A yellow solid obtained by eluting with benzene containing 0.5% acetone was identified as **34** (~10% yield) by its infrared spectrum and X-ray powder pattern.

2. With $RhCl(CO)(Ph_3P)_2$. Attempted reaction as in method 1 gave unchanged carbonyl complex.

3. With $RhCl(C_8H_{14})_2$. To a stirred solution of the stilbene ligand (0.25 g) in 30 ml of benzene was added 0.15 g of the cyclooctene complex. An orange-yellow solution formed immediately, which was stirred at room temperature for 5 hr. Evaporation to dryness at 15 mm gave a yellow residue of **34a**, identified by its infrared spectrum and X-ray powder pattern. The solid was treated with sodium thiocyanate (0.52 g) in 30 ml of boiling acetone. The orange crystals (0.25 g, 75%) were identical (infrared, nmr, and X-ray) with **36**.

Rhodium(I) Complexes of Tri-*p*-tolylphosphine and Tri-*m*-tolylphosphine. 1. $RhCl\{(p\text{-}CH_3C_5H_4)_3P\}_3$. Treatment of μ,μ'-dichloro-bis(1,5-cyclooctadiene)dirhodium(I)[59] (0.1 g) with $(p\text{-tol})_3P$ (0.7 g) in 30 ml of boiling *n*-hexane under nitrogen gave initially a yellow suspension which on refluxing gave a red precipitate. After 1 hr the solution was cooled to room temperature and evaporated to *ca.* 15 ml at 15 mm; the red microcrystalline precipitate was filtered and washed with *n*-pentane, yield 0.29 g (70%). *Anal.* Calcd for $C_{63}H_{63}ClP_3Rh$: C, 71.9; H, 6.0; Cl, 3.4; P, 8.8. Found: C, 70.7; H, 6.3; Cl, 4.4; P, 9.1.

A similar reaction with $(m\text{-tol})_3P$ gave an orange precipitate which was soluble in all organic solvents and could not be purified from excess ligand.

2. $RhCl(CO)\{(p\text{-tol})_3P\}_2$ (11). i. Treatment of $RhCl\{(p\text{-tol})_3P\}_3$ (0.3 g) in 30 ml of benzene with CO at 25° (1 atm) gave a complex identical with that prepared by Vallarino[10] from $[RhCl(CO)_2]_2$ and the ligand.

ii. Hydrated rhodium(III) chloride (0.75 g) and $(p\text{-tol})_3P$ (4.5 g) in 150 ml of 2-methoxyethanol were heated under reflux in a nitrogen atmosphere for 6 hr. The solution was cooled to 0° and kept at this temperature overnight. Yellow crystals of **11** (1.5 g, 68%) were isolated. A similar reaction occurred in boiling 2-(2-methoxyethoxy)ethanol to give an 86% yield of crude product, 68% of recrystallized product.

3. $RhCl(CO)\{(m\text{-tol})_3P\}_2$ (10). i. An authentic sample was prepared by treating $[RhCl(CO)_2]_2$ (0.25 g) in 10 ml of benzene with $(m\text{-tol})_3P$ (0.78 g). The crude product was recrystallized from 1:1 dichloromethane–ethanol and dried at 80° (10^{-2} mm), ν(CO) 1975 cm^{-1} (Nujol).

ii. The reaction was carried out as under 2ii; the product (88% yield of crude, 63% yield of recrystallized) was identical with that obtained above.

Rhodium(I) Carbonyl Complexes of *o*-Tolylphosphines. Authentic samples of **7**, **8**, and **9** were prepared from $[RhCl(CO)_2]_2$ in benzene and the ligand. Solvent was removed at 15 mm, the residue washed with ethanol to remove excess ligand, and the product recrystallized from benzene–ethanol [in the case of $Ph_2(o\text{-tol})P$ and $Ph(o\text{-tol})_2P$] or chloroform–ethanol [in the case of $(o\text{-tol})_3P$].

