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The Synthesis and Characterization of Several Diacidobis(ethylenediamine)iridium(III) Salts

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The syntheses and characterizations of *cis*- and *trans*-$Ir(en)_2X_2^+$ (X = Cl, Br, I) (en = ethylenediamine) as well as *trans*-$Ir(en)_2XY^{n+}$ (X = Cl, Y = Br, I, H_2O, OH, NCS, NO_2, ONO; X = Y = NO_2, N_3) are described. *trans*-$Ir(en)_2Cl_2^+$ was prepared by a catalytic method using H_3PO_2, and the *cis* isomer was prepared by a method utilizing high ionic strength. The mixed complexes were prepared by a new photochemical method. Proof of structure is based on ir spectra and unequivocable geometric assignments were made by resolution of the *cis* isomer. The base hydrolyses of both *cis*- and *trans*-$Ir(en)_2Cl_2^+$ go with retention of geometry.

Introduction

Although cobalt(III) complexes of the type $Co(en)_2XY^+$ have long been known and extensively studied to elucidate the mechanisms of reactions in these systems,[1] only relatively recently were several of the analogous Rh(III) complexes prepared[2] and the rates of many of these have since been investigated.[3]

Both rhodium(III) and iridium(III) undergo substitution reactions with amines with difficulty. Owing to the basicity of most amines, the metal ions usually precipitate from aqueous reaction mixtures as hydrated hydroxides. When acidified, the amines react very slowly. Johnson[2] partially relieved this problem by carefully controlling the pH of the reaction solution. This method was particularly important in the synthesis of $Rh(en)_2Cl_2^+$ but the corresponding synthesis of $Ir(en)_2Cl_2^+$ was unsuccessful.[4]

The only iridium complex of this type which had been reported[5] at the start of this work was *cis*-$Ir(en)_2(NO_2)_2^+$. Since then Kida[6] reported the synthesis of *cis*- and *trans*-$Ir(en)_2Cl_2^+$. We have repeated his syntheses and have developed new synthetic methods to prepare these and other compounds of iridium(III).

It has been reported[7] that $Rh(py)_4Cl_2^+$ lends itself readily to substitution by ethylenediamine and ammonia to yield $Rh(en)_2Cl_2^+$ and $Rh(NH_3)_4Cl_2^+$, respectively. Earlier reports indicate that this synthesis fails and produces $[Rh(en)(py)_2Cl_2]Cl \cdot 3H_2O$ and $[Rh(en)_2(py)Cl]Cl_2$.[8] This method of preparation was attempted with ethylenediamine and the analogous iridium(III) complex, but the only products obtained were *cis*- and *trans*-$(enH_2)[Ir(py)_2Cl_4]_2$.

A number of investigations in rhodium chemistry show[9] that ethyl alcohol, hypophosphorous acid, hydrazine, and borohydride have a catalytic effect on substitution reactions. The nature of catalysis is uncertain, as although the catalysts are all reducing agents, they are potential donors of hydride ions as well. A method of preparation of *trans*-$Ir(en)_2Cl_2^+$ was developed utilizing hypophosphorous acid as a catalyst.[10] The mixed chloroacid complexes of the type *trans*-$Ir(en)_2ClX^+$ were prepared by a new photochemical method starting with *trans*-$Ir(en)_2Cl_2^+$.[11]

Experimental Section

K_2IrCl_6.—This compound was used as the starting material for other syntheses and was prepared in a method similar to that described by Gire.[12] Iridium metal was originally obtained from Engelhard Industries, Inc., and was recovered from residues produced during this investigation.

***trans*-$[Ir(en)_2Cl_2]ClO_4$.**—Twenty grams of K_2IrCl_6 was placed in 100 ml of hot (80°) water and reduced by slowly adding 3.82 g of $K_2C_2O_4 \cdot H_2O$. After effervescence had subsided, the solution was boiled to remove the remaining CO_2 and 20 g of ethylenediamine dihydrochloride was added. A green-brown precipitate was produced by the addition of 0.1 g of KH_2PO_2, and 20 ml of concentrated HCl was added to complete precipitation. The solution was cooled to room temperature and filtered, and the green-brown precipitate was washed with 20 ml of cold water. The precipitate was transferred to 100 ml of water and dissolved by the addition of 8 ml of neat ethylenediamine. The solution was boiled for 5 min and an additional 8 ml of neat ethylenediamine was added. After boiling for 1 hr and concentrating to 50 ml the solution was neutralized with concentrated HCl, boiled for 10 min, cooled, and treated with 10 ml of 70% $HClO_4$. The immediate precipitate was collected on a filter and recrystallized from 70 ml of hot water by adding 10 ml of 70% $HClO_4$ and allowing it to stand overnight. The yellow crystals were collected on a filter, washed with 10-ml portions of cold water, ethanol, and ether, and air dried; yield, 4.3 g (47%). Analyses of this and other complexes are listed in Table I.

