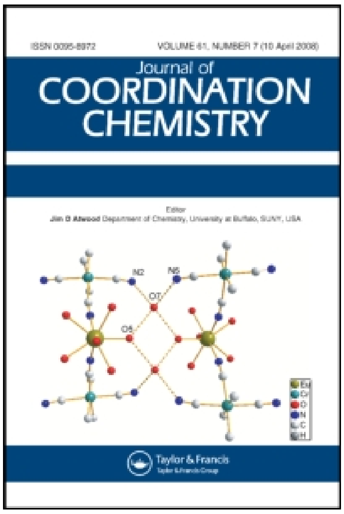

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CHIROPTICAL PROPERTIES OF FIVE-COORDINATE COMPLEXES OF NICKEL(II) AND COBALT(II) CONTAINING AN OPTICALLY ACTIVE LIGAND WITH NITROGEN AND PHOSPHORUS DONOR ATOMS

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CHIROPTICAL PROPERTIES OF FIVE-COORDINATE COMPLEXES OF NICKEL(II) AND COBALT(II) CONTAINING AN OPTICALLY ACTIVE LIGAND WITH NITROGEN AND PHOSPHORUS DONOR ATOMS

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A new tripodal ligand with an asymmetric carbon atom, $Ph_2PCH_2CH(Me)N(CH_2CH_2PPh_2)_2$ (S-mnp$_3$) was prepared using L-alanine as an optically active starting material; a series of its complexes, $[M(X)(S\text{-mnp}_3)]BPh_4$($M$ = Ni(II) and Co(II); X = NCS^-, Cl^-, Br^- and I^-) was prepared. Electronic spectra of these complexes indicated that their coordination geometries are essentially the same as those of corresponding complexes containing the tripodal ligand *tris* (diphenylphosphinoethyl) amine. Thus, all the present nickel complexes in solution exhibit electronic spectra typical of trigonal-bipyramidal complexes of diamagnetic configuration. CD spectra of these nickel complexes have been discussed on the basis of the selection rules for magnetic dipole transitions under C_{3v} symmetry. Cobalt(II) complexes are either high-spin or low-spin, depending on the nature of the unidentate ligand. The high-spin cobalt(II) complexes did not show CD spectra typical of trigonal-bipyramidal geometry.

KEYWORDS: five coordination, nickel(II), cobalt(II), circular dichroism, optical activity, aminophosphine.

INTRODUCTION

In 1985, one of the authors reported the chiroptical properties of five-coordinate complexes of copper(II), nickel(II), and cobalt (II) containing a chiral tripodal tetraamine, 2,4,8-trimethyl-5-(3-methyl-3-azabutyl)-2,5,8-triaza-4(-S)-nonane (S-tan).[1] All of these complexes showed electronic spectra typical of complexes with trigonal bipyramidal geometry; circular dichroism spectra reflected the selection rule for magnetic dipole transitions under C_{3v} symmetry, although the intensities of some CD bands reflected the selection rule under D_{3h} symmetry.

These results now lead to an investigation of chiral complexes with different electronic structure. Thus, preparation of a chiral tripodal ligand containing nitrogen and phosphorus as ligand atoms was sought and a chiral methyl derivative of *tris*(diphenylphosphinoethyl)amine (np$_3$)[2] was obtained. This paper describes the

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preparation and chiroptical properties of nickel(II) and cobalt(II) complexes containing a chiral ligand, 2-*S*-2-methyl-1,5-*bis*(diphenylphosphino)-3-(diphenylphosphinoethyl)-3-azapentane, *S*-mnp$_3$.

