It is not clear why P_2Mo_{18} should adopt a different structure from that of P_2W_{18}.[24] Some years ago it was pointed out that most of the then known isopoly- and heteropolymolybdates have structures with two (cis) terminal oxygens per molybdenum, whereas most polytungstates have structures with a single terminal oxygen per tungsten.[25] Although there are exceptions to both generalizations, such exceptions are relatively few.[26] The structure of P_2Mo_{18} therefore appears to be a compromise between the limitations of stoichiometry and the tendency of molybdenum(VI) to adopt a cis dioxo coordination.

Acknowledgment. The partial support of this research by NIH Grant No. GM23263 is gratefully acknowledged.

Registry No. $[(C_4H_9)_4N]_5HP_2Mo_{18}O_{62}$, 66018-03-9; (*l*-bru)$_5HP_2Mo_{18}O_{62}$, 66018-02-8; $[(C_4H_9)_4N]_5H_3P_2Mo_{18}O_{62}$, 66018-01-7; α-$P_2W_{18}O_{62}^{6-}$, 12269-70-4; $Mo_6O_{19}^{2-}$, 11132-40-4; α-$SiMo_{12}O_{40}^{4-}$, 50927-64-5; *l*-brucine sulfate, 4845-99-2.

References and Notes

(1) M. T. Pope, *Inorg. Chem.*, **15**, 2008 (1976).

(2) R. Strandberg, *Acta Chem. Scand., Ser. A*, **29**, 350 (1975).

(3) H. D'Amour, *Acta Crystallogr., Sect. B*, **32**, 729 (1976).

(4) Although the structure of the second isomer (labeled α for historical reasons, but see ref 1) was reported to have D_{3d} symmetry (K. Y. Matsumoto and Y. Sasaki, *J. Chem. Soc., Chem. Commun.*, 691 (1975)) there is now some uncertainty (Y. Sasaki, private communication). The ^{31}P NMR spectrum of β-P_2W_{18} shows the two phosphorus atoms to be nonequivalent (R. Massart, R. Contant, J. M. Fruchart, J. P. Ciabrini, and M. Fournier, *Inorg. Chem.*, **16**, 2916 (1977)).

(5) H. Wu, *J. Biol. Chem.*, **43**, 189 (1920).

(6) J. Fuchs and K. F. Jahr, *Z. Naturforsch. B*, **23**, 1380 (1968).

(7) L. Barcza and M. T. Pope, *J. Phys. Chem.*, **77**, 1795 (1973).

(8) E. Papaconstantinou and M. T. Pope, *Inorg. Chem.*, **6**, 1152 (1967).

(9) N. A. Tsvetkov and L. M. Karina, *Russ. J. Inorg. Chem.*, **20**, 694 (1975).

(10) C. Rocchiccioli-Deltcheff, R. Thouvenot, and R. Franck, *Spectrochim. Acta, Part A*, **32**, 587 (1976).

(11) If only a fraction of the heteropolyanion is precipitated, the filtrate shows no optical activity.

(12) E. Papaconstantinou and M. T. Pope, *Inorg. Chem.*, **9**, 667 (1970).

(13) B. Bosnich, *J. Am. Chem. Soc.*, **89**, 6143 (1967); B. Bosnich in "Fundamental Aspects and Recent Developments in Optical Rotatory Dispersion and Circular Dichroism", F. Ciardalli and P. Salvadori, Ed., Heyden & Sons Ltd., London, 1971, p 254 ff; B. Norden, *Chem. Scr.*, **7**, 14 (1975); see also P. E. Schipper, *Chem. Phys.*, **12**, 15 (1976), and references therein.

(14) P. Pfeiffer and K. Quehl, *Ber. Dtsch. Chem. Ges. A*, **64**, 2667 (1931); **62**, 560 (1932). For a recent study involving the Pfeiffer effect see R. J. Pollock, S. Kirschner, and S. Policec, *Inorg. Chem.*, **16**, 522 (1977).

(15) When *d*-cinchonine hydrochloride is used to precipitate the heteropolyanion, the resulting ORD in dimethylformamide indicates that conversion to the $(-)_{380}$ enantiomer has occurred.

(16) H. So and M. T. Pope, *Inorg. Chem.*, **11**, 1441 (1972).

(17) If the ORD illustrated in Figure 3 had been induced by ion pairing and did not result from the inherent chirality of P_2Mo_{18}, the reduced anion should have exhibited an effect of similar if not greater magnitude.

(18) R. A. Prados and M. T. Pope, *Inorg. Chem.*, **15**, 2547 (1976).

(19) J. M. Fruchart, G. Hervé, J. P. Launay, and R. Massart, *J. Inorg. Nucl. Chem.*, **38**, 1627 (1976).

(20) See, for example, M. T. Pope and G. M. Varga, Jr., *Inorg. Chem.*, **5**, 1249 (1966).

(21) P. Souchay, R. Contant, and J. M. Fruchart, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **264**, 976 (1967).

(22) R. Contant and J. M. Fruchart, *Rev. Chim. Miner.*, **11**, 123 (1974).

(23) M. T. Pope and E. Papaconstantinou, *Inorg. Chem.*, **6**, 1147 (1967).

(24) D'Amour[3] has suggested that the differences may be traced to differences in the compressibilities of the core electrons of Mo^{6+} and W^{6+} (resulting from the lanthanide contraction) and to differences between the radial extensions of 4d and 5d orbitals.

(25) M. T. Pope, *Inorg. Chem.*, **11**, 1973 (1972).

(26) To date, the only confirmed exceptions are $Mo_6O_{19}^{2-}$, the Keggin anions $XMo_{12}O_{40}^{n-}$, X = P, As, Si, Ge (all monooxo terminal groups), $NiW_6O_{24}H_6^{4-}$, $NiW_6O_{24}^{8-}$, and probably $IW_6O_{24}^{5-}$ and $TeW_6O_{24}^{6-}$ (all cis dioxo terminal groups). Some polytungstates (e.g., $H_2W_{12}O_{42}^{10-}$) contain both dioxo and monooxo groups.

Contribution from the Chemistry Department, Tohoku University, Sendai, Japan,
and the William Albert Noyes Laboratory of Chemistry, University of Illinois at Urbana, Urbana, Illinois 61801

Stereochemistry of Complex Inorganic Compounds. 36. Ammoniation Reactions of Some Optically Active 1,2-Dihalobis(ethylenediamine) Complexes of Rhodium(III) and Iridium(III) Ions

HIROSHI OGINO[1] and JOHN C. BAILAR, JR.*

Received April 27, 1977

Ammonation reactions of dihalobis(ethylenediamine) complexes of rhodium(III) and iridium(III) ions proceed with retention of configuration. The absolute configuration of optically active 1,2-dihalobis(ethylenediamine) complexes and their ammoniated complexes were inferred by comparison of the electronic and CD spectra of these complexes with those of the corresponding cobalt(III) complexes.

Introduction

The inversion of chiral 1,2-$[Co(en)_2Cl_2]^+$ has been observed to occur in the ammoniation reaction of the complex at liquid ammonia temperature.[2] In the reactions described in this paper, the ammoniation reactions of several dihalobis(ethylenediamine) complexes of rhodium(III) and iridium(III), including optically active complexes, were examined.

Experimental Section

A. Preparation of Complexes. The complexes 1,2-$[Co(en)_2Cl_2]Cl$,[3] 1,2-$[Co(en)_2(NH_3)Cl]Cl_2$,[4,5] 1,2- and 1,6-$[Co(en)_2(NH_3)_2](NO_3)_3$,[6] 1,2-$[Rh(en)_2Cl_2]Cl$,[7,8] 1,2- and 1,6-$[Rh(en)_2(NH_3)Cl](NO_3)_2$,[8] 1,6-$[Rh(en)_2Br_2]NO_3$,[8] 1,2- and 1,6-$[Rh(en)_2I_2]I$,[8] and 1,2- and 1,6-$[Ir(en)_2Cl_2]Cl$[9,10] were prepared as reported in the literature. 1,6-$[Rh(en)_2Cl_2]Cl$ was prepared by the method of Basolo et al.,[7,8] but the crystals obtained by the concentration of the aqueous solution were found to contain one molecule of water of crystallization. Anal. Calcd for $[Rh(en)_2Cl_2]Cl\cdot H_2O$: C, 13.83; H, 5.22; N, 16.12. Found: C, 13.87; H, 5.10; N, 16.38. The water of crystallization can be removed easily by heating the crystals at 100 °C for 30 min. Anal. Calcd for $[Rh(en)_2Cl_2]Cl$: C, 14.58; H, 4.87; N, 17.00. Found: C, 14.40; H, 4.95; N, 16.73.

1,2-$[Rh(en)_2Br_2]Br$. 1,2-$[Rh(en)_2Cl_2]Cl$ (0.65 g) was dissolved in 30 mL of water. After the addition of NaBr (1.5 g), the solution was refluxed for 30 min. Upon cooling the solution, yellow-orange crystals appeared. To complete the precipitation, 25 mL of ethanol and 25 mL of ether were added. A total of 0.48 g of 1,2-$[Rh(en)_2Br_2]Br$ was obtained. Anal. Calcd for $[Rh(en)_2Br_2]Br$: C, 10.38; H, 3.49; N, 12.11. Found: C, 10.81; H, 3.84; N, 12.23.

