Conclusions

The salt/molecule technique has allowed for the synthesis of the $Cs^+PF_4^-$ ion pair in argon matrices, through the codeposition of CsF and PF_3. The spectra obtained here represent the first spectral data obtained for the PF_4^- anion and support the notion that PF_3 has a least limited acceptor properties. The spectrum is suggestive of a folded-square, C_{2v}, structure for the anion, and normal coordinate calculations support this structure as well. In addition, normal coordinate calculations support a structure for the ion pair which has the Cs^+ cation sitting along an axial P–F bond, in a monodentate arrangement. The salt/molecule reaction technique also leads to the synthesis of the $PClF_3^-$ anion and the possible synthesis of the $PCl_2F_2^-$ anion, while the synthesis of the PCl_3F^- and PCl_4^- anions could not be achieved.

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Registry No. $Cs^+PF_4^-$, 76173-91-6; $Cs^+PClF_3^-$, 76173-92-7; PF_3, 7783-55-3; $PClF_2$, 14335-40-1; CsCl, 7647-17-8; CsF, 13400-13-0.

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Proton Magnetic Resonance Study of *cis*-Bis(ethylenediamine)cobalt(III) Complexes. Assignment and Deuteration of Amine Hydrogens and the Structure of Ion Pairs and Ion Triplets[1]

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The amine portion of the ^1H NMR spectra has been investigated for *cis*-bis(ethylenediamine)cobalt(III) complexes, *cis*-$[Co(en)_2(X)_2]^{n+}$, with $(X)_2 = (CN)_2$, $(NO_2)_2$, acetylacetonate, malonate, and oxalate, in dimethyl-d_6 sulfoxide and D_2O. One of the NH hydrogens undergoes large, counterion-dependent shifts in dimethyl-d_6 sulfoxide and is assigned to the trans hydrogens pointing approximately parallel to the molecular twofold axis. In the nitro compound, this hydrogen is deuterated first in D_2O. In the other complexes, this hydrogen is exchanged with deuterium second, the fastest exchanging hydrogen being the other trans NH. The peculiar behavior of the nitro compound has been explained by intramolecular hydrogen bonding between nitro oxygen and trans amine hydrogen(s). The structure of ion pairs between complex cations and counteranions (Cl^-, Br^-, I^-) and of the ion triplet in the acetylacetonato complex, in dimethyl-d_6 sulfoxide, has been deduced.

Recently, we have reported that the magnetic anisotropy of a cobalt(III) ion dominates the proton chemical shift of coordinated amine groups. Yoneda and Nakashima[2] advanced a theory of proton chemical shift based on this hypothesis. More recently, Nakashima, Sakaguchi, and Yoneda[3] refined the theory so as to be suitable for practical applications and established a correlation between ^{59}Co chemical shifts and proton chemical shifts. The theory has been tested for a series of pentaamminecobalt(III) complexes with quantitative sucess, except for the trans (to substituent) ammine groups of cyano- and nitropentaamminecobalt(III) ions. The theory has also been examined on various types of complexes[4] and supported in the main by other groups of workers. The disparity noted for the trans ammine groups of the cyano and nitro complexes suggested an increase in the electron density on these ammine hydrogens. To test this view, we have measured the hydrogen-exchange rates at ammine groups.[5] The results of HD exchange studies pointed to the importance of the trans influence in $[Co(NH_3)_5(X)]^{2+}$ complexes; trans ammine hydrogens are deuterated faster than cis ones for weak-field ligand X, whereas for strong-field ligands, CN^- and possibly NO_2^-, trans hydrogens are slower exchanging. The effect of the X ligand upon the exchange rate is less prominent for cis ammines.

In contrast to the nitropentaammine complex, the *cis*-$[Co(en)_2(NO_2)_2]^+$ ion[6] suggested smaller rate of deuteration for cis amine than for trans ones.[5] The reason for this difference and the assignment of NH absorptions were not clear at that time. The chemical shift of amine hydrogens in a series of *cis*-$[Co(en)_2(X)_2]^+$ has been calculated by using a procedure similar to that used for the pentaammine series, but the agreement with the observed shifts was not so good, especially again for the cyano complex.[7] Further, the amine portion of the ^1H NMR spectra of *cis*-$[Co(en)_2(X)_2]^+$ in trifluoroacetic acid solvent exhibited two to four absorptions depending upon the X ligand, and the assignment of each of these absorptions could not be made. Though the ^1H NMR spectra of this type of complexes have been reported previously by several workers, no definite conclusions has been reached about the assignment of the NH absorptions.[8-11]

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(6) Abbreviations: en, ethylenediamine; acac 2,4-pentanedionate ion; mal, malonate ion; ox, oxalate ion; Me_2SO, dimethyl sulfoxide; DMF, dimethylformamide.

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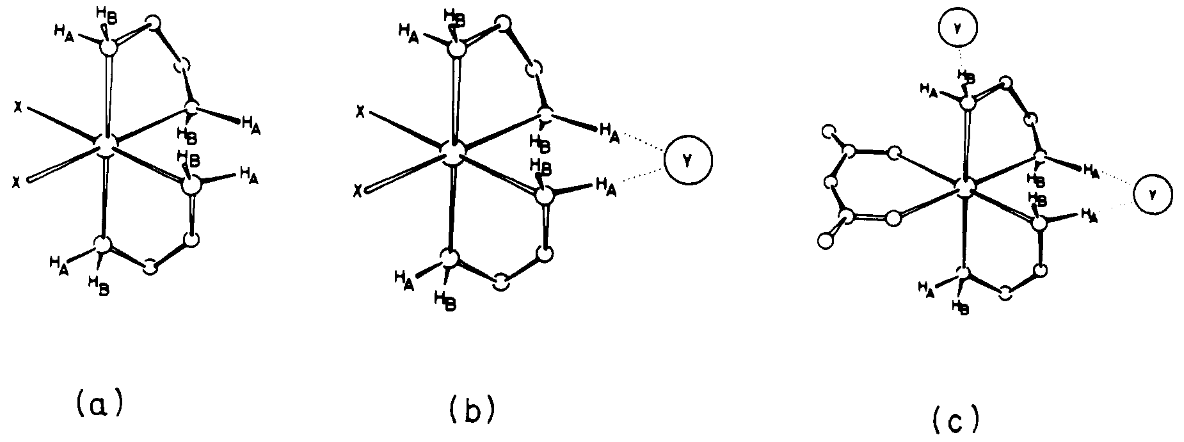