EXPERIMENTAL

Preparation of the Ligand

The lignad, *S*-mnp$_3$, was prepared as shown in Scheme 1.

$$
\begin{array}{lr}
L\text{-Alanine} & \\
\downarrow \ \mathrm{LiAlH_4} & \\
\mathrm{HOCH_2CH(Me)NH_2} & \mathrm{I} \\
\downarrow \ \mathrm{O(CH_2CH_2)}\ \text{(ethylene oxide)} & \\
\mathrm{HOCH_2CH(Me)N(CH_2CH_2OH)_2} & \mathrm{II} \\
\downarrow \ \mathrm{SOCl_2} & \\
\mathrm{ClCH_2CH(Me)N(CH_2CH_2Cl)_2} & \mathrm{III} \\
\downarrow \ \mathrm{NaPPh_2} & \\
\mathrm{Ph_2PCH_2CH(Me)N(CH_2CH_2PPh_2)_2} & S\text{-mnp}_3
\end{array}
$$

Scheme 1

S-Alaninol I

S-alaninol was prepared by the reduction of 50.0 g (0.561 mol) of *L*-alanine by 32.3 g (0.850 mol) of lithium aluminium hydride using tetrahydrofuran as a solvent according to the method of Vogl and Pohm.[3] Distillation of the product under reduced pressure gave 27.6 g (0.367 mol) of *S*-alaninol.

Methyl Derivative of Triethanolamine II

The alaninol was dissolved in water (27.4 g in 70 cm^3 of water) and chilled with an ice bath. Under diminished pressure, ethylene oxide was generated by adding an aqueous solution of sodium hydroxide (50 g in 120 cm^3 of water) to a hot solution of 97 g of 2-chloroethanol in 20 g of water, and was condensed in a round-bottomed flask. About 40 grams of the oxide was collected. The flask was connected with a tube to a round-bottomed flask, which contained the solution of *S*-alaninol. After the latter flask was filled with gaseous ethylene oxide, the system was sealed and the oxide was allowed to be absorbed in the *S*-alaninol solution at a temperature of 25–30°C. The flask containing the *S*-alaninol solution was shaken, occasionally, for about four hours. Elongated absorption of ethylene oxide produced indefinable product(s) and markedly lowered the yield. The reaction was followed by the detection of secondary amine, the disappearance of which was taken to be the end of the reaction. Copper sulfate and carbon disulfide were used to detect the secondary amine.[5] Evaporation of the reaction mixture gave the *tris*(alcohol) amine, II, as a colourless liquid. It was purified by converting to the hydrochloride, $HOCH_2CH(Me)N(CH_2CH_2OH)_2 \cdot HCl$. Yield, 56.8 g (78%). $[\alpha]_D = +64.5°$ (2% aqueous solution). Carbon-13 NMR of an alkaline solution (TMS as external standard): 9.26 (1C), 50.66 (2C), 56.19 (2C), 58.89 (2C), 62.07 (1C).

Methyl Derivative of Tris(chloroethyl)amine III

To a slurry of the hydrochloride of the alcoholamine, II, in benzene, 30% excess of thionyl chloride was added dropwise with stirring. After evolution of SO_2 and HCl ceased, the mixture was heated for an hour. Then, the reaction mixture was rotatory evaporated. Recrystallizing the residue from acetone gave the hydrochloride of III, $ClCH_2CH(Me)N(CH_2CH_2Cl)_2 \cdot HCl$. Carbon-13 NMR of a $CDCl_3$ solution (TMS as internal standard): 10.30 (1C), 36.69 (2C), 41.54 (1C), 51.38 (2C), 60.16 (1C).

Methyl Derivatives of Tris(diphenylethyl)amine, S-mnp$_3$

The hydrochloride, $ClCH_2CH(Me)N(CH_2CH_2Cl)_2 \cdot HCl$ (25.5 g, 0.1 mol) was converted to the free amine, III, by treating its aqueous solution with sodium carbonate. The liberated oil was extracted repeatedly with small amounts of diethyl ether and the combined extract was dried over anhydrous sodium sulfate. After evaporation of ether, III was obtained as a viscous liquid.

In an atmosphere of nitrogen, a solution of $NaPPh_2$ was prepared by adding 26.2 g (0.1 mol) of triphenylphosphine in small portions into a solution of 4.6 g (0.2 mol) of sodium metal in 200 cm^3 of liquid ammonia.[7] The deep blue solution changed to an orange-red slurry, into which 9.8 g (0.1 mol) of ammonium bromide was added in small portions. The free base, III, which was prepared as described above, was added to the resulting bright orange slurry, and the mixture was left to stand overnight at a room temperature. About 500 cm^3 of water was then added. The final product, *S*-mnp$_3$ was obtained as colourless, viscous oil. It was washed several times with ethanol and used without further purification.

