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Solvent Dependence of the Circular Dichroism Spectra of Some *cis*-Dianionobis(ethylenediamine)cobalt(III) Complexes

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The circular dichroism spectra of some *cis*-bis(ethylenediamine)cobalt(III) complexes have been measured in several solvents. Among these complexes, the diisothiocyanato complex was found to exhibit a marked solvent dependence; the dominant circular dichroism band in the lowest energy spin-allowed transition region changed its sign upon going from, *e.g.*, water, dimethyl sulfoxide, methanol, or acetone to pyridine or its analogues. Coupled with the proton NMR spectra and a similar solvent dependence of the circular dichroism spectra of nitroisothiocyanatobis(ethylenediamine)cobalt(III) and diisothiocyanatobis(ethylenediamine)chromium(III) complexes, we ascribed the origin of the sign inversion of the diisothiocyanato complex to the stereoselective hydrogen bonding of *cis* N–H$_B$ with pyridine-like molecules, where *cis* N–H$_B$ is the hydrogen bonded to the nitrogen atom *cis* to NCS$^-$ and directed off the molecular twofold axis.

It has been known for some time that the optical activity of some organic compounds is solvent dependent and this effect has been used, for example, for conformational analysis.[1] In the field of coordination chemistry, however, no systematic studies have been made on the effect of solvents upon the optical activity of metal complexes.[2] Recently, Bosnich and Harrowfield[3] found that the circular dichroism (CD) spectra of bobalt(III) complexes of the type *trans*-[Co(N)$_4$(X)$_2$]$^+$ are particularly sensitive to solvents, where (N)$_4$ represents chiral quadridentate amine ligands. Depending upon the solvent, some of these complexes changed even the sign of rotational strength of the lowest energy spin-allowed $^1A_{1g}$ to $^1T_{1g}(D_{4h})$ circular dichroism, which owes its origin to the so-called vicinal effect. Although they examined many closely related systems extensively, no definite conclusion was reached about the origin of the large CD variations observed. Subsequently, Hawkins *et al.*[4] investigated the CD and proton NMR spectra of some *trans*-[Co(*R*-pn)$_2$(X)$_2$]$^{n+}$ and related complexes in several solvents, where *R*-pn is (*R*)-1,2-propanediamine. They ascribed the prominent solvent dependence of the CD spectra to the stereoselective hydrogen bonding that is formed between the equatorial amino hydrogens of the complex cation and the solvent molecule, rendering the coordinated nitrogens asymmetric.

Though several other scattered examples can be found in the literature[5] which describes significant solvent variation of CD spectra of metal complexes, no further attempt appears to be made at the elucidation of the solvent variation *per se*. In the above, we confined our interest to such systems that contain no chiral solvents, because in chiral solvents additional sources of complication might arise due to, *e.g.*, induced CD,[6] asymmetric transformation,[7] or the Pfeiffer effect.[8]

We have studied the CD spectra of some optically stable *cis*-dianionobis(ethylenediamine)cobalt(III) complexes, *cis*-[Co(en)$_2$(X)$_2$]$^{n+}$, in several solvents, where en=ethylenediamine and (X)$_2$=(CN)$_2$, (NO$_2$)$_2$, (NCS)$_2$, (N$_3$)$_2$, oxalate, acetylacetonate, (NH$_3$)$_2$, and en. These substituents range from strong- to weak-field ligands in the spectrochemical series. The diisothiocyanato and dicyano complexes were found to exhibit marked solvent dependences; the dominant and minor CD bands, respectively, changed their signs in some solvents. This paper describes the results of such studies and discusses, in particular, the origin of the CD variation of the diisothiocyanato complex with solvents.