Figure 1. Schematic illustration of (a) the *cis*-$[Co(en)_2(X)_2]^{n+}$ ion, showing that there are four kinds of NH hydrogens, (b) the postulated structure of ion pairs in Me_2SO, and (c) the postulated structure of ion triplet between $[Co(en)_2(acac)]^{2+}$ and Cl^- or Br^- in Me_2SO.

To solve these problems, we here examined the amine portion of the ^1H NMR spectra of *cis*-$[Co(en)_2(X)_2]^{n+}$ in Me_2SO-d_6 and D_2O, with X covering the strong-field ligands CN^- and NO_2^- and the weak-field ligands $acac^-$, ox^{2-}, and mal^{2-}. The *cis*-$[Co(en)_2(X)_2]^{n+}$ ions contain four types of NH hydrogens; see Figure 1(a). Of these four, trans H_A and cis H_A are directed approximately parallel to the molecular C_2 axis while the remaining trans H_B and cis H_B hydrogens are not. Here trans H_A, for example, is the hydrogen on the nitrogen atom trans to the substituent X.

Experimental Section

Materials. The literature methods were used to prepare *cis*-$[Co(en)_2(CN)_2]ClO_4$,[12] *cis*-$[Co(en)_2(NO_2)_2]NO_2$,[13] $[Co(en)_2(acac)]I_2 \cdot H_2O$,[14] $[Co(en)_2(ox)]Cl \cdot H_2O$,[15] and $[Co(en)_2(mal)]I \cdot 0.5H_2O$.[16] The chloride salt of the *cis*-dicyano compound was made from the perchlorate by metathesis with potassium chloride. The bromide and iodide salts were obtained metathetically from the chloride.

The *cis*-dinitro nitrate was converted to the iodide, and the iodide was in turn treated with silver acetate to obtain the solution of the acetate salt. Addition of solid NaCl, NaBr, and $NaClO_4$ to the acetate solution yielded the corresponding salts of the *cis*-dinitro complex.

The acetylacetonato complex was treated in a manner similar to that for the *cis*-dinitro complex, and the chloride, bromide, iodide, and perchlorate salts were obtained.

The bromide, iodide, and perchlorate salts of the oxalato complex were obtained metathetically from the chloride.

The (malonato)bis(ethylenediamine)cobalt(III) iodide was ground with equimolar amount of AgCl and a small amount of water in a mortar. The mixture was filtered, and the filtrate was concentrated and cooled in ice to yield the chloride salt. The bromide and perchlorate salts were obtained from the chloride. All the complexes used in the present work were recrystallized from warm water and identified by the visible absorption and ^1H NMR spectra.

Measurements. All the ^1H NMR measurements were made at 25 °C on a JEOL PS-100 spectrometer operating at 100 MHz. The spectra were run either in deuterium oxide (Merck, 99.75 atom % D minimum) or in perdeuteriodimethyl sulfoxide (Me_2SO-d_6, Merck, 99 atom % D minimum) with an internal reference of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) or tetramethylsilane (Me_4Si), respectively.

Partial Deuteration Experiments. The chloride salt of each complex was dissolved in D_2O, and after the appropriate time of deuteration, a few drops of concentrated hydrochloric acid was added, which served to stop effectively the deuteration of amine hydrogens. The acidic solution was divided into four portions, to which solid NaCl, NaBr, NaI, or $NaClO_4$ was added and cooled in ice to obtain the precipitate of the corresponding salt. These partially deuterated salts were dissolved in acidified deuterium oxide and Me_2SO-d_6, and the ^1H NMR spectra were recorded. Thanks to the difference in deuteration rates among four types of NH hydrogens of each complex, the correspondence of each signal in the spectrum taken in acidified D_2O to that in Me_2SO-d_6 was readily apparent. This partial deuteration

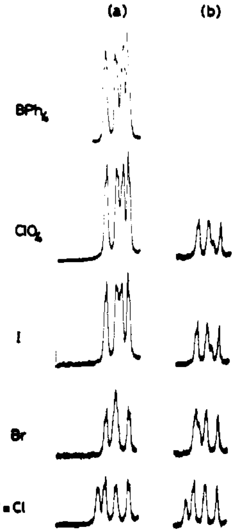

Figure 2. NH portion of the spectra of *cis*-$[Co(en)_2(NO_2)_2]Y$ in Me_2SO-d_6 (a) before and (b) after partial deuteration at amine group. Deuteration was made for the chloride salt in D_2O (0.16 M) for 55 min at 25 °C. The complex concentration is about 20 mg/mL.

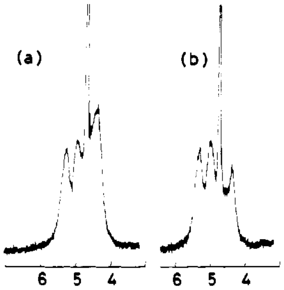

Figure 3. Amine portion of the spectra of *cis*-$[Co(en)_2(NO_2)_2]Cl$ in D_2O containing 1% DCl (a) before and (b) after partial deuteration. Conditions for deuteration are the same as in Figure 2. The peak at δ 4.74 is due to solvent HDO.