Preparation of Metal Complexes

The ligand, *S*-mnp$_3$, gave pure metal complexes when it was used immediately after the synthesis. The ligand seemed to change gradually upon prolonged standing in air, since the aged ligand gave metal complexes of different colour with indefinite composition. Thus, the ligand was stored in an atmophere of nitrogen and washed several times with ethanol just before it was used for the preparation of the complexes. Since the complexes, especially those of nickel, were photo-sensitive, they were handled under a shaded light.

[M(X) (S-mnp$_3$)]BPh$_4$ (M = Co or Ni, and X = Cl or Br).

In an atmosphere of nitrogen, 10 cm^3 of a 0.05 M ethanol solution of cobalt(II) or nickel(II) halide was added to 40 cm^3 of a saturated ethanol solution of the ligand. To the resulting solution, sodium tetraphenylborate in ethanol was added. The precipitated solid was washed several times with ethanol. The crude nickel complex was recrystallized by dissolving it in acetone followed by addition of ethanol to the filtered solution. The cobalt(II) complex was recrystallized by dissolving it in 1,2-dichloroethane followed by addition of ethanol. *Anal.*: [Ni (Cl)(*S*-mnp$_3$)]BPh$_4$, calcd. for $C_{67}H_{64}NP_3ClBNi$: C, 74.43; H, 5.97; N, 1.30%. Found: C, 74.22; H, 5.84; N, 1.21%. [Ni(Br)(*S*-mnp$_3$)]BPh$_4$, calcd. for $C_{67}H_{64}NP_3BrBNi$: C, 71.50; H, 5.73; N, 1.24%. Found: C, 70.39; H, 5.58; N, 1.17%. [Co(Cl)(*S*-mnp$_3$)]BPh$_4$, calcd. for $C_{67}H_{64}NP_3ClBCo$: C, 74.42; H,5.97; N, 1.30%. Found: C, 73.35; H, 5.97; N, 1.30%. [Co(Br)(*S*-mnp$_3$)]BPh$_4$, calcd. for $C_{67}H_{64}NP_3BrBCo$: C, 71.48; H, 5.73; N, 1.24%. Found: C, 70.92; H, 5.60; N, 1.24%.

[M(X)(S-mnp$_3$)]BPh$_4$ (M = Co or Ni, and X = I or NCS)

To 1 cm^3 of a 0.5 M solution of metal perchlorate, 2.2 cm^3 of a 0.5 M solution of potassium iodide or thiocyanate was added, and after about an hour in a refrigerator, liberated potassium perchlorate was filtered. To the filtrate, 0.3 mmol of sodium tetraphenylborate was added, and the resulting precipitate was also filtered off. A saturated ethanol solution (40 cm^3) of the ligand was added to the filtrate, followed by the addition of 0.5 mmol of sodium tetraphenylborate. Resulting crude complex was purified in a similar manner to the recrystallization of the chloro or the bromo complex. *Anal.*: [Ni(I)(*S*-mnp$_3$)]BPh$_4$, calcd. for $C_{67}H_{64}NP_3IBNi$: C, 68.63; H, 5.50; N, 1.19%. Found: C, 67.75; H, 5.38; N, 1.16%. [Ni(NCS)(*S*-mnp$_3$)]BPh$_4$, calcd. for $C_{68}H_{64}N_2P_3SBNi$: C, 74.00; H, 5.84; N, 2.54%. Found: C, 73.01; H, 5.81; N, 2.48%. [Co(I)(*S*-mnp$_3$)]BPh$_4$, calcd. for $C_{67}H_{64}NP_3IBCo$: C, 68.62; H, 5.50; N, 1.19%. Found: C, 67.79; H, 5.37; N, 1.14%. [Co(NCS)(*S*-mnp$_3$)]BPh$_4$, calcd. for $C_{68}H_{64}N_2P_3SBCo$: C, 73.98; H, 5.84; N, 2.54%. Found: C, 73.92; H, 5.71; N, 2.99%.

