region between 16200 and 20300 cm^{-1}. The CD spectrum of $[Cu(R\text{-pn})_2]^{2+}$ has been reported by Gillard and resembles that of $[Cu(R\text{-chxn})_2]^{2+}$.[23] Both have shoulders at 16000 cm^{-1} with intensities of $+0.05$ in $\Delta\varepsilon$. These CD spectra have been discussed by Kida and Nishida.[24] They resolved the absorption spectra into three absorptions by means of Gaussian curves. Three CD components corresponding to the resolved absorptions are estimated to have a small positive, a small negative, and a large positive signs at 15600, 17500, and 19800 cm^{-1} respectively. The single-electron transfer for these three components are assigned to $d_{z^2}\to$, $d_{xy}\to$, and d_{xz}, $d_{yz}\to d_{x^2-y^2}$ respectively. The sign of each component does not change in Cu(II) complexes from that of the *trans*-dichlorocobalt(III) complexes of these diamines.

The CD spectrum of $[Cu(R\text{-cptn})_2]^{2+}$ in water showed a single positive CD component with a maximum at 17800 cm^{-1}. It shifted to an energy lower by 1800 cm^{-1} from the positive CD component of $[Cu(R\text{-chxn})_2]^{2+}$. In the region between 16000 and 20000 cm^{-1}, two transitions may be expected for $[Cu(R\text{-cptn})_2]^{2+}$, and the observed CD spectrum seems to arise from two positive components spaced with a small energy difference. A very small negative component is found at *ca.* 12500 cm^{-1} and is assigned to the transition of $d_{z^2}\to d_{x^2-y^2}$.

Circular Dichroism in Charge-transfer Region. The CD components of *cis*-isomers of $[Co(CN)_2(R\text{-cptn})_2]^+$ resembled those of the corresponding isomers of $[Co(CN)_2(R\text{-chxn})_2]^+$ with a decrease in the wave numbers by 1600 cm^{-1} and so were used to identify the absolute configurations. The empirical rule for assigning absolute configurations from these components holds for the cptn complexes. A further characteristic of the *R*-cptn complexes is a moderately strong positive CD component which appears at 37800 and 35600 cm^{-1} for the *trans*-dicyanocobalt(III) and copper(II) complexes respectively. This positive component seems also to be present in the vicinal curve shown in Fig. 5. The origins of this enhancement are, however, ambiguous for the present.

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References

1) Throughout this paper, the following abbreviations are used for diamines: en, ethylenediamine; *R*-pn, (*R*)-1,2-propanediamine; *R*-bn, (2*R*,3*R*)-2,3-butanediamine; *R*-cptn, (1*R*,2*R*)-1,2-cyclopentanediamine; *R*-chxn, (1*R*,2*R*)-1,2-cyclohexanediamine: *R*-phenen, (*R*)-1-phenyl-1,2-ethanediamine; *R*-stien, (1*R*,2*R*)-1,2-diphenyl-1,2-ethanediamine.

2) S. F. Mason, "Fundamental Aspects and Recent Developments in Optical Rotatory Dispersion and Circular Dichroism," ed by F. Ciardelli and P. S. Salvadori, Heyden, London (1973), Chap. 3, 6.

3) P. L. Fereday and S. F. Mason, *J. Chem. Soc. Chem. Commun.*, **1971**, 1314.

4) S. Yano, M. Saburi, S. Yoshikawa, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **49**, 101 (1976).

5) F. M. Jaeger and H. B. Blumendal, *Z. Anorg. Allg. Chem.*, **175**, 161 (1928).

6) M. Ito, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **27**, 2178 (1971); Y. Saito, F. Marumo, and M. Ito, *Proc. Jpn. Acad.*, **47**, 495 (1971).

7) H. Toftlund and E. Pedersen, *Acta Chem. Scand.*, **26**, 4019 (1972).

8) C. J. Hawkins, G. A. Lawrance, and R. M. Peachey, *Aust. J. Chem.*, **30**, 2115 (1977).

9) H. Lund and J. Bjerrum, *Ber. Dtsch. Chem. Ges.*, **64**, 210 (1931).

10) E. M. Arnett and C. F. Douty, *J. Am. Chem. Soc.*, **86**, 409 (1964).

11) C. C. Hach, C. V. Banks, and H. Diehl, *Org. Synth.*, Coll. Vol. IV, 229 (1963).

12) L. Long, Jr., and L. F. Fieser, *J. Am. Chem. Soc.*, **62**, 2670 (1940).

13) R. S. Treptow, *Inorg. Chem.*, **5**, 1593 (1966).

14) K. Kashiwabara, T. Yamanaka, K. Saito, N. Komatsu, N. Hamada, H. Nishikawa, and M. Shibata, *Bull. Chem. Soc. Jpn.*, **48**, 3631 (1975).

15) K. Ogino, K. Murano, and J. Fujita, *Inorg. Nucl. Chem. Lett.*, **4**, 351 (1968).

16) M. Goto, M. Takeshita, and T. Sakai, *Inorg. Chem.*, **17**, 314 (1978).

17) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 202 (1965).

18) B. Bosnich and J. MacB. Harrowfield, *J. Am. Chem. Soc.*, **94**, 3425 (1972).

19) R. Kuroda and Y. Saito, *Bull. Chem. Soc. Jpn.*, **49**, 433 (1976).

20) K. Matsumoto, S. Ooi, and H. Kuroda, *Bull. Chem. Soc. Jpn.*, **44**, 2721 (1971).

21) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, **1965**, 5094.

22) B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).

23) R. D. Gillard, *J. Inorg. Nucl. Chem.*, **26**, 1455 (1964).

24) Y. Nishida and S. Kida, Paper presented at the 21st Symposium on Coordination Chemistry, Nagoya, 1971.