Experimental

Materials. The literature methods were used for the preparation and optical resolution of *cis*-[Co(en)$_2$(X)$_2$]$^{n+}$ complexes, where (X)$_2$=(CN)$_2$,[9] (NO$_2$)$_2$,[10] (NCS)$_2$,[11] (N$_3$)$_2$,[12] en,[13] acetylacetonate,[14] (NH$_3$)$_2$,[15] and oxalate.[16] The methods for the preparation and optical resolution of the chromium(III) analogue *cis*-[Cr(en)$_2$(NCS)$_2$]$^+$ and *cis*-[Co(en)$_2$(NO$_2$)(NCS)]$^+$ were those of House[11] and Yamazaki *et al.*,[12] respectively. Each of these complexes was obtained in the form of chloride, bromide, iodide, perchlorate, and tetraphenylborate (BPh$_4^-$) by metathesis. For complexes containing monodentate ligands, ion-exchange chromatography with SP-Sephadex C-25 resin was used to confirm the absence of any *trans* impurities. The identity of these complexes was confirmed by unpolarized absorption spectra, proton NMR spectra, and CD spectra.

The nonaqueous solvents used for the CD measurements were of spectroscopic grade or of highest grade commercially available, mostly from Katayama Chemical Industries Co., Ltd. (Osaka) or Tokyo Kasei Kogyo Co., Ltd. (Tokyo), and used as supplied. Dimethyl-d_6 sulfoxide (DMSO-d_6, 99 atom% D minimum) and pyridine-d_5 (99 atom% D minimum) were purchased from E. Merck (Darmstadt).

Measurements. The CD spectra were obtained on a JASCO J-40CS recording spectropolarimeter at ambient temperature. Tetraphenylborate salts were used throughout for nonaqueous solvents and the complex concentration was typically 1.1×10^{-3} to 2.7×10^{-3} mol dm^{-3}.

Proton magnetic resonance spectra were run on a JEOL JNM-PMX60 spectrometer at 36 °C or on a JEOL PS-100 spectrometer at ambient temperature. Chemical shifts were referenced to internal tetramethylsilane (TMS).

Results and Discussion

The utility of CD spectra in assigning the stereochemistry and the absolute configuration of metal complexes relies upon the structure-spectrum correlation in the d-d transition and/or exciton band region.[17]

The correlation has now been believed to be well established both theoretically and experimentally, especially for configurational CD spectra. Usually, the configurational effects dominate over the conformational and vicinal effects for five-membered chelate ring systems.[17)] The CD spectra due to the latter two effects have been shown,[3–5)] in some complexes, to vary with solvents. For configurational CD spectra, however, no examples appear to be reported in which the sign of rotational strength changes with solvents. This spectral stability seems to be the basis of the utility of configurational CD spectra in the determination of absolute configuration. The absolute configuration of *cis*-$[Co(en)_2(X)_2]^+$ complexes has been determined based on the sign of the rotational strength of the dominant CD band in the first d-d transition region.[18)] Thus, if the sign of the rotational strength of the dominant CD band changed with the environment or the medium for unknown reasons, it might lead to the undesired situation where CD spectra are unreliable and useless in the study of the stereochemistry and absolute configuration of metal complexes.

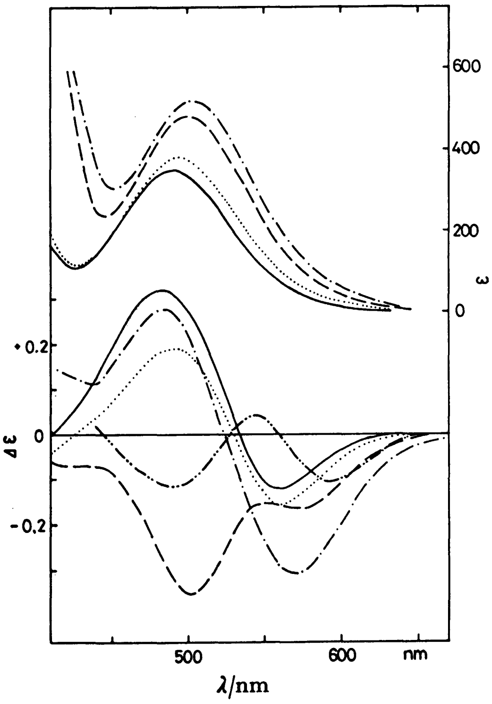

Fig. 1. The unpolarized absorption and CD spectra in the first d-d transition region of Λ-*cis*-$[Co(en)_2(NCS)_2]^+$ in water (——), DMSO (······), THF (-·-·-·-), and pyridine (------), and the CD spectrum in nitrobenzene (-··-··-··-).