***cis*-$[Ir(en)_2Cl_2]Cl$.**—Potassium hexachloroiridate(IV) (20.0 g) was stoichiometrically reduced to $IrCl_6^{3-}$ in 100 ml of hot (80°) water by the slow addition of 3.82 g of $K_2C_2O_4 \cdot H_2O$. After the vigorous evolution of CO_2 had subsided, the solution was boiled

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TABLE I
ELEMENTAL ANALYSES

Compound	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
trans-$[Ir(en)_2Cl_2]ClO_4$	9.95	9.71	3.34	3.23	11.61	11.42
trans-$[Ir(en)_2Br_2]ClO_4$	8.40	8.42	2.82	2.85	9.80	9.82
trans-$[Ir(en)_2I_2]I$	6.93	7.10	2.33	2.26	8.09	8.25
trans-$[Ir(en)_2(NO_2)_2]ClO_4$	9.54	9.64	3.20	2.95	16.7	17.93
trans-$[Ir(en)_2(N_3)_2]PF_6$	8.87	8.83	2.98	3.11	25.87	25.32
trans-$[Ir(en)_2BrCl]ClO_4$	9.11	9.12	3.06	3.02	10.63	10.70
trans-$[Ir(en)_2ICl]ClO_4$	8.36	8.54	2.81	2.89	9.76	9.94
trans-$[Ir(en)_2(NO_2)Cl]ClO_4$	9.74	9.75	3.27	3.32	14.20	14.18
trans-$[Ir(en)_2(NCS)Cl]ClO_4$	11.84	10.64	3.19	2.49	13.86	13.88
trans-$[Ir(en)_2(H_2O)Cl](ClO_4)_2$	8.51	8.66	3.21	3.24	9.92	9.99
$(enH_2Cl)[Ir(en)Cl_4]\cdot H_2O$	9.43	9.43	3.96	4.12	11.00	10.65
cis-$[Ir(en)_2Cl_2]ClO_4$	9.95	9.95	3.34	3.45	11.61	11.35
cis-$[Ir(en)_2Br_2]Br\cdot H_2O$	8.43	8.47	3.18	2.99	9.83	9.88
cis-$[Ir(en)_2I_2]Cl\cdot H_2O$	7.75	7.73	2.93	2.88	9.04	9.08

for 2 min to complete the reduction and remove CO_2. A solution of 8 ml of 90% aqueous ethylenediamine in 100 ml of H_2O was neutralized and buffered at pH 7 with glacial acetic acid. The two solutions were combined and heated to boiling. Solid NaCl and water were added until the boiling solution was saturated in NaCl and had a total volume of 600 ml. The solution was refluxed for 4 hr. The volume of the solution was reduced to 50 ml in several operations of successively boiling, quickly cooling to room temperature, and removing the precipitated NaCl. Upon standing at room temperature for 2 hr, large, light yellow crystals of *cis*-$[Ir(en)_2Cl_2]Cl$ were collected on a filter, washed with 5 ml of cold water, redissolved in 20 ml of hot (80°) water, and recrystallized by adding 10 ml of concentrated HCl and allowing it to stand at room temperature overnight. The crystals were collected on a filter, washed with 5-ml portions of cold H_2O, ethanol, and ether, and allowed to air dry; yield, 2.3 g.

Upon standing 24 hr at room temperature 2.5 g of orange *cis*-$[Ir(en)_2Cl_2][Ir(en)Cl_4]$ precipitated from the reaction solution. The orange crystals were dissolved in 50 ml of hot water and passed through an anion-exchange column, Cl^- form. The resulting solution (eluate) was evaporated to 10 ml. Upon the addition of 10 ml of concentrated HCl, *cis*-$[Ir(en)_2Cl_2]Cl$ precipitated, was collected on a filter after 3 hr, and washed and dried as before; yield, 1.0 g.

$(enH_2Cl)[Ir(en)Cl_4]\cdot H_2O$.—Further evaporation of the reaction solution in the preparation above (and removal of the NaCl) to 5 ml yielded 1.0 g of the sodium or potassium salt of $Ir(en)Cl_4^-$. This salt was dissolved in 10 ml of H_2O and 1.0 g of ethylenediamine dihydrochloride was added when an immediate red powder precipitated. This powder was collected and redissolved in 20 ml of H_2O and the addition of 2 ml of concentrated HCl caused immediate recrystallization. The red microcrystalline material was collected on a filter, washed with 5 ml of 1 *N* HCl, 5 ml of ethanol, and 10 ml of ether, and air dried.

trans-**$[Ir(en)_2I_2]I$.**—To a solution of 0.250 g of *trans*-$[Ir(en)_2Cl_2]ClO_4$ (0.55 mmol) in 30 ml of H_2O was added 0.750 g of NaI (5.5 mmol). The solution was refluxed for 65 hr. The volume of the solution was reduced to 20 ml on a steam bath at which point red-orange needles began to precipitate. The solution was cooled for 2 hr at 10° and the well-formed crystals were collected on a filter, washed with separate 5-ml portions of cold water, ethanol, and ether, and air dried; yield after recrystallization from water, 0.260 g (70%).

trans-**$[Ir(en)_2I_2]ClO_4$.**—The same preparatory solution was prepared as described above and was then heated in a glass polymer pressure bottle for 2 hr at 140°. The complex was precipitated in 80% yield by adding 10 ml of 70% $HClO_4$ while the reaction solution was still warm and then allowing it to cool to room temperature.

trans-**$[Ir(en)_2Br_2]ClO_4$.**—The experiment immediately above was duplicated using 5.5 mmol of NaBr instead of NaI. The solution was heated in a glass polymer pressure bottle for 2 hr at 140°. The yellow-orange crystals separated from the solution at room temperature after the addition of 10 ml of 70% $HClO_4$ were collected on a filter, washed with 5-ml portions of cold water, ethanol, and ether, and allowed to air dry; yield, 80%.