Physical Measurements

Electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Circular dichroism spectra were recorded on a Jasco J-500C spectropolarimeter in the range 14000 cm^{-1} – 30000 cm^{-1}. Nuclear magnetic resonance spectra were obtained using a JEOL JNM-GX 400 spectrometer equipped with a superconducting magnet.

Magnetic moments of chloroform-d_1 and nitromethane-d_3 solutions were measured by the NMR method[8] using coaxial tubes, the ambient temperatures of which were changed from 298 K to 350 K. The outer tube was a normal 5 mm o.d. tube and the inner tube was a 3 mm o.d. (2 mm i.d.) tube, both of which were the products of the Shigemi Standard Joint Industrial Co. Ltd. The solvent and markers, TMS and cyclohexane, were set in the inner tube and the sample solution containing the same solvent and marker was set in the outer tube. The concentration of the sample solution was varied from *ca* 2 mg to 10 mg in each 260 μl of chloroform-d_1 or nitromethane-d_3. Mass susceptibilities of the samples, χ, were calculated using the equation of Evans,[8] with a modification[9] as follows,

$$\chi = -\frac{3\Delta f}{4\pi f m} + x_o + \frac{x_o(d_o - d_s)}{m}$$

where symbols have the same meanings as those used by Evans. Diamagnetic corrections were derived from molar susceptibilities of appropriate organic substances and Pascal's constants.[10]

RESULTS AND DISCUSSION

Preparation and Properties of S-mnp$_3$ and Its Complexes

One of the authors previously reported[1] the preparation and chiroptical properties of complexes containing a chiral tripodal ligand, *S*-tan, which was a methyl derivative of *tris*(dimethylaminoethylamine) (Me$_6$tren). The report revealed that the introduction of a methyl group to the tripodal ligand, Me$_6$tren, scarcely affected the properties and the structure of its metal complexes, except for the fact that the chiral conformation of the chelate rings was fixed.

The present ligand, *S*-mnp$_3$, is a methyl derivative of *tris*(diphenylaminoethyl)-amine (np$_3$) and is expected to form metal complexes possessing properties similar to those of np$_3$. This is reflected in the electronic spectra of the *S*-mnp$_3$ complexes. Positions and molar absorption coefficients of absorption maxima of the *S*-mnp$_3$ complexes are quite similar to those of np$_3$ complexes. Although the magnetic behavior of *S*-mnp$_3$ complexes is somewhat different from that of np$_3$ complexes, the molecular and electronic structure of the present complexes are considered to be approximately the same as those of np$_3$ complexes.

Magnetic Properties

Sacconi and Bertini reported that all the nickel(II) complexes of np$_3$ are diamagnetic but the cobalt(II) complexes of np$_3$ exist as both high-spin and low-spin complexes.[2] This is also the cases for the *S*-mnp$_3$ complexes, although the magnetic moments of [Co(X)(*S*-mnp$_3$)]BPh$_4$ are somewhat lower than those of the corresponding np$_3$ complexes. Magnetic moments of five-coordinate cobalt(II) complexes are reported to lie between those of the tetrahedral complexes (4.4–4.7 B.M.) and octahedral complexes (4.7–5.2 B.M.).[11] Actually, the moments of high-spin complexes, [Co(X)(np$_3$)]BPh$_4$, lie in this range. However, even [Co(Cl)(*S*-mnp$_3$)]BPh$_4$, the magnetic moment of which was the highest of the present four complexes, exhibited lower moments than those expected of tetrahedral complexes. The magnetic moment of [Co(I)(S-mnp$_3$)]BPh$_4$ is extremely low. Table 1 lists magnetic moment data for the complexes.