Diisothiocyanato Complex. Figure 1 shows the absorption and CD spectra of Λ-*cis*-$[Co(en)_2(NCS)_2]^+$ in several solvents, including water (solid curve) and pyridine (broken curve). The counter anions were chloride and BPh_4^- in water and nonaqueous solvents, respectively. In the absorption spectra, it is noted that the peak position and the intensity of the first d-d band are affected by solvents to some extent. Though the CD spectra in water, DMSO, and tetrahydrofuran (THF) differ in magnitude, their shapes are not so drastically different, as with ordinary solvents like methanol, acetone, and acetonitrile. The lowest energy CD peak, which was assigned[18)] to the B_1 transition, has a minus sign in these solvents, while the higher energy component, assigned to the A_2+B_2 transition, is plus. These notations follow those of McCaffery, Mason, and Norman.[18)] In contrast to these minus-plus couplets, the pyridine solution yielded a minus-minus couplet; the sign of the dominant CD band is changed from plus to minus, while leaving the minor CD band relatively unaffected. This may be the most spectacular example ever reported. If we judge simply from the sign of the dominant CD band, the pyridine spectrum is almost enantiomeric to the water or DMSO spectrum.

The CD variation shown in Fig. 1 does not seem to be primarily due to the counter anions. The CD spectrum in water did not show any noticeable change upon changing the counter anion from chloride to perchlorate. Also, addition of ten-fold excess of sodium perchlorate did not affect the spectrum in water. It is only addition of ten-fold excess of chloride to the DMSO solution that gave rise to measurable, though small, CD changes.[19)] The tetraphenylborate anion is believed to show little tendency to ion association in nonaqueous solvents with bulk dielectric constants greater than 15.[20)] Note that the dielectric constants of pyridine, THF, and DMSO are about 13, 7, and 47, respectively. Thus, we may safely eliminate the possibility of the counter anions generating these CD variations. That the observed CD change is not an artifact nor due to any chemical reactions was confirmed by the stability of the

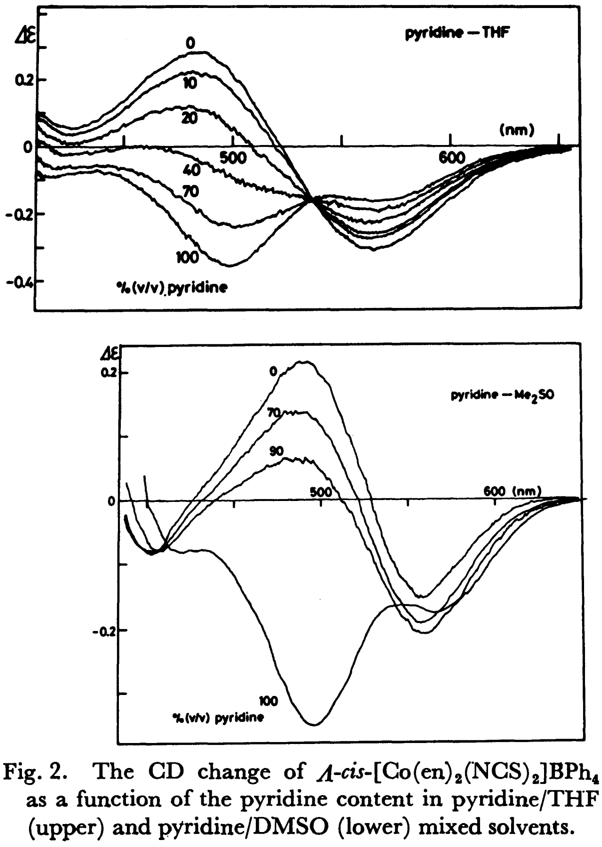

Fig. 2. The CD change of Λ-*cis*-$[Co(en)_2(NCS)_2]BPh_4$ as a function of the pyridine content in pyridine/THF (upper) and pyridine/DMSO (lower) mixed solvents.

spectra against time and by recovering the identical compound from the pyridine solution.