trans-**$[Ir(en)_2(N_3)_2]PF_6$.**—*trans*-$[Ir(en)_2Cl_2]ClO_4$ (0.35 g) and NaN_3 (0.5 g) were dissolved in 30 ml of H_2O in a sealed polymer pressure bottle and heated at 140° for 6 hr. The resulting solution was evaporated to 5 ml on a steam bath and cooled at 5° for 2 hr. The resulting yellow crystals were collected on a filter, redissolved in a minimum amount of water (10 ml), and precipitated by the addition of 0.7 g of NH_4PF_6. The fluffy yellow needles were recrystallized from 5 ml of hot (90°) water, washed with 5 ml of H_2O, 10 ml of ethanol, and 10 ml of ether, and air dried. The compound was not isolated as the N_3^- or ClO_4^- salt in order to prevent its decomposition.

trans-**$[Ir(en)_2(NO_2)_2]ClO_4$.**—*trans*-$[Ir(en)_2Cl_2]ClO_4$ (0.35 g) and $NaNO_2$ (0.60 g) were dissolved in 30 ml of H_2O in a polymer pressure bottle and heated at 140° for 6 hr. The solution was filtered, evaporated to 5 ml, and precipitated by the addition of 2 ml of 70% $HClO_4$. The white precipitate was collected on a filter and redissolved in 10 ml of hot water, filtered, and recrystallized by adding 2 drops of 70% $HClO_4$. The precipitate was collected on a filter, washed, and dried as above.

trans-**$[Ir(en)_2(NCS)Cl]ClO_4$.**—*trans*-$[Ir(en)_2Cl_2]ClO_4$ (0.35 g) and NaNCS (0.6 g) were dissolved in 30 ml of H_2O in a sealed polymer pressure bottle and heated at 140° for 6 hr. The resulting solution was evaporated to 5 ml on a steam bath and 2 ml of 70% $HClO_4$ was added. The solution was cooled to 5° for 24 hr when the small yellow plates were collected on a filter, washed, and dried as above.

cis-**$[Ir(en)_2Br_2]Br\cdot H_2O$.**—*cis*-$[Ir(en)_2Cl_2]I$ (1.0 g) was shaken in hot (65°) water for 5 min with 2 g of freshly precipitated AgCl. The solution was filtered and diluted to 60 ml and 3.5 g of NaBr was added. The solution was refluxed for 25 hr and evaporated to 25 ml. The solution was filtered hot, and upon cooling to room temperature for 3 hr, large, bright yellow needles were collected on a filter, washed with 5 ml of H_2O, 5 ml of ethanol, 5 ml of ether, and air dried; yield, 0.55 g (51%).

cis-**$[Ir(en)_2I]_2Cl\cdot H_2O$.**—*cis*-$[Ir(en)_2Cl_2]I$ (1.0 g) was dissolved in 60 ml of H_2O and 3.0 g of NaI was added. The solution was refluxed for 20 hr, evaporated to 20 ml, and filtered while hot. Upon cooling to room temperature for 2 hr, orange crystals were collected on a filter, washed with three separate 5-ml portions of H_2O, ethanol, and ether, and air dried; yield, 1.1 g. Analyses of this compound and a perchlorate salt of these crystals were unsatisfactory. The crystals were dissolved in a minimum amount of hot water and 2 ml of concentrated HCl was added. The resulting orange crystals were collected on a filter and washed and dried as above.

trans-**$[Ir(en)_2BrCl]ClO_4$.**—A solution of 0.5 g of *trans*-$[Ir(en)_2Cl_2]ClO_4$ in 50 ml of H_2O was irradiated for 2 hr in a water-cooled (25°) reaction dish 25 cm from a GE UA11 1200-W Vycor-

TABLE II

VISIBLE–ULTRAVIOLET SPECTRA OF IRIDIUM(III) COMPLEXES

Complex	λ, mμ	ε, l. mol^{-1} cm^{-1}
trans-[Ir(en)$_2$Cl$_2$]Cl	425, 345, 273 sh	12.7, 51.5, 58.4
trans-[Ir(en)$_2$Br$_2$]ClO$_4$	450, 364, 285 sh, 230 sh	12.5, 73.5, 46.5, 3010
trans-[Ir(en)$_2$I$_2$]ClO$_4$	490 sh, 398, 282.5, 230	18, 183, 1.37 × 10^4, 4.72 × 10^4
trans-[Ir(en)$_2$(N$_3$)$_2$]PF$_6$	412, 341, 255 sh	78, 511, 3490
trans-[Ir(en)$_2$(NO$_2$)$_2$]ClO$_4$	250	3790
trans-[Ir(en)$_2$BrCl]ClO$_4$	358, 275 sh	57.4, 37.4
trans-[Ir(en)$_2$ICl]ClO$_4$	393, 356, 280 sh	65.5, 58.6, 314
trans-[Ir(en)$_2$(NCS)Cl]ClO$_4$	295	336
trans-[Ir(en)$_2$(H$_2$O)Cl](ClO$_4$)$_2$, pH 2	~350 sh, ~285 sh	20, 52
trans-[Ir(en)$_2$(OH)Cl]$^+$,[a] pH 11	~360 sh, ~290	30, 90
trans-[Ir(en)$_2$(NO$_2$)Cl]ClO$_4$	280, 258 sh	1.04 × 10^3, 963
trans-[Ir(en)$_2$(ONO)Cl]ClO$_4$	288	1.11 × 10^3
trans-[Ir(en)$_2$IBr]ClO$_4$	400, 258	267, 6810
(enH$_2$Cl)[Ir(en)Cl$_4$]	405, 362, 294	61.1, 88.3, 121
cis-[Ir(en)$_2$Cl$_2$]Cl	380, 315, 293, 255	17, 92, 120, 127
cis-[Ir(en)$_2$Br$_2$]Br	310, 265 sh, 230 sh	205, 210, 1730
cis-[Ir(en)$_2$I$_2$]Cl	346, 283, 226	393, 2750, 2.9 × 10^4