In order to obtain information to elucidate this kind of curious behavior, the magnetic properties in solution were examined for the present complexes using an NMR spectrometer and a coaxial tube. The samples were dissolved in chloroform-*d$_1$* or in nitromethane-*d$_3$* which contained tetramethylsilane and cyclohexane as markers. Since a superconducting magnet was used, the magnetic field applied was parallel to the coaxial tube. This caused shifts of the markers in solution to lower field with respect to the markers in the solvent, due to the paramagnetism of the solution . It was pointed out that the shifts are twice as large as those observed for iron core magnets, the field of which was perpendicular to the sample tube.[9] Thus the susceptibility was calculated using the modified equation of Evans (*vide supra*). In order to examine the effectiveness

Table 1 Magnetic moments of cobalt complexes in the solid state and in solution.

Complex	Solid		$CDCl_3$ Soln.		CD_3NO_2 Soln.	
	t/°C	μ_{eff}/BM	t/°C	μ_{eff}/BM	t/°C	μ_{eff}/BM
$[Co(Cl)(S\text{-}mnp_3)]BPh_4$	20.3	3.96	30.1	4.35	30.1	4.36
			35.1	4.34	39.9	4.35
			40.4	4.33	50.0	4.33
					60.0	4.34
$[Co(Br)(S\text{-}mnp_3)]BPh_4$	18.0	3.42	30.0	4.29	30.0	4.37
			40.0	4.27	40.0	4.36
			50.0	4.25	50.0	4.38
					60.0	4.38
$[Co(I)(S\text{-}mnp_3)]BPh_4$	18.8	2.80	30.0	3.31	30.0	3.25
			40.0	3.36	40.0	3.32
			49.9	3.41	50.0	3.39
					60.0	3.46
$[Co(NCS)(S\text{-}mnp_3)]BPh_4$	19.8	1.86	30.1	2.69	30.0	2.55
			35.1	2.71	39.9	2.58
			40.4	2.73	50.0	2.64
			45.3	2.75	60.0	2.74

of this method, the susceptibilities of some familiar complexes were measured. Their molar susceptibilities obtained at 298.2 K were as follows: *tris*(acetylacetonato)iron(III) in $CDCl_3$, 14320×10^{-6}; *tris*(acetylacetonato)chromium(III) in $CDCl_3$, 5940×10^{-6}; copper(II) sulfate pentahydrate in D_2O, 1476×10^{-6}; potassium hexacyanoferrate(III) in D_2O, 1918×10^{-6}. Diamagnetic corrections for the molar susceptibility gave the magnetic moment for each complex as 5.88, 3.82, 1.95, and 2.17 B.M., respectively. These values are comparable to reported values.[8,12]

The magnetic moments of the cobalt(II) complexes in solution are tabulated in Table 1. The chloro and bromo complexes are high-spin and their values are comparable to those of corresponding np_3 complexes in the solid state,[2] while the value of the isothiocyanato complex is somewhat higher than the value for low-spin, five-coordinate complexes (2.0–2.5 BM).[13]

The magnetic moments of the iodo complex in both solvents are quite abnormal in that they are lower than moments of tetrahedral complexes, but higher than those of low-spin complexes. The effect of temperature was examined and results are also shown in Table 1. These solution moments can be understood assuming that the iodo complex exists as an equilibrium mixture of a high-spin form and a low-spin form. The equilibrium seems to shift to the high-spin form when temperature is raised or the solvent is changed from nitromethane to chloroform. A similar situation is observed for the isothiocyanato complex, although the low-spin form is predominant in this case. Sacconi pointed out that the spin state of $[Co(X)(np_3)]Y$ depends on the softness of the monodentate ligand X.[14] He elucidated that the observed tendency of the ligand X to stabilize the low-spin state was $Cl = Br = I < NCS$ for solid $[Co(X)(np_3)]BPh_4$ and $Br < I$ for solid $[Co(X)(np_3)]X$. This tendency, $Cl = Br < I < NCS$, is the same as that found for the solution magnetic moments of the present S-mnp_3 complexes.

