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Notes

Notes

Solvent–Dependent Circular Dichroism Spectra of *trans*–Dichlorobis (*S,S*–1,3–diphenyl–1,3–propanediamine)cobalt(III) Complex

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Figure 1. CD spectra, *trans*-[Co(S,S-dppn)$_2$Cl$_2$]ClO$_4$ in methanol (——), in acetonitrile (- - -), in benzonitrile (·····), in nitromethane (----), and in tetrahydrofurane (-·-·-·-).
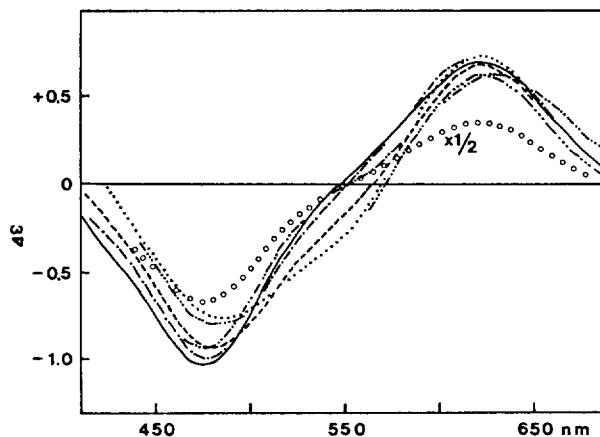

Figure 2. CD spectra, *trans*-[Co(S,S-dppn)$_2$Cl$_2$]ClO$_4$ in methanol (ooooo) and *trans*-[Co(S,S-dppn)$_2$Cl$_2$]Cl·HCl·H$_2$O in methanol (——), in acetonitrile (- - -), in benzonitrile (·····), in nitromethane (----), in dimethylsulfoxide (-·-·-·-), and in acetone (-·-·-·-·-).

The solvent dependence of circular dichroism(CD) spectra has been reported for many optically active metal complexes[1-4]. In a previous paper[5], we showed that the CD spectra of optically active [Co(acac)$_2$(diamine)]$^+$ complexes were sensitive to the type of organic solvents, where acac is acetylacetonato anion and diamine is ethylenediamine or trimethylenediamine. The CD spectra of *trans*-[CoL$_2$X$_2$]$^{n+}$ complexes were also reported in a large number of solvents, where L is (R)-propane-1,2-diamine(R-pn)[1] or (R)-1-phenylethane-1, 2-diamine[2] and X is Cl$^-$, Br$^-$, or NH$_3$. Among these the dihalo complexes showed a preferential solvation *via* hydrogen-bond formation with the equatorial N–H protons of chiral diamine ligands(L)[1,2].

In this study, we have studied the effect of counteranions upon the solvent-dependent CD spectra of *trans*-[Co(S,S-dppn)$_2$Cl$_2$]$^+$ complexes in a number of organic solvents, where S,S-dppn is S,S-1,3-diphenyl-1,3-propanediamine.

Experimental

Optically active ligand dppn and complexes were prepared and characterized according to the literature[6]. Circular dichroism spectra were measured with a JASCO J-500C spectropolarimeter. All the solvents were of analytical grade and used without further purification.

Results and Discussion

The CD spectra of the complexes, *trans*-[Co(S,S-dppn)$_2$-Cl$_2$]ClO$_4$ and *trans*-[Co(S,S-dppn)$_2$Cl$_2$]Cl·HCl·H$_2$O, in some solvents are shown in Figures 1 and 2. The patterns and intensities of CD spectra for the two complexes are somewhat different. The CD spectra of the chloride complex in some solvents (acetonitrile, benzonitrile, and acetone) bear no resemblance to those of the perchlorate complex.

Furthermore, the patterns of the solvent-dependent CD spectra of both complexes at about 540 nm are somewhat different when the counteranions of the complex are different. The CD spectra of *trans*-[Co(S,S-dppn)$_2$Cl$_2$]ClO$_4$ complex have one isodichroic point at 545 nm (Figure 1), while *trans*-[Co(S,S-dppn)$_2$Cl$_2$]Cl·HCl·H$_2$O complex does not (Figure 2). Since the complex cation and solvents used are the same, the
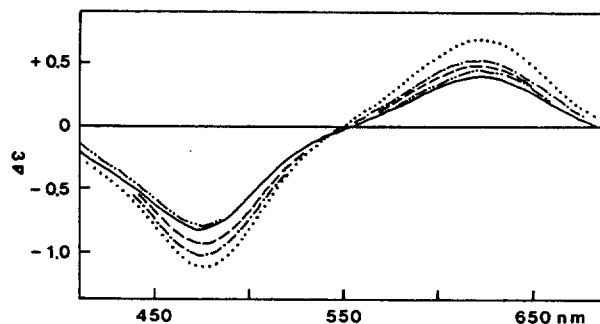
difference in the spectra of the two complexes may be attributed to different counteranions.

The above results may be an indication of the difference in the degree of ion–association between the complex cation and counteranion in organic solvents. Hawkins *et al.*[1] reported the solvent-dependent CD spectra of *trans*-[Co(R-pn)$_2$X$_2$]$^{n+}$ complexes and concluded that ion–association with counteranions of complex is more important than the stereoselective solvation in the dihalo complexes. It has also been reported[7] that the ion–association constant between complex and counteranion in dipolar aprotic solvents increase in order of counteranions; ClO$_4$$^-$<I$^-$<Br$^-$<Cl$^-$. The perchlorate anion is not a hydrogen–bond acceptor and the perchlorate complex is completely dissociated in dipolar aprotic solvents[7,8]. Since the completely dissociated species are present in solution, it seem that the perchlorate complex has one isodichroic point at 545 nm (Figure 1).

