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Chiroptical Properties of Trigonal-Bipyramidal Complexes of Copper(II), Nickel(II), and Cobalt(II) Containing an Optically Active Tetraamine

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A new tripodal tetraamine, $Me_2NCH_2CH(Me)N(CH_2CH_2NMe_2)_2$ (*S*-tan), was synthesized from L-alanine, and a series of its complexes, $[MX(S\text{-tan})](ClO_4)_n$ (M = Cu(II), Ni(II), Co(II); X = CN^-, $^1/_2$ CN^-, NH_3, CH_3CN, NCS^-, H_2O, $^1/_2$ OH^-, Cl^-, Br^-, I^-) were prepared. All the complexes exhibit electronic spectra typical of trigonal-bipyramidal complexes in the solid state and in solution. The structure of $[Co(NCS)(S\text{-tan})]ClO_4$ was determined by the X-ray diffraction method and subsequently refined by a block-diagonal least-squares method to give $R = 0.094$. The bluish green crystals of $C_{14}H_{32}ClCoN_5O_4S$ were orthorhombic with the space group $P2_12_12_1$, $a = 12.800$ (6) Å, $b = 17.530$ (11) Å, $c = 9.630$ (5) Å, and $Z = 4$. The complex cation has a trigonal-bipyramidal structure with the conformation of three chelate rings being δ,δ,δ. The CD spectra of these complexes are discussed on the basis of the selection rules for magnetic dipole transitions under C_{3v} symmetry.

Introduction

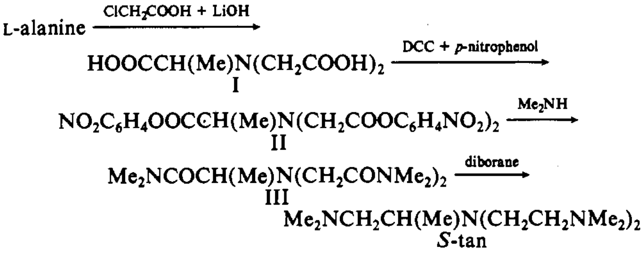
Few studies have been carried out on the chiroptical properties of five-coordinate complexes.[1-6] In 1966, Ciampolini and Nardi reported the preparation of five-coordinated complexes containing tris((dimethylamino)ethyl)amine (Me_6tren).[7a] The crystal structure analysis of $[CoBr(Me_6tren)]Br$ revealed that the complex ion had a trigonal-bipyramidal structure with C_3 symmetry.[8] The same structure was also found in the corresponding Ni(II) and Cu(II) complexes and other Me_6tren complexes.[9-11]

Recently, Mason predicted on the basis of the ligand-polarization model that the CD maximum for the $d_{xz}, d_{yz} \rightarrow d_{z^2}$ transition of $[Cu(NCS)(tren)]NCS$ should be negative when the ligand took a δ,δ,δ conformation.[4] A preliminary report of the present study revealed that the prediction was correct.[5] This paper describes the preparation, X-ray crystallography, and some properties of a series of Cu(II), Ni(II), and Co(II) complexes containing a chiral derivative of Me_6tren.

Experimental Section

Preparation of the Ligand. The ligand 2,4,8-trimethyl-5-(3-methyl-3-azabutyl)-2,5,8-triaza-4(*S*)-nonane (*S*-tan) was prepared as Scheme I shows.

Scheme I



$$\text{L-alanine} \xrightarrow{ClCH_2COOH\ +\ LiOH} \underset{\text{I}}{HOOCCH(Me)N(CH_2COOH)_2} \xrightarrow{\text{DCC} + p\text{-nitrophenol}} \underset{\text{II}}{NO_2C_6H_4OOCCH(Me)N(CH_2COOC_6H_4NO_2)_2} \xrightarrow{Me_2NH} \underset{\text{III}}{Me_2NCOCH(Me)N(CH_2CONMe_2)_2} \xrightarrow{\text{diborane}} \underset{S\text{-tan}}{Me_2NCH_2CH(Me)N(CH_2CH_2NMe_2)_2}$$

Alaninediacetic Acid (I). This was prepared by the method of Koine et al.[12]

Tris(*p*-nitrophenyl ester) (II). Solid *p*-nitrophenol, $p\text{-}NO_2C_6H_4OH$ (36.5 g, 263 mmol), was added to a warm solution (ca. 50 °C) of I (15.4 g, 75 mmol) in 60 cm^3 of dry dimethylformamide, and the resulting solution was chilled below 5 °C with ice–salt mixture. A mixture of dicyclohexylcarbodiimide, $C_6H_{11}NCNC_6H_{11}$ (DCC) (51.6 g, 250 mmol), and dry dimethylformamide (10 cm^3) in limited amount was added with stirring, keeping the reaction mixture below 5 °C. After the addition of DCC, the slurry was left in a refrigerator overnight, followed by being warmed at 30 °C for 24 h. The solid was filtered off and was washed with acetonitrile repeatedly. Excess DCC was converted to solid urea, $C_6H_{11}NHCONHC_6H_{11}$, by adding glacial acetic acid (2 cm^3). Evaporation of the solvents by a rotary vacuum evaporator gave the ester, II, as a liquid.

Tris(dimethylamide) (III). The crude ester was converted to the amide, III, by a reaction with dimethylamine in methanol. The amide was purified by adsorbing in a column of SP-Sephadex C-25 (H^+ form, bed volume 700 cm^3) and by eluting with aqueous ammonia (3 M), followed by passing through a column of QAE-Sephadex A-25 (OH^- form, bed volume 50 cm^3). The colorless solution and the washings were combined and evaporated to dryness to give an oily residue, which was dissolved in diethyl ether and dried with anhydrous sodium sulfate. After removal of the ether, III was obtained as a viscous liquid, yield 16.0 g (75%). ^{13}C NMR (H_2O, Me_4Si as an external standard): δ 12.98 (1 C), 36.84 (3 C), 38.06 (3 C), 53.97 (2 C), 56.97 (1 C), 173.11 (2 C), 175.63 (1 C).

Reduction of III. Into a chilled solution of diborane in tetrahydrofuran (350 cm^3 of 1.34 M B_2H_6)[13] was added 34.9 g (122 mmol) of III in 100 cm^3 of tetrahydrofuran slowly with stirring under nitrogen. Then, the mixture was refluxed for 1 h. To the chilled reaction mixture was added 70 cm^3 of a 2:1 mixture of tetrahydrofuran and water, and subsequently, 73 cm^3 of 6 M HCl was added in small portions. The tetrahydrofuran was removed by distillation. The slurry was filtered, and the filtrate and washings were combined and diluted to 10 dm^3. Half of the solution was passed through a column of SP-Sephadex C-25 (H^+ form, 5 cm in diameter and 36 cm in length). After the column was washed with water, the adsorbed amine was eluted with 1 dm^3 of 0.25 M NaOH, followed by 1 dm^3 of water. The amine in the eluate was detected by a drop of a solution, which contained cobalt(II) chloride in 0.02 M and pyridinium chloride, $C_5H_5N\cdot HCl$, in 1 M. The eluate was acidified with hydrochloric acid and then was concentrated by a rotary evaporator. The free amine was obtained as a colorless oil from the resulting slurry by treating with a concentrated solution of sodium hydroxide and by a subsequent extraction with diethyl ether. Another half of the solution was treated in the same way; yield of the crude amine 27.6 g (92%). ^{13}C NMR (H_2O, Me_4Si as an external standard): δ 15.05 (1 C), 45.81 (4 C), 46.38 (2 C), 49.38 (2 C), 55.14 (1 C), 58.43 (2 C), 63.46 (1 C).