In order to see what type of spectrum is obtained in a mixed solvent, we measured the CD spectrum of the diisothiocyanato complex as a function of solvent composition. The results are given in Fig. 2 for the combination of pyridine/THF and pyridine/DMSO. The figure clearly indicates that the band positions are not affected greatly but the sign of the dominant CD band changed with the solvent composition. The change is, however, not a smoothly varying function of the solvent composition and a strong preference for one component can be recognized. For example, the 70%(v/v) pyridine solution in pyridine/DMSO systems yielded the CD spectrum similar to that of DMSO rather than the pyridine spectrum. This indicates that the immediate solvation sphere of the complex cation is not a smoothly varying function of the solvent composition, a phenomenon known as preferential solvation.[21] Thus, the observed CD changes are not primarily due to a change in the energy positions of the bands but due to the immediate solvation of the complex cation, causing the inversion of the intrinsic sign of the dominant band. Further, all the CD curves obtained for the pyridine/THF systems have isodichroic points, which is evidence for the presence of only two species in solution and therefore the presence of a substantial, well-defined entity that generates the sign inversion. Thus, the changes observed in Figs. 1 and 2 result most probably from some specific solute-solvent interaction. To see the nature of this interaction, we examined (i) the effect of other pyridine-like solvents, (ii) whether or not two isothiocyanato groups are essential to the sign inversion of the dominant band, and (iii) the effect of the central metal ion, by replacing cobalt(III) by chromium(III).

Figure 3 gives the CD spectra of the diisothiocyanato complex in various solvents, mostly nitrogen-containing heterocycles. From this figure, the following points will be noted. The solvents that cause the sign inversion of the dominant band are unsaturated *N*-heterocycles and the nitrogen center should not be sterically crowded. For example, solvents that contain a saturated nitrogen center, such as *N*-methylmorpholine, piperidine, pyrrolidine, and aniline, do not give rise to inversion. The sterically crowded 2,6-lutidine solvent behaves similarly, whereas the less crowded 3,5-lutidine solvent does cause the inversion. These structural features necessary for the inversion suggest that the nitrogen centers are interacting with the complex cation through their lone electron pairs. Further, since only unsaturated or aromatic solvents caused the inversion, these unsaturated parts of the solvent molecules too should be considered to interact with the complex cation. This latter point will be discussed later. The site of interaction with a lone electron pair may be either the isothiocyanato group or the N–H group of the complex cation. But the former group is anionic and its interaction with a lone electron pair is unlikely. Interaction with the N–H group(s) of the complex cation is thus the only possibility. The donor power of pyridine and its derivatives are rather large[22] and the acidity of the coordinated amino groups are also comparatively high, allowing for, *e.g.*, pK_a measurements,[23] electrophilic attach by several Lewis bases at deprotonated amino groups,[24] and the exchange with deuterium in neutral deuterium oxide solution.[25] Therefore, the hydrogen bonding between pyridine and coordinated amino group(s) is highly likely. In fact, the same type of interaction with pyridine has been postulated by Hawkins *et al.*[2,4] to play a major role in the solvent variations of the CD spectra of some *trans*-$[Co(N)_4(X)_2]^{n+}$ type of complexes.

