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Iridium(III) and Rhodium(III) Mono- and Bis(1,10-phenanthroline) Complexes and the Optical Isomers of Iridium(III), Rhodium(III), Chromium(III), and Cobalt(III) Dihalogenobis(1,10-phenanthroline) Complex Cations

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phenH[IrCl$_4$phen] (phen = 1,10-phenanthroline) has been prepared, characterized, and used to synthesize new mono and bis complexes of Ir(III) and the tetrachloro-1,10-phenanthrolineiridium(IV) species. Similar reactions have led to greatly improved syntheses of the corresponding Rh(III) complexes. Separate thermal and photochemical aquation reactions of IrCl$_4$phen$^-$ have given tentative "*fac*"- and "*mer*"-IrX$_3$(H$_2$O)phen (X = Cl or Br), respectively. Chromatographic resolution on cellulose has enabled the assignment of cis configurations to iridium(III), rhodium(III), chromium(III), and cobalt(III) dihalogenobis(1,10-phenanthroline) complex cations. Infrared, nmr, and X-ray diffractometric measurements are also in agreement with a cis geometry. Infrared, ultraviolet, and visible spectra and X-ray diffraction data are reported for the new compounds.

Introduction

Failure of the reported method[1] to give the *trans*-dichlorobis(1,10-phenanthroline)iridium (III) cation has led us to investigate further the chemistry of this metal–ligand system.

In a preliminary note[2] the reaction of 1,10-phenanthroline with ammonium hexachloroiridate(III) in dilute hydrochloric acid was shown to give 1,10-phenanthrolinium tetrachloro(1,10-phenanthroline)iridate(III) instead of *trans*-dichlorobis(1,10-phenanthroline)iridium(III) chloride. We now report the results of these reactions in detail together with a wider study of the synthesis, characterization, and isomerism of other new iridium(III)- and -(IV)–1,10-phenanthroline complexes. For comparative purposes some related reactions of Rh(III), Co(III), and Cr(III) compounds with this ligand have been investigated.

Although iridium(III) complexes are characteristically inert, the presence of strong sunlight is known to accelerate reactions.[3] Delepine[4] reported photochemical effects in his studies of iridium–pyridine complexes and subsequent workers[5–7] have made use of this to synthesize new compounds. In the present work the different reactions of IrCl$_4$phen$^-$ in the dark and in the light enable the isolation of both facial and meridional isomers of IrCl$_3$H$_2$Ophen. Further, the photochemical aquation of *cis*-IrCl$_2$(phen)$_2^+$ provides an opportunity to attempt an asymmetric synthesis by utilizing circularly polarized light as the radiation. This type of experiment has been tried unsuccessfully by Jaeger and Berger[8] using Co(C$_2$O$_4$)$_3^{3-}$ and by Garvan[9] using the rhodium(III)–ethylenediamine- and –propylenediaminetetraacetic acid complexes.

The total resolution of a complex cation using ion-exchange chromatography was first described by Brubaker, Legg, and Douglas.[10] Our previously reported resolution[1] of *cis*-dichlorobis(1,10-phenanthroline)iridium(III) was not in fact produced by the sodium arsenyl (+)-tartrate employed but rather was a consequence of the cellulose ion exchangers used to remove the resolving agent. We now find that the use of cation-exchange cellulose provides a general method of resolution for Ir(III), Rh(III), Co(III), and Cr(III) bis(1,10-phenanthroline)metal complexes.

Experimental Section

Materials.—Ammonium and sodium hexachloroiridate(III) were obtained from Johnson Matthey and Co. and rhodium(III) chloride trihydrate was from Fluka, Buchs, Switzerland. The compounds formulated as IrO$_2\cdot$2H$_2$O and Rh$_2$O$_3\cdot$3H$_2$O were prepared by published methods.[11,12] Purple *cis*-[CoCl$_2$(phen)$_2$]Cl$\cdot$3H$_2$O and brown-green [CrCl$_2$(phen)$_2$]Cl were prepared by the methods of Ablov[13] and Burstall and Nyholm,[14] respectively.

1,10-Phenanthrolinium Tetrachloro(1,10-phenanthroline)iridate(III), (C$_{12}$H$_9$N$_2$)[IrCl$_4$(C$_{12}$H$_8$N$_2$)].—Ammonium hexachloroiridate(III) dihydrate (0.5 g) in water (20 ml) was added to a solution of 1,10-phenanthroline hydrate (0.6 g) in hot water (40 ml) containing hydrochloric acid (0.04 ml, 10 *M*). The solution was stirred magnetically and heated at the boil for a period of 2 hr. The product began to precipitate after the first 10 min as shiny red-orange crystals. The product was filtered off

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from the cooled reaction mixture and washed with water. The yield was 0.65 g (90%). *Anal.* Calcd for $C_{24}H_{17}N_4Cl_4Ir$: C, 41.4; H, 2.5; N, 8.0; Cl, 20.4. Found: C, 41.4; H, 2.6; N, 8.0; Cl, 20.5.

1,10-Phenanthrolinium Tetrabromo(1,10-phenanthroline)iridate(III), $(C_{12}H_9N_2)[IrBr_4(C_{12}H_8N_2)]$.—Hydroxonium hexabromoiridate(IV) was prepared *in situ* by dissolution of $IrO_2 \cdot 2H_2O$ (1 g) in concentrated hydrobromic acid (50 ml) the bromine evolved being boiled off, followed by reduction to the iridium(III) state with hydrazinium dihydrobromide (0.23 g). During this reaction the original royal blue of the solution changed to green. 1,10-Phenanthroline hydrate (2.5 g) in hot water (150 ml) containing hydrobromic acid (0.1 ml, 7 *M*) was added. The solution was then heated at the boil and stirred magnetically for a period of 20–30 min. The product began to separate from the hot solution as deep red crystals. The reaction mixture was cooled to room temperature and the product was filtered off at the pump and washed with water. The yield was 3.1 g (84%). *Anal.* Calcd for $C_{24}H_{17}N_4Br_4Ir$: C, 33.0; H, 2.0; N, 6.41; Br, 36.6. Found: C, 33.0; H, 2.2; N, 6.50; Br, 37.0.

1,10-Phenanthrolinium Tetrachloro(1,10-phenanthroline)rhodate(III), $(C_{12}H_9N_2)[RhCl_4(C_{12}H_8N_2)]$.—Rhodium(III) chloride trihydrate (0.3 g) was dissolved in concentrated hydrochloric acid (10 ml) and the solution was heated under reflux for 3 hr. 1,10-Phenanthroline hydrate (0.5 g) was added and heating was continued for a further 20 min during which time the volume of the reaction mixture was increased to 150 ml by the addition of hot water. The orange crystalline complex which separated on cooling was collected at the pump and washed with water. The yield was 0.59 g (85%). *Anal.* Calcd for $C_{24}H_{17}N_4Cl_4Rh$: C, 47.55; H, 2.83; N, 9.24; Cl, 23.4. Found: C, 47.78; H, 2.91; N, 9.27; Cl, 23.8.

1,10-Phenanthrolinium Tetrabromo(1,10-phenanthroline)rhodate(III), $(C_{12}H_9N_2)[RhBr_4(C_{12}H_8N_2)]$.—Rhodium(III) bromide was prepared *in situ* by dissolution of $Rh_2O_3 \cdot 3H_2O$ (0.3 g) in 6 *M* hydrobromic acid (10 ml) and the resulting solution was heated under reflux for 30 min. 1,10-Phenanthroline hydrate (0.9 g) was added and heating was continued for a further 20 min during which time the volume of the reaction mixture was increased to 150 ml by the addition of hot water. The maroon crystalline complex which separated was filtered off from the cooled reaction mixture and washed with water. The yield was 1.35 g (90%). *Anal.* Calcd for $C_{24}H_{17}N_4Br_4Rh$: C, 36.76; H, 2.18; N, 7.14; Br, 40.7. Found: C, 36.81; H, 2.40; N, 7.20; Br, 41.2.