[a] This compound has not been isolated.

filtered mercury arc lamp. The depth of the solution was 1 cm. The free chloride in the solution after irradiation was precipitated by adding 0.177 g of AgNO$_3$ dissolved in 20 ml of H$_2$O (Ag:Ir = 1:1). The solution was centrifuged and filtered and 0.1070 g of NaBr was added and dissolved. A drop of 70% HClO$_4$ was added and the solution was boiled for 15 min and evaporated on a steam bath to 25 ml. The solution deposited large yellow feathery crystals upon cooling to room temperature. These were collected after 3 hr, washed with 5 ml of H$_2$O, 10 ml of ethanol, and 20 ml of ether, and air dried; yield, 0.30 g (60%).

***trans*-[Ir(en)$_2$Cl]ClO$_4$.**—The method of preparation was exactly analogous to the preparation of *trans*-[Ir(en)$_2$ClBr]ClO$_4$ above, except that 0.156 g of NaI was substituted for NaBr.

***trans*-[Ir(en)$_2$BrI]ClO$_4$·H$_2$O.**—In a method analogous to those above, 0.60 g of *trans*-[Ir(en)$_2$I$_2$]ClO$_4$ was dissolved in 50 ml of H$_2$O and irradiated for 1 hr. A solution of 0.25 g of AgNO$_3$ in 25 ml of H$_2$O was added and then 0.2 g of NaBr in 20 ml of H$_2$O was added. The solution was centrifuged, filtered, and evaporated to 20 ml on a steam bath. After the addition of 2 ml of 70% of HClO$_4$, the solution was allowed to crystallize at room temperature for 1 hr. The orange crystals were collected on a filter, washed with 5 ml of H$_2$O, and recrystallized from 10 ml of hot H$_2$O by adding 2 ml of 70% HClO$_4$. The crystals were washed with H$_2$O, ethanol, and ether and air-dried.

***trans*-[Ir(en)$_2$Cl(H$_2$O)](ClO$_4$)$_2$.**—A 130-ml solution containing 1.0 g of *trans*-[Ir(en)$_2$Cl$_2$]ClO$_4$ and 0.02 *M* in NaOH was irradiated for 1.5 hr in a method similar to those above. The solution was reduced in volume on a steam bath to 7 ml and 1 drop of 70% HClO$_4$ was added to precipitate unreacted *trans*-[Ir(en)$_2$Cl$_2$]ClO$_4$. After filtration the solution was cooled at room temperature for 24 hr when white crystals of *trans*-[Ir(en)$_2$-Cl(H$_2$O)](ClO$_4$)$_2$ were collected on a filter, washed with 10 ml of ice-cold water, 10 ml of ethanol, and 10 ml of ether, and air-dried; yield, 0.30 g (26%).

***trans*-[Ir(en)$_2$(ONO)Cl]ClO$_4$.**—A solution of 0.50 g of *trans*-[Ir(en)$_2$Cl$_2$]ClO$_4$ in 75 ml of H$_2$O was irradiated 1 hr as above. The solution was treated with 0.200 g of AgClO$_4$ and 1 ml of 70% HClO$_4$, reduced to 20 ml on a steam bath, filtered, cooled to 5° for 30 min, and filtered again. The solution was cooled in an ice bath to 0–5° and 0.9 g of NaNO$_2$ was added and stirred until dissolved. The solution was maintained at this low temperature for 20 min and then filtered to remove the light yellow product. The crystals of the nitrito isomer were washed with 5 ml of cold water and separate 10-ml portions of ethanol and ether and air dried; yield, 0.25 g.

***trans*-[Ir(en)$_2$(NO$_2$)Cl]ClO$_4$.**—The nitro isomer was prepared from the nitrito isomer *in situ* either in solution by heating at 100° for at least 5 min or in the solid state by heating at 100° for 3 days.

Resolution of *cis*-[Ir(en)$_2$Cl$_2$]Cl.—The resolution of *cis*-Ir(en)$_2$Cl$_2^+$ was successfully accomplished with the ammonium salt of (+)-α-bromocamphor-π-sulfonic acid ((+)-BCS). *cis*-[Ir(en)$_2$Cl$_2$]Cl (4.0 g) was dissolved in 75 ml of H$_2$O at room temperature and 5.87 g of NH$_4$[(+)-BCS] were added and quickly filtered after it had dissolved. The filtrate began to crystallize on standing for 2 min and was allowed to crystallize for 30 min with occasional stirring. The solution was then cooled to 10° for 10 min and filtered, and the light yellow fluffy precipitate was washed with H$_2$O (5 ml), ethanol (20 ml), and ether (20 ml) and air dried; yield, 2.5 g. The precipitate was converted to the chloride by grinding it in an ice-cold mortar for 10 min with 12 ml of cold 1:1:1 HCl–ethanol–ether. The precipitate was collected on a filter, washed with 5 ml of ethanol and 10 ml of ether, and air dried; yield, 1.1 g. The chloride was converted to the perchlorate salt by dissolving it in 20 ml of H$_2$O and adding 5 ml of 70% HClO$_4$. The fluffy yellow needles were collected, washed, and dried as above; yield, 1.0 g of (−)-[Ir(en)$_2$Cl$_2$]ClO$_4$. The optical data are recorded in Table II and in Figure 1.

