Structural and Mechanistic Studies of Co-ordination Compounds. Part 38.[1] Syntheses and Characterization of Several Quadridentate Macrocyclic Amine Complexes of Iridium(III)

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Several macrocyclic amine complexes of the type *cis*-$[IrL^3(A)X]^+$ [L^3 = 1,4,8,11-tetra-azacyclotetradecane, (A)X = Cl_2, Br_2, or (Cl)Br], *trans*-$[IrLX_2]^+$ [L = L^3, X = Cl or NO_2; L^4 (1,4,8,12-tetra-azacyclopentadecane) or L^5 (*C*-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane), X = Cl or Br; and L^6 (*C*-*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane, X = Cl], and *trans*-$[IrL(Cl)Br]^+$ (L = L^4 or L^5) have been prepared and characterized. All these complexes are diamagnetic monomeric species. The i.r. and electronic absorption spectra of the complexes are discussed.

As part of our programme to study the photochemical, electrochemical, and thermal substitution and redox reactions of platinum amine complexes, we have reported the syntheses of some dianionotetra-amine complexes of ruthenium(III)[2-4] and osmium(III).[5] It is our intention to extend the studies to iridium(III) systems. One of the earliest known iridium(III) amine complexes was $[Ir(NH_3)_5Cl]^{2+}$, first reported by Palmaer[6] in 1895. Basolo and Hammaker[7] in 1962 then reported an improved synthetic procedure for this complex cation. Later, Schmidtke[8] successfully prepared an extensive series of related complexes of the type $[Ir(NH_3)_5X]^{2+}$ where X represents an anionic ligand. As for L^1 complexes (L^1 = two ethane-1,2-diamine ligands), the first known complex was *cis*-$[IrL^1(NO_2)_2]^+$.[9] The synthesis of *cis*- and *trans*-$[IrL^1Cl_2]^+$ was first reported by Kida.[10] Baranovskii *et al.*[11] then reported an improved method by treating $K_2[IrCl_6]$ with ethane-1,2-diamine in acetic acid. At much the same time, Bauer and Basolo[12,13] independently devized a catalytic method for the synthesis of *cis*- and *trans*-$[IrL^1Cl_2]^+$ from which they were able to prepare several other L^1 complexes of the type *trans*-$[IrL^1(A)X]^+$ where A and X are unidentate anionic ligands. Using the same catalytic method, they also prepared *trans*-$[IrL^2Cl_2]^+$ (L^2 = 3,6-diazaoctane-1,8-diamine). The synthesis of the L^2 complex was later improved by Bowker *et al.*[14] Very recently, Galsbøl and Rasmussen[15] commented that all the previous methods for the synthesis of *cis*- and *trans*-$[IrL^1Cl_2]^+$ were not really satisfactory and they suggested a modified procedure for the isolation of both isomers in good yields.

So far, no macrocyclic amine complexes of iridium(III) have been reported. This paper describes the syntheses and characterization of several iridium(III) complexes containing the following quadridentate macrocyclic amines: L^3 = 1,4,8,11-tetra-azacyclotetradecane; L^4 = 1,4,8,12-tetra-azacyclopentadecane; L^5 and L^6 = *C*-*meso*- and *C*-*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane, respectively.

Experimental

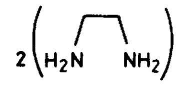
cis-*Dichloro*(1,4,8,11-*tetra-azacyclotetradecane*)*iridium*(III) *Perchlorate*.—Methanol (30 cm³, G.R. grade) was heated under reflux in a two-necked round-bottomed flask (500 cm³) for *ca.* 15 min. A methanolic solution (230 cm³) of $Na_2[IrCl_6]$ (1 g, Johnson Matthey) was added dropwise to the refluxing methanol through the condenser. After *ca.* 2 min a methanolic solution of L^3 (0.5 g in 230 cm³) was also added dropwise to the same refluxing solution at a slightly slower rate (*ca.* 5/6 of the former addition rate), the whole process taking about 6 h. After further heating under reflux overnight (about 18 h), the solution was acidified with HCl and was then filtered whilst hot. The filtrate was evaporated to dryness and the yellowish brown solid dissolved in the minimum quantity of hydrochloric acid (2 mol dm^{-3}). Dropwise addition of a concentrated solution of $NaClO_4$ precipitated out a yellow solid which was filtered off, washed with a small quantity of ice-cold water, ethanol, and diethyl ether, and finally dried *in vacuo* at 78 °C (yield 35%).