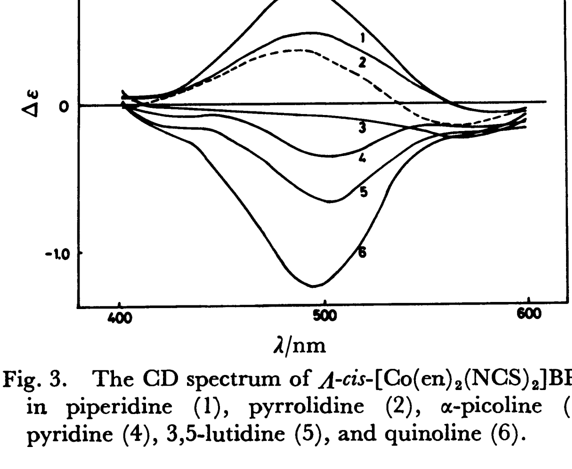

Fig. 3. The CD spectrum of *Λ-cis*-$[Co(en)_2(NCS)_2]BPh_4$ in piperidine (1), pyrrolidine (2), α-picoline (3), pyridine (4), 3,5-lutidine (5), and quinoline (6).

TABLE 1. THE AMINE PROTON CHEMICAL SHIFTS (δ) OF *cis*-$[Co(en)_2(NCS)_2]X$ IN DMSO-d_6[a)]

X	*cis* NH		*trans* NH	
BPh_4	(6.15)6.08	5.68(5.62)	4.48	
ClO_4	(6.08)6.00	5.67(5.55)	4.45	
I	(6.15)6.05	5.72(5.60)	4.55	
Br	(6.08)5.97	5.80(5.68)	5.37,5.27	4.57,4.47
Cl	(6.07)5.95	5.77(5.65)	5.90,5.80	4.53,4.42

a) From TMS internal standard. Numbers in parentheses refer to shoulders. Accuracy ±0.07 ppm.

In order to ascertain the actual site of hydrogen bonding with pyridine, we investigated the amine portion of the proton NMR spectrum of *cis*-$[Co(en)_2(NCS)_2]^+$. Table 1 lists the amine proton chemical shifts of *cis*-$[Co(en)_2(NCS)_2]X$ in DMSO-d_6, where X was varied from BPh_4^- through ClO_4^-, I^-, Br^- to Cl^-. We can note a particular hydrogen whose chemical shift is, among others, susceptible to the counter anion. As for other *cis*-$[Co(en)_2(X)_2]^+$ complexes with $(X)_2=$ $(CN)_2$, $(NO_2)_2$, oxalate, malonate, $(Cl)_2$, and $(N_3)_2$, the chemical shift changes of this particular hydrogen brought about by the counter anions are considered to be due to the ion-pair formation with the counter anions *via* hydrogen bonding.[19,26] Thus, this hydrogen can be assigned to the amine hydrogen that is bonded to the nitrogen atom *trans* to NCS^- and pointing approximately parallel to the molecular C_2 axis. This hydrogen will be called *trans* H_A. The other *trans* hydrogen, *trans* H_B, is thus assigned to the peak at about δ 4.50 and the

Table 2. The amine proton chemical shifts (δ) of *cis*-[Co(en)$_2$(NCS)$_2$]BPh$_4$ in mixed pyridine-d_5/DMSO-d_6 solvents[a)]

Pyridine %(v/v)	*cis* NH		*trans* NH
0	(6.15)6.08	5.68(5.62)	4.48
17	(6.20)6.08	5.77(5.67)	4.55
33	(6.43)6.33	5.98(5.87)	4.75
67	*ca.*6.7[b)]	6.25(6.13)	5.00
83	*ca.*7.2[b)]	6.43(6.30)	5.23
100	8.32, 8.27	6.33, 6.28	5.76

a) From TMS internal standard. Numbers in parentheses refer to shoulders. Accuracy ±0.07 ppm. b) Overlapped with the phenyl resonances of BPh$_4$$^-$.

low field AB quartet to two *cis* hydrogens.