Acknowledgments. We thank Dr. R. Bramley for esr and nmr measurements and for helpful discussion, Professor J. Lewis and Mr. R. B. Bentley, Manchester University, for the temperature-range magnetic measurements, and Dr. R. S. Coffey, Research Department, ICI Heavy Organic Chemicals Division, Billingham Co., Durham, England, for enabling us to use the analytical facilities of the division and for helpful discussion. This work would not have been possible without a generous loan of rhodium(III) chloride from Johnson Matthey Co. We also acknowledge the award of a Science Research Council studentship to P. A. L.

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[59] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

Stereospecificity of the Dichlorobis(ethylenediamine)cobalt(III) Ion in an Optically Active Solvent

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Abstract: A stereospecific substitution reaction for the two chloride ligands in *cis*-dichlorobis(ethylenediamine)cobalt(III) chloride by an optically active solvent, 1,2-propanediol, has been observed. The study follows the reactions of the optical and geometrical isomers of the complex when they are dissolved in a particular optical isomer of the solvent. Absorption spectra and circular dichroism data have been interpreted as showing the solvent coordinated as a bidentate ligand with stereospecificity imposed upon the system by conformational interactions.

In the past, much work has been done on the production of optically active ions in solutions of optically inactive complexes. These effects have been named asymmetric syntheses, asymmetric inductions, and asymmetric transformations. Although these effects have generally been observed in common solvents, some interesting examples have been produced in optically active solvents. Asymmetric inductions in metal complexes have been demonstrated,[1-3] while asymmetric syntheses in an optically active solvent have been observed in a very limited number of systems.[4] One of these involved the observation of circular dichroism activity in a solution of racemic *cis*-dichlorobis(ethylenediamine)cobalt(III) tetraphenylborate, *rac-cis*-$[Co(en)_2Cl_2]B(C_6H_5)_4$, in the optically active solvent L-2,3-butanediol.[4] It was concluded from that study that an antiracemization reaction was occurring with the production of only one optical antipode of the complex ion in solution. A subsequent paper[5] indicated that the optically active species in solution was actually a solvolysis product with the solvent acting as a unidentate ligand. We wished to examine the reaction further in a similar optically active solvent, 1,2-propanediol, and to extend the study by using the optical and

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[1] B. Bosnich, *J. Amer. Chem. Soc.*, **88**, 2606 (1966).

[2] R. A. Haines and A. A. Smith, *Can. J. Chem.*, **46**, 1444 (1968).

[3] A. A. Smith and R. A. Haines, *ibid.*, **47**, 2727 (1969).

[4] B. Bosnich, *J. Amer. Chem. Soc.*, **89**, 6143 (1967).

[5] B. Bosnich and D. W. Watts, *ibid.*, **90**, 6228 (1968).

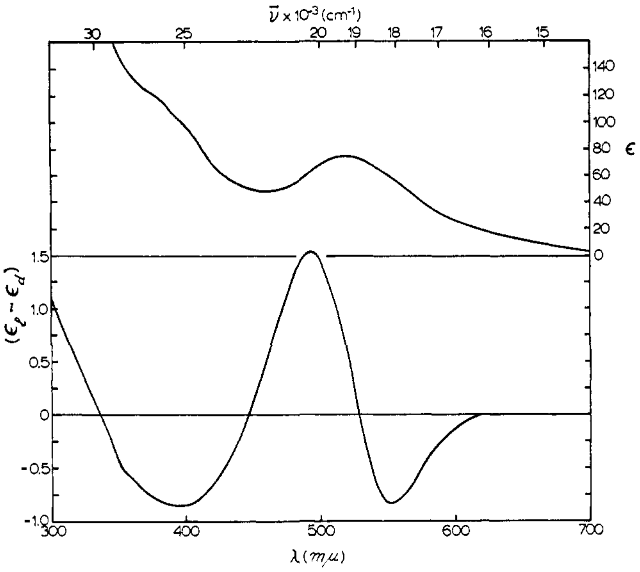

Figure 1. Equilibrium absorption and CD spectra for racemic *cis*-$[Co(en)_2Cl_2]Cl$ in L(−)-1,2-propanediol.