cis-*Dibromo*(1,4,8,11-*tetra-azacyclotetradecane*)*iridium*(III) *Bromide*.—A suspension of $K_2[IrBr_6]$ (1 g, Johnson Matthey) in absolute ethanol (230 cm³) was heated under reflux and with vigorous stirring for *ca.* 15 min. An ethanolic solution of L^3 (0.5 g in 230 cm³) was then added dropwise to the refluxing solution, over a period of about 6 h. After further heating under reflux overnight, the solution was acidified with HBr and then filtered whilst hot. The filtrate was evaporated to dryness and the yellowish brown residue dissolved in a minimum quantity of hot HBr (2 mol dm^{-3}). The solution was reduced to *ca.* 20 cm³, filtered whilst hot, and the filtrate set aside to cool. A yellowish brown solid slowly appeared, which was collected, washed with a small quantity of ice-cold water, ethanol, and diethyl ether, and dried *in vacuo* at 78 °C (yield 30%).

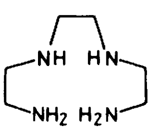
cis-*Bromochloro*(1,4,8,11-*tetra-azacyclotetradecane*)-*iridium*(III) *Bromide*.—A hot aqueous solution of *cis*-$[IrL^3Cl_2]ClO_4$ (0.5 g in 50 cm³) was treated with NaBr (7 g) and the resulting solution was heated under reflux and with vigorous stirring for 3 d. The yellowish solution was then evaporated down to *ca.* 20 cm³, filtered whilst hot, and cooled in a refrigerator overnight. A yellow solid, *cis*-$[IrL^3(Cl)Br]Br$, crystallized out, and was collected, washed with ethanol and diethyl ether, and dried *in vacuo* at 78 °C (yield 40%).

trans-*Dinitro*(1,4,8,11-*tetra-azacyclotetradecane*)*iridium*(III) *Perchlorate*.—An aqueous solution (80 cm³) of *cis*-$[IrL^3Cl_2]ClO_4$ (0.5 g) and $NaNO_2$ (5 g) was transferred to 10 Pyrex tubes which were sealed and heated to 150 °C for 18 h. The resulting solution was cooled, filtered, and rotary evaporated down to *ca.* 50 cm³. Addition of $NaClO_4$ precipitated out a pale yellow solid which was recrystallized from hot water. The final product was collected, washed with a small quantity of ice-cold water, ethanol, and diethyl ether, and dried *in vacuo* at 78 °C (yield 30%).

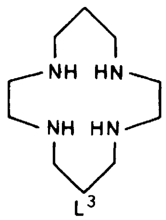
trans-*Dichloro*(1,4,8,11-*tetra-azacyclotetradecane*)-*iridium*(III) *Perchlorate*.—An aqueous solution (80 cm³) of *trans*-$[IrL^3(NO_2)_2]ClO_4$ (0.5 g) in $Na_2B_4O_7$–NaOH buffer at



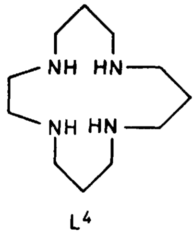
L^1



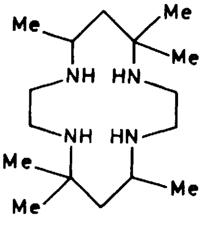
L^2



L^3



L^4



L^5 (*C-meso*)
or
L^6 (*C-rac*)

ca. pH 10 was transferred to 10 Pyrex tubes which were sealed and heated to 150 °C for 120 h. The solution was cooled, filtered, and treated with concentrated hydrochloric acid (*ca.* 20 cm^3). The resulting solution was heated under reflux for 20 h, filtered whilst hot, and then rotary evaporated down to *ca.* 80 cm^3. Addition of $NaClO_4$ precipitated out a light yellow solid which was collected and recrystallized from hot water (yield 20%).