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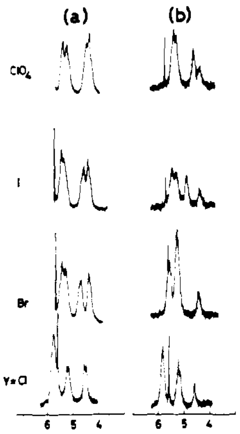

Figure 4. Amine portion of the spectra of $[Co(en)_2(acac)]Y_2$ in Me_2SO-d_6 (a) before and (b) after partial deuteration. The complex concentration is about 20 mg/mL.

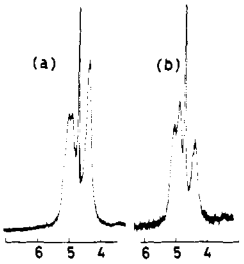

Figure 5. Amine portion of the spectra of $[Co(en)_2(acac)]Cl_2$ in D_2O containing 1% DCl (a) before and (b) after partial deuteration.

Table I. Chemical Shifts (δ) in Me_2SO-d_6^{a}

cis-$[Co(en)_2(NO_2)_2]Y$ (20 mg/mL)

Y	cis NH	cis NH	trans H_A	trans H_B
BPh_4	(5.26) 5.19	4.68 (4.62)	(4.36) 4.28	4.08 (4.00)
ClO_4	(5.26) 5.18	4.68 (4.62)	(4.38) 4.32	4.10 (4.02)
I	(5.26) 5.20	4.70 (4.64)	(4.44) 4.40	4.11 (4.04)
Br	(5.30) 5.21	4.74^{b} (4.64)^{b}	(4.85)^{b} 4.74^{b}	4.11 (4.01)
Cl	(5.32) 5.24	4.73 4.66	5.62	4.10 (4.00)

$[Co(en)_2(acac)]Y_2$ (20 mg/mL)

Y	cis NH_B	cis NH_A	trans H_A	trans H_B
ClO_4	(5.38) 5.30	5.16 (5.10)	(4.44) 4.39	4.29 (4.20)
I	(5.44) 5.38	5.28 (5.24)	(4.59) 4.53	4.36 (4.30)
Br	(5.46) 5.40	5.28 (5.24)	(4.74) 4.66	4.38 (4.30)
Cl	(5.84)^{b} 5.79^{b}	5.26 5.19	5.79^{b}	4.59 (4.54)

cis-$[Co(en)_2(CN)_2]Y$ (10 mg/mL)

Y	trans H_A	cis NH	cis NH	trans H_B
ClO_4	[4.48,^{b} 4.45,^{b} 4.37^{b}]			4.05 (3.99)
I	[4.48^{b} (4.40)^{b}]			4.06 (3.98)
Br	4.80	[4.57,^{b} 4.48^{b} (4.41)^{b}]		4.10 (4.04)
Cl	(5.41) 5.34	(4.49)^{b} 4.40	(4.32)^{b}	4.10 (4.02)

$[Co(en)_2(ox)]Y$ (10 mg/mL)

Y	cis NH	trans H_B	trans H_A
ClO_4	5.00	4.50	4.14
Br	4.98	4.45	

$[Co(en)_2(mal)]Y$ (20 mg/mL)

Y	cis NH	trans NH
ClO_4	5.24	4.12

^{a} For assignments, see text. The chemical shifts in parentheses refer to shoulders. ^{b} Overlapping peak.

technique was employed to correlate the D_2O spectra and the Me_2SO-d_6 spectra.

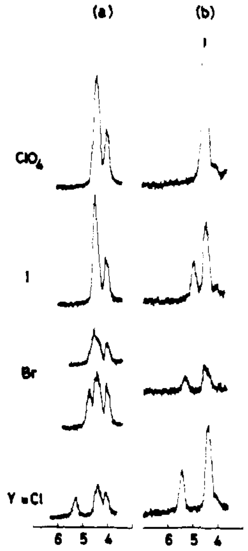

Figure 6. Amine portion of the spectra of *cis*-$[Co(en)_2(CN)_2]Y$ in Me_2SO-d_6 (a) before and (b) after partial deuteration. Deuteration was made for the chloride in D_2O (0.38 M) for 35 min at 25 °C. The complex concentration is about 10 mg/mL except for the upper spectrum of the bromide of (a), for which the concentration is halved.

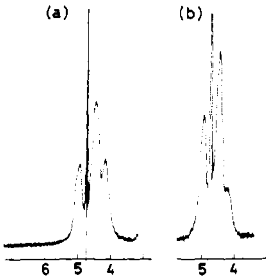

Figure 7. Amine portion of the spectra of *cis*-$[Co(en)_2(CN)_2]Cl$ in D_2O containing 1% DCl (a) before and (b) after partial deuteration. Conditions for deuteration are the same as in *Figure 6*. The peak at δ 4.74 is due to HDO.

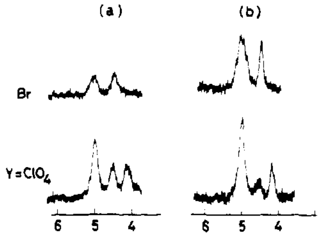

Figure 8. Amine portion of the spectra of $[Co(en)_2(ox)]Y$ in Me_2SO-d_6 (a) before and (b) after partial deuteration. Deuteration was made in D_2O (0.11 M) for 11 min at 25 °C. The complex concentration is about 10 mg/mL.