Conversion of Phenanthrolinium Salts to the More Soluble Ammonium Salts, $(NH_4)[MX_4(C_{12}H_8N_2)] \cdot H_2O$ (M = Ir, Rh).—The phenanthrolinium salt (0.5 g) was suspended in a saturated solution of ammonium chloride (25–30 ml). The pH of the solution was adjusted to 10–12 by the addition of dilute ammonium hydroxide. The reaction mixture was shaken mechanically for 30 min and the orange solid was collected at the pump and washed in turn with a solution of ammonium chloride (1 *M*) and then ethanol. The product was recrystallized from a hot solution of ammonium chloride. The shiny crystalline solid which separated was collected at the pump and washed with ice-cold water and then ethanol. The yield was almost quantitative. *Anal.* Calcd for $C_{12}H_{14}N_3Cl_4OIr$: C, 26.03; H, 2.56; N, 7.59; Cl, 25.6. Found: C, 25.94; H, 2.66; N, 7.59; Cl, 25.3. Calcd for $C_{12}H_{14}N_3Cl_4ORh$: C, 31.26; H, 3.06; N, 9.11; Cl, 30.8. Found: C, 31.31; H, 3.21; N, 9.17; Cl, 31.1.

Hydroxonium Tetrachloro(1,10-phenanthroline)iridate(III) Tetrahydrate, $(H_3O)[IrCl_4(C_{12}H_8N_2)] \cdot 4H_2O$.—1,10-Phenanthrolinium tetrachloro(1,10-phenanthroline)iridate(III) (1 g) was dissolved in water (50 ml) contained in a flask protected from the light. This was shaken mechanically with cation-exchange resin (20 g, Dowex 50W-X H^+ form) for a period of 2 hr. The resin was then filtered off and concentrated hydrochloric acid (50 ml) was added to the solution which was heated under reflux for 20 min. It was then evaporated to dryness and stored over sodium hydroxide pellets. The yield was quantitative (0.87 g). *Anal.* Calcd for $C_{12}H_{19}N_2Cl_4O_5Ir$: C, 23.8; H, 3.20; N, 4.60; Cl, 23.4. Found: C, 23.9; H, 3.30; N, 4.61; Cl, 23.0.

Hydroxonium Tetrachloro(1,10-phenanthroline)rhodate(III) Tetrahydrate, $(H_3O)[RhCl_4(C_{12}H_8N_2)] \cdot 4H_2O$.—1,10-Phenanthrolinium tetrachloro(1,10-phenanthroline)rhodate(III) was converted to the hydroxonium salt using the procedure already described for the iridium(III) analog. *Anal.* Calcd for $C_{12}H_{19}N_2Cl_4O_5Rh$: C, 27.93; H, 3.71; N, 5.43; Cl, 27.5. Found: C, 27.81; H, 3.65; N, 5.42; Cl, 27.9.

Hydroxonium Tetrabromo(1,10-phenanthroline)rhodate(III) Tetrahydrate, $(H_3O)[RhBr_4(C_{12}H_8N_2)] \cdot 4H_2O$.—1,10-Phenanthrolinium tetrabromo(1,10-phenanthroline)rhodate(III) (0.5 g) was dissolved in 6 *M* hydrobromic acid (25 ml). The solution was heated to ensure complete dissolution and then set aside to cool. The orange-brown product which crystallized was collected at the pump and washed with ice-cold hydrobromic acid and dried in a desiccator over sodium hydroxide pellets. The yield was 0.3 g (90%). The corresponding $(H_3O)[IrBr_4(C_{12}H_8N_2)] \cdot 4H_2O$ was prepared by a similar procedure. *Anal.* Calcd for $C_{12}H_{19}N_2Br_4O_5Rh$: C, 20.77; H, 2.76; N, 4.04; Br, 46.1. Found: C, 20.81; H, 2.82; N, 4.05; Br, 46.6. Calcd for $C_{12}H_{19}N_2Br_4O_5Ir$: C, 18.38; H, 2.43; N, 3.57; Br, 40.8. Found: C, 18.46; H, 2.76; N, 3.62; Br, 41.2.

Di-μ-chloro-tetrachlorobis(1,10-phenanthroline)diiridium(III), $[IrCl_3(C_{12}H_8N_2)]_2$.—Hydroxonium tetrachloro(1,10-phenanthroline)iridate(III) tetrahydrate was heated to constant weight in a thermogravimetric recording balance to a final temperature of 240°. Weight loss: found, 21.1%; calcd for loss of $5H_2O$ + HCl, 20.9%. *Anal.* Calcd for $C_{24}H_{16}N_4Cl_6Ir_2$: C, 30.04; H, 1.68; N, 5.84; Cl, 22.1. Found: C, 29.66; H, 1.83; N, 5.90; Cl, 21.8.

Di-μ-bromo-tetrabromobis(1,10-phenanthroline)diiridium(III), $[IrBr_3(C_{12}H_8N_2)]_2$.—"*mer*"-Tribromoaquo(1,10-phenanthroline)iridium(III) (0.3 g) was heated to constant weight at a temperature of 150°. Weight loss was 8.7 mg (2.9%). That calculated for loss of H_2O was 2.85%. *Anal.* Calcd for $C_{24}H_{16}N_4Br_6Ir_2$: C, 23.51; H, 1.32; N, 4.57; Br, 39.1. Found: C, 23.64; H, 1.38; N, 4.62; Br, 38.7.

Tetrachloro(1,10-phenanthroline)iridium(IV), $IrCl_4(C_{12}H_8N_2)$.—Hydroxonium tetrachloro(1,10-phenanthroline)iridate(III) tetrahydrate (0.3 g) was dissolved in water (20 ml). Chlorine gas was then bubbled through the orange solution for 20 min. The solution became cloudy and brown before the purple-black product precipitated. The reaction was carried out in the absence of light. The solid was collected at the pump and washed with water, ethanol, and ether. The yield was quantitative. The compound decomposed when exposed to moist air and was stored in a desiccator over P_4O_{10}. The same product was obtained by the oxidation of phenH[$IrCl_4$phen] with concentrated nitric acid in the presence of sulfamic acid. *Anal.* Calcd for $C_{12}H_8N_2Cl_4Ir$: C, 27.98; H, 1.56; N, 5.44; Cl, 27.5. Found: C, 28.16; H, 1.76; N, 5.46; Cl, 28.0.

"*fac*"-Trichloro(or tribromo)aquo(1,10-phenanthroline)iridium(III), $IrCl_3$(or Br_3)$H_2OC_{12}H_8N_2$.—(N.B. The following operations must be carried out in the absence of light to avoid gross contamination with the "mer" isomer.) Ammonium tetrachloro(or tetrabromo)(1,10-phenanthroline)iridate(III) monohydrate (1.0 g) was refluxed and stirred magnetically in *p*-toluenesulfonic acid (75 ml, 0.1 *M*) for a period of 1 day. The reaction was then cooled to room temperature and a yellow solid collected at the pump. At this stage the crude product may contain some [$IrCl_3$phen]$_2$ (or [$IrBr_3$phen]$_2$). The product was therefore treated with sodium hydroxide (10 ml, 0.1 *M*) and filtered to remove any dimer. The filtrate gave the almost pure "fac" isomer upon acidification with *p*-toluenesulfonic acid. The yield of chloro complex was 0.54 g (60%). The corresponding "*fac*"-$IrBr_3H_2O$phen was prepared by a similar procedure. *Anal.* Calcd for $C_{12}H_{10}N_2Cl_3OIr$: C, 28.96; H, 2.02; N, 5.63; Cl, 21.4. Found: C, 29.24; H, 2.40; N, 5.56; Cl, 21.6. Calcd for $C_{12}H_{10}N_2Br_3OIr$: C, 22.84; H, 1.60; N, 4.44; Br, 37.9. Found: C, 22.81; H, 2.08; N, 4.46; Br, 37.6.