Purification of the Amine. The optical purity of the amine was improved by repeated recrystallization of its complex. $[Cu(NH_3)(S\text{-tan})](ClO_4)_2$ was chosen as the complex because of its moderate solubility in water.[14] It was prepared by mixing 10.2 g (41.7 mmol) of *S*-tan, 45

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cm^3 of 1 M Cu(ClO$_4$)$_2$, 10 cm^3 of 1 M NH$_4$ClO$_4$, and 5 cm^3 of 25% aqueous ammonia. After the mixture stood in a refrigerator for more than 3 h, the precipitate was filtered through a sintered-glass filter, washed with a chilled solution of 0.3 M NH$_4$ClO$_4$, which contained a small amount of ammonia, and then washed with ethanol and water; yield 18.6 g (85%).

The crude complex was recrystallized by dissolving it in 200 cm^3 of warm 0.5 M HClO$_4$ followed by the addition of 8 cm^3 of 25% ammonia. Recrystallization was repeated five times, until the optical rotation of the mother liquor was the same as that of the purified crystals in water containing NH$_3$ and NH$_4$ClO$_4$. The molar rotation of the final crystals in nitromethane was found to be +459° g^{-1} cm^3 dm^{-1} at 546 nm and 303 K.[15] The final crystals, which amounted to 9.0 g, were dissolved in a warm solution of tartaric acid (7.73 g in 100 cm^3 of water). The solution was diluted with 2 dm^3 of water and then passed through a column of SP-Sephadex C-25 (Na$^+$ form, 3 cm in diameter and 40 cm in length). The column was washed with water and then with a solution of 6 g of sodium tartrate and 0.6 g of tartaric acid in 2 dm^3 of water, followed by washing with 0.01 M Na$_2$H$_2$EDTA (sodium ethylenediaminetetraacetate). The column was finally washed with water and was treated in a similar manner to that described in the preparation of *S*-tan.

Preparation of the Complexes. [M(CH$_3$CN)(*S*-tan)](ClO$_4$)$_2$. An equimolar mixture of *S*-tan and metal perchlorate in water was evaporated to dryness on a rotatory evaporator. The residue was treated with a minimum amount of acetonitrile, and the resulting solution was filtered through a sintered-glass filter and washed with acetonitrile. The complex was crystallized by the addition of ethanol to the combined filtrate and washings. It was washed with ethanol and ether and dried over phosphorus pentoxide, P$_4$O$_{10}$; yield 94–96%. These complexes are unstable in open air to give aqua complexes especially in moist atmosphere.

[M(*S*-tan)(H$_2$O)](ClO$_4$)$_2$. Since the aqua complexes were difficult to crystallitze out from aqueous solutions,[16] they were obtained after the acetonitrile complexes stood for more than 3 days over water at ca. 50 °C. These crude crystals were used as the starting materials for the preparation of other complexes. Pure aqua complexes were obtained by dissolving the crude complexes in a minimum amount of hot methanol and letting the solution stand in a refrigerator for more than 2 days.

[MX(*S*-tan)]ClO$_4$ (X = Cl$^-$, Br$^-$, I$^-$, NCS$^-$). These were prepared by the addition of LiX or NaX in ethanol to hot methanol solutions of the aqua complexes and recrystallized by dissolving them in a minimum amount of hot acetonitrile followed by subsequent addition of ethanol; yield 61–69% (X = Cl$^-$), 83–91% (X = Br$^-$), 81–92% (X = I$^-$), 68–78% (X = NCS$^-$).

[M(NH$_3$)(*S*-tan)](ClO$_4$)$_2$. Nickel and cobalt complexes were prepared from the aqua complexes and 25% ammonia and recrystallized in a similar manner to that of the copper complex; yield 94–97%.

[M$_2$(OH)(*S*-tan)$_2$](ClO$_4$)$_3$·*n*H$_2$O (*n* = 1 for Cu, *n* = 1.5 for Ni and Co). These complexes were prepared under an atmosphere free from carbon dioxide. The crude complex was obtained by concentrating a mixture of a methanol solution of the corresponding aqua complex and an aqueous solution of 5 M sodium hydroxide with a molar ratio of 2:1. The residue was recrystallized from a minimum amount of hot ethanol and washed with 1:1 mixture of ethanol and ether; yield 34–50%.

[M$_2$(CN)(*S*-tan)$_2$](ClO$_4$)$_3$. To a solution of the aqua complex, [M(*S*-tan)(H$_2$O)](ClO$_4$)$_2$ (1.0 mmol in 5 cm^3 of methanol), was added 24 mg (0.49 mmol) of sodium cyanide, NaCN, in 10 cm^3 of ethanol. The precipitate that formed was recrystallized from boiling water. Needlelike crystals that separated from the solution after being allowed to cool to room temperature were washed with hot methanol; yield 55–73%. In the case of the cobalt complex, some undefined crystals were obtained by this purification procedure. Thus, the crude complex was recrystallized from a hot mixture of 20 cm^3 of acetonitrile and 5 cm^3 of ethanol; yield 34%.

[Cu(CN)(*S*-tan)]ClO$_4$. A mixture of 0.52 g (1.0 mmol) of the aqua complex, [Cu(*S*-tan)(H$_2$O)](ClO$_4$)$_2$, in 5 cm^3 of methanol and 0.055 g (1.1 mmol) of NaCN in 10 cm^3 of methanol was evaporated to dryness. The residue was extracted with nitromethane and filtered off. To the filtered nitromethane solution was added dry diethyl ether until the solution became turbid. After 24 h, the crystals that separated were collected on a sintered-glass filter and washed with a 1:1 mixture of diethyl ether and ethanol and then with diethyl ether; yield 0.32 g (74%).

Physical Measurements. Electronic absorption spectra were recorded on a Shimadzu MPS-50L spectrophotometer. Diffuse reflectance spectra were also obtained on the spectrometer equipped with reflectance attachments. Infrared spectra were recorded on a Hitachi EPI-G3 spectrophotometer. Each sample was prepared as a Nujol mull. Circular dichroism spectra were recorded on a Jasco J-40 C spectropolarimeter in the range of 10 000–30 000 cm^{-1}. Room-temperature magnetic moments were measured by the Gouy method. Electronic conductivities of some complexes were measured by a Yanaco MY-7 conductivity outfit.

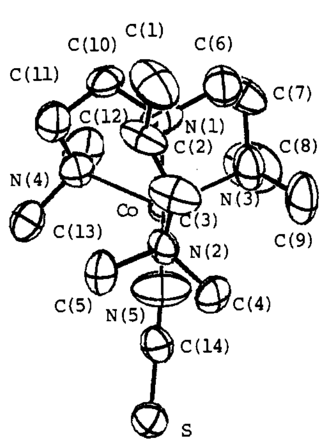

Figure 1. ORTEP[25] drawing of [Co(NCS)(*S*-tan)]$^+$.

X-ray Structure Determination. The crystal data are as follows: C$_{14}$H$_{32}$ClCoN$_5$O$_4$S, fw = 460.9, orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), a = 12.800 (6) Å, b = 17.530 (11) Å, c = 9.630 (5) Å, V = 2161 (2) Å^3, d(obsd) = 1.41 g cm^{-3} (by floatation in a mixture of carbon tetrachloride and *n*-hexane), d(calcd) = 1.42 g cm^{-3} (Z = 4), F(000) = 1548; monochromated Mo Kα radiation (λ = 0.7107 Å, μ = 10.7 cm^{-1}); specimen size 0.4 × 0.4 × 0.3 mm^3.