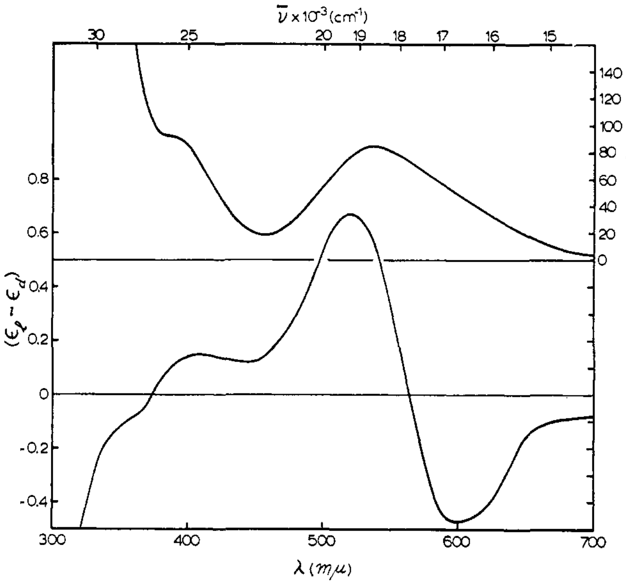

Figure 2. Absorption and CD spectra of a fresh solution of Λ-$(+)_{589}$-*cis*-$[Co(en)_2Cl_2]Cl$ in L(−)-1,2-propanediol.

geometrical isomers of the $[Co(en)_2Cl_2]^+$ ion, *i.e.*, *d-cis*, *l-cis*, *rac-cis*, and *trans*. Our results indicate the reaction in solution is not an asymmetric synthesis, but is actually a stereospecific substitution by the solvent molecules for the two chloride ions in the complex.

Results

Complexes in L(−)-1,2-Propanediol. 1. Racemic *cis*-$[Co(en)_2Cl_2]Cl$. The reaction observed in solution was essentially the same as that reported by Bosnich,[4] and the peak wavelengths of the CD curve were virtually identical with those obtained previously, with slight differences in intensity. When racemic *cis*-$[Co(en)_2Cl_2]Cl$ is dissolved in L(−)-1,2-propanediol and the reaction allowed to continue at room temperature, a strong CD curve is observed in the visible region, as shown in Figure 1. The curve first appeared within a few hours after dissolution, but 4 weeks was required for the solution to come to chiral equilibrium. Simultaneously, a change in the absorption spectrum was also observed. A fresh solution of the racemic complex gave a single peak at 534 mμ, which shifted to 519 mμ during the course of the reaction. A shift of this magnitude would indicate the presence of a ligand other than chloride.

2. Λ-$(+)_{589}$-*cis*-$[Co(en)_2Cl_2]Cl$. The CD and absorption spectra of a fresh solution of this compound in L(−)-1,2-propanediol are shown in Figure 2. Only slight differences in intensity are observed using water as solvent.[6] In L(−)-1,2-propanediol, the CD spectrum changed considerably with time, indicating a definite change in absorbing species. After 1 day in solution, the original negative CD peak at high wavelength disappeared completely, and a new negative peak started to form at ~550 mμ. Approximately 5 weeks was required for chiral equilibrium, with the peak values for the final CD curve being those shown in Table I. During this time, the absorption peak underwent a shift from 534 to 516 mμ.

3. Δ-$(-)_{589}$-*cis*-$[Co(en)_2Cl_2]Cl$. The CD curve of a fresh solution of this complex in L(−)-1,2-propanediol was almost the exact mirror image of the curve shown in Figure 2. This isomer was by far the fastest to reach chiral equilibrium in this solvent and gave constant CD values after 48 hr. The CD maxima are given in Table I, and the absorption spectrum maximum shifted from 534 to 518 mμ.

4. *trans*-$[Co(en)_2Cl_2]Cl$. The limiting CD spectrum observed for the *cis* complexes was also observed in this case, equilibrium being reached after 2 weeks. CD peak values are given in Table I. The absorption spectrum changed during this time from one with two peaks at 619 and 455 mμ to one with a single peak at 518 mμ.