"*mer*"-Trichloro(or tribromo)aquo(1,10-phenanthroline)iridium(III), $IrCl_3$(or Br_3)$H_2O(C_{12}H_8N_2)$.—Hydroxonium tetrachloro(or tetrabromo)(1,10-phenanthroline)iridate(III) tetrahydrate (0.5 g) dissolved in water (25 ml) and contained in a stoppered round-bottomed Pyrex flask was exposed to strong sunlight for about 2.5 hr. In this time orange crystals had separated which were collected at the pump and washed with water. The yield of "*mer*"-$IrCl_3H_2O$phen was 0.32 g (80%). Somewhat better yields were obtained for "*mer*"-$IrBr_3H_2O$phen. *Anal.* Calcd for $C_{12}H_{10}N_2Cl_3OIr$: C, 28.96; H, 2.02; N, 5.63; Cl, 21.4. Found: C, 29.28; H, 2.34; N, 5.67; Cl, 21.6. Calcd for $C_{12}H_{10}N_2Br_3OIr$: C, 22.84; H, 1.60; N, 4.44; Br, 37.9. Found: C, 23.04; H, 1.82; N, 4.52; Br, 37.6.

"*mer*"-Trichloro-*N*,*N'*-dimethylformamide(1,10-phenanthroline)iridium(III), $IrCl_3C_3H_7NO(C_{12}H_8N_2)$. **Method A.**—Hydroxonium tetrachloro(1,10-phenanthroline)iridate(III) tetrahydrate (0.5 g) was dissolved in *N*,*N'*-dimethylformamide (30 ml) and the orange solution contained in a stoppered round-

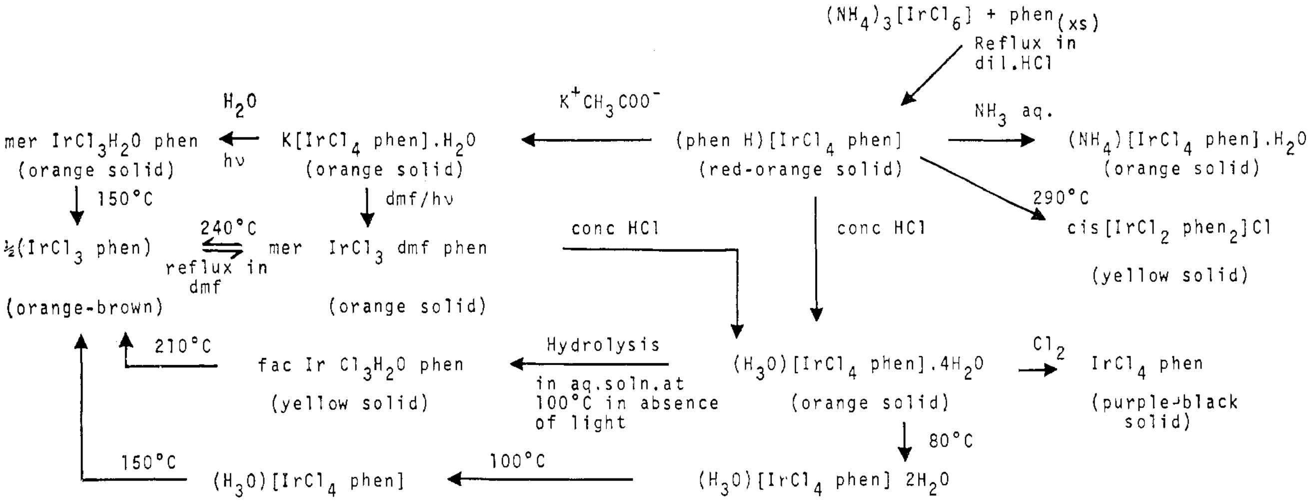

Figure 1.—Reactions of 1,10-phenanthrolinium tetrachloro(1,10-phenanthroline)iridate(III).

bottomed Pyrex flask was exposed to strong sunlight for 2 hr. Ether was then added to precipitate the orange crystalline complex which was washed in turn with water (four 10-ml portions) and then ethanol and ether. The yield was 0.37 g (82%). *Anal.* Calcd for $C_{15}H_{15}N_3Cl_3OIr$: C, 32.59; H, 2.74; N, 7.59; Cl, 19.3. Found: C, 32.42; H, 3.03; N, 7.56; Cl, 19.5.

Method B.—Di-μ-chloro-tetrachlorobis(1,10-phenanthroline)-diiridium(III) (0.3 g) was refluxed in *N,N'*-dimethylformamide (50 ml) for 6 hr. The solution was cooled and ether was added to precipitate the orange complex. The yield was 0.32 g (95%). Found: C, 32.67; H, 2.96; N, 7.63; Cl, 19.4.

***cis*-Dichlorobis(1,10-phenanthroline)iridium(III) Chloride Trihydrate, $[IrCl_2(C_{12}H_8N_2)_2]Cl \cdot 3H_2O$.**—Phenanthrolinium tetrachloro(1,10-phenanthroline)iridate(III) (0.5 g) in glycerol (20 g) was heated until it dissolved to give a deep red solution. The temperature was then raised to the boiling point (290°) and in about 1 min the solution became yellow. The reaction vessel was then immediately cooled to room temperature and water (50 ml) was added. The yellow solution was passed down a cellulose cation-exchange column (Whatman CM70) in the hydrogen form. The yellow product was thus separated from the glycerol solution which was washed through using several bed volumes of water. The yellow band was eluted with hydrochloric acid (100 ml, 0.1 *M*) and the solution was evaporated to a volume of 20 ml and cooled in ice. The yellow crystalline solid was filtered off at the pump and washed with cold dilute hydrochloric acid and then ice-cold water. The yield was 0.44 g (85%). *Anal.* Calcd for $C_{24}H_{22}N_4Cl_3O_3Ir$: C, 40.37; H, 3.10; N, 7.85; Cl, 14.9; Cl(ionic), 4.96. Found: C, 40.68; H, 3.15; N, 7.83; Cl, 15.2; Cl(ionic), 5.00.

***cis*-Dibromobis(1,10-phenanthroline)iridium(III) Perchlorate, $[IrBr_2(C_{12}H_8N_2)_2]ClO_4$.**—Phenanthrolinium tetrabromo(1,10-phenanthroline)iridate(III) (0.5 g) in glycerol was heated and stirred until it had dissolved. The deep red solution was then heated at the boiling point and the color changed rapidly to orange-yellow. The solution was immediately cooled and water (150 ml) was added. It was then passed through a cellulose pulp column to remove any solid. (The amount of this depends upon the reaction time which if prolonged gives a change from orange-yellow to brown.) The orange-yellow eluate was then exchanged onto a Whatman CM70 cellulose exchanger in the H^+ form and the column was washed with water to remove glycerol. The orange-yellow product was eluted from the column with 0.5 *M* acetic acid giving three fractions. The first fraction was obtained after the passage of 20 ml of acid. This was orange and readily eluted. It has not been characterized further. The second and third fractions were obtained with 20- and 160-ml volumes of acid, respectively, and were both yellow. Addition of either sodium perchlorate or sodium bromide to the third fraction gave *cis*-$[IrBr_2(phen)_2]ClO_4$ or *cis*-$[IrBr_2(phen)_2]Br \cdot 2H_2O$ in 70% yield. *Anal.* Calcd for $C_{24}H_{16}N_4Br_2ClO_4Ir$: C, 35.46; H, 2.98; N, 6.89; Br, 19.7. Found: C, 35.90; H, 2.13; N, 6.83; Br, 19.6. Calcd for $C_{24}H_{20}N_4Br_3O_2$: C, 34.75; H, 2.43; N, 6.75; Br, 28.9; Br(ionic), 9.6. Found: C, 34.71; H, 2.69; N, 6.71; Br, 29.0; Br(ionic), 9.5.