To the initial filtrate above was added 3 ml of concentrated HCl and the solution was heated at 80° for 5 min and then evaporated on a steam bath (55°) in a stream of air to 30 ml when 0.4 g of crystals separated on cooling to room temperature (fraction 2). The filtrate was evaporated to 10 ml at 55° in a stream of air and cooled to room temperature and fraction 3 was removed by filtration. Fraction 3 was dissolved in 10 ml of H$_2$O and crystallized by adding 2 g of NH$_4$I and cooling at 5° for 30 min. To the remaining filtrate was added 2 g of NH$_4$I, and it was allowed to crystallize at room temperature 1 hr. Fraction 4 was collected, washed with H$_2$O, ethanol, and ether, and air dried; yield, 0.8 g.

Fractions 2 and 3 were found to be (±)-*cis*-Ir(en)$_2$Cl$_2^+$ as the iodide and chloride salts and were contaminated with a large amount of resolving agent. Fraction 4, (+)-[Ir(en)$_2$Cl$_2$]I, was converted to the perchlorate salt by dissolving it in 30 ml of H$_2$O at 80° and adding 5 ml of 70% HClO$_4$, cooling to room temperature for 2 hr, filtering, washing with water (5 ml), ethanol (10 ml), and ether (10 ml), and air drying. The optical data for (+)-[Ir(en)$_2$Cl$_2$]ClO$_4$ are recorded in Table II.

Isomerization Experiments.—*trans*-Ir(en)$_2$Cl$_2^+$ is extremely stable in aqueous solution. No change in the ultraviolet spectrum of this compound was noted after heating it in 0.5 *M* Cl$^-$ for 5 hr at 140°. The base hydrolysis of *trans*-Ir(en)$_2$Cl$_2^+$ was determined to go with retention of geometry by heating a 2.5 × 10^{-3} *M* solution of *trans*-Ir(en)$_2$Cl$_2^+$ in a NaHPO$_4$–NaOH buffer

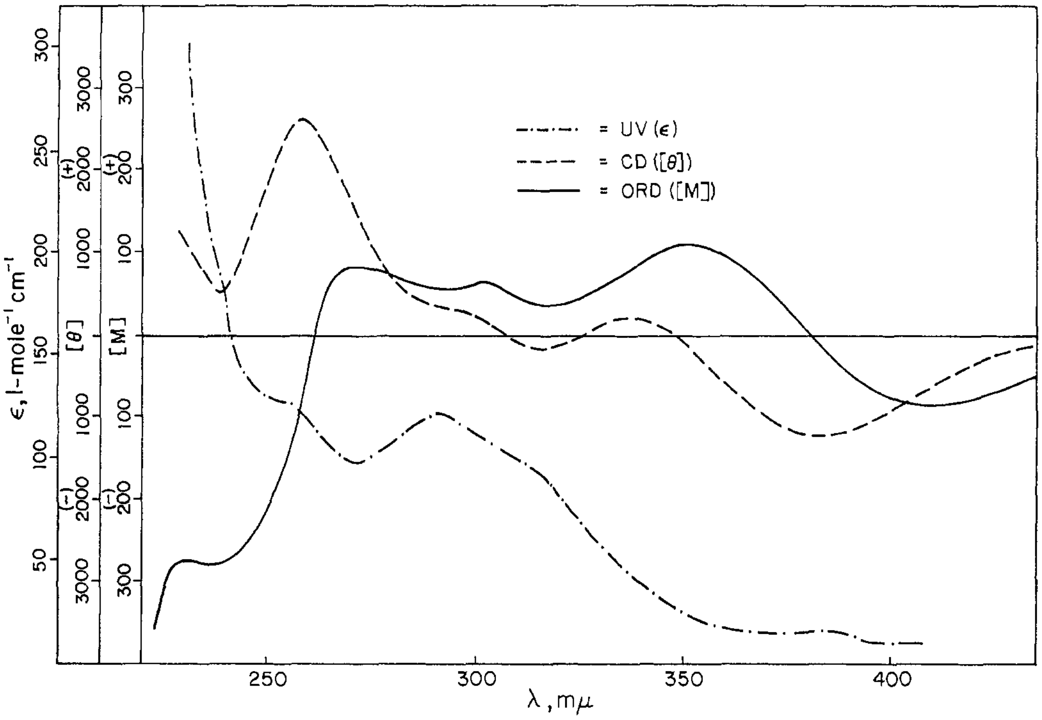

Figure 1.—Spectra of aqueous solutions of (−)-Ir(en)$_2$Cl$_2^+$.

at pH 11.5[13] for 2 hr at 140° (~75% reaction), cooling to room temperature, and adding enough concentrated HCl to bring the solution to pH 2. The solution was heated an additional 15 min at 140° and cooled to room temperature and the uv spectrum was recorded. After allowing for dilution, the final spectrum was identical with the initial spectrum within the accuracy of the method.

cis-[Ir(en)$_2$Cl$_2$]ClO$_4$ was heated with 0.2 M Cl$^-$ at 140° for 30 min. The uv spectrum showed a slight decrease in the intensity of the absorbance at 293 mμ, but no evidence of the formation of the *trans* isomer was found.