1,6-$[Rh(en)_2(NH_3)Br](NO_3)_2$. A solution of 1,6-$[Rh(en)_2Br_2]NO_3$ (0.57 g) in 30 mL of concentrated NH_4OH was refluxed for 30 min. After filtration, the filtrate was evaporated to dryness on a steam bath. The residue was dissolved in 3 mL of water. The solution was filtered and 3 mL of HNO_3 was added. After cooling, 50 mL of ethanol was carefully added. During the addition of ethanol, the desired yellow compound crystallized. This was collected, washed with ethanol and ether, and air-dried; yield 0.40 g. Anal. Calcd for $[Rh(en)_2(NH_3)Br](NO_3)_2$: C, 10.82; H, 4.31; N, 22.09. Found: C, 11.23; H, 4.43; N, 22.17.

* Correspondence to University of Illinois at Champaign-Urbana.

0020-1669/78/1317-1118$01.00/0 © 1978 American Chemical Society

1,6-[Rh(en)$_2$(NH$_3$)I]I$_2$. A solution of 1,6-[Rh(en)$_2$I$_2$]I (0.56 g) in 30 mL of concentrated NH$_4$OH was refluxed for 20 min. The color of the solution changed from brown to yellowish orange. It was evaporated to dryness on a steam bath. The residue was dissolved in 5 mL of warm water. The solution was filtered and 5 mL of saturated KI solution was added. Upon cooling, yellowish orange crystals deposited and were collected on a filter, washed with ethanol and then ether, and air-dried; yield 0.44 g. Anal. Calcd. for [Rh(en)$_2$(NH$_3$)I]I$_2$: C, 7.74; H, 3.08; N, 11.28. Found: C, 7.66; H, 3.29; N, 11.15.

1,2-[Rh(en)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$. 1,2-[Rh(en)$_2$Cl$_2$]ClO$_4$ and 1,2-[Rh(en)$_2$Br$_2$]ClO$_4$ were obtained by the addition of 60% HClO$_4$ to solutions of 1,2-[Rh(en)$_2$Cl$_2$]Cl and 1,2-[Rh(en)$_2$Br$_2$]Br.

Forty-five milliliters of liquid ammonia was placed in a reaction vessel in a dry ice–ethanol bath. Moisture was excluded by flushing the reaction vessel with gaseous ammonia prior to cooling. Then, the vessel was placed in a Dewar flask and a pellet of sodium metal was dissolved in the liquid ammonia. The amount of sodium metal was varied between 0.1 and 0.5 g without appreciably affecting the results. After the blue color due to solvated electrons disappeared, 100 mg of 1,2-[Rh(en)$_2$Cl$_2$]ClO$_4$ or 1,2-[Rh(en)$_2$Br$_2$]ClO$_4$ was added. The ammonia was allowed to evaporate from the vessel, which was fitted with a potassium hydroxide trap to avoid entrance of moisture. After the solution was kept overnight, the remaining liquid ammonia was evaporated through the trap by suction. The precipitate was dissolved in 100 mL of water, acidified with 60% HClO$_4$. This solution was poured into a column (1.5 × 5 cm) containing SP-Sephadex C-25 resin. The column showed two bands: a lower yellow band (very small amount) and an upper colorless band. After the yellow species (evidently starting material) was eluted with 0.2 M HCl, the upper species was eluted with 0.5 M HCl. To this eluate was added 0.5 mL of 60% HClO$_4$. Then, the solution was evaporated to small volume in a rotary evaporator. White crystals of 1,2-[Rh(en)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$ were collected. The crystals were recrystallized from water by the addition of 60% HClO$_4$; yield 50 mg from either 1,2-[Rh(en)$_2$Cl$_2$]ClO$_4$ or 1,2-[Rh(en)$_2$Br$_2$]ClO$_4$. Anal. Calcd for [Rh(en)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$: C, 8.65; H, 3.99; N, 15.13. Found: C, 8.41; H, 3.70; N, 14.92.

1,6-[Rh(en)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$. This was prepared from 100 mg of 1,6-[Rh(en)$_2$Cl$_2$]ClO$_4$ which was obtained by the addition of 60% HClO$_4$ to a solution of 1,6-[Rh(en)$_2$Cl$_2$]Cl. A Sephadex column showed two bands. The lower yellow species, which was characterized as the starting material, was eluted with a 0.05 M LiClO$_4$ solution and the upper species with a 0.5 M LiClO$_4$ solution. This eluate was evaporated to dryness. The remaining solid LiClO$_4$ was washed out with ethanol. The white precipitate which remained was dissolved in a minimum amount of water and 60% HClO$_4$ was added until white crystals appeared. Ethanol and then ether were added to ensure the precipitation of the crystals; yield 60 mg. Anal. Calcd for [Rh(en)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$: C, 8.65; H, 3.99; N, 15.15. Found: C, 8.39; H, 3.92; N, 15.22.

1,2-[Ir(en)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$. This complex was prepared from 320 mg of 1,2-[Ir(en)$_2$Cl$_2$]ClO$_4$ by a method similar to that used for the preparation of 1,2-[Rh(en)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$. A Sephadex column showed three bands: yellow (trace amount) at the bottom, colorless in the middle, and yellowish brown at the top of the column. The yellow species was eluted out with 0.2 M HCl and the colorless species with 0.5 M HCl. To this latter eluate was added 1 mL of 60% HClO$_4$, and the solution was evaporated to small volume in a rotary evaporator. White crystals of 1,2-[Ir(en)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$ were collected. The compound was recrystallized from water by the addition of 60% HClO$_4$; yield 250 mg. Anal. Calcd for [Ir(en)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$: C, 7.45; H, 3.44; N, 13.03. Found: C, 7.56; H, 3.56; N, 12.77.

The yellowish brown species remaining on the column was eluted with 1 M HCl solution. From the chromatographic behavior, this ion was considered to have tripositive or tetrapositive charge, but attempts to isolate crystals were unsuccessful.

B. Resolution of Complexes. 1,2-[Co(en)$_2$Cl$_2$]Cl[3] and 1,2-[Rh(en)$_2$Cl$_2$]Cl[7,8] were resolved as reported in the literature. The method of Werner and King[4] was used to resolve 1,2-[Co(en)$_2$(NH$_3$)Cl]Cl$_2$. The intensity of CD at 550 nm ($\Delta\epsilon_{550}$) was +0.27 ± 0.01. This did not change upon recrystallization. Attempts to resolve 1,2-[Rh(en)$_2$I$_2$]I with Ag[(+)-BCS] were unsuccessful.

Resolution of 1,2-[Rh(en)$_2$(NH$_3$)Cl]Cl$_2$. Method 1. 1,2-[Rh(en)$_2$(NH$_3$)Cl]Cl$_2$ (0.70 g), dissolved in 30 mL of hot water, was treated with an aqueous solution of Ag[(+)-BCS] (50 mL) which was prepared from 1.3 g of NH$_4$[(+)-BCS]. The precipitated silver chloride was removed and washed with 5 mL of water. The volume of the combined filtrate and washings was reduced to 30 mL in a rotary evaporator. When the solution was cooled in an ice bath, pale yellow crystals appeared. The diastereoisomer was collected by filtration and the filtrate was reserved for the isolation of 1,2-[$(-)^{\mathrm{CD}}_{362}$-Rh(en)$_2$(NH$_3$)Cl]Cl$_2$. For purification, the diastereoisomer was recrystallized from water and was dissolved in 5 mL of concentrated HCl and 5 mL of ethanol. Then, 10 mL of ether was added drop by drop with stirring. The pale yellow 1,2-[$(+)^{\mathrm{CD}}_{362}$-Rh(en)$_2$(NH$_3$)Cl]Cl$_2$ was collected and washed with ethanol and ether and air-dried; yield 0.28 g. Anal. Calcd for [Rh(en)$_2$(NH$_3$)Cl]Cl$_2$: C, 13.87; H, 5.53; N, 20.21. Found: C, 14.09; H, 5.71; N, 20.16. The recrystallized isomer showed $\Delta\epsilon_{362}$ = +0.51 ± 0.03. Further recrystallization did not change this.

When the filtrate which had been reserved was evaporated to 10 mL, pale yellow crystals appeared and were removed by filtration. The remaining filtrate was treated with 10 mL of concentrated HCl and 10 mL of ethanol. Then, 10 mL of ether was added drop by drop. The 1,2-[$(-)^{\mathrm{CD}}_{362}$-Rh(en)$_2$(NH$_3$)Cl]Cl$_2$ was collected and washed with ethanol and ether and air-dried; yield 0.2 g. The recrystallized isomer showed $\Delta\epsilon_{362}$ = −0.47 ± 0.03.

Method 2. 1,2-[$(-)^{\mathrm{CD}}_{393}$-Rh(en)$_2$Cl$_2$]Cl (100 mg) was dissolved in 10 mL of concentrated NH$_4$OH and the solution was refluxed for 20 min. During refluxing, the yellow color of the solution changed to a paler yellow. The solution was evaporated to dryness on a steam bath with a stream of air. The residue was dissolved in 3 mL of water and filtered. To the filtrate was added 3 mL of concentrated HCl and 10 mL of ethanol. Then, 10 mL of ether was added drop by drop. The resulting pale yellow precipitate of 1,2-[$(+)^{\mathrm{CD}}_{362}$-Rh(en)$_2$(NH$_3$)Cl]Cl$_2$ was collected; yield 90 mg. The complex was recrystallized from water by the addition of HCl, ethanol, and ether. $\Delta\epsilon_{362}$ = +0.50 ± 0.03. This was not changed by recrystallization.