***cis*-Dichlorobis(1,10-phenanthroline)rhodium(III) Chloride Trihydrate, $[RhCl_2(C_{12}H_8N_2)_2]Cl \cdot 3H_2O$.**—Phenanthrolinium tetrachloro(1,10-phenanthroline)rhodate(III) (0.5 g) was dissolved by warming in ethylene glycol (20 g) to give a deep orange solution. The temperature was then raised to the boil (190°) and the solution quickly became pale yellow. This was cooled to room temperature and water (50 ml) was added. The yellow solution was passed through a Whatman CM70 hydrogen ion exchanger and the product was isolated as for the iridium(III) analog. The yield was 0.46 g (90%). *Anal.* Calcd for $C_{24}H_{22}N_4Cl_3O_3Rh$: C, 46.21; H, 3.56; N, 8.98; Cl, 17.1; Cl(ionic), 5.68. Found: C, 46.45; H, 3.68; N, 9.05; Cl, 17.3; Cl(ionic), 5.75.

***cis*-Dibromobis(1,10-phenanthroline)rhodium(III) Perchlorate, $[RhBr_2(C_{12}H_8N_2)_2]ClO_4$.**—Phenanthrolinium tetrabromo(1,10-phenanthroline)rhodate(III) was dissolved in warm ethylene glycol (20 g) to give a deep red solution. This was immediately raised to the boil whereupon the color changed to yellow. The solution was cooled to room temperature and water (50 ml) was added. The product was isolated in a manner analogous to that described for *cis*-$[IrBr_2phen_2]ClO_4$ except that fractionation of the column eluate was unnecessary. The yield was 0.4 g. *Anal.* Calcd for $C_{24}H_{16}N_4Br_2ClO_4Rh$: C, 35.46; H, 2.98; N, 6.89; Br, 19.7. Found: C, 35.90; H, 2.13; N, 6.83; Br, 19.6.

Resolution of Bis(1,10-phenanthroline)metal Complexes Using Cation-Exchange Cellulose.—About 30 g of Whatman CM70 carboxymethylcellulose ion exchanger was poured as a slurry into a column (3 × 60 cm) and converted to the hydrogen form by washing with acetic acid (0.05 *M*, 100 ml) followed by water (200 ml). An aqueous solution of the racemic complex (0.5 g in 25 ml) was poured onto the column and the bound complex was eluted with 0.4 *M* acetic acid. The eluate flow was 5 ml/min. Six successive fractions of 50 ml were collected as the complex moved off the column and the complex was precipitated from each by addition of sodium perchlorate. The precipitates were filtered off at the pump, washed with water, dried, and weighed. Each precipitate was then dissolved in dimethyl sulfoxde (5 ml) and the optical rotatory dispersion (ORD) of the fractions was measured. In all cases the first two fractions had positive rotations over the range recorded with the first having the bigger rotation. The third and fourth fractions had very little optical activity while the fifth and sixth showed negative rotations, with the sixth having the larger value. Repeating this procedure for the more active fractions led to increased rotations. Each complex was characterized by its X-ray diffractometer pattern and (in some instances) by analysis. The curves of Figure 5 concern the first and sixth fractions only.

Conductivity and Thermogravimetric Measurements.—All conductivities were measured at 25° in cells protected from the light using a Philips GM4249 direct-reading bridge. Thermograms were obtained on a Stanton automatic thermorecording balance.

Magnetic Susceptibilities.—Magnetic moments were measured by the Gouy method and the tube was calibrated using mercuric tetrathiocyanatocobaltate(II).[15,16]

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Spectral Measurements.—Infrared spectra in the region 500–200 cm^{-1} were recorded on a Grubb-Parsons DM$_4$ spectrophotometer calibrated against water vapor. All spectra were of Nujol mulls between polythene plates. Ultraviolet and visible spectra have been measured on a Cary 14 or Beckman DK-2A spectrophotometer using matched silica cells. Optical rotatory dispersion data were obtained with a JASCO UV-5 recording spectropolarimeter. Nmr spectra were obtained using a Perkin-Elmer R-10 instrument for solutions in dimethyl sulfoxide containing tetramethylsilane.

X-Ray Diffractometric Studies.—An automatic Philips PW 1049 diffractometer using Ni-filtered Cu Kα radiation was employed for the powder studies.

Results and Discussion

The various compounds derived from the reaction of ammonium hexachloroiridate(III) with 1,10-phenanthroline in dilute hydrochloric acid are conveniently summarized in Figure 1. phenH[IrCl$_4$phen] is the initial product from this reaction and there is no evidence for the formation of any *trans*-IrCl$_2$(phen)$_2^+$ species. Further, we find that the deep red crystals previously described[2] as [IrCl$_2$(phen)$_2$][IrCl$_4$phen], which separate from the mother liquor after the initial reaction, have an analysis and X-ray powder pattern identical with those of phenH[IrCl$_4$phen] and differ only in the size of the crystals from the first batch. The mono complex phenH[IrCl$_4$phen] is an excellent starting material for the synthesis of *cis*-[IrCl$_2$(phen)$_2$]Cl. This complex is obtained in high yield by the homogeneous reaction of the mono complex in glycerol as solvent. Previous workers[2] employed a melt of $(NH_4)_3IrCl_6$ and the base over a period of 14 hr, a reaction which gives a mixture of products.

Using analogous procedures and the hexahalogenorhodate(III) complexes the compounds phenH[RhCl$_4$phen] and phenH[RhBr$_4$phen] have been synthesized. These are readily converted in ethylene glycol as solvent to the corresponding *cis*-[RhX$_2$(phen)$_2$]X compounds (X = Cl, Br). Since the start of this work, the preparations of phenH[RhX$_4$phen] (X = Cl, Br, I) have been described[17] using conditions which may also give the bis complexes. In the present work use of acid conditions maintains a low concentration of 1,10-phenanthroline and at the same time a high concentration of the phenanthrolinium ion, both features which contribute to the clean synthesis of the mono complexes. The compounds described have been characterized by elemental analyses and a variety of physical measurements. All those formulated as 1:1 electrolytes gave molar conductivity values in dimethyl sulfoxide at 25° in the range 21–33 ohm^{-1} cm^2 mol^{-1} for 10^{-3} *M* solutions. These are to be compared with the value of 33 ohm^{-1} cm^2 mol^{-1} given by typical 1:1 electrolyte complexes such as *cis*-[CoCl$_2$(en)$_2$]Cl under the same conditions. In water the hydroxonium salts gave high molar conductances, *e.g.*, 306 ohm^{-1} cm^2 mol^{-1} for a 10^{-3} *M* solution of H$_3$O[IrCl$_4$phen]. Both these results are consistent with the formulations proposed.