The base hydrolysis of *cis*-Ir(en)$_2$Cl$_2^+$ goes with complete retention of both geometry and configuration. A solution of 0.290 g of (−)-[Ir(en)$_2$Cl$_2$]ClO$_4$ in 20 ml of 0.1 N NaOH solution had an observed rotation of 0.31° in a 1-dm polarimeter tube. The solution was heated at 100° for 2 hr and the observed rotation fell to 0.08°. The *cis*-Ir(en)$_2$Cl$_2^+$ complex was restored by adding 10 ml of a 0.4 N HCl solution and heating at 100° for 4 hr. The observed rotation of the solution (after correcting for dilution) was 0.28°. This value is the same as that for the original solution within the experimental error of the method. The possibility of a *cis* → *trans* → *cis* isomerization during the base hydrolysis of *cis*-Ir(en)$_2$Cl$_2^+$ is thus precluded.

Irradiation Techniques.—Preparative photochemical reactions were carried out by placing the solution to be irradiated in a shallow petri dish so that the liquid depth never exceeded 4 cm. Suitable reaction times were determined by monitoring the ultraviolet spectrum. The solution was stirred by placing it directly onto a cold-water-driven magnetic stirrer. The stirrer provided enough cooling so that the temperatures of the irradiated solutions never exceeded 30°. The stirrer and solution were placed 25 cm from a Vycor-filtered, water-jacketed GE UA11 1200-W mercury vapor lamp.

Quantitative kinetic reactions were carried out in stoppered 1-cm quartz cells placed on a bed of wet tissue paper in a water jacket. The circulating water in the jacket was maintained at 25° and the solutions were maintained at 25.0 ± 0.3°. The irradiation was done 25 cm from the lamp mentioned above. The cells were removed at various intervals of time and their ultraviolet spectra were recorded. No "dark" reaction occurred in any of the solutions when they were not under the irradiation source. Excellent first-order kinetics were observed with all reactions when $\ln ((A_\infty - A_0)/(A_\infty - A_t))$ was plotted *vs.* time, where A_∞, A_0, and A_t are absorbance readings at infinity reaction time (at least 7 half-lives), zero time, and time t, respectively.

Analyses.—Carbon, nitrogen, and hydrogen analyses were performed by Miss Hilda Beck, the departmental analyst, by Micro-Tech Laboratories, Inc., Skokie, Ill., or by Alfred Bernhardt, Mikroanalytisches Laboratorium in Max-Planck Institut für Kohlenforschung, Mülheim, West Germany.

Spectral Measurements.—Visible and uv spectra were recorded with a Cary Model 14 recording spectrophotometer in 1-cm quartz cells. Infrared spectra were recorded on a Perkin-Elmer recording spectrometer or a Beckman IR 10 either as KBr disks or in Nujol and hexachlorobutadiene mulls between KBr plates. Optical rotation studies at a single wavelength were made on a Rudolph photoelectric spectrophotometer equipped with an oscillation polarizer. ORD, CD, and uv spectra were recorded on a Jasco ORD/UV-5 recording spectrometer in 1-cm quartz cells.[14]

Results and Discussion

The principal features of the visible and ultraviolet spectra of the compounds are listed in Table II. The optical rotatory dispersion and circular dichroism data for the resolved isomers of *cis*-Ir(en$_2$)Cl$_2^+$ are shown in Figure 1 and Table III.

The *cis* and *trans* assignments to the complexes were made by the method of Baldwin.[15] The *cis* isomers have two infrared bands in each of the CH$_2$ rocking (800–900 cm^{-1}) and NH$_2$ asymmetric deformation (1600 cm^{-1}) regions, whereas the *trans* isomers exhibit only one band in each of these regions. This criterion has been used for establishing the *cis* configuration in

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[13] R. G. Bates, *J. Res. Natl. Bur. Std.*, **66A**, 172 (1962).

[14] The authors wish to express their thanks to Dr. C. F. Liu of the University of Illinois Circle Campus for the use of the Jasco ORD/UV-5 and to M. E. Foss Sheridan for instruction on the use of the instrument and the recording of spectra.

[15] M. E. Baldwin, *J. Chem. Soc.*, 4369 (1960).

TABLE III

OPTICAL ROTATORY DISPERSION, CIRCULAR DICHROISM, AND ULTRAVIOLET SPECTRAL DATA FOR (−)-$Ir(en)_2Cl_2^+$ [a]

ORD		CD		Uv	
λ, mμ	[*M*]	λ, mμ	[θ]	λ, mμ	ε
410	−78 (80)	380	−1212	380	17
350	107 (−97)	335	154		
300	58 (−62)	315	−175	315	92
270	−73 (−80)	295	245	293	120
240	−290 (365)	258	2570	255	127

[a] (−)-$[Ir(en)_2Cl_2]ClO_4$, 0.0081 g/10 ml of H_2O. Values in parentheses are for (+)-$[Ir(en)_2Cl_2]ClO_4$, 0.0035 g/10 ml of H_2O.

a number of chloroamminebis(ethylenediamine)cobalt(III) complexes[16] and is valid in the assignment of *cis*- and *trans*-diacidobis(ethylenediamine)rhodium(III) complexes as well.[2,3b] The assignment of the structure of *cis*-$Ir(en)_2Cl_2^+$ is proved to be correct by the resolution of its optical isomers.