Resolution of 1,2-[Rh(en)$_2$Br$_2$]$^+$. Method 1. 1,2-[Rh(en)$_2$Br$_2$]Br (0.92 g) was suspended in 40 mL of water at 60 °C. To the suspension (at 60 °C) was added 10 mL of Ag[(+)-BCS] solution which was prepared from 0.66 g of NH$_4$[(+)-BCS]. The mixture was stirred vigorously for several minutes, keeping the temperature above 60 °C. The precipitated silver bromide was removed by filtration and washed with 5 mL of hot water. The combined filtrate and washings were cooled in an ice bath. Yellow crystals of the [$(+)^{\mathrm{CD}}_{406}$-Rh(en)$_2$Br$_2$][(+)-BCS] salt were collected by filtration, and the salt was recrystallized. The filtrate was reserved. The solid was treated with 6 mL of *cold* 1:1:1 HCl–ethanol–ether. The precipitate was collected, washed with ethanol and ether, and air-dried; yield 0.3 g. Anal. Calcd for [Rh(en)$_2$Br$_2$]Cl: C, 11.48; H, 3.85; N, 13.39. Found: C, 11.63; H, 4.01; N, 13.38. $\Delta\epsilon_{406}$ = −0.62 ± 0.03. The same value was obtained after recrystallization.

The reserved filtrate was evaporated to 15 mL and cooled in an ice bath. A yellowish orange precipitate was obtained by filtration. The substance was treated as described above. Racemic 1,2-[Rh(en)$_2$Br$_2$]Cl was obtained; yield 0.2 g. The remaining filtrate was evaporated to dryness. The residue was stirred with 3 mL of 1:1 HCl–ethanol. Then, 3 mL of ether was added and the solution was cooled. The yellowish orange precipitate of 1,2-[$(+)^{\mathrm{CD}}_{406}$-Rh(en)$_2$Br$_2$]Cl was collected on a filter; yield 0.25 g. $\Delta\epsilon_{406}$ = +0.45 ± 0.04.

Method 2. 1,2-[$(-)^{\mathrm{CD}}_{393}$-Rh(en)$_2$Cl$_2$]Cl (130 mg) was dissolved in 6 mL of water. After the addition of 0.3 g of NaBr, the solution was refluxed for 30 min. Cooling the solution gave yellowish orange crystals. To complete the precipitation, 10 mL of 1:1 ethanol–ether was added. 1,2-[$(-)^{\mathrm{CD}}_{406}$-Rh(en)$_2$Br$_2$]Br was obtained; yield 95 mg. $\Delta\epsilon_{406}$ = −0.59 ± 0.03. This was not changed by recrystallization.

1,2-[$(+)^{\mathrm{CD}}_{325}$-Rh(en)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$. Under conditions identical with those described for the preparation of the racemic 1,2-[Rh(en)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$, 1,2-[$(-)^{\mathrm{CD}}_{393}$-Rh(en)$_2$Cl$_2$]ClO$_4$ or 1,2-[$(-)^{\mathrm{CD}}_{406}$-Rh(en)$_2$Br$_2$]ClO$_4$ was treated with liquid ammonia containing NaNH$_2$ and then put through the Sephadex column. The compound obtained, 1,2-[$(+)^{\mathrm{CD}}_{325}$-Rh(en)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$, gave $\Delta\epsilon_{325}$ = +0.43 ± 0.03 for the sample from 1,2-[$(-)^{\mathrm{CD}}_{393}$-Rh(en)$_2$Cl$_2$]ClO$_4$ and +0.48 ± 0.03 for the sample from 1,2-[$(-)^{\mathrm{CD}}_{406}$-Rh(en)$_2$Br$_2$]ClO$_4$. These values did not change upon recrystallization.

Resolution of 1,2-[Ir(en)$_2$Cl$_2$]Cl. Resolution of 1,2-[Ir(en)$_2$Cl$_2$]Cl was effected with NH$_4$[(+)-BCS] by the method of Bauer and Basolo.[10] An alternative method was also employed in this work: K[$(+)^{\mathrm{RD}}_{546}$-Co(edta)]·2H$_2$O[12] (2.8 g) was converted to an aqueous solution of Ag[$(+)^{\mathrm{RD}}_{546}$-Co(edta)] by use of Dowex 50W X-8 resin and Ag$_2$O.[13] The solution (200 mL) was mixed with a solution of 2.8 g

Table I. Electronic Spectra of Rhodium(III) and Iridium(III) Complexes

Complex	Obsd bands, $\tilde{\nu}$ in $cm^{-1} \times 10^3$ (log ϵ)	Previous workers, $\tilde{\nu}$ in $cm^{-1} \times 10^3$ (log ϵ)
1,6-$[Rh(en)_2Cl_2]Cl$	24.6 (1.90), 32 sh[a] (1.9), 34.6 (2.09), 41.4 sh[a] (3.2), 48.5 (4.60)	24.4–24.6 (1.88–1.92),[b–e] 34.5–35.0 (2.10, 2.11),[b–e] 41.7 (3.13),[d] 48.5 (4.59)[d]
1,2-$[Rh(en)_2Cl_2]Cl$	25.4 sh[a] (2.0), 28.4 (2.28), 33.9 (2.27), ca. 42 sh[a] (3.0)	28.4 (2.18, 2.19),[b,e] 33.9 (2.25, 2.26)[b,e]
1,6-$[Rh(en)_2Br_2]NO_3$[f]	23.3 (2.06), 30.6 sh[a] (1.96), 36.0 (3.41), 42.7 (4.57)	23.3–23.5 (2.00–2.08),[b–e] 35.8–36.2 (3.26–3.48),[b–e] 42.9, 43.3 (4.49, 4.58)[c,d]
1,2-$[Rh(en)_2Br_2]Br$	23 sh[a] (1.9), 27.2 (2.38), 36 sh[a] (3.0)	27.6 (2.32),[b] 36.2 (2.95)[b]
1,6-$[Rh(en)_2I_2]I$	21.5 (2.42), 29.4 (4.39), 37.1 (4.69), 44.8 (4.47)	21.5–21.7 (2.36–2.51),[b,d,e,g] 29.2–29.5 (4.00–4.34),[b,d,e,g] 36.9–37.2 (4.36–4.68),[b,d,e,g] 44.1–45.5 (4.23–4.30)[b,d,e,g]
1,2-$[Rh(en)_2I_2]I$	22.5 sh[a] (2.65), 26.7 (2.98), 34.5 (3.67), 44.4 (4.65)	26.7 (3.08)[b]
1,6-$[Rh(en)_2(NH_3)Cl](NO_3)_2$[f]	29.0 (2.02), 36.3 (2.12)	29.2 (1.98),[b] 36.4 (2.08)[b]
1,2-$[Rh(en)_2(NH_3)Cl]Cl_2$	29.1 (2.18), 36.2 (2.26)	29.2 (2.18),[b] 36.2 (2.29)[b]
1,6-$[Rh(en)_2(NH_3)Br](NO_3)_2$[f]	28.2 (2.07), ca. 35 sh[a] (2.2), 41 (2.96)	
1,6-$[Rh(en)_2(NH_3)I]I_2$	25.6 (2.54), ca. 30 sh[a] (2.68), 36.2 (3.62), 44.1 (4.69)	
1,6-$[Rh(en)_2(NH_3)_2](ClO_4)_3$	33.3 (2.26), 39.7 (2.22)	
1,2-$[Rh(en)_2(NH_3)_2](ClO_4)_3$	33.1 (2.31), 39.4 (2.20)	
1,6-$[Ir(en)_2Cl_2]Cl$	23.4 (0.68), 28.9 (1.64), 37 sh[a] (1.5)	23.5 (1.10),[h] 28.9–29.0 (1.66–1.71),[h,i] 36.6 (1.77)[h]
1,2-$[Ir(en)_2Cl_2]Cl$	26.4 sh[a] (1.27), 31 sh[a] (1.94), 34.1 (2.14), 39.2 sh[a] (2.19), 44.0 (2.78)	26.3 (1.23),[h] 31.7 (1.96),[h] 34.1–34.2 (2.08–2.15),[h,i] 39.2 (2.10)[h]
1,2-$[Ir(en)_2(NH_3)_2](ClO_4)_3$	ca. 33 sh[a] (1.31), 40.6 (2.20), ca. 45 sh[a] (2.23)	

[a] sh = shoulder. [b] From ref 8. [c] H. L. Bott and A. J. Poë, *J. Chem. Soc.*, 5931 (1965). [d] C. Burgess, F. R. Hartley, and D. E. Rogers, *Inorg. Chim. Acta,* **13**, 35 (1975). [e] M. M. Muir and W-L. Huang, *Inorg. Chem.*, **12**, 1831 (1973). [f] Absorption due to NO_3^- was corrected. [g] E. J. Bounsall and A. J. Poë, *J. Chem. Soc. A*, 286 (1966). [h] From ref 10. [i] From ref 9.

of 1,2-$[Ir(en)_2Cl_2]Cl$ in 50 mL of water at 70 °C. The precipitated silver chloride was removed by filtration and washed with 5 mL of water. The combined filtrate and washings were evaporated to 20 mL in a rotary evaporator. When the solution was cooled to room temperature, reddish violet needles appeared. These were collected, recrystallized, and washed with 1:3 water–ethanol, and then ether; yield 1.0 g. The diastereoisomer was dissolved in 50 mL of water. The solution was passed through a column (ϕ 1.5 × 6 cm) of SP-Sephadex C-25. The adsorbed 1,2-$[(-)^{CD}_{385}\text{-}Ir(en)_2Cl_2]^+$ was eluted with a 0.2 M HCl solution and the eluate was evaporated to 5 mL. To this solution was added 1 mL of 60% $HClO_4$. The resultant crystals weighed 0.54 g. Anal. Calcd for $[Ir(en)_2Cl_2]ClO_4$: C, 9.95; H, 3.34; N, 11.60. Found: C, 10.26; H, 3.39; N, 11.76. $\Delta\epsilon_{385} = 0.40 \pm 0.02$, unchanged after recrystallization.