The intensities were measured on a Rigaku AFC-5 four-circle diffractometer in conventional θ–2θ scan mode. Data were corrected for Lorentz and polarization effects but not for absorption (μ = 1.07 mm^{-1}) and extinction. A unique data set with $2\theta_{\max}$ = 60° yielded 3568 independent reflections, 2187 of these with $|F| \geq 3\sigma(|F|)$ considered "observed" and used in the solution and refinement by the heavy-atom method. Refinement was carried out by the block-diagonal least-squares method. Thermal parameters used were anisotropic, except for B_H (isotropic). A function, $\sum w(|F_o| - |F_c|)^2$ (w = 1.0 for $|F_o| < 70.0$ and w = 0.5 for $|F_o| \geq 70.0$) was minimized. Residuals (R, R_w) were 0.094 and 0.118, respectively. Two peaks (0.7–0.9 e Å^{-3}) remain around the cobalt atom (1.0–1.1 Å away from the cobalt atom) in the final difference Fourier map. They are almost on the equatorial N(2)–N(3)–N(4) plane and between the N(2) and N(3) and the N(2) and N(4) atoms, alternatively. Excepting these peaks, $\Delta\rho_{\max}$ = 0.6 e Å^{-3}. Neutral-atom scattering factors were used; all atoms except H were corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[17] When the absolute configuration of the C(2) atom was assumed to be *S*, the *R* factor dropped to 0.0938, while the *R* configuration gave the *R* factor of 0.0944. Thus, the *R* configuration was rejected. Computations were carried out with use of the UNICS III program system[18] on a FACOM M-160F computer at the Computer Center of Josai University. The atom-numbering system within the complex cation is shown in Figure 1 by an ORTEP drawing,[19] hydrogen atoms being numbered according to the parent carbon atoms with suffix 1–3. The unit cell contents projected down the c axis are shown in Figure 2.

Results and Discussion

Preparation and Properties of *S*-tan and Its Complexes. At an earlier stage of this work, *S*-tan was prepared by the reduction of the amide, III, with LiAlH$_4$.[5] However, the yield of *S*-tan was very poor (ca. 45%), because of the formation of some byproducts, amino alcohols. The yield was drastically improved when diborane was used as a reducing agent. Diborane was reported to be a useful reagent for the reduction of tertiary amides.[20]

All the present complexes were obtained as perchlorates. Table I shows their analytical values and some of their properties. In contrast with [MX(Me$_6$tren)]X,[7a] which is moisture sensitive, the present complexes, [MX(*S*-tan)]ClO$_4$, separated from their alcohol

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(15) If the final crystals were assumed to be optically pure, the optical purity of the first crude crystals was calculated to be 95%. This means that some racemization takes place in the course of the ligand synthesis.

(16) Instead of aqua complexe, [M(*S*-tan)(H$_2$O)](ClO$_4$)$_2$, hemihydroxo complexes, [M$_2$(OH)(*S*-tan)$_2$](ClO$_4$)$_3$·*n*H$_2$O, were sometimes obtained from aqueous solutions.

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Table I. Analytical Data and Some Properties of $[MX(S\text{-tan})](ClO_4)_n$

			elemental anal./%					
M	X		C	H	N	M	μ_{eff}/μ_B (*T*/K)	Λ^a/cm^2 Ω^{-1} M^{-1}
Cu	CN^-	found	38.67	7.69	16.34	14.65	1.85 (299)	94
		calcd	38.80	7.44	16.16	14.66		
	$^1/_2$ CN^-	found	34.45	6.89	13.61	13.49	1.73 (301)	148
		calcd	34.49	6.86	13.41	13.52		
	NH_3	found	29.76	6.68	13.33	12.16	1.89 (293)	193
		calcd	29.80	6.73	13.37	12.13		
	CH_3CN	found	32.80	6.41	12.73	11.63	1.91 (296)	202
		calcd	32.88	6.44	12.78	11.60		
	NCS^-	found	35.98	6.92	14.94	13.66	1.88 (295)	93
		calcd	36.12	6.93	15.04	13.65		
	H_2O	found	29.50	6.62	10.67	12.22	1.89 (293)	201
		calcd	29.75	6.53	10.67	12.11		
	$^1/_2$ OH^- [b]	found	32.75	6.98	11.64	13.38	1.92 (297)	151
		calcd	32.90	7.11	11.80	13.39		
	Cl^-	found	35.13	7.49	12.68	14.25	1.86 (296)	95
		calcd	35.26	7.28	12.65	14.35		
	Br^-	found	32.28	6.56	11.59	13.05	1.86 (297)	95
		calcd	32.04	6.62	11.50	13.04		
	I^-	found	29.24	5.95	10.61	11.89	1.85 (297)	96
		calcd	29.22	6.04	10.49	11.89		
Ni	$^1/_2$ CN^-	found	34.60	6.81	13.74	12.60	3.28 (298)	146
		calcd	34.85	6.93	13.55	12.62		
	NH_3	found	30.00	6.56	13.47	11.33	3.51 (297)	196
		calcd	30.08	6.80	13.49	11.31		
	CH_3CN	found	32.82	6.05	12.68	10.82	3.44 (294)	202
		calcd	33.17	6.50	12.90	10.81		
	NCS^-	found	36.14	7.07	14.95	12.76	3.33 (297)	93
		calcd	36.50	7.00	15.20	12.74		
	H_2O	found	29.72	6.41	10.73	11.30	3.41 (292)	201
		calcd	30.03	6.59	10.77	11.29		
	$^1/_2$ OH^- [c]	found	32.92	7.12	11.82	12.40	3.44 (298)	151
		calcd	32.92	7.22	11.81	12.37		
	Cl^-	found	35.50	7.07	12.71	13.24	3.42 (289)	95
		calcd	35.65	7.36	12.79	13.40		
	Br^-	found	32.23	6.63	11.54	12.14	3.46 (297)	95
		calcd	32.36	6.68	11.61	12.17		
	I^-	found	29.76	6.11	10.91	11.07	3.46 (296)	96
		calcd	29.49	6.09	10.58	11.09		
Co	$^1/_2$ CN^-	found	35.19	6.97	14.27	12.46	4.34 (298)	148
		calcd	34.83	6.93	13.54	12.66		
	NH_3	found	30.39	7.21	13.45	11.33	4.45 (297)	195
		calcd	30.07	6.79	13.49	11.35		
	CH_3CN	found	32.88	6.45	12.67	10.86	4.47 (297)	201
		calcd	33.16	6.49	12.89	10.85		
	NCS^-	found	36.28	7.01	15.12	12.77	4.45 (295)	93
		calcd	36.49	7.00	15.20	12.79		
	H_2O	found	29.92	6.54	10.76	11.40	4.44 (294)	201
		calcd	30.01	6.59	10.77	11.33		
	$^1/_2$ OH^- [c]	found	32.80	7.19	11.63	12.38	4.49 (297)	150
		calcd	32.90	7.22	11.81	12.42		
	Cl^-	found	35.52	7.88	12.63	13.33	4.44 (297)	95
		calcd	35.63	7.36	12.78	13.45		
	Br^-	found	32.35	6.42	11.62	12.25	4.49 (296)	95
		calcd	32.35	6.68	11.61	12.21		
	I^-	found	29.45	5.95	10.57	11.12	4.47 (296)	95
		calcd	29.48	6.09	10.58	11.13		

[a] Molar conductance for 10^{-3} M nitromethane solution at 25.0 °C. Reference values: $(C_4H_9)_4NBr$, 91; $(C_4H_9)_4NI$, 97.
[b] $Cu_2(OH)(S\text{-tan})_2(ClO_4)_3 \cdot H_2O$. [c] $M_2(OH)(S\text{-tan})_2(ClO_4)_3 \cdot 1.5H_2O$.

solutions and could be handled in open air. Some of the complexes were found to crystallize even from their aqueous solutions. These were cases for the ammine, isothiocyanato, chloro, bromo, and iodo complexes.