Table 2 gives the chemical shifts of amine hydrogens of *cis*-[Co(en)$_2$(NCS)$_2$]BPh$_4$ in mixed pyridine-d_5/DMSO-d_6 solvents. As the pyridine content in the solvent increases, *trans* hydrogens and one of the *cis* hydrogens move to low fields by about 1.28 and 0.64 ppm, respectively. In contrast, the other *cis* hydrogen suffers a downfield shift of as great as about 2.20 ppm by pyridine and it appears in neat pyridine at about δ 8.30, which is downfield of even the phenyl resonances of BPh$_4$$^-$. This may be taken as evidence for the stereoselective hydrogen bonding at *cis* N–H by pyridine. This *cis* hydrogen, pertaining to the stereoselective hydrogen bonding, may be *cis* N–H$_B$, the *cis* hydrogen directing off the molecular C$_2$ axis, in analogy with the assignment made previously for the acetylacetonato- and diazidobis(ethylenediamine)cobalt(III) complexes.[19,26)] Comparison of the values of Table 2 and the CD variation of Fig. 2(b) provides additional evidence for the stereoselective hydrogen bonding. The chemical shifts of the other *cis* hydrogen, *cis* N–H$_A$, and the two *trans* hydrogens are monotonic functions of the pyridine content, whereas the *cis* N–H$_B$ hydrogen suffers downfield shifts from pyridine in a manner quite similar to the CD variation due to pyridine in pyridine/DMSO systems. The similarity of the chemical shift variation of *cis* N–H$_B$ and the CD variation in pyridine/DMSO systems suggests strongly that this hydrogen plays a key role in the sign inversion of the dominant CD band.

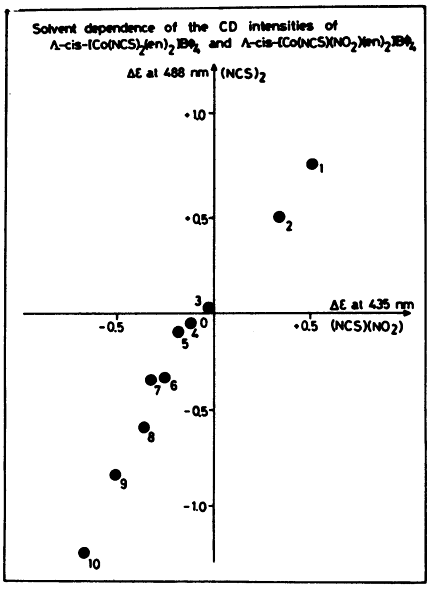

Fig. 4. The correlation of the CD intensities of Λ-*cis*-[Co(en)$_2$(NCS)$_2$]BPh$_4$ and Λ-*cis*-[Co(en)$_2$(NO$_2$)(NCS)]-BPh$_4$ in various solvents, including piperidine (1), pyrrolidine (2), pyrrole (3), aniline (4), α-picoline (5), β-picoline (6), pyridine (7), 3,5-lutidine (8), isoquinoline (9), and quinoline (10).

Table 3 gives the CD data of the monoisothiocyanato complex, Λ-*cis*-[Co(en)$_2$(NO$_2$)(NCS)]$^+$, and the chromium(III) complex, Λ-*cis*-[Cr(en)$_2$(NCS)$_2$]BPh$_4$. The reason for substitution of one NCS$^-$ by NO$_2$$^-$ is that among several Λ-*cis*-[Co(en)$_2$(X)$_2$]$^{n+}$ complexes investigated, the CD spectrum of the dinitro complex was the least sensitive to the change in solvents (see below). The solvent dependence of the CD spectrum of the monoisothiocyanato complex is very similar to that of the diisothiocyanato complex. This correlation will be seen most clearly by Fig. 4, in which the CD intensity of the diisothiocyanato complex in a solvent is plotted against that of the monoisothiocyanato complex in the same solvent. In this plot, we used the wavelengths at which the CD intensities change significantly with solvents. As seen from Fig. 4, the correlation is very good and more importantly, the change in the CD intensity of the diisothiocyanato complex is

Table 3. CD peaks of Λ-*cis*-[Co(en)$_2$(NO$_2$)(NCS)]BPh$_4$ and Λ-*cis*-[Cr(en)$_2$(NCS)$_2$]BPh$_4$