1,2-$[(+)^{CD}_{280}\text{-}Ir(en)_2(NH_3)_2](ClO_4)_3$. Under conditions identical with those described above for the preparation of racemic 1,2-$[Ir(en)_2(NH_3)_2](ClO_4)_3$, 1,2-$[(-)^{CD}_{385}\text{-}Ir(en)_2Cl_2]ClO_4$ was converted to 1,2-$[(+)^{CD}_{280}\text{-}Ir(en)_2(NH_3)_2](ClO_4)_3$. $\Delta\epsilon_{280} = +0.18 \pm 0.01$. The intensity of CD did not change upon recrystallization of the sample.

C. Spectral Measurements. Electronic spectra were recorded with a Cary Model 14 M or a Hitachi EPS-3 recording spectrophotometer. The data are shown in Table I. Infrared spectra (KBr disks) were recorded on a Perkin-Elmer or a Hitachi 285 recording spectrometer and CD spectra on a Jasco ORD/UV-5 recording spectrometer. ^1H NMR spectra were recorded with a Varian A-60 spectrophotometer (60 MHz) in trifluoroacetic acid (TFA) containing sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS) as the internal standard. Each complex salt was converted to the chloride salt with the aid of Dowex 1 X-4 resin in the chloride form, because the chloride is the soluble form in TFA. TFA has been shown to be a suitable solvent for ^1H NMR measurements of some cobalt(III) complexes.[14] In Table II, the ^1H NMR spectral data of rhodium(III) and iridium(III) complexes are summarized along with those of some cobalt(III) complexes.

Results and Discussion

The geometric structures of 1,2-$[Rh(en)_2Cl_2]^+$ and 1,2-$[Ir(en)_2Cl_2]^+$ have been proved unequivocally by resolutions into their optical isomers.[7,8] Those of 1,2-$[Rh(en)_2(NH_3)Cl]^{2+}$ and 1,2-$[Rh(en)_2Br_2]^+$ were newly proved in this work by their resolutions.

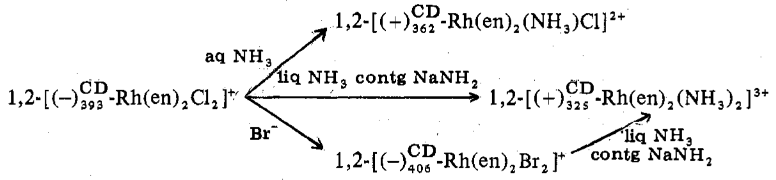
For the 1,2 and 1,6 assignment to various diacidobis(ethylenediamine) complexes of rhodium(III) and iridium(III), the infrared spectra have been measured.[7-10] The spectrum of the 1,6 isomer exhibits a single sharp peak in the NH_2 asymmetric deformation region (1600 cm^{-1}), whereas that of 1,2 isomer shows two peaks in the same region. This criterion is also valid for the assignment to 1,2- and 1,6-$[Rh(en)_2(NH_3)Cl]^{2+}$.[8] These results were confirmed in this work for 1,2 and 1,6 pairs of $[Rh(en)_2X_2]^+$ (X^- = Cl^-, Br^-, and I^-), $[Rh(en)_2(NH_3)Cl]^{2+}$, and $[Ir(en)_2Cl_2]^+$. The infrared spectra of $[Rh(en)_2(NH_3)X]^{2+}$ (X^- = Br^- and I^-), which were newly prepared in this work, show a sharp single peak at 1593 cm^{-1}

Table II. Proton Chemical Shifts and Bandwidths at Half-Height (*W*/2) of Some Cobalt(III), Rhodium(III), and Iridium(III) Complexes in TFA

	Chemical shifts vs. DSS, ppm (*W*/2, Hz)		
Complex	NH_2 protons	NH_3 protons	CH_2 protons
1,6-$[Rh(en)_2Cl_2]^+$	4.64 (13.5)		3.05 (9)
1,6-$[Ir(en)_2Cl_2]^+$	5.20 (13.5)		2.88 (7)
1,2-$[Rh(en)_2Cl_2]^+$	$\left\{\begin{matrix}5.04\\4.78\ \mathrm{sh}^b\end{matrix}\right\}$ (ca. 30)[a]		3.09 (10)
1,2-$[Ir(en)_2Cl_2]^+$	Doublet $\begin{cases}5.54\ \text{(ca. 19)}\\5.29\ \text{(ca. 18)}\end{cases}$		2.92 (11)
1,6-$[Rh(en)_2(NH_3)Cl]^{2+}$	Doublet $\begin{cases}5.09\ \text{(ca. 18)}\\4.84\ \text{(ca. 18)}\end{cases}$	3.71 (7)	3.09 (11)
1,6-$[Rh(en)_2(NH_3)Br]^{2+}$	Doublet $\begin{cases}5.02\ \text{(ca. 18)}\\4.78\ \text{(ca. 18)}\end{cases}$	3.67 (7)	3.10 (11)
1,6-$[Rh(en)_2(NH_3)I]^{2+}$	Doublet $\begin{cases}5.10\ \text{(ca. 22)}\\4.61\ \text{(ca. 22)}\end{cases}$	3.50 (9)	3.19 (20)
1,2-$[Rh(en)_2(NH_3)Cl]^{2+}$	Ca. 5 (very broad)	3.61 (8)	3.10 (9)
1,6-$[Co(en)_2(NH_3)_2]^{3+}$	5.20 (14)	3.27[c]	3.14[c]
1,6-$[Rh(en)_2(NH_3)_2]^{3+}$	5.28 (18)	3.81 (14)	3.12 (11)
1,2-$[Co(en)_2(NH_3)_2]^{3+}$	$\begin{cases}5.25\\4.93\end{cases}$ (ca. 47)[a]	3.64 (8)	3.12 (12)
1,2-$[Rh(en)_2(NH_3)_2]^{3+}$	5.18 (ca. 28)[a]	3.85 (7)	3.13 (10)
1,2-$[Ir(en)_2(NH_3)_2]^{3+}$	5.59 (ca. 27)[a]	4.53 (7)	3.01 (10)

[a] Distorted signal. [b] Shoulder. [c] The value of *W*/2 was not determined because the signals of the NH_3 and the CH_2 protons overlap.

Scheme I



for $X^- = Br^-$ and at 1568 cm^{-1} for $X^- = I^-$; hence the complexes must have the 1,6 configuration. The infrared spectra of the diammine complexes in the NH$_2$ asymmetric deformation region were compared with those of authentic samples of 1,2- and 1,6-$[Co(en)_2(NH_3)_2]^{3+}$. 1,2-$[Co(en)_2(NH_3)_2]^{3+}$ exhibits an absorption band at 1580 cm^{-1} with a shoulder at 1630 cm^{-1}, whereas the 1,6 isomer shows a single sharp band at 1585 cm^{-1}. Similar patterns are observed for 1,2- and 1,6-$[Rh(en)_2(NH_3)_2]^{3+}$ and 1,2-$[Ir(en)_2(NH_3)_2]^{3+}$.

^{1}H NMR measurements have been used to distinguish between 1,2 and 1,6 isomers of $[Co(en)_2X_2]^+$.[15] This method was found to be applicable to the rhodium(III) and iridium(III) complexes, also. The 1,6 isomer of $[Ir(en)_2Cl_2]^+$ shows a single NH$_2$ signal at 5.20 ppm, whereas the 1,2 isomer gives a doublet at 5.54 and 5.29 ppm. The 1,2 and 1,6 isomers of $[Rh(en)_2Cl_2]^+$ give corresponding patterns. Yoneda and Nakashima, using the same type of instrument as ours, reported that 1,2-$[Co(en)_2Cl_2]^+$ gives two well-separated signals due to NH$_2$ protons.[16] The signal at the lower magnetic field was assigned to out-of-plane NH$_2$ protons, the one at higher magnetic field to the in-plane protons. Although the separation of these two NH$_2$ signals is not significant in the present cases, a similar observation to this one was made by Hendrickson and Jolly for the acidopentaammine complexes of cobalt(III), rhodium(III), and iridium(III).[17] Only one peak due to NH$_3$ protons was detected for the rhodium(III) and iridium(III) complexes, whereas the cobalt pentaammines showed two peaks with an intensity ratio 4:1.

^{1}H NMR spectra of 1,2 and 1,6 isomers of $[M(en)_2(NH_3)_2]^{3+}$ (M = Co, Rh, and Ir) are compared in Table II. The 1,6 isomer of $[Co(en)_2(NH_3)_2]^{3+}$ shows a singlet NH$_2$ signal, whereas the signal of 1,2-$[Co(en)_2(NH_3)_2]^{3+}$ is much broader. A similar trend is recognizable for 1,2- and 1,6-$[Rh(en)_2(NH_3)_2]^{3+}$, though the curve for 1,2-$[Rh(en)_2(NH_3)_2]^{3+}$ is not as broad as that for 1,2-$[Co(en)_2(NH_3)_2]^{3+}$. The ^{1}H NMR spectral pattern of $[Ir(en)_2(NH_3)_2]^{3+}$ prepared in this work is very similar to that of 1,2-$[Rh(en)_2(NH_3)_2]^{3+}$, except for the values of the chemical shifts, and indicates the 1,2 configuration.