The cyano complexes were obtained as two kinds of complexes: $[M_2(CN)(S\text{-tan})_2](ClO_4)_3$ and $[M(CN)(S\text{-tan})]ClO_4$. All three metal ions formed the former complex, but only the copper ion formed the latter. The products of the other two ions after the same treatment as the preparation of $[Cu(CN)(S\text{-tan})]ClO_4$ were deep green granules for nickel and grayish purple crystalline powder for cobalt. Anal. Calcd for $Ni_3(CN)_4(S\text{-tan})_2(ClO_4)_2 \cdot 2H_2O$: C, 35.89; H, 6.83; N, 16.74; Ni, 17.54. Found: C, 36.17; H, 6.62; N, 16.80; Ni, 17.30. Anal. Calcd for $Co_5(CN)_6(S\text{-tan})_4(ClO_4)_5 \cdot H_2O$: C, 35.84; H, 6.74; N, 15.85; Co, 15.16. Found: C, 35.17; H, 6.65; N, 15.97; Co, 14.86. These must be polynuclear complexes with bridging cyanide groups, but their properties were not investigated further.

Coordination Geometry in the Solid State. Table II shows the position of the peaks of the diffuse reflectance spectra of the *S*-tan complexes. Since the complexes, $[MX(S\text{-tan})]ClO_4$ ($X = Cl^-$, Br^-, I^-, NCS^-), exhibit essentially the same diffuse reflectance spectra as those of the corresponding Me_6tren complexes, $[MX(Me_6tren)]X$,[7] the trigonal-bipyramidal structure[8,9,21,22] is assigned to the present *S*-tan complexes. A single-crystal structure de-

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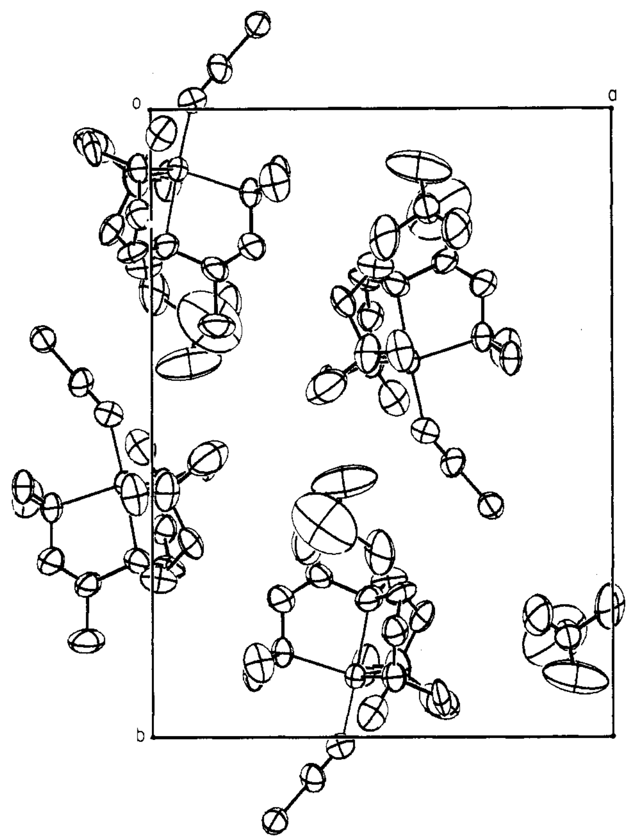

Figure 2. Packing geometry viewed down the *c* axis.

termination of [Co(NCS)(*S*-tan)]ClO_4 is consistent with this prediction (vide post).

Each hemicyano complex should be composed of the dimer with a bridging cyanide group, since each metal ion has a trigonal-bipyramidal chromophore and no signs of perchlorate coordination have been observed in the IR spectra of these three complexes. The IR absorption due to the stretching vibration of the cyanide ion also supports the presence of a cyanide-bridged structure; i.e., ν_{CN} of $[Cu_2(CN)(S\text{-tan})_2](ClO_4)_3$ at 2152 cm^{-1} is very close to that of $[Cu_2(CN)(tren)_2](PF_6)_3$ at 2150 cm^{-1}.[23] The magnetic moments of the three hemicyano complexes also seem to reflect a bridged structure; i.e., they possess somewhat subnormal moments compared to the other *S*-tan complexes, as Table I shows. The μ_{eff} value of the copper complex, 1.73 μ_B at 301 K, is close to that of $[Cu_2(CN)(tren)_2](PF_6)_3$, ca. 1.72 μ_B at 300 K.[23,24] Stuart models show that there exists no severe repulsion between two *S*-tan molecules in the cyanide-bridged dimer.

On the other hand, a similar dimer structure with a hydroxide bridge is impossible for the hemihydroxo complexes, $M_2(OH)(S\text{-tan})_2(ClO_4)_3\cdot nH_2O$. A very crowded dimer would result if two metal ions were connected by only one atom, oxygen in this case. One of the most probable structures is a hydrogen-bonded dimer of $[M(OH)(S\text{-tan})]^+$ and $[M(S\text{-tan})(H_2O)]^{2+}$. The presumed structure is consistent with the facts that the hemihydroxo complexes contain at least one molecule of water per two metal ions and that they show normal magnetic moments, in contrast to the subnormal magnetic moments of the hemicyano complexes.

Crystal Structure of [Co(NCS)(*S*-tan)]ClO_4. The structure of the complex cation is essentially the same as that of the corresponding Me_6tren complex, [Ni(NCS)(Me_6tren)]SCN·H_2O.[10] The cobalt ion is surrounded by five nitrogen atoms in approximately a trigonal-bipyramidal geometry. All the chelate rings were found to take δ conformation, which was quite reasonable, since the C(1) atom should be in an equatorial position of the chelate ring.