Table II. Chemical Shifts (δ) in D_2O

cis-$[Co(en)_2(NO_2)_2]^+$	5.31	4.98	4.46^{a}	
$[Co(en)_2(acac)]^{2+}$	5.08	4.97	4.43^{a}	
cis-$[Co(en)_2(CN)_2]^+$	4.95	4.46^{a}	4.17	
$[Co(en)_2(ox)]^+$	5.36	5.20	4.74^{b}	4.46
$[Co(en)_2(mal)]^+$	5.38	4.36		

^{a} Overlapping peak. ^{b} Overlapping with HDO resonance.

Results

Figures 2, 4, 6, and 8 show the tracings of the amine portion of the ^{1}H NMR spectra of *cis*-$[Co(en)_2(NO_2)_2]Y$, $[Co(en)_2(acac)]Y_2$, *cis*-$[Co(en)_2(CN)_2]Y$, and $[Co(en)_2(ox)]Y$, taken in Me_2SO-d_6.[2-9] In these figures, (a) and (b) give the spectra of undeuterated and partially deuterated (at amine

Figure 9. Time variation of the amine portion of the spectra of $[Co(en)_2(ox)]Cl$ in D_2O: bottom, immediately after dissolution; middle, 1 min after dissolution; top, after 20 min.

groups) complexes. The low solubility in Me_2SO-d_6 precluded the spectral measurements for the chloride and iodide salts of the oxalato complex and for the chloride, bromide, and iodide salts of the malonato complex. Figures 3, 5, 7, and 9 are the tracings of the amine portion of the ^1H NMR spectra of the complexes taken in D_2O or acidified D_2O. All the chemical shift values of the NH absorptions are summarized in Tables I and II, along with their assignments.

***cis*-[Co(en)$_2$(NO$_2$)$_2$]Y in Me$_2$SO-*d*$_6$.** As seen from Figure 2(a), the chloride, iodide, perchlorate, and tetraphenylborate salts give rise to four absorptions of equal intensities in the region of the NH resonances. A closer look at each line reveals that each is split into two absorptions. This point will be treated later. In the spectrum of the bromide salt, the central line has the intensity twice that of the low- and high-field signals and so this line is an overlap of two absorptions. Of these four, the chemical shifts of three absorptions are virtually unaffected by the counteranions. The remaining one, the lowest field absorption of the chloride spectrum, moves to higher magnetic fields as we go from the chloride, to the bromide, iodide, perchlorate, and tetraphenylborate. In the iodide, perchlorate, and tetraphenylborate spectra, this line appears at the second highest magnetic field. From Figure 2(b), it can be seen that this line is deuterated first of four absorptions, which is evidence for the identity of this line in these spectra. Further, the signals of Figure 2(b) resonating at the highest field changed from marginally resolved doublets into sharp singlets upon deuteration of the hydrogen responsible for the lowest field line of the chloride salt. This deuteration-induced decoupling indicates that these hydrogens are spin–spin coupled. Thus, in the chloride spectrum, for example, the outer pair and the inner pair of the four absorptions make respectively the AB-type quartet. In the iodide, perchlorate, and tetraphenylborate spectra, the low-field pair and the high-field pair make the respective AB quartet. Though the line width of each of four absorptions is rather large owing to the nuclear quadrupole relaxation of the nitrogen atoms, the spin–spin coupling constants in all these spectra can be seen to be the same within experimental errors, $J = 8 \pm 2$ Hz. The manner in which the spectral pattern of these AB quartets changes with the change in the AB chemical shift differences conforms rather well to that expected theoretically for the AB-type spectra.[17] The result of analysis of the spectra treated as the AB quartet is summarized in Table III.

It is noted that the highest field signal of the chloride, bromide, iodide, and perchlorate spectra is the second fastest in the hydrogen–deuterium exchange, as seen from its relative intensity in Figure 2(b).

Table III. Result of the AB Analysis for *cis*-$[Co(en)_2(NO_2)_2]Y$ in Me_2SO-d_6: Ratio of Intensities of the Inner Pair to the Outer Pair of the AB Quartet

	intens ratio (calcd^a)	
Y	cis amine	trans amine
BPh_4	1.2 (1.3)	1.5 (1.8)
ClO_4	1.2 (1.3)	1.4 (1.6)
I	1.2 (1.2)	1.2 (1.5)
Br	1.4 (1.4)	1.2 (1.3)
Cl	1.1 (1.3)	1.1 (1.1)

^{a} Calculated by using $J_{\text{trans}} = J_{\text{cis}} = 8 \pm 2$ Hz.

The spectra of the chloride and bromide showed concentration dependence; the lowest field line of the chloride, corresponding to the hydrogen deuterated first, undergoes a downfield shift with increasing complex concentration; see the two spectra of the bromide in Figure 2.

***cis*-[Co(en)$_2$(NO$_2$)$_2$]Cl in D$_2$O.** The compound in deuterium oxide gives rise to three broad absorptions with an intensity ratio of 1:1:2 from low to high magnetic fields. Therefore the intensity of the highest field line results from contributions from two kinds of NH hydrogens. The spectrum of the partially deuterated compound, Figure 3(b), tells that these two kinds of NH hydrogens are the fastest and the second fastest exchanging hydrogens, since the intensity of the highest field line in Figure 3(b) is smaller than the intensities of the remaining two absorptions.

Comparison of Figures 3(b) with 2(b) indicates that the NH hydrogens giving rise to the highest field line in the D_2O spectrum appear in the Me_2SO-d_6 spectrum as the highest and lowest field lines of the chloride or, equivalently, as the two high-field lines of the perchlorate. Our recent measurements established that the second lowest field line of Figure 3(a) is the slowest exchanging with deuterium.[18]

[Co(en)$_2$(acac)]Y$_2$ in Me$_2$SO-*d*$_6$. In Figure 4, the sharp peak at δ 5.65 is due to the C_3 hydrogen of the coordinated acetylacetonato moiety. (The chemical shift of this hydrogen in the chloride is δ 5.60.) Each spectrum of Figure 4(a) consists principally of four lines of equal intensities. In the chloride spectrum, the lowest field line is an overlap of two absorptions. If we look more closely at each line, each is split into two marginally resolved absorptions owing to the spin–spin coupling. This point will be discussed later.