trans-*Dichloro*(*tetramine*)*iridium*(III) *Perchlorate*, *trans*-$[IrLCl_2]ClO_4$ ($L = L^4$—L^6).—All these complexes were prepared by essentially the same method as that for *cis*-$[IrL^3Cl_2]ClO_4$ by treating $Na_2[IrCl_6]$ with the appropriate macrocyclic amine L in alcohol (methanol for L^4 and absolute ethanol for L^5 and L^6). For the preparation of L^5 and L^6 complexes, addition of $NaClO_4$ would probably have co-precipitated the perchlorate salts of the protonated L^5 or L^6, which could be removed by washing the product with a small quantity of hot water.

trans-*Dibromo*(*tetramine*)*iridium*(III) *Perchlorate*, *trans*-$[IrLBr_2]ClO_4$ ($L = L^4$ *or* L^5).—A suspension of $K_2[IrBr_6]$ (1 g) in absolute ethanol (230 cm^3) was heated under reflux with vigorous stirring for *ca.* 15 min. An ethanolic solution (230 cm^3) of L (L^4, 0.6 g; L^5, 0.7 g) was added dropwise to the refluxing solution over a period of about 6 h. After heating under reflux overnight, the solution was filtered whilst hot and the filtrate was evaporated to dryness. The yellow residue was dissolved in hot dilute hydrobromic acid (2 mol dm^{-3}, *ca.* 80 cm^3). The solution was filtered whilst hot and $NaClO_4$ added to the cooled solution, precipitating a yellow crystalline solid which was collected, washed with a small quantity of ice-cold water, ethanol, and diethyl ether, and dried *in vacuo* at 78 °C (yield 30%).

trans-*Bromochloro*(1,4,8,12-*tetra-azacyclopentadecane*)-*iridium*(III) *Bromide*.—This complex was prepared by essentially the same method as that of *cis*-$[IrL^3(Cl)Br]Br$ except that *trans*-$[IrL^4Cl_2]ClO_4$ was used as the starting material instead of *cis*-$[IrL^3Cl_2]ClO_4$ (yield 30%).

trans-*Bromochloro*(*C*-meso-5,5,7,12,12,14-*hexamethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*iridium*(III) *Perchlorate*.—A hot aqueous solution of *trans*-$[IrL^5Cl_2]ClO_4$ (0.5 g, in 150 cm^3) was treated with NaBr (10 g) and the resulting solution heated under reflux with vigorous stirring for 3 d. The yellow solution was filtered whilst hot and then rotary evaporated down to *ca.* 100 cm^3. On cooling, the yellow product gradually precipitated and was collected, washed with water, ethanol, and diethyl ether, and dried *in vacuo* at 78 °C (yield 40%).

Elemental analytical data of all new complexes are collected in Table 1.

Table 1. Elemental analytical data for some new iridium(III) macrocyclic amine complexes

Complex	Analysis */% C	H	N	Cl	Br
cis-$[IrL^3Cl_2]ClO_4$	21.3	4.3	9.7	18.7	
	(21.3)	(4.3)	(10.0)	(18.9)	
cis-$[IrL^3(Cl)Br]Br \cdot H_2O$	19.8	4.0	9.2	6.1	26.5
	(19.8)	(4.3)	(9.3)	(5.9)	(26.4)
cis-$[IrL^3Br_2]Br$	19.0	3.8	8.8		37.7
	(19.0)	(3.8)	(8.9)		(37.9)
trans-$[IrL^3Cl_2]ClO_4$	21.5	4.2	9.7	18.7	
	(21.3)	(4.3)	(10.0)	(18.9)	
trans-$[IrL^3(NO_2)_2]ClO_4$	20.3	3.9	14.1	6.1	
	(20.6)	(4.1)	(14.4)	(6.1)	
trans-$[IrL^4Cl_2]ClO_4 \cdot H_2O$	22.1	4.4	9.3	17.9	
	(22.2)	(4.7)	(9.4)	(17.9)	
trans-$[IrL^4(Cl)Br]Br \cdot H_2O$	21.4	4.4	9.1	5.6	25.6
	(21.3)	(4.5)	(9.0)	(5.7)	(25.8)
trans-$[IrL^4Br_2]ClO_4$	19.6	3.7	8.1		24.3
	(19.8)	(3.9)	(8.4)		(24.0)
trans-$[IrL^5Cl_2]ClO_4$	29.6	5.6	8.6	16.2	
	(29.7)	(5.6)	(8.7)	(16.4)	
trans-$[IrL^5(Cl)Br]ClO_4$	27.9	5.3	8.2	10.2	11.4
	(27.8)	(5.3)	(8.1)	(10.3)	(11.6)
trans-$[IrL^5Br_2]ClO_4$	26.1	4.8	7.4		21.7
	(26.1)	(4.9)	(7.6)		(21.7)
trans-$[IrL^6Cl_2]ClO_4$	29.6	5.8	8.5	16.1	
	(29.7)	(5.6)	(8.7)	(16.4)	