Table II. Diffuse Reflectance Spectra of [MX(*S*-tan)]$(ClO_4)_n$[a]

M = Cu

X	excited state (ground state $^2A_1'$)		X	excited state (ground state $^2A_1'$)	
	$^2E'$	$^2E''$		$^2E'$	$^2E''$
CN^-	13.0	16.5 sh	H_2O	10.6	15 sh
$^1/_2$ CN^-	12.0	16 sh	$^1/_2$	11.0	14.5 sh
NH_3	11.8	15.5 sh	Cl^-	10.4	13.1
CH_3CN	11.5	15.5 sh	Br^-	10.0	13.0
NCS^-	11.4	14.5 sh	I^-	9.6	12.9

M = Ni

X	excited state (ground state $^3E'$)				
	$^3E''$	$^3A_1''$, $^3A_2''$	$^3A_2'$	$^3E''$	$^3A_2'$
$^1/_2$ CN^-	8.3	13.1	16.4	22 sh	25.0
NH_3	7.8	13.0	15.7	21.5 sh	24.9
CH_3CN	8.2	13.0	15.9	22 sh	24.9
NCS^-	7.5	12.4	15.5	21.0 sh	24.3
H_2O	7.5	12 sh	15.0	21 sh	24.2
$^1/_2$ OH^-	6.9	11.4	15.2	21.0 sh	24.4
Cl^-	7.0	10.6	14.6	20.0 sh	23.2
Br^-	7.1	10.4	14.1	19.5 sh	22.7
I^-	7.1	10.1	13.6	19.0 sh	22.1

M = Co

X	excited state (ground state $^4A_2'$)			
	$^4E''$	$^4E'$	$^4A_2'$	$^4E''$
$^1/_2$ CN^-	6.0 sh	15.0 sh	17.2	20.4, 21.1 sh
NH_3	5.8	13.4	16.8	20.7, 21.5 sh
CH_3CN	5.7	13.3	17.4	20.4, 21.3 sh
NCS^-	5.6 sh	13.3	15.5 sh, 16.3	20.4, 21.3 sh
H_2O	5.7 sh	13.1	16.9	20 sh, 20.4, 21.3 sh
$^1/_2$ OH^-	5.8	13.2	15.4, 16.1 sh	20.8, 22.2 sh
Cl^-	5.6	12.5	15.6 sh, 16.1	19 sh, 20.0, 21 sh
Br^-	5.6	12.3	15.5 sh, 16.2	19.0, 19.6, 20.6 sh
I^-	5.4 sh	12.1	15.4 sh, 16.2	18.3, 19 sh, 20 sh

[a] The peaks are assigned on the basis of D_{3h} symmetry.[20]

Table III. Atomic Parameters[a] for [Co(NCS)(*S*-tan)]ClO_4

atom	*x*	*y*	*z*	$B_{eq}/Å^2$
Co	595 (1)	963 (1)	2597 (2)	3.32 (0.04)
Cl	4013 (3)	−3398 (2)	2518 (7)	5.76 (0.11)
S	2351 (3)	−1328 (2)	2620 (5)	4.63 (0.10)
N(1)	297 (9)	2192 (6)	2431 (20)	5.33 (0.37)
N(2)	2180 (8)	1339 (6)	2599 (14)	4.07 (0.28)
N(3)	−310 (10)	1101 (10)	4430 (14)	5.36 (0.41)
N(4)	−241 (10)	942 (8)	671 (13)	4.66 (0.35)
N(5)	936 (11)	−141 (7)	2688 (26)	7.65 (0.57)
C(1)	1408 (18)	3446 (10)	2162 (25)	7.34 (0.68)
C(2)	1363 (13)	2570 (9)	2030 (21)	5.76 (0.53)
C(3)	2196 (13)	2185 (10)	2753 (26)	6.79 (0.64)
C(4)	2800 (11)	1012 (11)	3738 (16)	4.84 (0.44)
C(5)	2701 (15)	1147 (13)	1290 (16)	5.91 (0.57)
C(6)	−119 (18)	2486 (10)	3651 (20)	6.17 (0.57)
C(7)	−843 (13)	1891 (12)	4221 (22)	6.31 (0.58)
C(8)	−1167 (24)	575 (15)	4523 (31)	10.08 (1.00)
C(9)	372 (14)	1119 (13)	5652 (18)	6.29 (0.58)
C(10)	−392 (14)	2276 (9)	1113 (19)	5.08 (0.48)
C(11)	−250 (13)	1680 (11)	45 (18)	5.11 (0.48)
C(12)	−1254 (11)	603 (12)	800 (20)	5.93 (0.55)
C(13)	235 (15)	391 (13)	−348 (19)	6.69 (0.61)
C(14)	1529 (11)	−647 (8)	2709 (16)	4.13 (0.36)
O(1)	3364 (12)	−3061 (11)	3421 (22)	11.12 (0.70)
O(2)	4932 (11)	−2943 (11)	2499 (31)	12.33 (0.69)
O(3)	3714 (28)	−3389 (18)	1196 (23)	20.16 (1.49)
O(4)	4168 (25)	−4064 (10)	2980 (29)	19.26 (1.31)

[a] Positional parameters are multiplied by 10^4. Thermal parameters are given by the equivalent temperature factors, $B_{eq} = {}^4/_3\Sigma_i\Sigma_jB_{ij}a_ia_j$.

In the Co–N bond distance between the cobalt atom and the *S*-tan moiety, the axial Co–N distance is longer than the equatorial

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(23) Bieksza, D. S.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 924.

(24) The μ_{eff} value was estimated from the curve that was given in ref 23.

Table IV. Bond Lengths (A) and Bond Angles (deg)

	Lengths		
Co-N(1)	2.20 (2)	N(4)-C(11)	1.43 (2)
Co-N(2)	2.13 (1)	N(2)-C(4)	1.47 (2)
Co-N(3)	2.13 (2)	N(2)-C(5)	1.47 (3)
Co-N(4)	2.14 (1)	N(3)-C(8)	1.44 (4)
Co-N(5)	1.99 (3)	N(3)-C(9)	1.47 (3)
N(1)-C(2)	1.57 (3)	N(4)-C(12)	1.43 (3)
N(1)-C(6)	1.40 (3)	N(4)-C(13)	1.51 (3)
N(1)-C(10)	1.55 (3)	S-C(14)	1.59 (2)
C(1)-C(2)	1.54 (3)	N(5)-C(14)	1.17 (3)
C(2)-C(3)	1.44 (3)	Cl-O(1)	1.34 (2)
C(6)-C(7)	1.50 (3)	Cl-O(2)	1.42 (3)
C(10)-C(11)	1.48 (3)	Cl-O(3)	1.33 (4)
N(2)-C(3)	1.49 (3)	Cl-O(4)	1.27 (3)
N(3)-C(7)	1.56 (3)		
	Angles		
N(1)-Co-N(2)	82.1 (6)	C(6)-N(1)-C(10)	116 (2)
N(1)-Co-N(3)	81.6 (7)	N(1)-C(2)-C(3)	109 (2)
N(1)-Co-N(4)	82.3 (6)	N(1)-C(6)-C(7)	107 (2)
N(2)-Co-N(3)	118.9 (6)	N(1)-C(10)-C(11)	116 (2)
N(2)-Co-N(4)	118.8 (5)	N(2)-C(3)-C(2)	114 (2)
N(3)-Co-N(4)	116.7 (6)	N(3)-C(7)-C(6)	113 (2)
N(2)-Co-N(5)	95.3 (8)	N(4)-C(11)-C(10)	110 (2)
N(3)-Co-N(5)	101.2 (9)	C(3)-N(2)-C(4)	108 (2)
N(4)-Co-N(5)	97.5 (8)	C(3)-N(2)-C(5)	108 (2)
Co-N(1)-C(2)	106 (1)	C(7)-N(3)-C(8)	104 (2)
Co-N(1)-C(6)	112 (1)	C(7)-N(3)-C(9)	110 (2)
Co-N(1)-C(10)	105 (1)	C(11)-N(4)-C(12)	114 (2)
Co-N(2)-C(3)	109 (1)	C(11)-N(4)-C(13)	108 (1)
Co-N(3)-C(7)	103 (1)	C(4)-N(2)-C(5)	108 (1)
Co-N(4)-C(11)	111 (1)	C(8)-N(3)-C(9)	115 (2)
Co-N(2)-C(4)	113 (1)	C(12)-N(4)-C(13)	99 (1)
Co-N(2)-C(5)	111 (1)	N(1)-C(2)-C(1)	116 (2)
Co-N(3)-C(8)	113 (2)	C(1)-C(2)-C(3)	114 (2)
Co-N(3)-C(9)	110 (1)	O(1)-Cl-O(2)	106 (2)
Co-N(4)-C(12)	113 (1)	O(1)-Cl-O(3)	116 (2)
Co-N(4)-C(13)	112 (1)	O(1)-Cl-O(4)	106 (2)
Co-N(5)-C(14)	152 (2)	O(2)-Cl-O(3)	103 (2)
S-C(14)-N(5)	176 (2)	O(2)-Cl-O(4)	113 (2)
C(2)-N(1)-C(6)	113 (2)	O(3)-Cl-O(4)	113 (2)
C(2)-N(1)-C(10)	105 (2)		