TABLE I

INFRARED SPECTRA (CM^{-1}) FOR METAL–PHENANTHROLINE COMPLEXES IN THE 500–200-CM^{-1} REGION

	Assignments			
Compound	γ_{M-O}	γ_{M-X}	γ_{M-N}	γ_{phen}
mer-IrCl$_3$H$_2$Ophen[a]	401 m, b	345 vs	257 m, b	439 m
		323 vs	243 m, b	
		310 vs	227 m	
fac-IrCl$_3$H$_2$Ophen[b]	420 m	330 vs	270 m	440 m
		309 s	256 m	
		296 vs	232 m	
mer-IrBr$_3$H$_2$Ophen[a]	406 m, b	238 vs	253 s	439 w
		217 sb	246 m	
		209 sb		
[IrCl$_3$phen]$_2$		345 s	280 w	441 w
		333 vs	260 sh	
		321 s	252 m	
		298 s		
[IrBr$_3$phen]$_2$		234 s	250 s	437 w
			241 sh	
phenH[IrCl$_4$phen]		340 s	249 s	461 m
		313 vs	236 m	439 m
		303 vs	223 s	420 w
		290 vs	220 sh	400 m
phenH[RhCl$_4$phen][c]		343 s	284 m	461 m
		332 sh	249 m	439 m
		319 s	237 m	422 w
			223 m	402 m
phenH[IrBr$_4$phen]		225 s	260 w	463 m
		215 s	248 m	440 w
			236 m	420 w
				398 m
IrCl$_4$phen		364 s	234 w	437 m
		339 vs	227 w	
		330 sh		
		317 s		
mer-IrCl$_3$(DMF)phen	424 m	343 vs	253 vw	438 s
		325 vs	249 vw	
		306 vs	236 vw	
			228 vw	
cis-[IrCl$_2$(phen)$_2$]Cl		338 s	270 w[d]	438 w
		313 s	260 w[d]	
cis-[RhCl$_2$(phen)$_2$]Cl		352 vs	315[d]	457 w
		331 s	295[d]	439 m
			284[d]	410 w
			268[d]	
			259[d]	
cis-[CoCl$_2$(phen)$_2$]Cl		375 vs	315 w[d]	439 m
			303 m[d]	
			265 m[d]	
			252 s[d]	
			245 sh[d]	
cis-[CrCl$_2$(phen)$_2$]Cl·3H$_2$O		363 vs	293 w	453 m
		333 s	280 w	438 m
			244 m	
cis-[IrBr$_2$(phen)$_2$]Br·2H$_2$O		238 s	270 m	437 w
		226 w	330 w[d]	
cis-[RhBr$_2$(phen)$_2$]Br		239 s	296 s	439 m
			274 m	
			311 m	
			329 m[d]	

[a] Nujol mulls between polythene disks. Compounds were photochemical aquation products. [b] Obtained by subtracting the spectrum of the mer isomer. [c] Peak at 296 cm^{-1} unassigned. [d] Not assigned.

Complexes of the general formula phenH[MX$_4$phen] (M = Ir(III) or Rh(III); X = Cl or Br) belong to the point group C_{2v} and should therefore have four infrared-active metal–halogen stretching frequencies. For phenH[IrCl$_4$phen] bands at 340, 313, 303, and 290 cm^{-1} (Table I) are assigned to iridium–chlorine stretching following comparisons with the corresponding bromo complexes. The overlap of metal–bromine and metal–nitrogen frequencies makes the various metal–ligand assignments for phenH[MBr$_4$phen] complexes less satisfactory. However, the fact that these complexes are isostructural (Table II) together with the analytical and conductivity data supports the formulas given. Kulasingham and coworkers[17] have previously reported only one metal–chlorine assignment for the rhodium(III) mono complex.

When phenH[IrCl$_4$phen] is heated in the solid state,

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[17] G. C. Kulasingham, W. R. McWhinnie, and J. D. Miller, *J. Chem. Soc. A*, 521 (1969).

TABLE II

BRAGG ANGLE VALUES (IN DEGREES AND MINUTES) AND INTENSITIES[a] FOR VARIOUS METAL–PHENANTHROLINE COMPLEXES USING Cu Kα RADIATION

phenH[IrCl$_4$phen]	phenH[IrBr$_4$phen]	phenH[RhCl$_4$phen]	*mer*-IrCl$_3$H$_2$Ophen	*mer*-IrBr$_3$H$_2$Ophen	[IrCl$_3$phen]$_2$	[IrBr$_3$phen]$_2$
7–24 w	7–15 w	7–18 w	8–48 w	8–27 s	10–27 vs	10–30 vs
8–24 w	8–9 ms	8–24 w	9–24 w	9–6 w	12–48 s	12–45 vs
8–57 m	8–48 s	8–54 m	10–12 w	9–54 vw	13–45 s	13–33 s
10–18 w	10–6 w	10–15 w	12 s	11–45 m	14–00 vs	14–19 vs
11–4 w	11–30 m	11–48 w	13–24 s	13–6 vs	17–57 m	17–37 m
12–30 s	12–21 s	12–23 s	14–51 s	14–24 m	18–12 m	18–9 m
13–6 s	12–45 s	13–6 s	16–3 ms	15–6 m	19–15 w	. . .
13–33 vs	13–12 vs	13–30 vs	16–42 s	15–36 m	19–54 m	19–24 m
14–6 s	13–45 s	14–3 s	18–12 m	16–54 m	21–12 m	20–51 m
14–12 s	14–00 s	14–9 s	18–48 m	17–42 m	22–12 w	21–48 w
15–51 m	15–24 m	15–45 m	19–42 vs	18–15 m	23–18 m	22–54 m
16–54 m	16–27 m	16–54 w	20–51 m	19–18 s	. . .	. . .
17–57 w	. . .	17–57 w	21–6 m	20–36 m	. . .	. . .
18–30 w	18–27 w	18–30 m	21–45 w	21–30 w	. . .	. . .
19–21 w	19–15 w	19–21 w	23–39 m	22–54 w	. . .	. . .
20–51 m	20–15 m	20–54 m	26–12 m	25–21 m	. . .	. . .
			26–54 m	26–21 m		

cis-[RhCl$_2$(phen)$_2$]ClO$_4$	*cis*-[IrCl$_2$(phen)$_2$]ClO$_4$	*cis*-[CrCl$_2$(phen)$_2$]ClO$_4$	*cis*-[IrBr$_2$(phen)$_2$]ClO$_4$
8–6 s	8–6 m	8–6 s	8–00 s
8–24 m	8–20 s	8–27 w	8–12 m
9–54 w	9–57 w	9–54 w	9–54 w
10–24 w	10–30 w	10–24 w	10–18 s
11–33 w	11–54 w	11–42 w	11–48 w
13–00 vs	12–57 vs	12–54 vs	12–51 vs
14–39 m	14–45 m	14–30 m	14–36 s
15–48 sh	15–42 w	15–48 w	15–42 w
16–15 m	16–00 m	16–27 m	16–24 m
19–24 m	19–24 m	19–18 m	19–18 m

[a] Abbreviations: s, strong; m, medium; w, weak.

loss of hydrogen chloride is evident. The reaction, which commences at about 250°, does not yield a single pure product but *cis*-[IrCl$_2$(phen)$_2$]Cl can be identified in the residue from its ion-exchange behavior and spectrum. On the other hand thermogravimetric studies using NH$_4$[IrCl$_4$phen]H$_2$O show loss of water at 80° and further heating of this complex to 450° results in decomposition. Unlike the phenanthrolinium compound there is no clearly identified step corresponding to loss of hydrogen chloride and coordination of the ammonia ligand. The formulation H$_3$O[IrCl$_4$phen]·4H$_2$O is preferred for the hydroxonium salt as three distinct stages can be observed in its thermogravimetric analysis (Figure 2) with weight losses corresponding to the reactions