The spectra of the chloride and bromide show concentration dependence; the lowest field line of the chloride and the second highest field line of the bromide undergo downfield shifts with increasing complex concentration; see the two bromide spectra of Figure 4.

From Figure 4(b), the identity of the highest field lines of these spectra is readily apparent, being the smallest of four lines. The chemical shift of this line undergoes a small upfield shift as we go from the chloride to the perchlorate: δ 4.59 for chloride, δ 4.38 for bromide, δ 4.36 for iodide, and δ 4.29 for perchlorate. Integration of Figure 4(b) indicates that the second fastest exchanging hydrogen corresponds to the signal at the second highest field in the perchlorate and iodide, to the overlapping peak in the chloride, and to the overlapping peak (the second highest field peak in Figure 4(a)) in the bromide.

We can see from Table I that the chemical shift of the peak at about δ 5.2–5.3 (the second highest field peak of the chloride or the second lowest field peak of the bromide) is virtually unaffected by the counteranions. Thus, we can assign this peak to the same hydrogen. After all, we could identify all four lines of these spectra: (1) the highest field peak of all the salts is due to one type of NH hydrogen, which is deuterated first; (2) the second highest field peak of the bromide, iodide, and perchlorate and the lowest field overlapping peak of the

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(17) See, for example; J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, 1959.

Table IV. Result of the AB Analysis for $[Co(en)_2(acac)]Y_2$ in Me_2SO-d_6: Intensity Ratio of the Inner Pair to the Outer Pair of the AB Quartet

	intens ratio (calcd^a)	
Y	cis amine	trans amine
ClO_4	1.8 (2.0)	
I	1.8 (2.0)	1.5 (1.7)
Br	1.7 (1.8)	1.3 (1.6)
Cl	1.0 (1.2)	1.1 (1.1)

^{a} Calculated by using $J_{trans} = J_{cis} = 7 \pm 2$ Hz.

chloride are due to a second type of NH hydrogen, which is deuterated second fastest; (3) the peak that exhibits little counteranion dependence is due to a third type of NH hydrogen, which is deuterated last[18] (this is the second highest field peak of the chloride and the second lowest field peak of the bromide, iodide, and perchlorate); (4) the remaining peak, the lowest field peak of all the salts, is due to the fourth type of NH hydrogen, which is deuterated third fastest.[18] The two hydrogens, exchanging first and second, as well as the other two, are spin–spin coupled, and altogether two sets of AB quartets can be recognized in the Me_2SO-d_6 spectra. The results of the AB analysis are given in Table IV.

$[Co(en)_2(acac)]Cl_2$ in D_2O. The spectrum of Figure 5(a) consists of three peaks with an intensity ratio of 1:1:2. Comparison of the spectra of the undeuterated and partially deuterated complexes, coupled with our recent data,[11] reveals that the two hydrogens giving rise to the highest field peak are deuterated first and second, followed by the lowest field peak, and the second lowest field peak is deuterated last. From Figures 4(b) and 5(b), it follows that the two NH hydrogens, exchanging first and second, are assigned to the highest and the second highest field peaks of the perchlorate spectrum in Me_2SO-d_6.

***cis*-$[Co(en)_2(CN)_2]Y$ in Me_2SO-d_6.** The chloride, bromide, and iodide salts in Me_2SO-d_6 exhibit a strong concentration dependence. As an illustration of this, two bromide spectra are provided in Figure 6(a), in which the concentration of the upper spectrum is half that of the spectrum below. These spectra indicate that only the lowest field peak undergoes a downfield shift with increasing complex concentration. This peak appears in the chloride spectrum at the lowest magnetic field and in the perchlorate as an overlapping peak. The highest field peaks of all the salts show little dependence upon the complex concentration and the counteranions and have almost the same chemical shifts. Thus, the highest field peak is due to the same type of NH hydrogen. This assignment is further substantiated by the spectra of partially deuterated compounds; the highest field peaks of all the salts were deuterated first and almost disappeared.

Spectra were measured at several stages of deuteration, and it was found that the second fastest exchanging hydrogen corresponds to the peak that undergoes the counteranion-dependent shifts, the peak resonating at the lowest magnetic field in the chloride and bromide.[18] Extensive deuteration leaves only the peak at about δ 4.52 ± 0.02 for all the salts, so that this hydrogen is deuterated last.

***cis*-$[Co(en)_2(CN)_2]Cl$ in D_2O.** The spectrum of this compound in D_2O consists of three absorptions with an intensity ratio of 1:2:1; see Figure 7. Figure 7(b) reveals that the highest field peak diminishes its intensity first. Our recent results on the deuteration rates of this compound established that the lowest field peak is the slowest in hydrogen–deuterium exchange.[18] Comparison with the spectra in Figure 6 correlates the highest field peak of the D_2O spectrum with the highest field peaks in the Me_2SO-d_6 spectra. The lowest field peak of the D_2O spectrum, the slowest exchanging one, corresponds in the Me_2SO-d_6 spectra to the peak at about δ 4.52 ± 0.02. The central peak of the D_2O spectrum contains, therefore, contributions from two types of NH hydrogens that are deuterated second and third.

$[Co(en)_2(mal)]ClO_4$ in Me_2SO-d_6. Only the perchlorate salt dissolved in Me_2SO-d_6 to an appreciable extent and showed two well-separated resonances at δ 5.24 and 4.12 with equal intensities. The high-field peak is deuterated first.