In the 1,2- and 1,6-$[Rh(en)_2(NH_3)Cl]^{2+}$ complexes, the NH$_2$ signal of the 1,6 isomer is a distinct doublet, that of the 1,2 isomer being much broader than that of 1,6 isomer. The $[Rh(en)_2(NH_3)Br]^{2+}$ and $[Rh(en)_2(NH_3)I]^{2+}$ complexes prepared in this work give almost identical patterns with that of 1,6-$[Rh(en)_2(NH_3)Cl]^{2+}$ and the spectra allow us to assign the 1,6 configuration to these complexes.

In order to know whether the stereochemical changes occur or not during the course of the ammoniation reactions, the following experiments were carried out: The product solution derived from the reaction of 1,2-$[(-)^{\mathrm{CD}}_{393}$-$Rh(en)_2Cl_2]^+$ with NH$_4$OH was put through a Sephadex column. After the very small amount of the starting material was eluted with 0.2 M HCl, all rhodium(III) ions remaining in the column were collected by elution with 0.5 M HCl. This eluate was evaporated to dryness. The residue was dissolved in water and the solution was subjected to measurements of the electronic and CD spectra. The electronic spectrum showed that the rhodium(III) species was $[Rh(en)_2(NH_3)Cl]^{2+}$. From the CD spectrum, the product was found to be optically active and its pattern, the same as that of 1,2-$[(+)^{\mathrm{CD}}_{362}$-$Rh(en)_2(NH_3)Cl]^{2+}$. The value of $\Delta\epsilon_{362}$ was found to be 0.49, and agreed with that of the isomer forming the less soluble (+)-BCS salt obtained by the independent resolution of 1,2-$[Rh(en)_2(NH_3)Cl]Cl_2$. The product solutions derived from the reactions of 1,2-$[(-)^{\mathrm{CD}}_{393}$-$Rh(en)_2Cl_2]^+$ and 1,2-$[(-)^{\mathrm{CD}}_{406}$-$Rh(en)_2Br_2]^+$ with liquid ammonia containing NaNH$_2$ were put through Sephadex columns. The solutions containing all tripositively charged species which were eluted with 0.5 M HCl were treated in the way described for $[Rh(en)_2(NH_3)Cl]^{2+}$. The electronic spectra showed that the species in the solutions were $[Rh(en)_2(NH_3)_2]^{3+}$. The CD patterns indicated that the products were 1,2-$[(+)^{\mathrm{CD}}_{325}$-$Rh(en)_2(NH_3)_2]^{3+}$ and their values of $\Delta\epsilon_{325}$ agreed with those of the samples isolated by recrystallization as described in the Experimental Section. Furthermore, it was found that the crystals of $[Rh(en)_2(NH_3)_2]Cl_3$ obtained here were needles, whereas those of $[Rh(en)_2(NH_3)_2]Cl_3$ which was derived from 1,6-$[Rh(en)_2Cl_2]^+$ were micaceous plates. A similar experiment to these was also made for the ammoniation reaction of 1,2-$[(-)^{\mathrm{CD}}_{385}$-$Ir(en)_2Cl_2]ClO_4$ in liquid ammonia containing NaNH$_2$. The value of $\Delta\epsilon_{280}$ was +0.18. Various reactions attempted with 1,2-$[(-)^{\mathrm{CD}}_{393}$-$Rh(en)_2Cl_2]^+$ are summarized in Scheme I. It is known that the ammoniation of 1,2-$[Co(en)_2Cl_2]^+$ gives 1,6-$[Co(en)_2(NH_3)_2]^{3+}$ as well as the 1,2 isomer.[1,2] If the monoammine and diammine complexes obtained by the ammoniation of 1,2-$[Rh(en)_2X_2]^+$ and 1,2-$[Ir(en)_2Cl_2]^+$ contained 1,6 isomers as well as 1,2 isomers, it would be expected that the intensities of the CD spectra would change upon recrystallization. However, this was not observed. These facts indicate that the ammoniation of these dihalo complexes proceeds with complete retention or complete inversion of configuration. However, no reactions of octahedral metal complexes which proceed with the complete inversion have been found so far and it is difficult to consider a pathway proceeding with complete inversion. Hence it is inferred that all the optically active complexes given in Scheme I have the same relative configuration. Similarly, the absolute configuration of 1,2-$[(-)^{\mathrm{CD}}_{385}$-$Ir(en)_2Cl_2]^+$ must be the same as that of 1,2-$[(+)^{\mathrm{CD}}_{280}$-$Ir(en)_2(NH_3)_2]^{3+}$.

The electronic absorption data for the rhodium(III) and iridium(III) complexes prepared in this work were compared with those of the corresponding cobalt(III) complexes whose d–d transitions have been investigated extensively. All complexes in question can be classified into four categories: MN$_6$ (approximated as O_h symmetry), MN$_5$X (C_{4v}), 1,6-MN$_4$X$_2$ (D_{4h}), and 1,2-MN$_4$X$_2$ (C_{2v}). From the spectroscopic investigations of cobalt(III) complexes, it is known that the first absorption band of the CoN$_6$ type complex ($A_1 \rightarrow T_1$) splits into two components in the MN$_5$X and MN$_4$X$_2$ complexes and the magnitude of the shifts of the splitting components can be predicted.[18-21] In Table III are summarized the predicted positions of splitting components under the first absorption bands for the complexes of the four types in question,[18,21] where σ_{CoN_6} and σ_{CoX_6} represent the positions in μm^{-1} of the first absorption bands of the complexes having CoN$_6$ and CoX$_6$ moieties, respectively. The energy of the nondegenerate component, I$_b$, of 1,6-CoN$_4$X$_2$ is the same as that of the CoN$_6$ complex. The degenerate component of 1,6-CoN$_4$X$_2$ (I$_a$) is located at the averaged position of σ_{CoN_6} and σ_{CoX_6}. If the intensity of the absorption due to each

Table III. Predicted Positions of the First Absorption Bands of the Complexes of $\mathrm{CoN}_{6-n}\mathrm{X}_n$ Type

Type of the complex	Components of first band	Degeneracy no. of the component	Band designation[a]
$\mathrm{CoN_6}$ (O_h)	$\sigma_{\mathrm{CoN_6}}$	3	I
	$^{3}/_{4}\sigma_{\mathrm{CoN_6}} + {}^{1}/_{4}\sigma_{\mathrm{CoX_6}}$	2	$\mathrm{I_a}$
$\mathrm{CoN_5X}$ (C_{4v})	$\sigma_{\mathrm{CoN_6}}$	1	$\mathrm{I_b}$
	$^{1}/_{2}\sigma_{\mathrm{CoN_6}} + {}^{1}/_{2}\sigma_{\mathrm{CoX_6}}$	1	$\mathrm{I_b}$
1,2-$\mathrm{CoN_4X_2}$ (C_{2v})	$^{3}/_{4}\sigma_{\mathrm{CoN_6}} + {}^{1}/_{4}\sigma_{\mathrm{CoX_6}}$	2	$\mathrm{I_a}$
	$^{1}/_{2}\sigma_{\mathrm{CoN_6}} + {}^{1}/_{2}\sigma_{\mathrm{CoX_6}}$	2	$\mathrm{I_a}$
1,6-$\mathrm{CoN_4X_2}$ (D_{4h})	$\sigma_{\mathrm{CoN_6}}$	1	$\mathrm{I_b}$

[a] When an absorption band is split into two components, the degenerate one is labeled $\mathrm{I_a}$ and another nondegenerate one, $\mathrm{I_b}$.

component is assumed to be proportional to the degeneracy number, it can be predicted that the $\mathrm{I_a}$ absorption band will be stronger than $\mathrm{I_b}$, that is, the $\mathrm{I_a}$ band will be the major one. In $\mathrm{CoN_5X}$ complexes, as the energy separation between the major absorption band ($\mathrm{I_a}$) and the minor one ($\mathrm{I_b}$) is small, the latter band would be a shoulder of the $\mathrm{I_a}$ band. In the 1,2-$\mathrm{CoN_4X_2}$ complex, the major band ($\mathrm{I_a}$) will also be accompanied by a shoulder band ($\mathrm{I_b}$).

These findings and aspects obtained for cobalt(III) complexes allow one to identify the d–d transitions of the rhodium(III) and iridium(III) complexes correctly because these metal ions have the same spin-paired $\mathrm{d^6}$ electronic structures as cobalt(III) ions.