Complexes in D(+)-1,2-Propanediol. In general, the complexes in D-1,2-propanediol gave the mirror image of the final equilibrium curves of the complexes in L-1,2-propanediol after the completion of the reaction. Table II gives the CD maxima for each isomer.

It should be mentioned that the reaction was also studied in D-1,2-propanediol using the hydrated chloride salts of the complex *cis*-$[Co(en)_2Cl_2]Cl \cdot H_2O$. The spectra for these compounds gave curves similar to those of the anhydrous samples, but with much lower intensities. In all cases the absorption spectrum changed from that of the complex chloride salt to that with an absorption peak at 518 mμ.

The tetraphenylborate salt, racemic *cis*-$[Co(en)_2Cl_2]B(C_6H_5)_4$, was also dissolved in D-1,2-propanediol to give a direct comparison with Bosnich's work.[4] The CD spectrum observed was identical, within experimental error, with that obtained using chloride as anion. Hence, the effect is probably associated with the cationic portion of the molecule.

Complexes in Racemic 1,2-Propanediol. All solutions prepared using racemic solvent showed no CD activity after standing for 2 days. Under anhydrous conditions, the violet *cis* isomers produced a green color after a few hours, and spectral analysis indicated these solutions contained over 95% of the *trans* isomer.

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[6] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

Table I. Circular Dichroism in L(−)-1,2-Propanediol

Racemic *cis*[a]		Λ-(+)$_{589}$-*cis*[a]		Δ-(−)$_{589}$-*cis*[a]		*trans*[a]	
λ, mμ	CD	λ, mμ	CD	λ, mμ	CD	λ, mμ	CD
552	−0.83	554	−1.24	551	−2.29	552	−1.55
492	1.53	495	3.36	491	3.39	493	3.42
396	−0.85	390	−1.82	390	−1.73	390	−1.78
368 (sh)	−0.69	368 (sh)	−1.39	368 (sh)	−1.25	368 (sh)	−1.38

[a] $[(Co(en)_2Cl_2]^+$.

Table II. Circular Dichroism in D(+)-1,2-Propanediol

Racemic *cis*[a]		Λ-(+)$_{589}$-*cis*[a]		Δ-(−)$_{589}$-*cis*[a]		*trans*[a]	
λ, mμ	CD	λ, mμ	CD	λ, mμ	CD	λ, mμ	CD
555	0.65	551	1.73	556	0.34	556	0.34
497	−1.05	491	−1.48	500	−0.78	492	−0.26
412	0.60	408	1.06	400	0.42	401	0.31
371 (sh)	0.44	371 (sh)	0.73	374 (sh)	0.39	365 (sh)	0.23
2[b]		3[b]		7[b]		13[b]	

[a] $[Co(en)_2Cl_2]^+$. [b] Days required for chiral equilibrium.

When the *cis* isomers were put in racemic solvent which also contained a small amount of water, the solutions turned pink, with an absorption peak at 518 mμ, suggesting the presence of the same species as in the optically active solvents.

Various tests were performed in racemic solvent to determine whether or not any chloride ions were coordinated to the cobalt. A fresh solution of Δ-*cis*-$[Co(en)_2Cl_2]Cl$ in racemic solvent was treated with $AgNO_3$ solution and the AgCl was filtered off. Absorption spectra taken before and after introduction of silver ion showed a shift in the absorption maximum from 534 to 505 mμ (possibly due to aquo- or nitrato-containing species). An equilibrium solution of the same complex in racemic 1,2-propanediol gave an absorption spectrum at 517 mμ, and after addition of silver ion and removal of precipitate, this was observed at 516 mμ. This indicates no chloride ions are coordinated in the final equilibrium species. This conclusion is supported by conductivity titrations, which have given values from 2.6 to 2.8 for the number of chloride ions in solution at equilibrium. Conclusive support is available from the fact that the compounds racemic *cis*-bis(dimethylformamide) bis (ethylenediamine) cobalt(III) perchlorate, *cis*-$[Co(en)_2(DMF)_2]\ (ClO_4)_3$, and racemic *cis*-diaquobis(ethylenediamine)cobalt(III) nitrate, *cis*-$[Co(en)_2(H_2O)_2]\ (NO_3)_3$, when dissolved in L-1,2-propanediol, exhibit CD spectra differing only in intensity from that of *cis*-$[Co(en)_2Cl_2]Cl$ at equilibrium. Moreover, the absorption spectra of these complexes change to give absorption peaks at 516 and 517 mμ, respectively, in L(−)-1,2-propanediol.