Chiroptical Properties

Electronic spectra of present complexes in solution were measured in the range 5000–30000 cm^{-1} and CD spectra were measured in the range 14000 to 30000 cm^{-1}. They are shown in Figures 1–3, and the selection rules for magnetic dipole transitions are shown in Table 2.

Figure 1 shows that a weak positive CD maximum and two negative maxima were observed for the nickel complex between 14000 and 30000 cm^{-1}. The two longer wavelength bands originate from the ^1D configuration. The longest wavelength band with weak positive intensity is assigned to the $^1A_1{}' \rightarrow {}^1E'$ transition and the negative band at about 18000–20000 cm^{-1} to the $^1A_1{}' \rightarrow {}^1E''$ transition under D_{3h} symmetry.[15] There is clearly an inverse relation between the intensities of the CD bands and those of the absorption bands. This is expected, as Table 2 shows. For the two transitions, the selection rules for the magnetic dipole transitions are the inverse of those for the electric dipole transitions under D_{3h} symmetry. This situation is quite similar to that found in five-coordinate copper(II) complexes of *S*-tan, [CuX(*S*-tan)].[1] Regarding five-coordinate complexes with D_{3h} symmetry, the ground and excited states of the copper(II) complex are the same as those of the diamagnetic nickel(II) complex except for the spin multiplicity of both complexes.

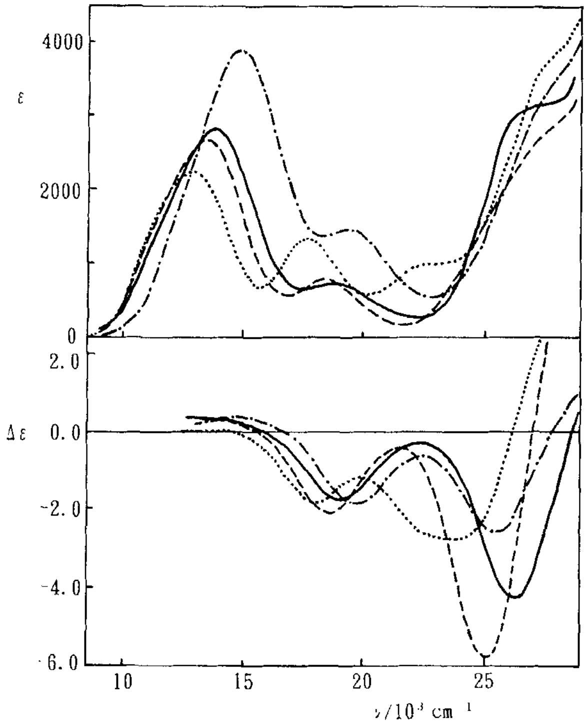

Figure 1 Electronic absorption and CD spectra of [Ni(X)(*S*-mnp$_3$)]BPh$_4$ in dichloroethane. X = Cl (——), X = Br (– – – – –), X = I (.....), and X = NCS (–.–.–).

Table 2 Selection rules for electronic (E) and magnetic dipole (M) transitions under D_{3h} and C_{3v} symmetry.*

Low-spin nickel(II) complex					
D_{3h}			C_{3v}		
Transition	E	M	Transition	E	M
${}^1A_1' \rightarrow {}^1E''$	⊥	X	${}^1A_1 \rightarrow {}^1E$	⊥	⊥
${}^1A_1' \rightarrow {}^1E'$	X	⊥	${}^1A_1 \rightarrow {}^1E$	⊥	⊥
High-spin cobalt(II) complex					
D_{3h}			C_{3v}		
Transition	E	M	Transition	E	M
${}^4A_2' \rightarrow {}^4A_2''$	∥	X	${}^4A_2 \rightarrow {}^4A_2(F)$	X	∥
${}^4A_2' \rightarrow {}^4A_1''$	X	X	${}^4A_2 \rightarrow {}^4A_1(F)$	∥	X
${}^4A_2' \rightarrow {}^4E''(F)$	X	⊥	${}^4A_2 \rightarrow {}^4E(F)$	⊥	⊥
${}^4A_2' \rightarrow {}^4E'$	⊥	X	${}^4A_2 \rightarrow {}^4E(F)$	⊥	⊥
${}^4A_2' \rightarrow {}^4A_2'$	X	X	${}^4A_2 \rightarrow {}^4A_2(P)$	∥	X
${}^4A_2' \rightarrow {}^4E''(P)$	X	⊥	${}^4A_2 \rightarrow {}^4E(P)$	⊥	⊥

*The symbols ∥ and ⊥ denote whether a transition is allowed parallel or perpendicular to the C_3 axis, respectively; X denotes a transition forbidden in any direction.