Solvent	λ/nm	$\Delta\varepsilon$	Solvent	λ/nm	$\Delta\varepsilon$
		Λ-*cis*-[Co(en)$_2$(NO$_2$)(NCS)]BPh$_4$			
Piperidine	484	+0.829	β-Picoline	450	−0.178
Pyrrolidine	488	+0.659		526	+0.073
Pyrrole	496	+0.287	Pyridine	450	−0.407
Aniline	435	+0.161		525	+0.065
	500	−0.468	3,5-Lutidine	453	−0.472
α-Picoline	448	−0.277		557	+0.024
	507	+0.277	Quinoline	455	−0.953
		Λ-*cis*-[Cr(en)$_2$(NCS)$_2$]BPh$_4$			
Pyrrolidine	485	+0.93	3,5-Lut dine	460	+0.17
Pyridine	472	+0.34		525	−0.32
	486	+0.31	Quinoline	488	−0.27
				510	−0.27

approximately twice as large as that of the mono complex. This indicates (i) that the isothiocyanato group is essential to the CD change, as is also trivial from the fact that the CD changes of the other *cis*-$[\mathrm{Co(en)_2(X)_2}]^+$ complexes examined here were much smaller, if any (see below), and (ii) that the two isothiocyanato groups interact independently with pyridine-like molecules. In the case of Λ-*cis*-$[\mathrm{Cr(en)_2(NCS)_2}]\mathrm{BPh_4}$, the CD variation is not so drastic as to produce an enantiomeric spectrum but the essential features of the cobalt(III) complexes are retained; the order of increasing tendency to invert the dominant CD band observed here (pyrrolidine$\ll$pyridine$<$3,5-lutidine$<$quinoline) parallels that of the di- and mono-isothiocyanato complexes of cobalt(III). This suggests that the sign inversion as observed for the cobalt(III) complexes is due to specific ligand-solvent interactions. It should be pointed out that the above order and a similar order in Fig. 4 can not be correlated in a simple way with common solvent parameters, such as the dielectric constant, dipole moment, E_T or Z value, or the basicity.[22]

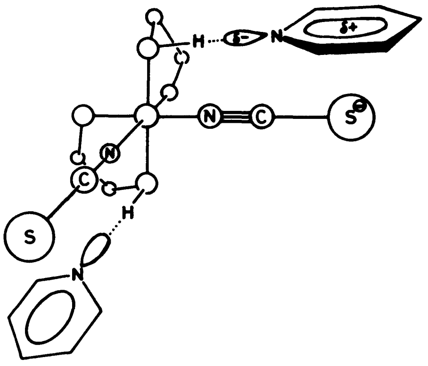

Fig. 5. The proposed model for the interaction of Λ-*cis*-$[\mathrm{Co(en)_2(NCS)_2}]^+$ and pyridine.

From all the above observations, we propose a model for the interaction of the isothiocyanato complexes with pyridine-like molecules in solution, as illustrated schematically in Fig. 5. For convenience, this figure is drawn for pyridine and Λ-*cis*-$[\mathrm{Co(en)_2(NCS)_2}]^+$. The nitrogen lone electron pair of pyridine is involved in the *cis* N–H$_\mathrm{B}$···N type hydrogen bonding, as deduced from the NMR spectra. A crystal structure analysis[27] established that the Co(III)–NCS bond is linear, indicating Co–N≡C–S$^-$ as the dominant resonance form. Molecular models show that the pyridine ring