Unfortunately, the equilibrium species could not be obtained in the crystalline state, although attempts were made to precipitate the complex from various solvent mixtures and by using high molecular weight anions, including tetraphenylborate ($B\,(C_6H_5)_4^-$) and hexabromobismuthate ($BiBr_6^{3-}$). Removal of the solvent from solution caused a return to the dichloro compounds, generally as the *trans* isomer.

Discussion

The fact that the CD spectra in D- and L-1,2-propanediol were mirror images of each other indicates that the equilibrium species present in the two solvents are exact enantiomers. It is now quite certain that this compound contains no chloride ion as ligand. This is shown by the shift in absorption maximum, conductivity titrations, reactions using silver ion, and the fact that the equilibrium CD and absorption spectra for *cis*-$[Co(en)_2(DMF)_2]^{3+}$ and *cis*-$[Co(en)_2)H_2O)_2]^{3+}$ in L-1,2-propanediol were identical with those obtained for the dichloro complex in that solvent.

The significance of water in the determination of the final color of the solutions in racemic 1,2-propanediol shows that it must play an important role in the reaction. The water, however, cannot remain coordinated to the cobalt atom in the equilibrium species since the absorption spectra are inconsistent with the presence of water as a ligand. Also, the new species must be one in which stereospecificity is possible and molecular models have shown that an aquopropanediol species should not be stereospecific and therefore should not give rise to any CD activity in the optically active solvents. It may therefore be concluded that 1,2-propanediol is the only ligand filling the coordination sites vacated by chloride. It should be noted that infrared spectra of the optically active solvents before use showed a very small water peak at 1630 cm^{-1}. The amount of water is also critical. If too much water is present, the complex may react in a nonstereospecific manner to yield aquo-containing species, thus causing a quenching of the CD intensities. This was observed for the hydrated *cis*-dichloro compounds in D-1,2-propanediol where lower intensities for the CD maxima were observed than for the anhydrous salts. Alternatively, too little water present leads to isomerization of the complex to the *trans* form as has been observed in other alcohols.[7] This may have been the case in Bosnich's original work,[4] where the absorption spectra showed that a large proportion of *trans* isomer was present.

The only stereospecific substitution reaction possible is one in which the solvent molecule coordinates in a bidentate manner. This would produce a molecule closely analogous to the bis(ethylenediamine)propylenediaminecobalt(III) ion, $[Co(en)_2pn]^+$. Stereospecificity

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[7] (a) D. D. Brown and C. K. Ingold, *J. Chem. Soc.*, 2680 (1953); (b) D. D. Brown and R. S. Nyholm, *ibid.*, 2696 (1953); (c) B. Bosnich, C. K. Ingold, and M. L. Tobe, *ibid.*, 4074 (1965); (d) R. C. Brasted and C. Hirayama, *J. Amer. Chem. Soc.*, 80, 788 (1958).