* Calculated values are given in parentheses.

Physical Measurements.—Infrared spectra were recorded in Nujol mulls on a Perkin-Elmer 577 spectrophotometer (200—4 000 cm^{-1}). Electronic absorption spectra of freshly prepared solutions were measured with a Beckman Acta CIII spectrophotometer. Magnetic susceptibilities of solid samples were measured by the Gouy method using mercury tetrathiocyanatocobaltate(II) as the calibrant.[16]

Results and Discussion

It is well known[13] that the syntheses of iridium(III) amine complexes are not straightforward and the yields are low. While most of the starting materials for the syntheses of first-row transition-metal amine complexes are usually simple metal halides in the +2 oxidation state, such as $CoCl_2 \cdot 6H_2O$, no simple bivalent second- or third-row transition-metal salts exist. Simple trivalent metal chlorides are available, however they are usually impure, substitutionally inert, and sensitive to base, precipitating as hydrated oxides from aqueous reaction mixtures. It seems that if these simple trivalent metal chlorides were to be used as starting materials, drastic reaction conditions coupled with a long reaction time and careful pH control might be necessary. It is, therefore, not unexpected that most synthetic reactions are usually accompanied by many side reactions, such as hydrolysis and redox reactions, thus leading to a low yield of the desired products.

The ' controlled dropwise addition method ' developed for the high-yield syntheses of tetra-amine complexes of ruthenium(III)[2-4] and osmium(III)[5] has now been employed successfully, with minor modifications, for the syntheses of various quadridentate macrocyclic amine complexes of iridium(III) using $Na_2[IrCl_6]$ as the starting material. It was proposed[13] that the successful synthesis of *trans*-$[IrLCl_2]^+$ ($L = L^1$ or L^2), using $K_2H_2PO_2$ or $NaBH_4$ as a catalyst, would probably involve the reduction of $[IrCl_6]^{2-}$ to iridium(I) which then would promote amine substitutions. In the present work, no reducing agent was added and alcohol is not a powerful agent for reducing iridium(IV) to iridium(I). It might reduce $[IrCl_6]^{2-}$ to $[IrCl_6]^{3-}$ which, however, would not be the reactive species for the successful synthesis of the desired amine complexes. In fact several reactions have been tried in vain to synthesize *cis*- or *trans*-$[IrLCl_2]^+$ ($L = L^3$—L^6) directly from $[IrCl_6]^{3-}$.

An important feature for the successful syntheses of these iridium(III) amine complexes was the use of methanol (or ethanol) as the reaction medium. Various other solvents, such as water, tetrahydrofurane, dimethyl sulphoxide, dimethylformamide, and acetonitrile, have been tried, but in every case the reaction was either unsuccessful or proceeded inefficiently with many side products. It should be noted that the use of absolute alcohol is extremely important as the addition of a small amount of water to the reaction solution would seriously lower the overall yield, probably due to hydrolysis of the starting material in basic medium. Another important feature was the controlled dropwise addition of amine to the refluxing solution of the starting $[IrCl_6]^{2-}$ which was also freshly introduced continually at a slow rate. The syntheses of the corresponding ruthenium(III) and osmium(III) complexes are believed to involve the generation of the corresponding reactive hydrido-intermediates by the initial refluxing of the starting materials in a basic alcoholic medium. The dropwise mode of addition of the amine is employed because of the slow formation of these intermediates, and so that a roughly stoicheiometric ratio of the intermediate to amine is maintained without an excessive build-up of the free amine in the reaction solution. In the present case, a reactive hydrido-intermediate is also probably formed. Such an intermediate has also been postulated in the syntheses of some related rhodium(III) complexes.[17] If the amine was not added dropwise, yellowish brown solids, probably iridium oxo- or hydroxo-species, precipitated during the reactions. Furthermore, $Na_2[IrCl_6]$ should also be introduced slowly into the reaction solution. If its rate of addition was fast, the yield of the final product was very low. The reason might be that the reactive intermediate was formed rather slowly. If the concentration of $[IrCl_6]^{2-}$ had been built up at a faster addition rate, it might have gradually changed into some other species on prolonged heating in solution. For the syntheses of L^5 and L^6 complexes, ethanol (higher b.p.) was found to be a better solvent than methanol, which probably reflects the steric effects of the ligands on their approach to the metal to form the products.