TABLE 4. ABSORPTION AND CD PEAKS OF Λ-*cis*-$[\mathrm{Co(en)_2(X)_2}]^{n+}$

$(\mathrm{X})_2$		Solvent			
		$\mathrm{H_2O}$	DMSO	THF	Pyridine
$(\mathrm{CN})_2$	AB	400(78.3)	421(79.7)	416(79.7)	419(83.0)
	CD	443(+0.315)	447(+0.273)	443(+0.206)	433(+0.198)
		366(+0.206)	398(−0.154)	342(+0.095)	342(+0.062)
			337(+0.105)		
$(\mathrm{NO_2})_2$	AB	435(173)	438(201)	436(218)	440(227)
	CD	458(+1.66)	462(+1.68)	461(+1.49)	463(+1.01)
		405(−0.60)	410(−0.85)	405(−0.72)	410(−0.80)
$(\mathrm{N_3})_2$	AB	520(332)	523(394)	524(369)	525(397)
	CD	568(−0.80)	589(−0.92)	607(−0.86)	608(−0.77)
		501(+1.17)	508(+4.22)	516(+5.22)	517(+4.26)
$(\mathrm{NCS})_2$	AB	490(351)	493(380)	503(521)	499(482)
	CD	559(−0.12)	561(−0.16)	571(−0.31)	573(−0.16)
		483(+0.32)	495(+0.19)	484(+0.28)	501(−0.35)
$(\mathrm{Cl})_2$	AB	534(92.6)	539(104)		
	CD	613(−0.60)	622(−0.77)		
		538(+0.70)	540(+0.68)		
ox[a)]	AB	496(118)	561(140)	C)	504(151)
		335(154)	363(154)		363(162)
	CD	523(+2.60)	530(+2.65)	C)	532(+2.52)
		385(+0.118)	383(+0.194)		386(+0.204)
		335(+0.212)	338(+0.164)		339(+0.135)
acac[b)]	AB	498(138)	498(138)	490(250)	498(144)
	CD	495(+2.6)	530(+1.49)	490(+1.70)	489(+2.92)
		373(−1.3)	372(−0.90)	377(−0.75)	383(−1.28)
$(\mathrm{NH_3})_2$	AB	467(84)	470(87)	472(115)	
	CD	494(+0.49)	497(+0.49)	500(+0.32)	
		433(−0.03)	440(−0.08)	446(−0.10)	
en	AB	466(91)	468(97)	463(100)	469(106)
	CD	490(+1.89)	492(+1.88)	497(+1.26)	495(+1.28)
		429(−0.11)	433(−0.24)	441(−0.42)	425(−0.31)

a) ox: Oxalate. b) acac: Acetylacetonate. c) Insoluble.

can be situated over the sulfur atom, which carries a negative charge. In this model, the aromatic ring is tentatively assumed to interact with the negatively charged sulfur atom, which is reminiscent of the case of tetrabutylammonium bromide in nitrobenzene, where the bromide anion was assumed to be situated on the aromatic phenyl group.[28] The production of such a well-defined entity in solution may alter the CD spectrum of the complex cation either by rendering the hydrogen-bonded N–H center asymmetric (vicinal effects[17]) or by simply attaching a large "*N*-substituent" (regional rules[29]) which is orientated stereospecifically. Such a two-site interaction would be conceivable not only for pyridine but also for other aromatic molecules, if they satisfy steric requirements for this type of interaction. For example, nitrobenzene may interact in a similar fashion, though this molecule appears a little too large for such an interaction and its basicity is very much weaker than the basicity of pyridine.[22] In fact, the nitrobenzene solution gave the CD spectrum which is a weaker imitation of the pyridine spectrum rather than the water or DMSO spectrum, as shown in Fig. 1.

Other Complexes. We describe briefly the effect of solvents upon the CD spectra of the other complexes. Table 4 summarizes the absorption and CD data of all the bis(ethylenediamine) type of complexes examined here. The dicyano complex shows a relatively large CD variation especially for DMSO; the higher-energy B_1 transition, which was placed in water at 366 nm, appears to have shifted to a longer wavelength and changed the sign of its rotational strength in DMSO. The spectrum of the dinitro complex undergoes a comparatively small variation upon changing the solvents. The CD intensity of the higher-energy dominant band of the diazido complex[30] is enhanced by a factor of more than four upon going from water to DMSO, THF, or pyridine. For the oxalato and acetylacetonato complexes, prominent solvent effects are noted also for the higher-energy transitions rather than for the lower-energy ones. The peak positions and the intensities of the first d-d band of all the complexes are affected by these solvents. The origin and the nature of these spectral variations are not clear as yet.

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