Table IV shows the data for the electronic absorptions of the complexes of the $\mathrm{MN_6}$ and 1,6-$\mathrm{MN_4X_2}$ types (M = Rh and Ir) in the d–d transition regions; the data for cobalt(III) complexes are included for comparison. As the ligand X in question is halide ion in which the strength of the ligand field is less than that of the nitrogen atom, the absorption of 1,6-$\mathrm{MN_4X_2}$ at the lowest wavenumber can be assigned to $\mathrm{I_a}$. Therefore, the values of $\sigma_{\mathrm{MN_6}}$ and $\sigma_{\mathrm{MX_6}}$ can be estimated from the positions of the absorption bands based on both I band of the $\mathrm{MN_6}$ complex and the $\mathrm{I_a}$ band of the 1,6-$\mathrm{MN_4X_2}$: $\sigma_{\mathrm{CoN_6}} = 21.3_5$, $\sigma_{\mathrm{CoCl_6}} = 1.63 \times 2 - 2.13_5 = 1.12_5$, $\sigma_{\mathrm{RhN_6}} = 3.32$, $\sigma_{\mathrm{RhCl_6}} = 2.46 \times 2 - 3.32 = 1.60$, $\sigma_{\mathrm{RhBr_6}} = 1.34$, $\sigma_{\mathrm{IrN_6}} = 4.06$, and $\sigma_{\mathrm{IrCl_6}} = 1.72$ in $\mu\mathrm{m}^{-1}$. The data on the electronic absorption spectra of the complexes of $\mathrm{MN_6}$, $\mathrm{MN_5X}$, and 1,2-$\mathrm{MN_4X_2}$ types are summarized in Table V. This table also shows the positions of the splitting components under the first bands which were predicted from the σ values estimated above. The positions of the first absorption bands for all complexes shown in Table V agree with the predicted values satisfactorily. However, it should be noted that the $\sigma_{\mathrm{MX_6}}$ values estimated from Table IV do not agree with the values observed for $\mathrm{MX_6}$ complexes. The position of the first band of $\mathrm{MX_6}$ has been reported to be 1.39 $\mu\mathrm{m}^{-1}$ for $\mathrm{RhCl_6}^{3-}$, 1.81 $\mu\mathrm{m}^{-1}$ for $\mathrm{RhBr_6}^{3-}$, and 2.41 $\mu\mathrm{m}^{-1}$ for $\mathrm{IrCl_6}^{3-}$, respectively.[22] When these observed values of $\mathrm{MX_6}$ are used as $\sigma_{\mathrm{MX_6}}$ values, there are big discrepancies between the predicted values and the observed values, especially for 1,6-$\mathrm{MN_4X_2}$ and 1,2-$[\mathrm{Ir(en)_2Cl_2}]^+$ complexes. This indicates that the difference between the absorption positions of $\mathrm{MN_6}$ and $\mathrm{MX_6}$ complexes is too large to allow the prediction of the positions of the splitting components of mixed $\mathrm{MN}_{6-n}\mathrm{X}_n$ complexes accurately. For example, the difference between the absorption positions of $\mathrm{IrN_6}$ and $\mathrm{IrCl_6}$ complexes is 1.65 $\mu\mathrm{m}^{-1}$. The positions of the splitting components of 16 complexes of $[\mathrm{Co(en)}_{3-x-y}(\mathrm{gly})_y(\mathrm{ox})_x]$ type were predicted from the values for $[\mathrm{Co(en)_3}]^{3+}$ ($\sigma_{\mathrm{CoN_6}}$) and $[\mathrm{Co(ox)_3}]^{3-}$ ($\sigma_{\mathrm{CoO_6}}$), where ox and gly denote oxalate and glycinate, respectively.[21] Although the values predicted are in good agreement with the observed values, the difference between $\sigma_{\mathrm{CoN_6}}$ and $\sigma_{\mathrm{CoO_6}}$ is only 0.49 $\mu\mathrm{m}^{-1}$.

Table IV. Electronic Absorptions of the Complexes of the $\mathrm{MN_6}$ and 1,6-$\mathrm{MN_4X_2}$ Types

Complex ion (approx symmetry)	Absorption $\tilde{\nu}$, cm × 10^3 (log ϵ)	Transition	Ref for spectral data
1,6-$[\mathrm{Co(en)_2(NH_3)_2}]^{3+}$ (O_h)	21.4 (1.77)	I band	*a*
	29.7 (1.73)	Second band	
1,2-$[\mathrm{Co(en)_2(NH_3)_2}]^{3+}$ (O_h)	21.3 (1.86)	I band	*b*
	29.3 (1.79)	Second band	
1,6-$[\mathrm{Co(en)_2Cl_2}]^+$ (D_{4h})	16.3 (1.58)	$\mathrm{I_a}$ band	*c*
	21.6 (1.41)	$\mathrm{I_b}$ band	
	25.8 (1.68)	Second band	
1,6-$[\mathrm{Rh(en)_2(NH_3)_2}]^{3+}$ (O_h)	33.3 (2.26)	I band	*d*
	39.7 (2.22)	Second band	
1,2-$[\mathrm{Rh(en)_2(NH_3)_2}]^{3+}$ (O_h)	33.1 (2.31)	I band	*d*
	39.4 (2.20)	Second band	
1,6-$[\mathrm{Rh(en)_2Cl_2}]^+$ (D_{4h})	24.6 (1.90)	$\mathrm{I_a}$ band	*d*
	32 sh[e] (1.9)	$\mathrm{I_b}$ band	
	34.6 (2.09)	Second band	
1,6-$[\mathrm{Rh(en)_2Br_2}]^+$ (D_{4h})	23.3 (2.06)	$\mathrm{I_a}$ band	*d*
1,2-$[\mathrm{Ir(en)_2(NH_3)_2}]^{3+}$ (O_h)	ca. 33 sh[e] (1.31)	Triplet band	*d*
	40.6 (2.20)	I band	
	ca. 45 sh[e] (2.23)	Second band	
1,6-$[\mathrm{Ir(en)_2Cl_2}]^+$ (D_{4h})	23.4 (0.68)	Triplet band	*d*
	28.9 (1.64)	$\mathrm{I_a}$ band	

[a] Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, 29, 311 (1956). [b] From ref 26. [c] Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, 28, 572 (1955). [d] This work. [e] Shoulder band.

All the electronic and CD spectra of the optically active complexes prepared in this work are shown in Figures 1–3, and their CD data are given in Table V. The absolute configurations of various complexes have been inferred by comparing the signs of the CD peaks with that of the standard complex, whose absolute configuration is known. The principle underlying this method is that two related optically active complexes have the same absolute configuration if they give a Cotton effect of the same sign in the absorption wavelength region of an electronic transition common to both complexes.[23] This empirical rule was applied to the present complexes.

The absolute configuration of 1,2-$[(-)^{\mathrm{CD}}_{608}\text{-}\mathrm{Co(en)_2Cl_2}]^+$ has been determined as Λ by x-ray diffraction.[24,25] The CD spectrum of this isomer shows a − and a + peak from the lower wavenumber side of the first band and a + peak under the second band.[26] Since this CD pattern resembles that of the respective 1,2-$[(-)^{\mathrm{CD}}_{393}\text{-}\mathrm{Rh(en)_2Cl_2}]^+$, 1,2-$[(-)^{\mathrm{CD}}_{406}\text{-}\mathrm{Rh(en)_2Br_2}]^+$, and 1,2-$[(-)^{\mathrm{CD}}_{385}\text{-}\mathrm{Ir(en)_2Cl_2}]^+$ as shown in Figure 1, each isomer may have the Λ configuration. Two additional CD peaks observed for 1,2-$[(-)^{\mathrm{CD}}_{385}\text{-}\mathrm{Ir(en)_2Cl_2}]^+$ at 2.60 and 2.94 $\mu\mathrm{m}^{-1}$ are considered to be due to the triplet transitions.

If it is accepted that ammoniations of the rhodium(III) and iridium(III) complexes proceed through retention of configuration, 1,2-$[(+)^{\mathrm{CD}}_{362}\text{-}\mathrm{Rh(en)_2(NH_3)Cl}]^{2+}$, 1,2-$[(+)^{\mathrm{CD}}_{325}\text{-}\mathrm{Rh(en)_2(NH_3)_2}]^{3+}$, and 1,2-$[(+)^{\mathrm{CD}}_{280}\text{-}\mathrm{Ir(en)_2(NH_3)_2}]^{3+}$ must be the Λ configuration. This inference seems to be supported when CD spectra of these complexes shown in Figure 2 and 3 are compared. The CD pattern of 1,2-$[(+)^{\mathrm{CD}}_{362}\text{-}\mathrm{Rh(en)_2}$-

Table V. Electronic Absorption and Circular Dichroism of Some Cobalt(III), Rhodium(III), and Iridium(III) Complexes