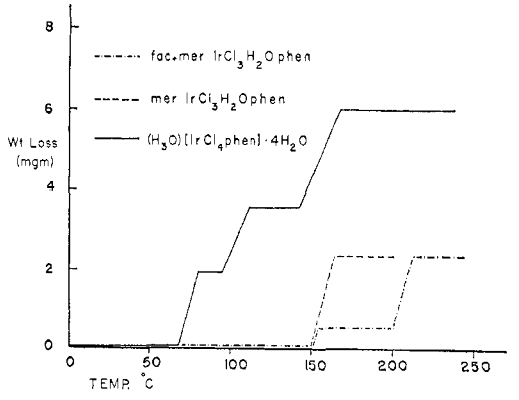

Figure 2.—Thermogravimetric analysis of mono(1,10-phenanthroline)iridium(III) complexes. Initial sample weights were as follows: *fac*- + *mer*-IrCl$_3$H$_2$Ophen, 66.4 mg; *mer*-IrCl$_3$H$_2$Ophen, 65.9 mg; H$_3$O[IrCl$_4$phen]·4H$_2$O, 30.2 mg.

$$H_3O[IrCl_4phen]\cdot 4H_2O = H_3O[IrCl_4phen]\cdot 2H_2O + 2H_2O \quad (1)$$

$$H_3O[IrCl_4phen]\cdot 2H_2O = H_3O[IrCl_4phen] + 2H_2O \quad (2)$$

$$H_3O[IrCl_4phen] = [IrCl_3phen]_2 + H_2O + HCl \quad (3)$$

In reaction 3 loss of hydrogen chloride to yield the aquo complex IrCl$_3$H$_2$Ophen which then undergoes loss of water might perhaps be expected. However, despite variations in the rate of heating efforts to observe this as a separate reaction were unsuccessful. From the shapes of the thermograms it is likely that both reactions occur together. If the aquo complex is produced and it is "*mer*"-IrCl$_3$H$_2$Ophen, then an immediate water loss (at 150°) is to be expected. Figure 2 shows that the corresponding "fac" isomer does not lose water until 210° which suggests that this isomer is not formed. The truth of the fac and mer labels used for these compounds rests for the present on differences in solubility and color. For IrCl$_3$H$_2$Ophen the "fac" isomer is the more soluble and is yellow in contrast to the orange "mer" isomer. For the bromo analog the "fac" isomer is orange and the "mer" orange-brown. We regard these as tentative designations and for this reason use quotes.

Pure "*mer*"-IrCl$_3$H$_2$Ophen has been obtained by the photochemical aquation of IrCl$_4$phen$^-$. The thermal aquation yields mainly the "fac" isomer which is contaminated with the "mer" form. This is seen by comparison of their infrared spectra (Figure 3). The formula IrCl$_3$H$_2$Ophen is supported by analysis and the presence of a frequency in the infrared spectrum attributed to metal–oxygen stretching (Table I). Either isomer loses water when heated beyond 150° and this is accompanied by disappearance of the metal–oxygen peak. Similar behavior was found for the IrBr$_3$H$_2$Ophen isomers.

Magnetic moment measurements serve to confirm an oxidation state of III for the majority of complexes studied (see Table III). The small degree of paramag-

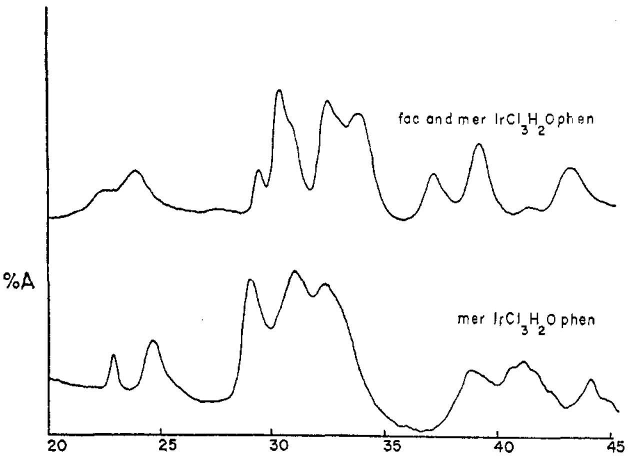

Figure 3.—Far-infrared spectra of the isomers of IrCl$_3$H$_2$Ophen.

TABLE III

MAGNETIC DATA FOR IRIDIUM AND RHODIUM 1,10-PHENANTHROLINE COMPLEXES

Compd	μ, BM	Temp, °K
(phenH)[IrCl$_4$phen]	0.60	295
Ag[IrCl$_4$phen]	0.55	296
(phenH)[RhCl$_4$phen]	0.45	300
(phenH)[IrBr$_4$phen]	0.69	295
cis-[IrCl$_2$(phen)$_2$]Cl·3H$_2$O	0.38	301
cis-[IrBr$_2$(phen)$_2$]Br·2H$_2$O	0.39	302
cis-[RhCl$_2$(phen)$_2$]NO$_3$	0.51	300
mer-[IrCl$_3$H$_2$Ophen]	0.47	297
[IrCl$_3$phen]$_2$	0.43	296
IrCl$_4$phen	2.06	298

netism generally observed is certainly not unusual for iridium(III) complexes.[16]

The orange hydroxonium tetrachloro(1,10-phenanthroline)iridate(III) could be oxidized with chlorine in a cooled aqueous solution to the deep violet, insoluble, paramagnetic tetrachloro(1,10-phenanthroline)iridate(IV) species. This complex is a powerful oxidizing agent and is readily reduced by water to the orange Ir(III) complex. It may be stored in a desiccator without appreciable decomposition. Its magnetic moment of 2.06 BM is somewhat larger than those found for other Ir(IV) complexes but nevertheless agrees with the presence of a low-spin d^5 configuration. It dissolves in nitrobenzene and has the conductance of a nonelectrolyte in this solvent. It is soluble in dry *N,N'*-dimethylformamide and in dry dimethyl sulfoxide but reacts rapidly with either solvent being reduced to the orange IrCl$_4$phen$^-$ anion. The other products of these oxidations have not yet been investigated. The Ir(IV) complex could also be obtained using concentrated nitric acid as oxidant. The product is soluble in this acid and the spectrum of the nitric acid solutions agrees with that of nitrobenzene solutions of IrCl$_4$phen prepared by chlorine oxidation (see Table IV). However the deep violet color is sensitive to the presence of the nitric acid reduction products and fades with time. For example, addition of trace amounts of sodium nitrite gives rapid decoloration of the nitric acid solutions while subsequent addition of sulfamic acid, a reagent for nitrite, completely restores the IrCl$_4$phen spectrum.

Comparison of the infrared spectra of phenH[IrCl$_4$phen] and IrCl$_4$phen given in Table I shows that oxidation of the metal has shifted the metal–chlorine stretching frequencies uniformly by 26 ± 2 cm^{-1} to higher values. An explanation may be offered in terms of decreased metal–ligand back-bonding consequent on oxidation. A similar effect has been noted for K$_3$[IrCl$_6$] and K$_2$[IrCl$_6$] for which the iridium–chlorine frequencies are 296 and 333 cm^{-1}, respectively.[18] It is not clear whether a similar shift has occurred for the iridium–nitrogen bands as only two are found in the spectrum of the oxidized complex. Since ligand π orbitals of different energies are certainly involved, then different degrees of back-bonding would be expected for the two types of donor atom with the two metal oxidation states.