$[Co(en)_2(mal)]Cl$ in D_2O. The compound exhibits two signals with equal intensities. Of these, the high-field peak has a larger deuteration rate. Thus, the high-field peak in both Me_2SO-d_6 and D_2O spectra results from the same NH hydrogens.

$[Co(en)_2(ox)]Y$ in Me_2SO-d_6. While the bromide of this complex showed only two peaks, the perchlorate gives three absorptions; see Figure 8(a). Of these three, two peaks have the same chemical shifts as the bromide. Thus, the high-field peak of the bromide is an overlap of the two high-field resonances of the perchlorate. Figure 8(b) indicates the fastest exchanging peak to be the high-field one of the bromide and the second highest field one of the perchlorate.

$[Co(en)_2(ox)]Cl$ in D_2O. Figure 9 illustrates the time variation of the spectrum of the oxalato complex in pure D_2O. The bottom figure was measured immediately after dissolution and consists of four peaks of equal intensities. Of these four, one peak is overlapped with strong HDO absorption and the two low-field peaks are overlapped with each other to some extent. The rate of deuteration is largest either for the highest field peak or for the second highest field peak but the relative rate of deuteration of these two peaks could not be determined with any certainty.

Discussion

Assignment. The results of *cis*-dinitro, acetylacetonato, dicyano, and oxalato complexes indicated the presence of one particular hydrogen that undergoes a large chemical shift variation from the counteranions. The chemical shift of this hydrogen moves to low fields by counteranions on going from the perchlorate to the iodide, bromide, and chloride, in this order. The chemical shifts of this hydrogen showed also concentration dependence in the case of chlorides, bromides, and iodides; the higher the complex concentration, the lower the resonance field of this hydrogen. The effect of the counteranions and of the complex concentration upon the chemical shifts of the other three types of NH hydrogens is less prominent.

When dissolved in D_2O, each of these complexes gives the same spectral patterns and chemical shifts, irrespective of the counteranion used.

These results indicate the importance of ion association between the complex cation and the counteranion in Me_2SO-d_6. To our knowledge, the ion-association constants for the present complexes in Me_2SO do not appear to be reported. The ion-association constant for *cis*-$[Co(en)_2Cl_2]Cl$ in Me_2SO is determined at $K = 397$ (25 °C).[19] If we assume the K value of a similar magnitude for the present complexes, our complexes are expected to be ion-associated to an appreciable degree. Further it is generally accepted[20] that the ion-association constant in dipolar aprotic solvents increases in the order of counteranions: $Cl^- > Br^- > I^- > ClO_4^-$. The perchlorate anion is not a hydrogen-bond acceptor and is shown

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[19] W. A. Millen and D. W. Watts, *J. Am. Chem. Soc.*, **89** 6858 (1967).

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to be completely dissociated in dipolar aprotic solvents.[21] The tetraphenylborate anion is believed to show little tendency to ion association in nonaqueous solvents with bulk dielectric constants greater than 15.[22] The hydrogen-bonding ability of the anions exactly parallels the above order. All these facts are consistent with the postulate that the chemical shift changes of one particular hydrogen are brought about by ion association with counteranions, via hydrogen bonding through NH. For electrostatic reasons and for the reasons mentioned below, the actual site occupied by the counteranions should be as depicted in Figure 1(b). A similar mode of association was proposed by Yoneda and coworkers[11] and by Watts[23] from kinetic studies. This model will be shown later to be consistent with previous studies. Thus, we assign the peak exhibiting the greatest counteranion dependence to trans H_A. In the *cis*-dinitro compound, trans H_A is the hydrogen that is detuerated first and shows the most downfield shift as the chloride in $Me_2SO\text{-}d_6$. In D_2O, this hydrogen resonates at δ 4.46. Trans H_A of the acetylacetonato complex is deuterated second fastest and appears in $Me_2SO\text{-}d_6$ at the second highest magnetic field in the perchlorate and the lowest field in the chloride. In D_2O, this hydrogen appears at δ 4.43. Trans H_A of the *cis*-dicyano compound appears at the lowest magnetic field in all salts in $Me_2SO\text{-}d_6$. (In actuality, it is involved in the overlapping peak in the perchlorate and iodide). For the oxalato compound, Figure 8(a) indicates that trans H_A is to be assigned to the peak at δ 4.14 in the perchlorate and is downfield shifted by the bromide ion to δ 4.45.

The assignment of trans H_B is made as follows. In the *cis*-dinitro compound, deuteration of trans H_A results in decoupling of the highest field peak of all the salts in $Me_2SO\text{-}d_6$. Since the two trans hydrogens are expected to be spin-spin coupled, this highest field peak of $Me_2SO\text{-}d_6$ spectra is assigned to trans H_B. As is evident from Figure 2(b), trans H_B of the *cis*-dinitro complex is deuterated second fastest and resonates at the highest field in all salts in $Me_2SO\text{-}d_6$. In D_2O, it appears at δ 4.46, overlapping with trans H_A. In the acetylacetonato compound, trans H_A is decoupled upon deuteration of the highest field peak of all salts; see Figure 4(b). Therefore, the highest field peak is due to trans H_B. This assignment is supported by the observation that they give rise to an AB-type quartet.

Trans H_B, being deuterated first, is overlapped with trans H_A in the D_2O spectrum to give a singlet at δ 4.43. The *cis*-dicyano complex shows its trans H_B at the highest magnetic field in $Me_2SO\text{-}d_6$. This assignment follows from the observation that the lowest and the highest field signals of the chloride salt are spin-spin coupled to give an AB quartet. Trans H_B of the cyano compound is the first to be deuterated, so that it corresponds to the peak at δ 4.17 in the D_2O spectrum. Trans H_B of the oxalato compound is assigned to the peak at δ 4.50 in the perchlorate and at δ 4.45 in the bromide because sharpening of trans H_A resonance is brought about by deuteration of trans H_B. The spectrum of the perchlorate salt in Figure 8(b) shows that deuteration of trans H_B sharpens the trans H_A peak at δ 4.14.