in propylenediamine-containing cobalt complexes has been previously demonstrated,[8–11] and the same arguments apply in this case. Considering L-1,2-propane diol, a five-membered ring coordination is possible with the ring in the δ (or k) or λ (or k′) conformations. Figure 3 shows the absolute configurations of L(−)-1,2-propanediol (a) and the two conformations possible, b and c. The ligand orients itself in the most thermodynamically favorable form, that being the one in which the methyl group is equatorial. In the Λ-*cis* complex, the most stable conformation will be $\Lambda\delta\delta\delta$, while for the Δ isomer, the preferred conformation will be $\Delta\delta\lambda\lambda$, where the two ethylenediamine ligands are also in their more stable conformation in both cases. For $[Co(en)_2pn]^{3+}$, the difference in energy between these two conformations has been calculated as being $\sim$0.6 kcal/mol.[8] It is reasonable to assume the energy difference in this case will be of the same order of magnitude; the majority of molecules should, therefore, be in the $\Lambda\delta\delta\delta$ form for L-1,2-propanediol as ligand. Conversely, the favored complex in D-1,2-propanediol solution would be expected to be *cis*-$\Delta\lambda\lambda\lambda$-$[Co(en)_2$(D-1,2-p*l*$]^{3+}$. Since the most stable configurations in the two solvents are exact mirror images, the CD spectra should be exact mirror images also. Allowing for a lower optical purity for the D(+)-1,2-propanediol compared with that for L(−)-1,2-propanediol, this is indeed seen to be the case.

A band analysis of the CD spectra shows some interesting features. For the Λ-*cis*-$[Co(en)_2Cl_2]^+$ ion, the CD and absorption spectrum of which is shown in Figure 2, the absorption band at approximately 530 mμ is the magnetic dipole allowed transition ${}^1A_{1g} \rightarrow {}^1T_{1g}$ in O_h symmetry. For the C_2 symmetry of this ion, the upper state has its degeneracy removed into two components, giving rise to the transitions ${}^1A \rightarrow {}^1A$, ${}^1B$ and ${}^1A \rightarrow {}^1B$. These correspond to the CD bands at 530 and 610 mμ, respectively.[6] In addition, the band at 410 mμ is assigned as the ${}^1A \rightarrow {}^1A$, ${}^1B$ and ${}^1A \rightarrow {}^1A$ transitions, arising from ${}^1A_{1g} \rightarrow {}^1T_{2g}$, which are also magnetic dipole allowed for C_2 symmetry. When the compound is dissolved in L-1,2-propanediol, with the subsequent formation of the $\Lambda\delta\delta\delta$-$[Co(en)_2$(L-1,2-p*l*)$]^{3+}$ complex ion, the CD and absorption spectra change to those shown in Figure 1. We assign the CD bands in this spectrum as ${}^1A \rightarrow {}^1B$ for the 550-mμ band and ${}^1A \rightarrow {}^1A$, ${}^1B$ for the 500-mμ band, where both transitions again arise from the removal of the degeneracy of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition on going to C_2 symmetry. The 400-mμ CD band contains the ${}^1A \rightarrow {}^1A$, ${}^1B$ and ${}^1A \rightarrow {}^1A$ transitions derived from the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition. This is in accord with the assignment of the absolute configuration as Λ in L-1,2-propanediol. It is interesting to notice that there are two CD bands under the first absorption band in the equilibrium complex with approximately equal intensities. This type of curve is most generally observed for bis(ethylenediamine)cobalt(III) complexes in which there are two monodentate ligands. A chelating ligand generally gives rise to a single CD band under the first absorption band.

We conclude, therefore, that instead of an asymmetric synthesis occurring in this solvent, there is very stereospecific substitution taking place by the solvent molecules for the Cl^- ions. The similarity between the CD spectra obtained here and those observed by Bosnich[4] indicate that an exactly analogous reaction occurs in optically active 2,3-butanediol. In fact, the substitution reaction could also be occurring for other compounds examined in that study, such as *cis*-dichlorotriethylenetetraminecobalt(III) tetraphenylborate (*cis*-$[Co(trien)Cl_2]B(C_6H_5)_4$) and *trans*-chlorohydroxobis(ethylenediamine)cobalt(III) chloride (*trans*-$[Co(en)_2ClOH]Cl$, for which the spectra are very similar to those observed for the *cis*-$[Co(en)_2Cl_2]B(C_6H_5)_4$ complex in L(−)-2,3-butanediol and to those obtained here using 1,2-propanediol. It should be emphasized that only the *majority* of molecules are in the stereospecific form which gives rise to the CD spectrum. Other forms, although less favored thermodynamically, are almost certainly present and could conceivably make a small contribution to the CD.