The enH_2^{2+} group is recognizable by a characteristic sharp doublet at 1630 and 1670 cm^{-1}. This is common to enH_2Cl_2 and enH_2Br_2 and $enH_2Cl(Ir(en)Cl_4]$ but not to complexes containing only coordinated ethylenediamine.

trans-$[Ir(en)_2(N_3)_2]PF_6$ shows characteristic N_3^- ir absorptions at 1955 (w) cm^{-1} and a doublet at 2040 and 2060 (s) cm^{-1}. *trans*-$[Ir(en)_2(NO_2)_2]ClO_4$ exhibits NO_2^- ir absorptions at 825 cm^{-1} and *trans*-$[Ir(en)_2NCSCl]ClO_4$ shows thiocyanate infrared absorptions at 2065, 2155, and 1720 cm^{-1}. *trans*-$[Ir(en)_2(ONO)Cl]ClO_4$, the nitrito isomer, exhibits ir bands at 1440 (s) and 828 (m) cm^{-1}, whereas the rearranged nitro isomer absorbs at 1405, 1385 (s), and 833 (m) cm^{-1}.

The assignment of structure to derivatives of $Ir(en)_2Cl_2^+$ was also based on the assumption that no *cis* ↔ *trans* isomerizations occurred during their preparation. Although *cis*-$Rh(en)_2I_2^+$ has been observed[2] to isomerize to the *trans* isomer and during base hydrolysis *trans*-$Rh(en)_2(py)Cl^{2+}$ was shown to rearrange to the *cis* isomer,[3b] no *cis* ↔ *trans* isomerizations occurred during any of the preparative reactions of iridium(III) complexes. The spectra of the reaction solutions, monitored during preparations, showed the appearance of only one set of absorptions. *trans*-$Ir(en)_2Cl_2^+$ and (−)-$Ir(en)_2Cl_2^+$ were allowed to react with excess alkali to generate the hydroxo complexes, and these were allowed to react with excess hydrochloric acid to regenerate the dichloro complexes. Within the limit of experimental error, there were no *cis* ↔ *trans* isomerizations of the complexes, which suggests that all of these substitutions take place with retention of configuration.

The bonding of thiocyanate in *trans*-$[Ir(en)_2NCSCl]ClO_4$ was deduced to be Ir–NCS linkage from the ultraviolet spectrum of this complex. Owing to the different ligand field strengths of M–S and M–N bonds, complexes containing M–S bonds should absorb between M–Cl and M–Br, whereas M–N should absorb at shorter wavelengths than M–Cl.[17] The following is the ordering in *trans*-$Ir(en)_2XCl^+$ complexes: X = NCS (295 mμ), X = Cl (345 mμ), X = Br (355 mμ).

trans-$[Ir(en)_2(N_3)_2]PF_6$ decomposes in the solid state with loss of molecular weight when exposed to normal room illumination over a period of several days, changing from yellow to light brown. Stored in the dark, the compound showed no noticeable decomposition over a period of several months. Kept in the dark, aqueous solutions of the compound are relatively stable at temperatures as high as 140°, the temperature at which the complex is prepared. If acidified, solutions of *trans*-$[Ir(en)_2(N_3)_2]PF_6$ in either acetone or water decompose at room temperature with *vigorous evolution of nitrogen*. Behavior of this type has not been reported in the literature with the cobalt(III) and rhodium(III) analogs, although the hydronium ion has been used in catalyzing the removal of N_3^- from these complexes,[18] presumably through the formation of HN_3. Johnson[4] noticed, however, that *trans*-$[Rh(en)_2(N_3)_2]N_3$ decomposed in the solid state but that decomposition was slower with chloride as the counteranion and when kept in the dark. Under quantitative experimental conditions, it was determined that 2.08 mol of pure nitrogen was evolved per mole of iridium when *trans*-$[Ir(en)_2(N_3)_2]PF_6$ was allowed to react with a 30% aqueous solution of HCl. The nature of the products of the reaction is not known and is presently under study.

Although quantitative kinetic studies have not yet been made, the rearrangement of *trans*-$Ir(en)_2(ONO)Cl^+$ to the more stable nitro isomer in aqueous solution with a half-life of about 80 sec at 78° was observed by monitoring the uv spectrum. No appreciable rearrangement occurs in aqueous solution at room temperature over several hours. The solid complex chloride salt is nearly completely rearranged to the nitro isomer after 3 days at 110°.

A general method for the preparation of *trans*-dichlorotetraammineiridium(III) complexes has been developed[10] which depends on the use of reducing agents such as KH_2PO_2 and $NaBH_4$. However, the nature of this catalysis remains elusive. *trans*-$Ir(en)_2Cl_2^+$ in aqueous solution is extremely resistant to attack by reducing agents. The ease of reduction of this complex was examined by means of the dropping mercury electrode and a recording polarograph. The height of the polarographic wave obtained was not proportional to the concentration of the complex, and the position of the wave was dependent upon the concentration of the complex and varied with supporting electrolyte as well. Although no conclusion could be reached as to the reversibility of the reduction nor as to the number of electrons involved, the reduction potential of the reducible species ($E_{1/2} \approx 2.0$ V) appears to be too high for the complex to be reduced by common reducing agents. Therefore catalysis seems to depend upon the reduction of $IrCl_6^{3-}$, which then promotes substitution by amines. Since this method of synthesis gives exclusively *trans*-$Ir(en)_2Cl_2^+$, it may suggest

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(16) C. S. Chan and F. Leh, *J. Chem. Soc., A*, 760 (1966).