The malonato complex exhibits only two resonances in both $Me_2SO\text{-}d_6$ and D_2O. In both solvents the faster exchanging peak is the high-field one. From the discussion made above for the other complexes, it has become clear that trans hydrogens are deuterated faster than cis ones. If we apply this criterion to the malonato complex, the high-field resonance in both solvents corresponds to trans hydrogens.

Recently we have shown that added malonate anion can be used to assign the amine signals of $[Co(en)_2(acac)]^{2+}$ in deuterium oxide.[11] The malonate anion worked in two ways in the deuteration of amine groups; stereoselective association with only one type of trans NH (trans H_A) decelerates the deuteration rate of this particular hydrogen, while the malonate anion works as general-base catalyst for hydrogen exchange. On the basis of these observations, we assigned the high-field signal of Figure 5 to the two trans hydrogens and the second highest field peak to cis H_A, which is poised over the acetylacetonato chelate. This assignment is fully consistent with the present one. The previous assignment made for the *cis*-dicyano and *cis*-dinitro complexes in D_2O on the basis of the magnetic anistropy of the central cobalt(III) ion needs some modification, though the 60-MHz spectra of these two complexes gave only two resonances.[5,7] It is now clear that the two trans NH hydrogens of the *cis*-dinitro complex resonate at a higher magnetic field than cis ones in D_2O. For the *cis*-dicyano complex, the foregoing discussion indicated that the fastest and the second fastest exchanging hydrogens are trans H_B and trans H_A, respectively. In the D_2O spectrum of Figure 7, the highest and lowest field peaks are deuterated first and last, respectively, and thus the central overlapping peak is due to one trans NH plus one cis NH. After all, the three peaks of the D_2O spectrum are assigned to trans H_B, trans H_A plus cis NH, and cis NH from high to low fields, in this order.

Since the D_2O spectra of all the complexes did not depend upon the counteranions and the perchlorate is most probably completely dissociated in $Me_2SO\text{-}d_6$,[20] the difference in the spectra of perchlorate salts in both solvents can be attributed solely to solvent effects. Though the contribution of the magnetic anisotropy of the S=O group of Me_2SO to the N—H···O=S chemical shift is not clear,[24] it is believed to be small.[25] Therefore spectral difference in both solvents is most probably brought about by D_2O. If we compare the chemical shift of each hydrogen of all the complexes measured in both solvents, it is apparent that the D_2O solvent causes a downfield shift for all the NH resonances except the cis amine resonances of the acetylacetonato complex. This result may be interpreted by regarding D_2O as a stronger hydrogen-bonding solvent than $Me_2SO\text{-}d_6$ since it is established that hydrogen bonding causes downfield shifts.[17] The peculiar behavior of the cis hydrogens of the acetylacetonato complex may be reconciled with the hydrophobic nature of the acetylacetonato ligand and a poor solvation by D_2O about this ligand.

Structure of Ion Triplets. The foregoing discussion has demonstrated the structure of ion pairs in $Me_2SO\text{-}d_6$ solvent, as illustrated in Figure 1(b). Unlike the *cis*-dinitro, *cis*-dicyano, and oxalato compounds, the acetylacetonato complex is dipositive and carries two counteranions per cation. From its counteranion dependence, trans H_A is identified and assigned. If we compare the spectra of the chloride and bromide of Figure 4(a), we note the presence of another peak whose chemical shift is also susceptible to counteranions. This is the peak at about δ 5.8 in the chloride and at about δ 5.4 in the bromide. Since the two high-field peaks in the bromide spectrum are assigned to trans H_A and trans H_B, this is attributed to one of the cis NH hydrogens. As is clear from the preceding discussion, this is cis H_B, being deuterated third fastest. Therefore, the first-step association takes place between trans H_A and one of the two counteranions and the second-step of association between cis H_B and the second

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counteranion. The structure of the postulated ion triplet is depicted schematically in Figure 1(c).

The importance of the structure of ion-associated species is readily appreciated if we note that kinetic forms and steric courses of many reactions of metal complexes in nonaqueous solvent are affected by ion association. These aspects of complex reactions have been emphasized by Watts in his recent review.[23] For example the kinetic forms and the steric courses of the anation reaction in dimethylformamide

$$cis\text{-}[Co(en)_2(DMF)Br]^{2+} + Br^- \xrightarrow{DMF} cis\text{- and } trans\text{-}[Co(en)_2(Br)_2]^+ + DMF \quad (1)$$

could not be explained without the consideration of ion-association preequilibria. Watts stated that the actual sites occupied by the bromide ion are of primary importance in determining the steric course of the substitution reaction. In reaction 1, the formation of the ion triplet which has the counteranion in the cis NH sites is postulated to favor the cis product.[23]