TABLE IV

ULTRAVIOLET AND VISIBLE SPECTRAL DATA IN VARIOUS SOLVENTS

Compd	λ_{max}, mμ
IrCl$_4$phen	605 sh (1660),^{a,b} 509 (4670),^{a} 509 (4590)^e
(phenH)[IrCl$_4$phen]	549 sh (802)^c
H$_3$O[IrCl$_4$phen]	267 (24,200)^d
K[IrBr$_4$phen]·H$_2$O	267 (27,130)^d
fac-[IrCl$_3$H$_2$Ophen]	512 sh (660),^{c} 412 (2880),^{c} 362 (3676)^c
mer-[IrCl$_3$H$_2$Ophen]	512 sh (767),^{c} 383 sh (3505),^{c} 359 (3736)^c
mer-[IrCl$_3$(DMF)phen]	507 sh (708),^{c} 410 (3033),^{c} 362 (3959)^c
cis-[IrCl$_2$(phen)$_2$]Cl·3H$_2$O	228 (48,706),^{d} 275 (53,680)^d
cis-[IrBr$_2$(phen)$_2$]Br·2H$_2$O	276 (49,300)^d
cis-[RhCl$_2$(phen)$_2$]Cl	272 (57,340),^{d} 335 (3058),^{d} 350 (2867)^d

[a] Solvent concentrated HNO$_3$. [b] Extinction coefficients (M^{-1} cm^{-1}) in parentheses. [c] In dimethylformamide. [d] In H$_2$O. [e] In nitrobenzene.

It is interesting that the photochemical aquation of IrCl$_4$phen$^-$ yields only the "mer" isomer. Also the photolysis rules of Adamson[19] do not apply. The ultraviolet spectrum of H$_3$O[IrCl$_4$phen] in aqueous solution consists of a single intense charge-transfer band (Table IV) and therefore does not permit separate evaluation of the photoactivity in terms of d–d or charge-transfer processes.

Thermogravimetric studies of the reaction in which water is lost from either "*fac*"- or "*mer*"-IrCl$_3$H$_2$Ophen are shown in Figure 2. Loss of coordinated water is evident at 150°. The thermal aquation product displays two weight loss stages, the first at 150° and the second at 210°. This observation, together with the far-infrared spectra (Figure 3), confirms the belief that a mixture of "fac" and "mer" isomers is present. From this we estimate that in thermal aquation the "fac" isomer predominates in the approximate ratio of 70% "fac":30% "mer."

Both "*fac*"- and "*mer*"-IrCl$_3$H$_2$Ophen belong to the point group C_s and should each have three metal–chlorine stretching vibrations (2 A' + A''). Two metal–nitrogen (2 A') and one metal–oxygen stretching vibration are also predicted. The infrared spectra are given in Table I. Assignments of the iridium–chlorine stretching frequencies were confirmed by comparison with "*mer*"-IrBr$_3$H$_2$Ophen. With one exception there is also agreement between the predicted number of bands and those observed. The additional band in the iridium–nitrogen stretching region may be a result of crystal symmetry effects.

(18) J. G. Gibson and E. D. McKenzie, *J. Chem., Soc., A*, 2637 (1969).

(19) A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).

The product obtained after heating $IrCl_3H_2Ophen$ in the solid state is found to be the same no matter which isomeric form is used. This was shown by the identical X-ray powder patterns, analyses, and infrared spectra. It is formulated as a dimer $[IrCl_3phen]_2$ rather than a monomeric five-coordinated complex. Unfortunately its insolubility and lack of volatility precluded molecular weight measurements while suggesting the presence of a polymer. The infrared spectrum showed four bands attributed to iridium–chlorine stretching (Table I). If the complex is monomeric and square-pyramidal or trigonal-bipyramidal geometry applies, then the C_s symmetry predicts only three iridium–chlorine modes. Thus a dimer formulation is favored. Further information on likely structures for $[IrCl_3phen]_2$ comes both from infrared measurements and from the reaction with dimethylformamide. Direct loss of a water ligand from either "*fac*"- or "*mer*"-$IrCl_3H_2Ophen$ will lead first to a five-coordinate stage. If we examine in theory how this could combine with itself to give dimers, we find that there are four possible structures. These are shown in Figure 4 together with the appropriate symmetry point group. All four structures may arise from the "mer" isomer while the "fac" isomer can give only II and III. These conclusions make the assumption (reasonable for iridium(III)) that there is no rearrangement accompanying loss of water. Table V summarizes the expected total of iridium–chlorine stretching vibrations for both terminal and bridged ligands. As only four bands are observed structures III and IV are eliminated. It is noteworthy that the dimer reacts with *N,N'*-dimethylformamide to give a high yield of "*mer*"-$IrCl_3(DMF)phen$. Assignment of the "mer" geometry to the last-mentioned complex is based on the close similarity of its infrared spectrum in the iridium–chlorine stretching region with that of "*mer*"-$IrCl_3H_2Ophen$. Both structures I and II (Figure 4) could give "*mer*"-$IrCl_3(DMF)phen$, but I would give only this whereas II would give "fac" and "mer" products with equal probability. Since isomerization at the reaction temperatures used cannot be eliminated, final choice between structures I and II requires a crystal structure determination.

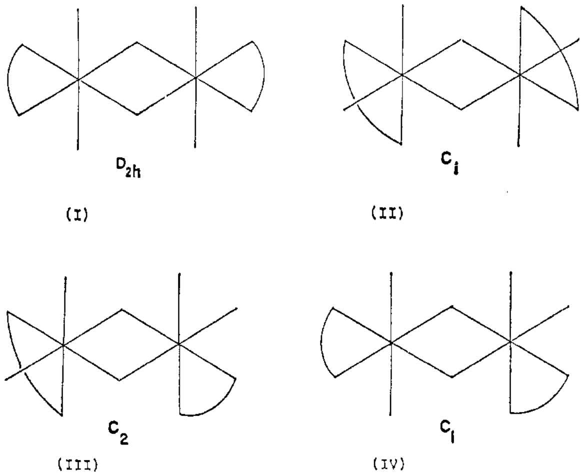

Figure 4.—Possible structures for $[IrCl_3phen]_2$.

TABLE V

IRIDIUM–CHLORINE STRETCHING MODES FOR COMPLEXES OF THE TYPE $[IrCl_3phen]_2$

Structure	Symmetry point group	γIr–Cl terminal	γIr–Cl bridged	Total
I	D_{2h}	$B_{1u} + B_{2u}$	$B_{2u} + B_{3u}$	4
II	C_i	$2A_u$	$2A_u$	4
III	C_2	$2A + 2B$	$2A + 2B$	8
IV	C_1	$4A$	$4A$	8

Although trans effects have been observed in the infrared spectra or iridium(III)–halogeno complexes containing tertiary arsines or phosphines,[20] there is little support for similar effects here. The Ir–Cl stretching frequency is reported at 335 cm^{-1} in *trans*-$IrCl_2(py)_4^+$ (py = pyridine) and at 333, 327 cm^{-1} in *cis*-$IrCl_2(py)_4^+$.[21] Table I shows that frequencies close to these are observed for *cis*-$IrCl_2(phen)_2^+$ and $phenH[IrCl_4phen]$.