Figure 2 shows the absorption and CD spectra of high-spin complexes, $[Co(X)(S\text{-}mnp_3)]^+$ (X = Cl and Br). It was pointed out that the CD spectra of [Co(X)(*S*-

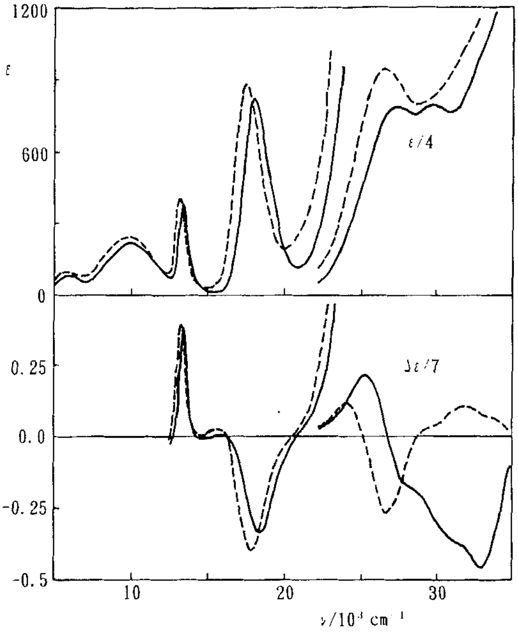

Figure 2 Electronic absorption and CD spectra of $[Co(X)(S\text{-}mnp_3)]BPh_4$ in dichloroethane. X = Cl (——) and X = Br (-----)

tan)]$^{n+}$ lacked a CD peak around 17000 cm^{-1} assigned to the $^4A_2 \rightarrow {}^4A_2$ transition under C_{3v} symmetry. This means that the selection rule for magnetic dipole transition was effective for these kinds of complexes. This was the only one of all the transitions which was not observed for the *S*-tan complexes of cobalt(II), nickel(II) and copper(II). In contrast to the *S*-tan complexes, high-spin *S*-mnp$_3$ complexes, [Co(X)(*S*-mnp$_3$)]$^+$ (X = Cl and Br), exhibit the CD peak corresponding to the $^4A_2 \rightarrow {}^4A_2$ transition. This fact may imply that the present cobalt complexes are distorted from trigonal bipyramidal geometry. Sacconi *et al.*,[16] reported an X-ray crystal analysis of [Co(Cl)(np$_3$)]ClO$_4$. The complex cation was regarded as being a very distorted trigonal bipyramid or a capped tetrahedron, since the cobalt-nitrogen bond was quite long (2.675 Å). The corresponding *S*-mnp$_3$ complex is expected to possess a similar structure. It is rather striking that this kind of gross distortion did not reflect on the electronic absorption spectrum of the *S*-mnp$_3$ complex in solution (*i.e.*, it resembles the spectrum of the *S*-tan complex).[1] The sensitivity of the CD spectra to the stereochemistry of metal complexes is more pronounced than with absorption spectra.