Rate of Deuteration. The rate of deuteration was greatest for trans H_A in the *cis*-dinitro compound whereas in the acetylacetonato, *cis*-dicyano, and oxalato complexes, trans H_B showed the largest rate of deuteration. We have previously reported that cis and trans amine or ammine groups of $[Co(NH_3)_5X]^{n+}$ and *cis*-$[Co(en)_2(X)_2]^{n+}$ ions are deuterated in D_2O at unequal rates.[5] While the trans ammine group of $[Co(NH_3)_5CN]^{2+}$ is deuterated more slowly than cis groups, the complexes $[Co(NH_3)_5X]^{2+}$ with X = NCS^-, Cl^-, $NH_2CO_2^-$, $CH_3CO_2^-$, and F^- showed the opposite behavior.[4a,5] We ascribed this difference to the trans influence of the sixth ligand. The present result established that in the *cis*-$[Co(en)_2(X)_2]^{n+}$ complexes, trans amine groups are deuterated faster than cis ones. Thus, for at least present *cis*-bis(ethylenediamine) complexes, the discussion based on the trans influence does not seem pertinent. The reason for the larger rate of trans amine groups in *cis*-$[Co(en)_2(X)_2]^{n+}$ may be the electrostatic one; the negatively charged OD^- catalyst attacks NH groups preferably from the side opposite to negatively charged X ligands. It is well established that the deuteration at coordinated amine groups is catalyzed by the hydroxide ion.[5] It is interesting to note that in the *cis*-dicyano, oxalato, and acetylacetonato complexes the hydrogen, trans H_B, that is deuterated first by OD^- is not the one that is most perferably associated with the counteranions in Me_2SO. In contrast, the *cis*-dinitro complex, the fastest exchanging hydrogen is the preferential site for ion association. This disparity may be explained by an intramolecular hydrogen bonding between the oxygen atoms of the nitro group and trans NH hydrogen(s). This type of intramolecular hydrogen bonding is found frequently in the structure of crystals containing the *cis*-$[Co(en)_2(NO_2)_2]^+$ cation.[26] In crystals, the orientation of the nitro groups are regulated either by this type of hydrogen bonds and/or by intermolecular forces. One piece of evidence for the strength of such regulation is the occurrence of two isomers due to the orientation of nitro groups.[27] We may expect also in solution that the nitro groups are hydrogen bonded to trans NH_B hydrogens. If this intramolecular hydrogen bonding is operative in solution, trans H_B is considered to be blocked effectively from the attack of the OD^- catalyst. This may be the reason for trans H_A, not trans H_B, being deuterated first in only the *cis*-dinitro compound.

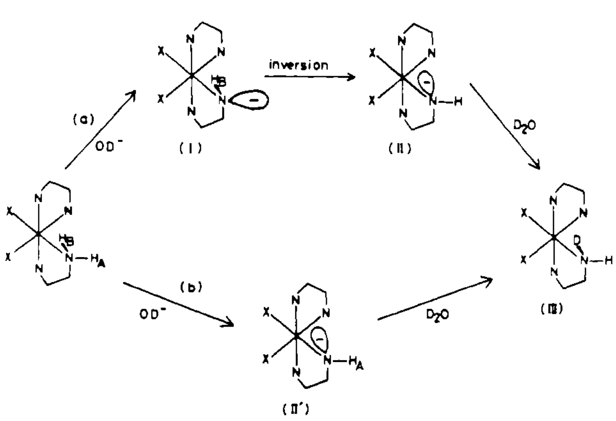

Figure 10. A scheme which gives a larger rate of deuteration for trans H_B than for trans H_A.

In the *cis*-dicyano, oxalato, and acetylacetonato compounds, trans H_B is deuterated faster than the other three NH hydrogens. The reason for this is not readily apparent, even if we accept that trans amine groups are universally exchanged with deuterium faster than cis ones. One plausible mechanism is illustrated in Figure 10. Process a assumes that the deprotonation takes place first at NH_A while process b is initiated by hydrogen abstraction at NH_B. If we postulate that the negatively charged OD^- catalyst approaches the complex cation along the molecular C_2 axis and from the side opposite to the negatively charged X ligands for electrostatic reasons, process b appears less likely. However, in process a, the resulting "amido" lone-pair electrons of intermediate I should invert rapidly into intermediate II, followed by the deuteration by D_2O donating D^+ to II to give the N-deuterated product III. The rate of inversion at coordinated nitrogen centers has been investigated by several workers.[28–31] In all such works, coordinated nitrogen centers are asymmetric and N methylated and so the methyl substituents suffer steric interactions form the rest of the molecule. Thus, inversion at these N centers is restricted.[30,31] In the complexes examined here, such steric interactions are expected to be greatly alleviated and the rate of inversion might as well become large. The N-substituents are known to prefer to orient themselves between the ethylenediamine chelate and X ligand (structure II), thus avoiding nonbonded interactins which are expected to be greater for structure I. This conformational preference will favor rapid inversion of I into II. In all cases investigated so far, however, the rate of inversion is very small as compared with the rate of hydrogen exchange. Thus, we cannot at present rule out either possibilities, but it seems tempting to assume that the OD^- catalyst attacks first trans H_B rather than trans H_A.

Registry No. *cis*-$[Co(en)_2(NO_2)_2]BPh_4$, 76233-04-0; *cis*-$[Co(en)_2(NO_2)_2]ClO_4$, 14781-32-9; *cis*-$[Co(en)_2(NO_2)_2]I$, 51321-45-0; *cis*-$[Co(en)_2(NO_2)_2]Br$, 20298-24-2; *cis*-$[Co(en)_2(NO_2)_2]Cl$, 15079-78-4; $[Co(en)_2(acac)](ClO_4)_2$, 54361-33-0; $[Co(en)_2(acac)]I_2$, 15627-56-2; $[Co(en)_2(acac)]Br_2$, 76250-73-2; $[Co(en)_2(acac)]Cl_2$, 15079-89-7; *cis*-$[Co(en)_2(CN)_2]ClO_4$, 76250-74-3; *cis*-$[Co(en)_2(CN)_2]I$, 76233-05-1; *cis*-$[Co(en)_2(CN)_2]Br$, 76232-97-8; *cis*-$[Co(en)_2(CN)_2]Cl$, 16773-79-8; $[Co(en)_2(ox)]ClO_4$, 36527-75-0; $[Co(en)_2(ox)]Br$, 15713-71-0; $[Co(en)_2(mal)]ClO_4$, 76232-98-9; deuterium, 7782-39-0; $[Co(en)_2(ox)]Cl$, 17439-00-8.

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