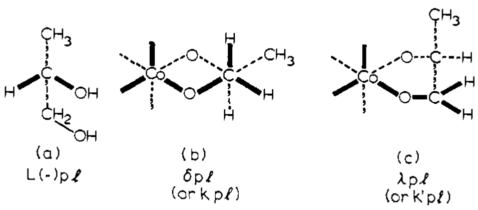

Figure 3. Stereochemistry of L(−)-1,2-propanediol (p*l* = propanediol).

Experimental Section

The compounds *trans*-$[Co(en)_2Cl_2]Cl$ and *cis*-$[Co(en)_2Cl_2]Cl \cdot H_2O$ were prepared by the method of Bailar.[12] The *cis* isomer was resolved using ammonium *d*-α-bromocamphor-π-sulfonate to precipitate the *l*-*cis*-dichlorobis(ethylenediamine)cobalt(III) *d*-α-bromocamphor-π-sulfonate[13] as the least soluble diastereoisomer. The same procedure was used to prepare *d*- or Δ-$(-)_{589}$-*cis*-$[Co(en)_2Cl_2]Cl$, except that ammonium *l*-α-bromocamphor-π-sulfonate was used as resolving agent. The resolved compounds had $[\alpha]_D$ values of +629 and −643°, respectively, as compared with the previously obtained value of ±660°.[15] The hydrated *cis*-$[Co(en)_2Cl_2]Cl$ salts were dried at 90° under vacuum to yield the anhydrous compounds.

Racemic 1,2-propanediol was obtained from Fisher Scientific Co. as propylene glycol (USP). Optically active D-1,2-propanediol was purchased from Aldrich Chemical Co., Milwaukee, Wis. ($[\alpha]_D$ 11.8 to 12.5°), while L-1,2-propanediol was prepared by Research Organic/Inorganic Chemical Co. ($[\alpha]_D$ 15.0°). An acid impurity in the latter solvent was removed by adding sodium hydroxide, vacuum subliming the solvent onto a coldfinger and finally, distilling the solvent to remove water. The optically active solvents were recovered from solutions by vacuum sublimation onto a coldfinger at liquid nitrogen temperature.

Absorption spectra were measured on a Beckman DK 1 spectrophotometer, and ORD and CD measurements on a Durrum-Jasco ORD-UV-5 spectropolarimeter. Solutions were prepared by weighing both solvent and solute into a weighing bottle and calculating concentrations on the basis of solvent density. The solutions were all $\sim 10^{-3}$ *M*.

Racemic *cis*-$[Co(en)_2(DMF)_2](ClO_4)_3$, where DMF = dimethylformamide, was prepared by the method of Lantzke and Watts.[16] The only modification was washing the complex with ice-cold

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[8] E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

[9] F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *ibid.*, **85**, 2913 (1963).

[10] Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Jap.*, **35**, 1131 (1962).

[11] Y. Saito, H. Iwasaki, and H. Ota, *ibid.*, **36**, 1543 (1963).

[12] J. C. Bailar, *Inorg. Syn.*, 2, 222 (1946).

[13] Much confusion has arisen from this nomenclature, since the complex named *l*-*cis*-$[Co(en)_2Cl_2]Cl$ in the resolution procedure[14] is actually Λ-$(+)_{589}$-*cis*-$[Co(en)_2Cl_2]Cl$.

[14] J. C. Bailar, *Inorg. Syn.*, 2, 224 (1946).

[15] F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *J. Amer. Chem. Soc.*, **85**, 1215 (1963).

[16] I. R. Lantzke and D. W. Watts, *Aust. J. Chem.*, 20, 35 (1967).

concentrated lithium perchlorate solution, ethanol, and ether and drying by suction.

Anal. Calcd for $[Co(en)_2(DMF)_2](ClO_4)_3$: C, 19.26; H, 4.85; Cl, 17.05; N, 13.48. Found: C, 19.02; H, 4.93; Cl, 17.18; N, 13.27.