During the course of this work studies on the preparation and characterization of *cis*-$IrCl_2(phen)_2^+$ and *cis*-$RhCl_2(phen)_2^+$ were published.[22] However the methods given here constitute greatly improved syntheses of these complexes. There has also been much discussion in the recent literature centered around the isomers of bis(1,10-phenanthroline)metal complexes including the demonstration that the Ir, Rh, and Co complexes are isomorphous.[17,18,22,23] Table II shows

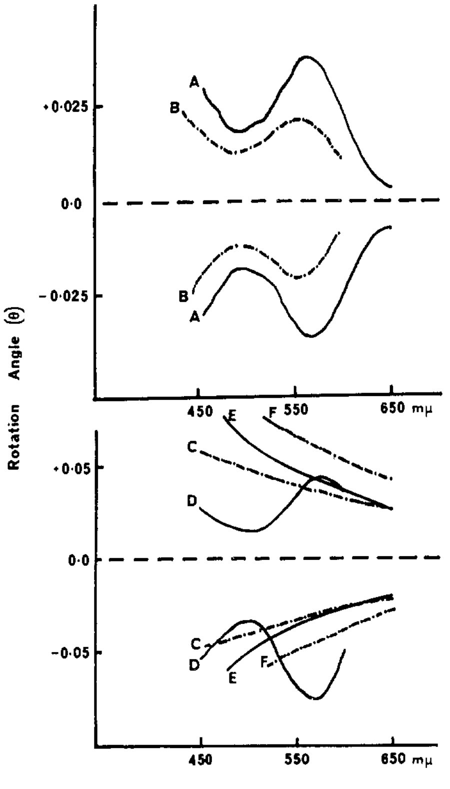

Figure 5.—ORD curves for various metal complex perchlorates Per cent concentrations (w/v) in dimethyl sulfoxide are given in parentheses for solutions corresponding to (+) and (−) rotations: curve A, $CrCl_2(bipy)_2^+$ (~1.5+, ~1.5−); curve B, $CrCl_2(phen)_2^+$ (1.06+, 1.70−); curve C, $RhCl_2(phen)_2^+$ (5.56+, 4.52−); curve D, $CoCl_2(phen)_2^+$ (~2+, ~2−); curve E, $IrCl_2(phen)_2^+$ (1.83+, 1.22−); curve F, $IrBr_2(phen)_2^+$ (2.3+, 2.3−).

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[20] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 6789 (1965).
[21] M. Delepine and F. Lareze, *C. R. Acad. Sci.*, **257**, 772 (1963).
[22] R. D. Gillard and B. T. Heaton, *J. Chem. Soc. A*, 451 (1969).
[23] J. D. Miller and R. H. Prince, *ibid.*, *A*, 519 (1969).

that the compounds labeled *cis*-[$MCl_2(phen)_2$]ClO_4 where M = Ir, Rh, or Cr and *cis*-[$IrBr_2(phen)_2$]ClO_4 are isomorphous thus confirming and extending the previous work[20] to include the chromium(III) complex. These perchlorate salts have an advantage compared to the halide salts used previously in that water of crystallization is absent.

The *cis*-dihalogenobis(1,10-phenanthroline)metal complexes have C_2 symmetry and therefore two infrared-active modes are expected. Table I shows that two frequencies are observed for iridium(III), chromium(III), and rhodium(III). Only one broad band could be assigned to the cobalt(III) complex but in this case the crystal structural work has verified the cis configuration. Also the metal–halogen assignments have been made by a comparison of the spectra for the dichloro and dibromo complexes. The spectral shift produced after the replacement of Cl^- ligands by Br^- moved the metal–bromine frequencies into the same region as other metal–phenanthroline vibrations. Therefore the metal–bromine modes have not been assigned. Definitive evidence that the dihalobis(1,10-phenanthroline)iridium(III) halides are the cis isomers is provided by the resolution of the optical forms. Though the rotations are small, it is clear from the ORD curves (Figure 5) that both optical forms have been separated. The resolution of $CoCl_2(phen)_2^+$, $RhCl_2(phen)_2^+$, $CrCl_2(phen)_2^+$, and $CrCl_2(bipy)_2^+$ as well as $IrCl_2(phen)_2^+$ by the cellulose ion-exchange technique is further evidence of the cis configuration for all of these complexes.

It has recently been argued[20] that an optical resolution is not proof of a cis configuration for complexes of the type $MX_2(phen)_2^+$. This arises because water might add across the C=N bond in 1,10-phenanthroline to give new asymmetric centers at the N and the C as shown in Figure 6. The ^1H nmr spectrum of the complex with formula B should give an aliphatic-type peak upfield at about τ 4. However, there was no evidence for such a peak in the spectrum of this ligand in dilute sulfuric acid, which corresponded to the presence of eight aromatic protons.[23] Similarly other nmr studies with 1,10-phenanthrolinemetal complexes have disclosed only aromatic protons.[17,24] In this work the ^1H nmr spectra of *cis*-[$IrBr_2(phen)_2$]$Br \cdot 2H_2O$, (−)-*cis*-[$IrBr_2(phen)_2$]ClO_4, and *cis*-[$RhCl_2(phen)_2$]ClO_4 have been measured in dimethyl sulfoxide relative to tetramethylsilane. The compounds are not sufficiently soluble in water. The results are given in Figure 7. The presence of only aromatic protons is again evident.

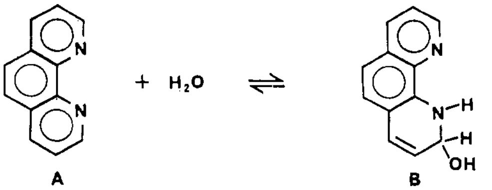

Figure 6.—Suggested water addition across C=N bond.

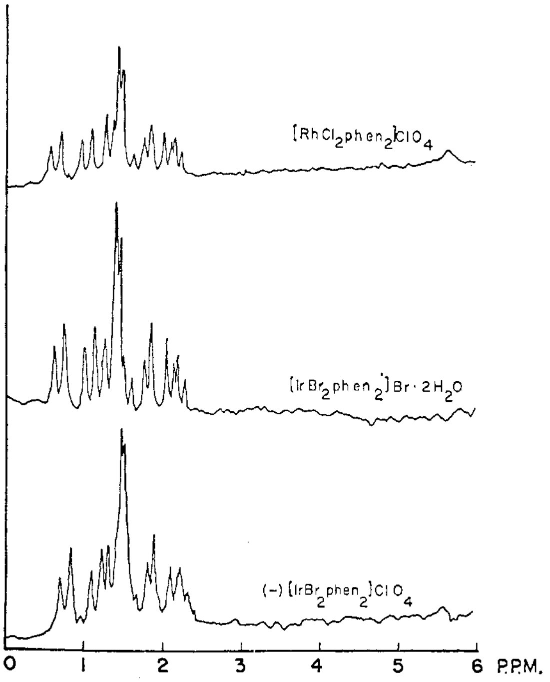

Figure 7.—Nmr spectra of bis(1,10-phenanthroline)metal complexes.

In contrast to the ease of oxidation of $IrCl_4phen^-$ no bis(1,10-phenanthroline)iridium(IV) compounds are obtainable, even with chlorine, nitric acid, or aqua regia as oxidants. Also *cis*-$IrCl_2(phen)_2^+$ is very inert so that attempts to acid-hydrolyze the complex at 100° for 1 week failed. However, by exposure to strong sunlight the loss of a chloro ligand is 95% complete in 6 hr. This suggests the possibility of an asymmetric synthesis since circularly polarized light is absorbed to different extents by optical antipodes and both are present in racemic *cis*-$IrCl_2(phen)_2^+$. Although photoaquation using a circularly polarized xenon light source could be taken to 90% completion, there was no optical activity produced. The dibromo complex behaved similarly. Finally we mention that all our attempts to prepare *trans*-dihalobis(1,10-phenanthroline)iridium(III) compounds have been unsuccessful. These have included catalytic methods involving the use of either hydrazine, zinc amalgam, or hypophosphorous acid.

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(24) J. D. Miller and R. H. Prince, *J. Chem. Soc.*, 4706 (1965).