Co–N distances by about 0.07 Å. This trend coincides with the previous study, although all these Co–N bonds are slightly longer than those in the previous one.[8]

The averaged value of the N–Co–N bond angle within the chelate rings is 82.0 (6)°, which is slightly larger than that of 81.1° found in $[\mathrm{CoBr(Me_6tren)}]\mathrm{Br}$[8] and slightly smaller than those of 84.7, 84.2, and 84.7° found in $[\mathrm{Ni(NCS)(Me_6tren)}]\mathrm{SCN{\cdot}H_2O}$,[10] $[\mathrm{NiBr(Me_6tren)}]\mathrm{Br}$,[9] and $[\mathrm{CuBr(Me_6tren)}]\mathrm{Br}$,[9] respectively. This causes the metal atom to lie 0.30 (1) Å below the equatorial plane of the three nitrogen atoms of the *S*-tan molecule. This trend was also observed in the $\mathrm{Me_6tren}$ complexes.[8-10]

The short Co–N(5) distance indicates the existence of π bonding between the metal and the NCS moiety. This short distance of Co–NCS bond seems to correlate with the fact that all the isothiocyanato complexes, $[\mathrm{M(NCS)}(S\text{-tan})]^+$ exhibit the absorption maxima of the electronic spectra at wavenumbers that are higher than or nearly equal to those of the aqua complexes, although the ligand field strength of the isothiocyanato ligand is weaker than that of water.[25] π bonding was also suggested between a cobalt ion and a bromide ion in $[\mathrm{CoBr(Me_6tren)}]\mathrm{Br}$.[8]

The N(1), Co, and N(5) atoms are almost in a line, and this is considered to be a principal axis of the cation. The axis is nearly parallel to *b* as is shown in Figure 2.

Behavior in Solution. All the present complexes were found to be soluble in nitromethane. The absorption spectra of most complexes in nitromethane correspond well to their diffuse reflectance spectra. These are the cases for the cyano, hemicyano, ammine, isothiocyanato, chloro, bromo, and iodo complexes. Exceptional are the aqua and hemihydroxo complexes. $[\mathrm{Co}(S\text{-tan})(\mathrm{H_2O})](\mathrm{ClO_4})_2$ shows a drastic color change from beige to purple when it is dissolved in nitromethane. This change was found to be due mainly to the enhanced intensity of the band at around 17 000 $\mathrm{cm^{-1}}$ and to the blue shift of that band. As Table I shows, the aqua complexes behave as 2:1 electrolytes in nitromethane; thus, coordination of a perchlorate ion in nitromethane can be excluded. Consequently, the color change may be ascribed to the displacement of a coordinated water molecule by a nitromethane molecule.

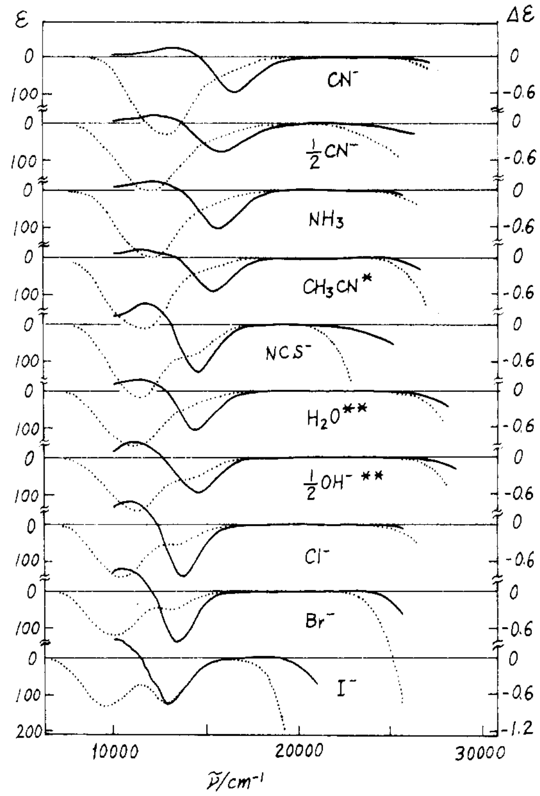

Figure 3. Absorption (···) and CD spectra (—) of $[\mathrm{CuX}(S\text{-tan})]^{n+}$ in nitromethane, acetonitrile (*), and water (**). The ordinate of the absorption spectra is taken inversely to the usual expression.

Although the aqua complexes of copper and nickel do not exhibit such a drastic color change on dissolution in nitromethane, they are expected to behave similarly to the cobalt complex. Therefore, spectral properties of all the aqua complexes should be investigated in aqueous solutions. However, there is an indication of ligand dissociation in an aqueous solution of the aquacobalt complex, the absorption spectrum of which in water is shown in Figure 5. At least three bands were observed in the region from 10 000 to 18 000 $\mathrm{cm^{-1}}$, in which two spin-allowed transitions are possible and all the other cobalt complexes exhibit two maxima.[22,26,27] The broad band at 15 000 $\mathrm{cm^{-1}}$ may be ascribed to the presence of a hydroxo complex in solution, since the band is absent in the solid spectrum of the aqua complex, and moreover, it appears more clearly in the aqueous solution spectra of the hemihydroxo complex, which is expected to dissociate into the aqua and the hydroxo complex in water. Therefore, it is plausible to conclude that the aqua complex dissociates partly in water to produce the hydroxo complex.

$$4[\mathrm{Co}(S\text{-tan})(\mathrm{H_2O})]^{2+} \rightarrow 3[\mathrm{Co(OH)}(S\text{-tan})]^{+} + S\text{-tan} + 3\mathrm{H}^{3+} + \mathrm{Co}^{2+} + \mathrm{H_2O}$$

Since it was not possible to find a more suitable solvent for the aqua and hemihydroxo complexes, the solution spectra were determined with water as solvent.

Chiroptical Properties. The CD spectra of the present complexes are shown in Figures 3–5, and the selection rules of

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(25) Shimura, Y.; Tsuchida, R. *Bull Chem. Soc. Jpn.* **1956**, *29*, 311.

(26) Wood, J. S. *Prog. Inorg. Chem.* **1972**, *16*, 227–486.

(27) Bertini, I.; Gatteschi, D.; Scozzafava, A. *Inorg. Chem.* **1975**, *14*, 812.