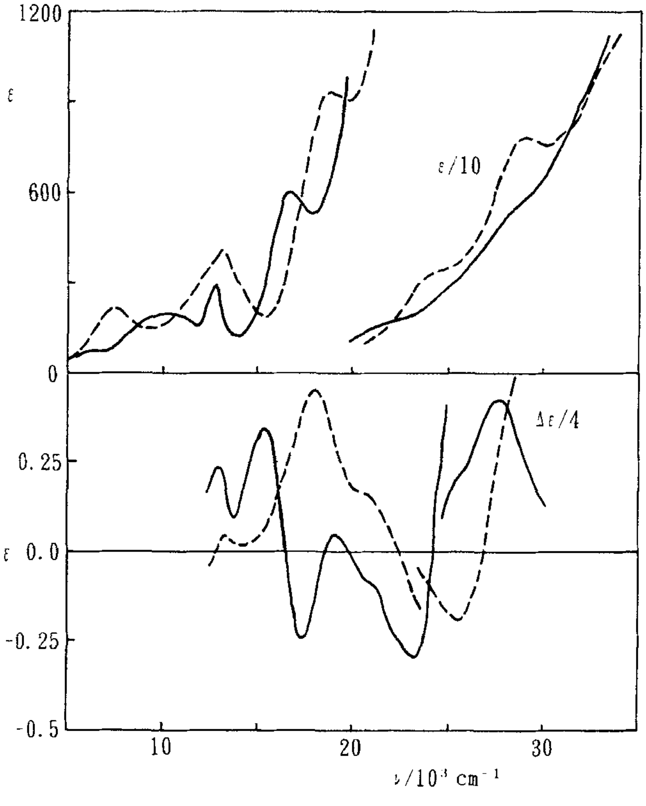

Figure 3 Electronic absorption and CD spectra of [Co(X)(*S*-mnp$_3$)]BPh$_4$ in dichloroethane. X = I (——) and X = NCS (-----)

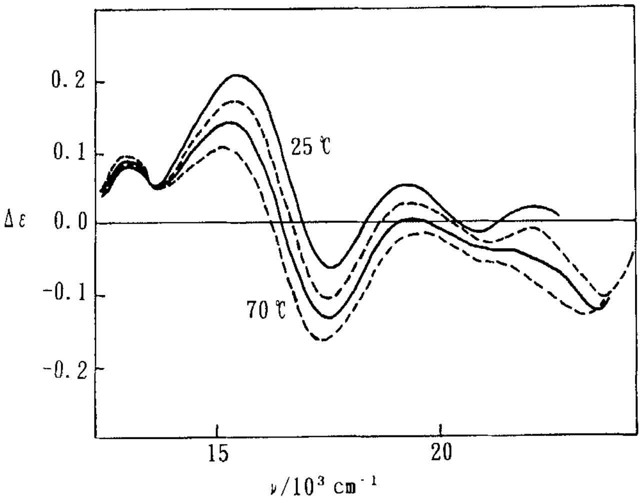

Figure 4 CD spectra of [Co(I)(*S*-mnp$_3$)]BPh$_4$ in nitromethane at 25, 40, 55 and 70 °C.

Figure 3 shows absorption and CD spectra of [Co(I)(*S*-mnp$_3$)]$^+$ together with those of the isothiocyanato complex. The CD spectrum of the iodo complex seems to exhibit characteristics of both high-spin and low-spin species. That is to say, a positive band at *ca* 13,000 cm^{-1} and a negative band at *ca* 17,000 cm^{-1} are also observed for the chloro and bromo complexes, while a positive band at *ca* 15,000 cm^{-1} seems to correspond to a band at *ca* 18,500 cm^{-1}, which is observed for the isothiocyanato complex.

The iodo complex has an abnormal magnetic moment both in the solid state and in solution, and the solution moment changed with temperature. Thus the spectra of the iodo complex in nitromethane have been recorded at various temperatures. Although the absorption spectrum did not show any significant temperature effect, the CD spectrum changed appreciably with temperatue. Figure 4 shows the CD spectra obtained. The bands around 13000 cm^{-1} and 17500 cm^{-1} increase and the bands around 15000 cm^{-1} and 19000 cm^{-1} decrease with temperature. Solution magnetic moments of the iodo complex indicate that the high-spin form corresponds to higher temperatures. Therefore the bands at 13000 cm^{-1} and 17500 cm^{-1} of the iodo complex in dichloromethane should be assigned to the high-spin form. This is consistent with the above mentioned characteristics observed for the CD spectrum of the iodo complex in dichloroethane.

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