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Nuclear Magnetic Resonance Studies of N–H Proton Dissociation and Inversion of Platinum(II) Complexes of Substituted Ethylenediamines

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Abstract: The effects of high KOH concentrations on nmr chemical shifts of ligand protons have been used to determine the fractional extent of titration and pK_a's of weakly acidic N–H protons of several Pt(II) complexes. For five methyl-substituted bipyridyl–ethylenediamine complexes, pK_a's range from $0.07K_w$ to $0.20K_w$ at $\mu = 1.3$. For $Pt(NH_3)_2(N,N'\text{-dmen})^{2+}$ and $Pt(NH_3)_2(EDDA)$, p$K_a \cong 0.01K_w$. For asymmetric complexes, rate constants for OH^--catalyzed inversion (k_{in}') have also been determined by analysis of nmr line shapes as a function of pH. Coupled with the pK_a determinations, these data permit calculation of k_3 ($=10^5$–10^6 sec^{-1} at 30° for four complexes), the rate constant for inversion of deprotonated complex. More limited temperature-dependence data suggest that $\Delta H°_{N-H}$ for the ionization of N–H for three complexes $\cong \Delta H°_{H_2O}$, which requires that ΔH_{in}^*, the activation energy derived from the temperature dependence of k_{in}', $\cong \Delta H_3^*$, the activation energy for inversion of deprotonated complex.

The increased acidity of N–H protons resulting from coordination of nitrogen by a metal ion has been recognized for a long time. Although for small highly charged cations, including the proton, the increase in acidity is sufficient to permit pK_a determination by titration in aqueous solution, for N–H protons of Pt(II) and Co(III) complexes of NH_3, amines, and amino acids, K_a for the dissociation represented by (1) is gen-

$$\text{N-H} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{N:}^- + H_3O^+ \qquad (1)$$

erally $<10^{-12}$ so that such determinations are not feasible.[1] Interest in the determination of pK_a's of these weakly acidic protons can often be traced to their importance to the interpretation of kinetic data for basic hydrolysis of metal complexes in terms of the SN1CB mechanism proposed originally by Garrick.[2,3] However, our interest in the problem originated in our attempts to interpret rate data for the inversion of $Pt(NH_3)_2(N,N'\text{-dmen})^{2+}$ [4] and $Pt(NH_3)_2(EDDA)$.[5] Since inversion requires prior proton abstraction, the rate of inversion of the deprotonated nitrogen species can be obtained from the observed over-all rate of inversion of the complex, derived from analysis of nmr line shapes, only if the extent of dissociation is known.

Protonation equilibria in aqueous solutions have been investigated extensively by nmr spectroscopy.[6,7] In general, pK_a's of weak acids can be determined from the inflection point in a plot of chemical shift *vs.* pH. On the basis of k_1's (eq 1) determined from the rate of water-catalyzed N–H exchange of these and similar complexes (10^{-4}–10^{-6} sec^{-1})[4,5,8] and an estimate of k_{-1} for the recombination of N:$^-$ and H_3O^+ as 10^{10} l. mole^{-1} sec^{-1},[9] we estimated that K_a would lie in the range 10^{-14}–10^{-16}. Therefore, it appeared to be feasible to determine pK_a's from the effect of 0.1–10 *M* KOH in chemical shifts of ligand protons. In this paper, we report the results of such investigations for the two complexes noted above and for several substituted ethylenediamine–bipyridyl complexes of Pt(II). The latter were selected for a detailed study because they do not have potentially titratable NH_3 protons so that deprotonation sites are unambiguous. In addition, recent studies of deprotonation in liquid ammonia by Watt and coworkers[10] indicated that bipyridyl complexes are more acidic than corresponding ammine complexes and hence more accessible to study by the nmr technique.

In view of the difficulties and uncertainties encountered in earlier studies of EDDA[5] and N,N'-dmen[4] complexes, which have two asymmetric centers and exist in both *meso* and *dl* forms, we also investigated or rein-

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[1] For a more complete discussion of this subject and a table of pK_a's and corresponding references, see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 33.

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