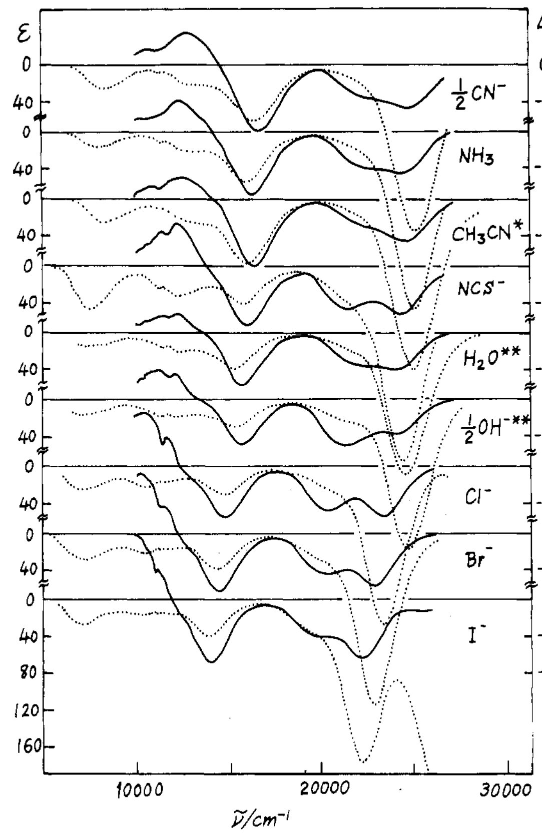

Figure 4. Absorption (···) and CD spectra (—) of [NiX(*S*-tan)]$^{n+}$ in nitromethane, acetonitrile (*), and water (**). The ordinate of the absorption spectra is taken inversely to the usual expression.

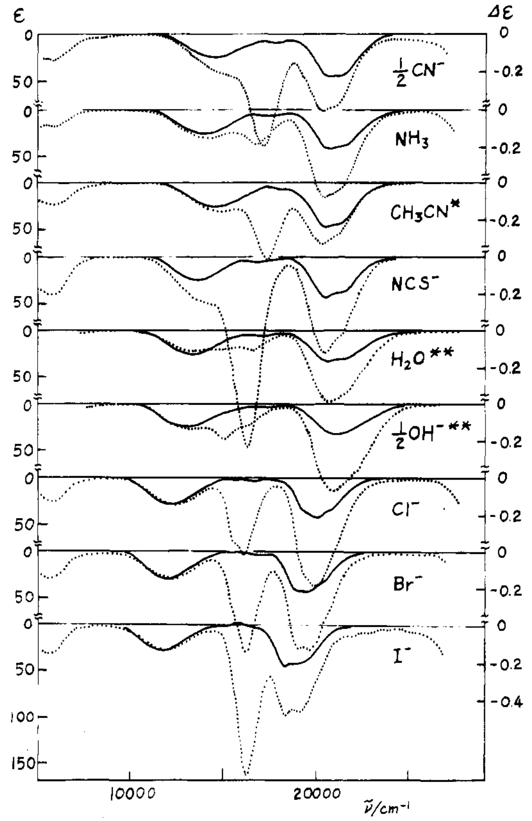

Figure 5. Absorption (···) and CD spectra (—) of [CoX(*S*-tan)]$^{n+}$ in nitromethane, acetonitrile (*), and water (**). The ordinate of the absorption spectra is taken inversely to the usual expression.

Table V. Selection Rules of Electronic (E) and Magnetic Dipole (M) Transitions under D_{3h} and C_{3v} Symmetries[a]

D_{3h}			C_{3v}		
transition	E	M	transition	E	M
Copper(II) Complex					
$^2A_1{}' \rightarrow {}^2E'$	⊥	×	$^2A_1 \rightarrow {}^2E$	⊥	⊥
$^2A_1{}' \rightarrow {}^2E''$	×	⊥	$^2A_1 \rightarrow {}^2E$	⊥	⊥
Nickel(II) Complex					
$^3E' \rightarrow {}^3E''(F)$	∥	⊥	$^3E \rightarrow {}^3E(F)$	⊥, ∥	⊥, ∥
$^3E' \rightarrow {}^3A_1{}''$	×	⊥	$^3E \rightarrow {}^3A_2(F)$	⊥	⊥
$^3E' \rightarrow {}^3A_2{}''$	×	⊥	$^3E \rightarrow {}^3A_1(F)$	⊥	⊥
$^3E' \rightarrow {}^3A_2{}'(F)$	⊥	×	$^3E \rightarrow {}^3A_2(F)$	⊥	⊥
$^3E' \rightarrow {}^3E''(P)$	∥	⊥	$^3E \rightarrow {}^3E(P)$	⊥, ∥	⊥, ∥
$^3E' \rightarrow {}^3A_2{}'(P)$	⊥	×	$^3E \rightarrow {}^3A_2(P)$	⊥	⊥
Cobalt(II) Complex					
$^4A_2{}' \rightarrow {}^4A_2{}''$	∥	×	$^4A_2 \rightarrow {}^4A_1(F)$	×	∥
$^4A_2{}' \rightarrow {}^4A_1{}''$	×	×	$^4A_2 \rightarrow {}^4A_2(F)$	∥	×
$^4A_2{}' \rightarrow {}^4E''(F)$	×	⊥	$^4A_2 \rightarrow {}^4E(F)$	⊥	⊥
$^4A_2{}' \rightarrow {}^4E'$	⊥	×	$^4A_2 \rightarrow {}^4E(F)$	⊥	⊥
$^4A_2{}' \rightarrow {}^4A_2{}'$	×	×	$^4A_2 \rightarrow {}^4A_2(P)$	∥	×
$^4A_2{}' \rightarrow {}^4E''(P)$	×	⊥	$^4A_2 \rightarrow {}^4E(P)$	⊥	⊥

[a] The marks ∥ and ⊥ denote a transition allowed parallel and perpendicular to the C_3 axis, respectively, and × denotes a transition forbidden in any direction.

magnetic dipole transitions are shown in Table V.

Two CD maxima were observed for all the copper complexes. The longer wavelength band with weak positive intensity is assigned to the $^2A_1 \rightarrow {}^2E'$ transition and the other negative band to the $^2A_1{}' \rightarrow {}^2E''$ transition under D_{3h} symmetry. The former is forbidden under D_{3h} symmetry but is allowed under C_{3v} symmetry; on the other hand, the latter is allowed under both D_{3h} and C_{3v} symmetries. There is clearly an inverse relation between the intensities of the CD bands and absorption bands. This is expected because, for the two transitions, selection rules concerning the magnetic dipole are exactly inverse to those concerning the electric dipole under D_{3h} symmetry, as Table V shows. This situation is quite similar to that found in trivalent cobalt complexes, which usually exhibit very weak CD peaks in the region of the second absorption band. This was ascribed to the effect that the CD spectra of cobalt(III) complexes are mainly governed by a selection rule under O_h symmetry, even if they actually belong to lower symmetry groups.[28] Although the selection rules under C_{3v} symmetry or even the real symmetry of C_1 must be applied to the present copper complexes, the rules under D_{3h} symmetry also seem to affect their CD and electronic spectra.

The ligand, *S*-tan, possesses a chiral carbon atom with the *S* configuration. Therefore, when it coordinates to a metal ion, its chelate rings must take a δ,δ,δ conformation. This is confirmed by a single-crystal structure determination of [Co(NCS)(*S*-tan)]ClO$_4$ (vide ante). Then, the CD maximum corresponding to the transition $^2A_1 \rightarrow {}^2E''$ should be negative according to the prediction of Mason.[4] This is in accord with the observed spectra.

Only [Cu$_2$(CN)(*S*-tan)$_2$](ClO$_4$)$_3$ in water was found to exhibit two negative CD bands in the region of the transition $^2A_1 \rightarrow {}^2E''$. The complex ion in nitromethane does not show this tendency of splitting. Therefore, the hemicyano complex seems to dissociate in water to give mainly the aqua and cyano complexes. This conclusion is supported by the fact that its aqueous CD spectrum can be reproduced from those of the cyano and aqua complexes in water, as Figure 6A shows.