(17) F. M. Jaeger and L. Bijkerk, *Z. Anorg. Allgem. Chem.*, **233**, 97 (1937).

(18) H. L. Bott and A. J. Poë, *J. Chem. Soc., A*, 205 (1967); P. J. Staples, *ibid.*, *A*, 2731 (1968).

that the catalyst is Ir(I) and that a two-electron redox process is involved.[19]

The *cis* isomer is obtained in low yield from reaction mixtures to which no reducing agent has been added. An improved yield is obtained in the presence of a high concentration of sodium chloride. The reason for this is not known, but it may be due to the observation that *cis*-dichloro complexes form more stable ion pairs than do the *trans* isomers.[20] Thus at higher chloride ion concentration there is a greater tendency to generate the more stable ion pair of the *cis* isomer.

Photoinduced substitution reactions of *trans*-$Ir(en)_2Cl_2^+$ provide a convenient method of synthesis of *trans*-$Ir(en)_2XCl^+$. No evidence of photoreduction or photoisomerization was found in these reactions. The photoaquation (eq 1) has a half-life of 13 min at 25°

$$trans\text{-}Ir(en)_2Cl_2^+ \xrightarrow[H_2O]{h\nu} trans\text{-}Ir(en)_2Cl(H_2O)^{2+} + Cl^- \qquad (1)$$

under the experimental conditions employed. This is five times faster than the thermal aquation at 140° and 10^5 times faster than the thermal aquation is estimated to be at 25°. Furthermore, the relative rates of photoinduced aquation under the same conditions at 25° of the dichloro, dibromo, and diiodo complexes are 1, 2.5, and 50, respectively.

The photochemical reactions of *trans*-$Ir(en)_2X_2^+$ in aqueous solutions containing added nucleophiles were examined and are shown in Table IV. The photochemical reactions are much too fast to involve thermal substitutions, and all products are the results of photoinduced substitutions.

Adamson[21] has proposed empirical rules for determining photoinduced substitution sites on complexes of O_h symmetry; *i.e.*, the axis containing the two ligands of lowest combined ligand field strength and the one of highest ligand field strength on this axis will be photoactivated. Table IV shows this rule to fit the observations of the *trans*-$Ir(en)_2X_2^+$ photosubstitutions. Thus the photoinduced substitution of *trans*-$Ir(en)_2Cl_2^+$ in the presence of I^- yields the disubstituted *trans*-$Ir(en)_2I_2^+$ through the intermediate *trans*-$Ir(en)_2ICl^+$, whereas the photoinduced substitution of *trans*-$Ir(en)_2I_2^+$ in the presence of Cl^- yields *trans*-$Ir(en)_2ICl^+$, and the relative ligand field strengths are $Cl^- > I^-$. The exception is the photoinduced reaction of *trans*-$Ir(en)_2Cl_2^+$ in the presence of OH^-. The product of this reaction is *trans*-$Ir(en)_2(OH)_2^+$ and not the expected *trans*-$Ir(en)_2(OH)Cl^+$ because of the relative ligand strength order, $OH^- > Cl^-$. This may be due to the fact that the ligand field strengths of these anions are very similar and that hydroxide ion is generally a very strongly bonded ligand in most metal complexes. It should be pointed out that the products of the reactions are also those which would be expected on the basis of the *trans*-effect behavior in these systems.[3c]

TABLE IV

PHOTOINDUCED SUBSTITUTION REACTIONS OF *trans*-$Ir(en)_2X_2^+$

Reactant	Nucleophile	Major product
trans-$Ir(en)_2Cl_2^+$	H_2O	*trans*-$Ir(en)_2(OH_2)Cl^{2+}$
	OH^-	*trans*-$Ir(en)_2(OH)_2^+$ [a]
	I^-	*trans*-$Ir(en)_2I_2^+$
	Cl^-	*trans*-$Ir(en)_2(OH_2)Cl^{2+}$
	Br^-	*trans*-$Ir(en)_2Br_2^+$
trans-$Ir(en)_2Br_2^+$	Cl^-	*trans*-$Ir(en)_2BrCl^+$
trans-$Ir(en)_2I_2^+$	Br^-	*trans*-$Ir(en)_2IBr^+$
	Cl^-	*trans*-$Ir(en)_2ICl^+$

[a] The salt of this complex has not been isolated.

The photochemistry of the *cis* isomer of $Ir(en)_2Cl_2^+$ is not as well understood. An examination of the spectral changes involved during the photochemical reaction indicates chelate ring opening rather than chloride substitution. An irradiated solution of *cis*-$Ir(en)_2Cl_2^+$ showed no free chloride ion. Heating the solution and observing spectral changes showed rapid reconversion to *cis*-$Ir(en)_2Cl_2^+$. Initial chelate ring opening is also suggested by the Adamson[21] rules for photoinduced substitution in these systems.

The analogous *trans*-$Rh(en)_2X_2^+$ complexes behave in a fashion similar to those of Ir(III),[11] and this suggests that photoinduced substitution reactions may be a ubiquitous method of preparation of other transition metal complexes which previously have been difficult to obtain.

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[19] J. V. Rund, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 658 (1964); J. V. Rund, *ibid.*, **7**, 24 (1968).

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

[21] A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).