Complex ion (approx symmetry)	Electronic absorption $\tilde{\nu}$, cm × 10^3 (log ϵ)	Predicted Position of absorption, cm × 10^3	Band assignment	Circular dichroism $\tilde{\nu}$, cm × 10^3 ($\Delta\epsilon$)
$1,2\text{-}[(+)^{\mathrm{CD}}_{492}\text{-Co(en)}_2(\mathrm{NH}_3)_2]^{3+}$ [a,b] (O_h)	21.3 (1.86)	21.3_5	I band	20.3 (+0.42)
				23.3 (−0.04)
	29.3 (1.79)		Second band	28.1 (+0.056)
$1,2\text{-}[(+)^{\mathrm{CD}}_{550}\text{-Co(en)}_2(\mathrm{NH}_3)\mathrm{Cl}]^{2+}$ [c] (C_{4v})	19.0 (1.87)	18.8	$\mathrm{I_a}$ band	18.2 (+0.27)
	ca. 21 sh (1.7)	21.3_5	$\mathrm{I_b}$ band	21.2 (+0.20)
	27.4 (1.89)		Second band	26.0 (+0.08)
$1,2\text{-}[(-)^{\mathrm{CD}}_{608}\text{-Co(en)}_2\mathrm{Cl}_2]^{+}$ [c] (C_{2v})	16.4 sh (1.65)	16.3	$\mathrm{I_b}$ band	16.4 (−0.40)
	18.6 (1.95)	18.8	$\mathrm{I_a}$ band	19.0 (+0.52)
	25.7 (1.93)		Second band	24.7 (+0.15)
$1,2\text{-}[(+)^{\mathrm{CD}}_{325}\text{-Rh(en)}_2(\mathrm{NH}_3)_2]^{3+}$ [d] (O_h)	33.1 (2.31)	33.2	I band	30.8 (+0.48)
				34.1 (−0.06)
	39.4 (2.20)		Second band	37.6 (+0.20)
$1,2\text{-}[(+)^{\mathrm{CD}}_{362}\text{-Rh(en)}_2(\mathrm{NH}_3)\mathrm{Cl}]^{2+}$ [c] (C_{4v})	29.1 (2.18)	28.9	$\mathrm{I_a}$ band	27.6 (+0.51)
	Masked	33.2	$\mathrm{I_b}$ band	34.4 (+0.77)
	36.2 (2.26)		Second band	ca. 38 (+0.2)
$1,6\text{-}[\mathrm{Rh(en)}_2(\mathrm{NH}_3)\mathrm{Cl}]^{2+}$ (C_{4v})	29.0 (2.02)	28.9	$\mathrm{I_a}$ band	
	Masked	33.2	$\mathrm{I_b}$ band	
	36.3 (2.12)		Second band	
$1,6\text{-}[\mathrm{Rh(en)}_2(\mathrm{NH}_3)\mathrm{Br}]^{2+}$ (C_{4v})	28.2 (2.07)	28.2_5	$\mathrm{I_a}$ band	
	Masked	33.2	$\mathrm{I_b}$ band	
	ca. 35 sh (2.2)		Second band	
			Triplet band	22.4 (−0.10)
$1,2\text{-}[(-)^{\mathrm{CD}}_{393}\text{-Rh(en)}_2\mathrm{Cl}_2]^{+}$ [c] (C_{2v})	25.4 sh (2.0)	24.6	$\mathrm{I_b}$ band	25.4 (−0.52)
	28.4 (2.28)	28.9	$\mathrm{I_a}$ band	29 (+0.33)
	33.9 (2.27)		Second band	32.9 (+0.72)
			Triplet band	21.4 (−0.15)
$1,2\text{-}[(-)^{\mathrm{CD}}_{406}\text{-Rh(en)}_2\mathrm{Br}_2]^{+}$ [c] (C_{2v})	23 sh (1.9)	23	$\mathrm{I_b}$ band	24.6 (−0.62)
	27.2 (2.38)	28.2_5	$\mathrm{I_a}$ band	28.6 (+0.62)
	36 sh (3.0)		Second band	33 (+0.20)
$1,2\text{-}[(+)^{\mathrm{CD}}_{280}\text{-Ir(en)}_2(\mathrm{NH}_3)_2]^{3+}$ [e] (O_h)	ca. 33 sh (1.31)		Triplet band	ca. 32 (+0.10)
	40.6 (2.20)	40.6	I band	35.7 (+0.18)
	ca. 45 sh (2.23)		Second band	42.5 (+0.15)
			Triplet band	26.0 (−0.40)
$1,2\text{-}[(-)^{\mathrm{CD}}_{385}\text{-Ir(en)}_2\mathrm{Cl}_2]^{+}$ [c,f] (C_{2v})	26.4 sh		Triplet band	29.4 (+0.09)
	31 sh (1.94)	28.9	$\mathrm{I_b}$ band	31.5 (−0.05)
	34.1 (2.14)	34.8	$\mathrm{I_a}$ band	34.2 (+0.14)
	39.2 sh (2.19)		Second band	38.6 (+0.95)

[a] Reference 26. [b] Prepared from $1,2\text{-}[(+)^{\mathrm{CD}}_{550}\text{-Co(en)}_2(\mathrm{NH}_3)\mathrm{Cl}]^{2+}$.[32] [c] The isomer forming the less soluble (+)-BCS salt. [d] Prepared from $1,2\text{-}[(-)^{\mathrm{CD}}_{406}\text{-Rh(en)}_2\mathrm{Br}_2]^{+}$. [e] Prepared from $1,2\text{-}[(-)^{\mathrm{CD}}_{385}\text{-Ir(en)}_2\mathrm{Cl}_2]^{+}$. [f] The isomer forming the less soluble $[(+)^{\mathrm{RD}}_{546}\text{-Co(edta)}]^{-}$ salt.

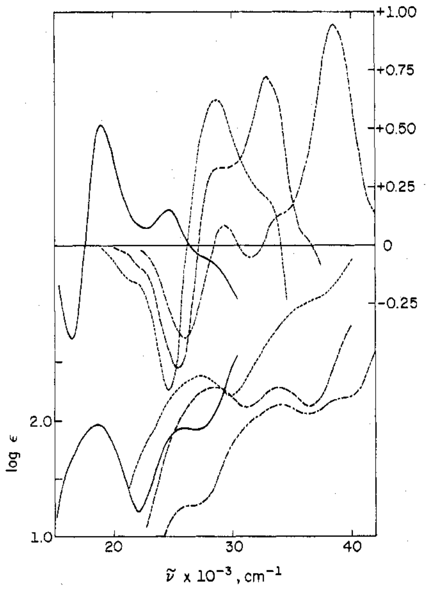


Figure 1. Electronic absorption (lower part) and circular dichroism (upper part) of $1,2\text{-}[(+)^{\mathrm{CD}}_{608}\text{-Co(en)}_2\mathrm{Cl}_2]^{+}$ (—), $1,2\text{-}[(-)^{\mathrm{CD}}_{406}\text{-Rh(en)}_2\mathrm{Br}_2]^{+}$ (- - -), $1,2\text{-}[(-)^{\mathrm{CD}}_{393}\text{-Rh(en)}_2\mathrm{Cl}_2]^{+}$ (— — —), and $1,2\text{-}[(-)^{\mathrm{CD}}_{385}\text{-Ir(en)}_2\mathrm{Cl}_2]^{+}$ (- — -).

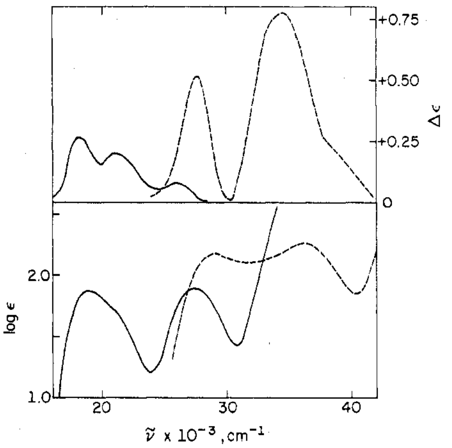


Figure 2. Electronic absorption (lower part) and circular dichroism (upper part) of $1,2\text{-}[(+)^{\mathrm{CD}}_{550}\text{-Co(en)}_2(\mathrm{NH}_3)\mathrm{Cl}]^{2+}$ (—) and $1,2\text{-}[(+)^{\mathrm{CD}}_{362}\text{-Rh(en)}_2(\mathrm{NH}_3)\mathrm{Cl}]^{2+}$ (- - -).

$(\mathrm{NH}_3)\mathrm{Cl}]^{2+}$ is +++ under the spin-allowed bands and similar to that of $1,2\text{-}[(+)^{\mathrm{CD}}_{550}\text{-Co(en)}_2(\mathrm{NH}_3)\mathrm{Cl}]^{2+}$ whose absolute configuration has been inferred as Λ.[27,28] The CD spectrum of $1,2\text{-}[(+)^{\mathrm{CD}}_{325}\text{-Rh(en)}_2(\mathrm{NH}_3)_2]^{3+}$ shows a strong positive and a weak negative peak under the first band and a positive band under the second band. This pattern is quite similar to those of $1,2\text{-}[(+)^{\mathrm{CD}}_{492}\text{-Co(en)}_2(\mathrm{NH}_3)_2]^{3+}$, $[(+)^{\mathrm{CD}}_{493}\text{-Co(en)}_3]^{3+}$, and $[(+)^{\mathrm{CD}}_{312}\text{-Rh(en)}_3]^{3+}$ whose absolute configurations have been determined or inferred as Λ.[23,27-30] Although the CD spectrum of $1,2\text{-}[(+)^{\mathrm{CD}}_{280}\text{-Ir(en)}_2(\mathrm{NH}_3)_2]^{3+}$ shows only two positive CD peaks under the spin-allowed bands, this pattern is considered to be similar to that of $1,2\text{-}[(+)^{\mathrm{CD}}_{492}\text{-Co(en)}_2(\mathrm{NH}_3)_2]^{3+}$, if a band which is expected to be weak negative is assumed to be hidden by the two positive CD peaks.

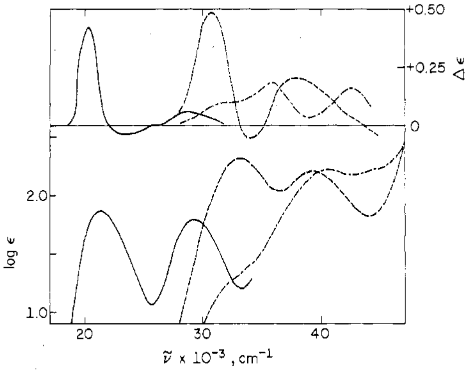


Figure 3. Electronic absorption (lower part) and circular dichroism (upper part) of 1,2-$[(+)^{CD}_{492}\text{-Co(en)}_2(\text{NH}_3)_2]^{3+}$ (—), 1,2-$[(+)^{CD}_{325}\text{-Rh(en)}_2(\text{NH}_3)_2]^{3+}$ (– – –), and 1,2-$[(+)^{CD}_{280}\text{-Ir(en)}_2(\text{NH}_3)_2]^{3+}$ (- - -). The data for 1,2-$[(+)^{CD}_{492}\text{-Co(en)}_2(\text{NH}_3)_2]^{3+}$ are taken from ref 27 and 28.