However, since the chloride complex is formed *via* strong ion–association between complex and counteranion (Cl$^-$), it seems that this complex is partially dissociated in organic solvents. Thus, the dissociated and associated species can coexist in solution. When different species coexist in solu-

tion, it is supposed that the intensity and the pattern of CD spectra can be different in a certain absorption band region and hence no isodichroic point. Thus, for the chloride complex, it seems that the observed irregular CD changes at about 540 nm are attributed to coexistance of the dissociated and associated species.

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Organocobalt(III) Complexes of the Tetraazamacrocyclic Ligand, $C_{32}H_{26}N_4^{2-}$ (I)

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A major factor affecting Co–C bond stability in Organocobalt(III) B_{12} models as well as cobalamins appears to be the coordination number. Most of the low spin d^6 cobalt(III) complexes are 6-coordinate with octahedral or pseudooctahedral structures, but 5-coordinate organocobalt(III) species have been suspected to exist either as reactive intermediates in ligand–exchange reaction or, less commonly, as relatively stable species.[1-3] However, the evidence for 5-coordinate cobalt (III) species is not clear. In connection with the research program toward the investigation of the effect of bases as the sixth ligands on the stability of Co–C bond in organocobalt(III) species, this paper reports on the chemistry of 5-coordinate organocobalt (III) complexes of completely conjugated dianionic macrocyclic ligand (L), 5,14-dihydro-6,15-dimethyl-8,17-diphenyldibenzo[b,i] [1,4,8,11] tetraazacyclotetradecinate.

As a starting material, Co(II)L was prepared by the addition of methanol solution of cobalt(II) acetate tetrahydrate to a solution of the ligand in DMF followed by 30 minutes reflux and obtained as a greenish brown crystal. The compound is air sensitive even in the solid state. The structure of Co(II)L determined by elemental analysis (Table 1), magnetic mo-

Table 1. Analytical Data for the Cobalt Complexes

Compound	Calcd, %			Found, %		
	C	H	N	C	H	N
Co(II)L· H₂O	71.9	5.05	10.5	72.2	4.92	10.5
CH₃Co(III)L	73.3	5.37	10.4	72.1	5.37	10.4
C₆H₅Co(III)L	75.7	5.15	9.30	74.9	5.10	9.34
C₆F₅Co(III)L	65.9	3.76	8.09	66.3	4.02	8.28

Table 2. Electronic Spectral Data for RCoL Complexes in the Range 16,000–30,000 cm⁻¹

Compound	Solvent	Absorption in cm⁻¹ (ε)
CoL	CHCl₃	27,800(47,400), 16,700(4,810)
CH₃CoL	CHCl₃	27,030(7,970), 23,810(3,910), 16,620(2,540)
C₆H₅CoL	CHCl₃	27,970(9,440), 23,120(5,000), 15,870(930)
C₆H₅CoL	CHCl₃	27,780(31,240), 22,990(6,650)

Table 3. Proton NMR Spectral Data for RCoL^a

Compound	Co–CH₃	Methyl 6.15-CH₃–	Methine –CH=	Aromatic
LH₂		2.30 (s)	5.14 (s)	6.10–7.94(m)
CH₃CoL	2.33(s)	2.53(s)	5.26(s)	5.76–7.16(m, benzenoid) 7.40(s, phenyl)
C₆H₅CoL		2.68(s)	4.89(s)	5.33–8.25(m)
C₆F₅CoL		2.45(s)	5.22(s)	6.17–8.30(m)

^{a}Chemical shifts in ppm from internal TMS. Measured in CDCl₃. s: singlet, m: multiplet.

ment (2.33 B.M.), IR spectrum and electronic spectrum is regarded as a 4–coordinate square planar complex which the macrocyclic ligand acts as a tetradentate chelating agent lying in the equatorial plane.

Five–coordinate organocobalt (III) complexes, RCo(III)L (where R = CH_3, C_6H_5, C_6F_5), were prepared similarly to that described for the synthesis of (py)Co(III) (salopha)(R)[1]. These green organocobalt complexes are also gradually decomposed in the air. The infrared spectra of these complexes show the change in the C = N stretching mode of the ligand, which enables us to distinguish between the coordinated and the free ligand. The absorption band for C = N of the free ligand which appears at 1613 cm⁻¹ with very strong intensity is shifted to the lower frequency region with decreased intensity; 1571 cm⁻¹ for CH_3CoL, 1570 cm⁻¹, 1570 cm⁻¹ for C_6H_5CoL and 1575 cm⁻¹ for C_6F_5CoL. This result indicates that the ligand is coordinated through for nitrogen atoms to the metal. Visible and ultraviolet spectral data covering 16,000–40,000 cm⁻¹ range are shown in Table 2.

These absorption bands are assigned to $\pi-\pi^*$ transitions within the ligand molecule and charge transfer transitions from metal to ligand since they have larger extinction coefficients (10^3–10^4 mol⁻¹dm³cm⁻¹) than expected for ligand field transitons.[4] Five coordinate organocobalt (III) complexes are known to show a band at ~440 nm[5]. Indeed, the ~430 nm band has been observed in chloroform in all the complexes of this work. This particular band is attributed to the intramolecular CT transitions for which the Co–CH_3 bond is