The nickel complexes exhibit CD maxima corresponding to all the spin-allowed electronic transitions, as expected from the selection rules under C_{3v} symmetry. However, the intensities of some CD maxima seem to reflect the selection rules under D_{3h} symmetry, analogously to the $^2A_1 \rightarrow {}^2E''$ transition of the copper complexes. This is particularly pronounced in a CD maximum at 22 000–25 000 cm^{-1}. Although the corresponding absorption maximum has the highest intensity of all, the CD maximum has

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[28] Fujita, J.; Shimura, Y. In "Spectroscopy and Structure of Metal Chelate Compounds"; Nakamoto, K., McCarthy, P. J., Eds.; Wiley: New York, 1968; pp 156–215.

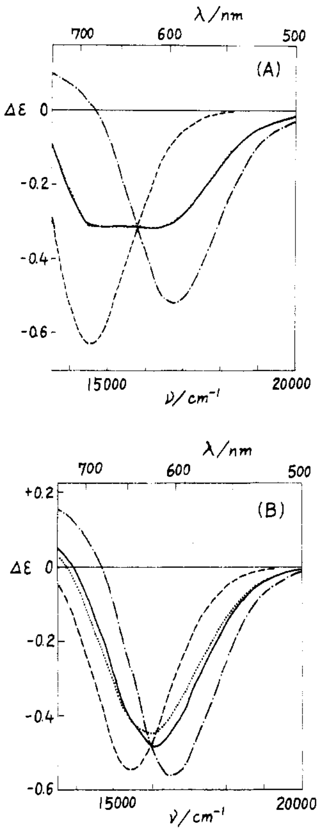

Figure 6. CD spectra of $[Cu_2(CN)(S\text{-tan})_2](ClO_4)_3$ (—), $[Cu(CN)(S\text{-tan})]ClO_4$ (–·–), and $[Cu(S\text{-tan})(H_2O)](ClO_4)_2$ (---) in (A) water and in (B) nitromethane. The dotted lines are the calculated curves for $^1/_2([Cu(CN)(S\text{-tan})]ClO_4 + [Cu(S\text{-tan})(H_2O)](ClO_4)_2)$.

the intensity of similar magnitude to the other maxima. Thus, the band at 22 000–25 000 cm^{-1} is assigned to the transition $^3E' \rightarrow {}^3A_2'$, which is magnetically forbidden under D_{3h} symmetry. Ciampolini et al., at an early stage of their studies,[7b] assigned the most intense absorption band at around 23 000 cm^{-1} observed for $[NiBr(Me_6tren)]Br$ to be the transition $^3E' \rightarrow {}^3E''$, but later they assigned it to be the transition $^3E' \rightarrow {}^3A_2'$ after the measurement of an absorption spectrum of a single crystal of $[Ni(NCS)(Me_6tren)]NCS\cdot H_2O$.[21] Present study confirms their later assignment.

In contrast to the copper and nickel complexes, the cobalt complexes do not show CD peaks corresponding to all spin-allowed transitions. Figure 5 shows the spectra of a series of cobalt complexes. The CD intensities at 16 000–17 000 cm^{-1} are very weak or negligible, although the electronic absorption peaks are fairly strong. These absorption bands are assigned to the transition $^4A_2 \rightarrow {}^4A_2$, which is magnetically forbidden under both D_{3h} and C_{3v}. Of all the transitions expected for copper, nickel, and cobalt coplexes in the region of 10 000–27 000 cm^{-1}, this is the only transition that is magnetically forbidden under C_{3v} symmetry. The spectra of these complexes agree with the selection rules under C_{3v} symmetry.

The ammine and isothiocyanato complexes, which possess the $[MN_5]$ chromophore, might obey the selection rules under D_{3h} symmetry. This is not the case, however. Their CD spectra are quite similar to those of the other $[MXN_4]$-type complexes, although the ligand, X, varies from $^1/_2$ CN^- to I^-. Even for the ammine or isothiocyanato complexes, effective symmetry is lowered by the presence of the chelate rings and also by the distortion of the trigonal-bipyramidal structure; i.e., each metal ion lies out of a plane formed by three dimethylamino nitrogen atoms. The distortion was found not only in the present isothiocyanato complex but also in all Me_6tren complexes studied crystallographically.[8-11]

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Registry No. I, 29578-05-0; II, 95420-19-2; III, 95408-34-7; S-tan, 95420-20-5; $[Cu(NH_3)(S\text{-tan})](ClO_4)_2$, 78063-15-7; $[Cu(CN)(S\text{-tan})]ClO_4$, 95407-95-7; $[Cu_2(CN)(S\text{-tan})](ClO_4)_3$, 95420-17-0; $[Cu(CH_3CN)(S\text{-tan})](ClO_4)_2$, 95407-97-9; $[Cu(NCS)(S\text{-tan})]ClO_4$, 95407-99-1; $[Cu(H_2O)(S\text{-tan})](ClO_4)_2$, 95408-01-8; $Cu_2(OH)(S\text{-tan})_2(ClO_4)_3\cdot H_2O$, 95408-03-0; $[CuCl(S\text{-tan})]ClO_4$, 95408-05-2; $[CuBr(S\text{-tan})]ClO_4$, 78063-09-9; $[CuI(S\text{-tan})]ClO_4$, 95408-07-4; $[Ni_2(CN)(S\text{-tan})_2](ClO_4)_3$, 95408-09-6; $[Ni(NH_3)(S\text{-tan})](ClO_4)_2$, 78063-17-9; $[Ni(CH_3CN)(S\text{-tan})](ClO_4)_2$, 95408-11-0; $[Ni(NCS)(S\text{-tan})]ClO_4$, 95408-13-2; $[Ni(H_2O)(S\text{-tan})](ClO_4)_2$, 95420-18-1; $Ni_2(OH)(S\text{-tan})_2(ClO_4)_3\cdot H_2O$, 95408-16-5; $[NiCl(S\text{-tan})]ClO_4$, 95408-18-7; $[NiBr(S\text{-tan})]ClO_4$, 78063-11-3; $[NiI(S\text{-tan})]ClO_4$, 95408-20-1; $[Co_2(CN)(S\text{-tan})_2](ClO_4)_3$, 95408-22-3; $[Co(NH_3)(S\text{-tan})_2](ClO_4)_2$, 78063-19-1; $[Co(CH_3CN)(S\text{-tan})](ClO_4)_2$, 95408-24-5; $[Co(NCS)(S\text{-tan})]ClO_4$, 95408-26-7; $[Co(H_2O)(S\text{-tan})](ClO_4)_2$, 95408-28-9; $Co_2(OH)(S\text{-tan})_2(ClO_4)_3\cdot H_2O$, 95464-03-2; $[CoCl(S\text{-tan})_2]ClO_4$, 95408-31-4; $[CoBr(S\text{-tan})]ClO_4$, 78063-13-5; $[CoI(S\text{-tan})]ClO_4$, 95408-33-6.

Supplementary Material Available: Tables giving comparison of the cation ligand geometries of $[Co(NCS)(S\text{-tan})]ClO_4$ with $[CoBr(Me_6tren)]^+$, mean square displacement tensor of atoms, atomic parameters (hydrogen atoms), packing geometries, and structure factor amplitudes and Figure 7 giving the conformation of the chelate ring (20 pages). Ordering information is given on any current masthead page.