The optically active complexes given in Table V form the less-soluble (+)-BCS salts except for the optically active diammine complexes. This also indicates that, from view of the solubility rule,[31] these enantiomers probably have the same absolute configuration.

Whole aspects of the ammoniation reactions of rhodium(III) and iridium(III) complexes studied in this work may suggest that the reactions proceed with complete retention of configuration and all optically active complexes listed in Table V have the Λ configuration.

Acknowledgment. The authors gratefully acknowledge the financial assistance of the National Science Foundation (Grants GP 5318 and GP 9370).

Registry No. 1,6-$[\text{Rh(en)}_2\text{Cl}_2]\text{Cl}$, 15444-63-0; 1,2-$[\text{Rh(en)}_2\text{Cl}_2]\text{Cl}$, 15444-62-9; 1,6-$[\text{Rh(en)}_2\text{Br}_2]\text{NO}_3$, 15529-89-2; 1,2-$[\text{Rh(en)}_2\text{Br}_2]\text{Br}$, 65761-17-3; 1,6-$[\text{Rh(en)}_2\text{I}_2]\text{I}$, 39561-35-8; 1,2-$[\text{Rh(en)}_2\text{I}_2]\text{I}$, 53368-51-7; 1,6-$[\text{Rh(en)}_2(\text{NH}_3)\text{Cl}](\text{NO}_3)_2$, 65802-28-0; 1,2-$[\text{Rh(en)}_2(\text{NH}_3)\text{Cl}]\text{Cl}_2$, 65794-88-9; 1,6-$[\text{Rh(en)}_2(\text{NH}_3)\text{Br}](\text{NO}_3)_2$, 65761-16-2; 1,6-$[\text{Rh(en)}_2(\text{NH}_3)\text{I}]\text{I}_2$, 65761-15-1; 1,6-$[\text{Rh(en)}_2(\text{NH}_3)_2](\text{ClO}_4)_3$, 65761-21-9; 1,2-$[\text{Rh(en)}_2(\text{NH}_3)_2](\text{ClO}_4)_3$, 65794-95-8; 1,6-$[\text{Ir(en)}_2\text{Cl}_2]\text{Cl}$, 15444-46-9; 1,2-$[\text{Ir(en)}_2\text{Cl}_2]\text{Cl}$, 15444-47-0; 1,2-$[\text{Ir(en)}_2(\text{NH}_3)_2](\text{ClO}_4)_3$, 65794-93-6; 1,6-$[\text{Co(en)}_2(\text{NH}_3)_2]\text{Cl}_3$, 36883-69-9; 1,2-$[\text{Co(en)}_2(\text{NH}_3)_2](\text{ClO}_4)_3$, 15079-83-1; Λ-1,2-$[\text{Co(en)}_2(\text{NH}_3)\text{Cl}]^{2+}$, 45837-30-7; Λ-1,2-$[\text{Co(en)}_2\text{Cl}_2]^+$, 18660-62-3; Δ-1,2-$[\text{Co(en)}_2\text{Cl}_2]^+$, 45837-15-8; Λ-1,2-$[\text{Rh(en)}_2(\text{NH}_3)_2]^{3+}$, 65794-91-4; Λ-1,2-$[\text{Rh(en)}_2(\text{NH}_3)\text{Cl}]^{2+}$, 65794-90-3; Δ-1,2-$[\text{Rh(en)}_2(\text{NH}_3)\text{Cl}]^{2+}$, 65794-89-0; Λ-1,2-$[\text{Rh(en)}_2\text{Cl}_2]^+$, 65830-10-6; Λ-1,2-$[\text{Rh(en)}_2\text{Br}_2]^+$, 65830-11-7; Δ-1,2-$[\text{Rh(en)}_2\text{Br}_2]^+$, 64598-98-7; Λ-1,2-$[\text{Ir(en)}_2(\text{NH}_3)_2]^{3+}$, 65830-12-8; Λ-1,2-$[\text{Ir(en)}_2\text{Cl}_2]^+$, 45838-56-0.

Supplementary Material Available: Figure for infrared spectra of bis(ethylenediamine)diammine complexes of cobalt(III), rhodium(III), and iridium(III) in the NH_2 asymmetric deformation region and figures for ^{1}H NMR spectra of bis(ethylenediamine) complexes of cobalt(III), rhodium(III), and iridium(III) (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Postdoctoral Research Associate, University of Illinois, 1968–1969.
(2) (a) J. C. Bailar, Jr., J. H. Haslam, and E. M. Jones, *J. Am. Chem. Soc.*, **58**, 2226 (1936); (b) R. D. Archer and J. C. Bailar, Jr., *ibid.*, **83**, 812 (1961).
(3) J. C. Bailar, Jr., *Inorg. Synth.* **2**, 222 (1946).
(4) A. Werner and V. L. King, *Ber. Dtsch. Chem. Ges.*, **44**, 1890 (1911).
(5) J. B. Work, Ph.D. Thesis, University of Illinois, 1942, p 44.
(6) A. Werner, *Justus Liebigs. Ann. Chem.*, **351**, 65 (1907).
(7) S. Anderson and F. Basolo, *J. Am. Chem. Soc.*, **82**, 4423 (1960).
(8) S. A. Johnson and F. Basolo, *Inorg. Chem.*, **1**, 925 (1962).
(9) S. Kida, *Bull. Chem. Soc. Jpn.*, **39**, 2415 (1966).
(10) R. A. Bauer and F. Basolo, *Inorg. Chem.*, **8**, 2231 (1969).
(11) In this paper, an optical isomer is designated mainly by $(+)^{CD}_{\lambda}$ or $(-)^{CD}_{\lambda}$, which is the sign of the circular dichroism (CD) curve. The suffix λ represents the wavelength (nm) used for the measurement. In some cases, $(+)^{RD}_{\lambda}$ or $(-)^{RD}_{\lambda}$ is used, where the sign represents the optical rotation at the given wavelength. 1,2-$[(-)^{CD}_{608}\text{-Co(en)}_2\text{Cl}_2]\text{Cl}$ correponds to the 1,2-$[(+)^{RD}_{589}\text{-Co(en)}_2\text{Cl}_2]\text{Cl}$ isomer.
(12) F. P. Dwyer and F. L. Garvan, *Inorg. Synth.*, **6**, 192 (1960).
(13) H. Ogino, M. Takahashi, and N. Tanaka, *Bull. Chem. Soc. Jpn.*, **43**, 424 (1970).
(14) H. Yoneda and Y. Morimoto, *Bull. Chem. Soc. Jpn.*, **39**, 2180 (1966).
(15) D. A. Buckingham, L. Durham, and A. M. Sargeson, *Aust. J. Chem.*, **20**, 257 (1967).
(16) H. Yoneda and Y. Nakashima, *Bull. Chem. Soc. Jpn.*, **47**, 669 (1974).
(17) D. N. Hendrickson and W. L. Jolly, *Inorg. Chem.*, **9**, 1197 (1970).
(18) H. Yamatera, *Bull. Chem. Soc. Jpn.*, **31**, 95 (1958).
(19) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709, 1524 (1965), and references cited therein.
(20) C. J. Hawkins, "Absolute Configuration of Metal Complexes", Wiley, New York, N.Y., 1971, p 157.
(21) N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **40**, 1868 (1967).
(22) C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 500 (1956).
(23) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).
(24) K. Matsumoto, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **43**, 3801 (1970).
(25) The symbols used here to denote absolute configurations are according to the IUPAC proposal: *Inorg. Chem.*, **9**, 1 (1970).
(26) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).
(27) A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.*, 132 (1965).
(28) S. F. Mason and B. J. Norman, *Chem. Commun.*, 73 (1965).
(29) Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **30**, 795 (1957).
(30) S. K. Hall and B. E. Douglas, *Inorg. Chem.*, **7**, 533 (1968).
(31) A. Werner, *Ber. Dtsch. Chem. Ges.*, **45**, 121, 865 (1912).
(32) T. E. MacDermott and A. M. Sargeson, *Aust. J. Chem.*, **16**, 334 (1963).

Contribution from the Departments of Chemistry, University of Houston,
Houston, Texas 77004, and California State University, Fullerton, California 92634

Reactions of Pyridine with a Series of Para-Substituted Tetraphenylporphyrincobalt and -iron Complexes

K. M. KADISH,*[1a] L. A. BOTTOMLEY,[1a,b] and D. BEROIZ

Received August 22, 1977

The effect of substituents on electrode reactions and ligand binding characteristics of para-substituted cobalt and iron tetraphenylporphyrins was investigated by the technique of cyclic voltammetry. The mechanism of electron transfer is discussed, and comparisons are made between the ligand binding reactions of TPPFeCl and TPPCo in several solvents. Equilibrium constants showed either a negative, positive, or zero Hammett relationship depending upon the charge on the central metal and the solvent.

During recent years a number of papers have been published which elucidate linear free energy relationships involving metalloporphyrins. These studies have focused on measuring polarographic half-wave potentials,[2-5] electron-transfer kinetics,[5] porphyrin spectroscopic properties,[6] phenyl ring rotation,[7a] kinetics of ligand exchange,[7b] and stability constants for axial ligand addition to form 1:1 and 2:1 complexes with metalloporphyrins.[3,8-14] It has been shown that the addition

0020-1669/78/1317-1124$01.00/0