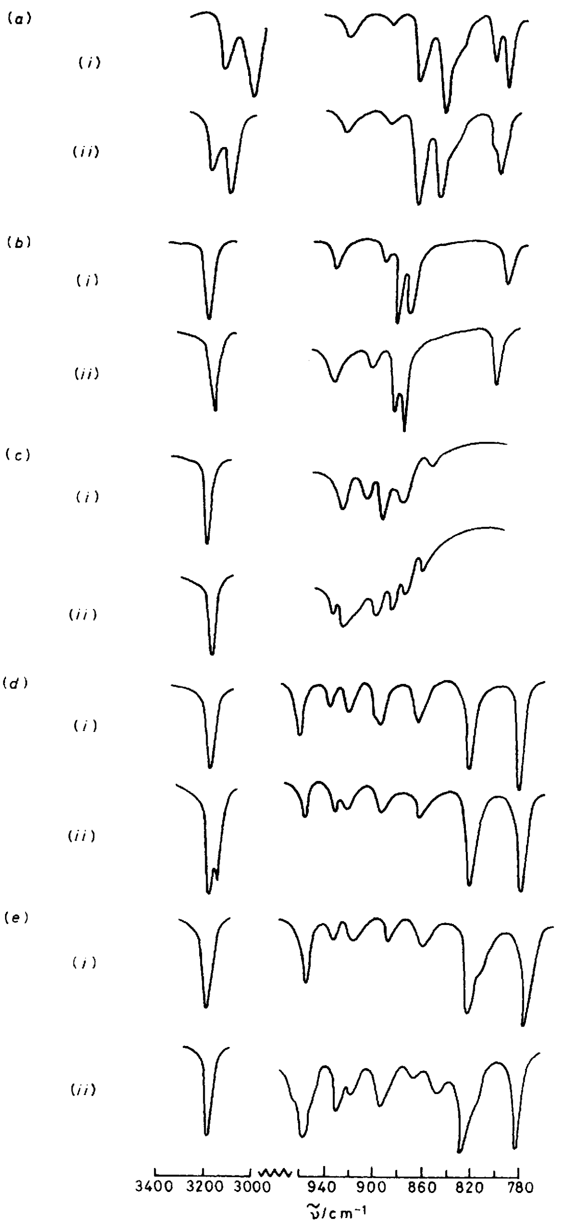


Figure. Infrared spectra of corresponding pairs of ruthenium(III) (*i*) and iridium(III) (*ii*) complexes: (*a*) *cis*-$[ML^3Cl_2]Y$ (Y = Cl for Ru^{III} and ClO_4 for Ir^{III}); (*b*)—(*e*) *trans*-$[MLCl_2]ClO_4$ [L^3(*b*), L^4(*c*), L^5(*d*), and L^6(*e*)]

It is known that iridium(III) amine complexes are inert to ligand substitutions.[13] There was no apparent formation of $[IrLX_2]^+$ when an aqueous solution of *cis*-$[IrL^3Cl_2]^+$ or *trans*-$[IrLCl_2]^+$ ($L = L^3$—L^5) was heated under reflux for 10 d in the presence of excess of NaX (X = Br or NCS). Reactions with NaBr only resulted in the formation of the corresponding $[IrL(Br)Cl]^+$. Furthermore, all substitution reactions are stereoretentive. The only geometrical isomerization observed was the reaction between *cis*-$[IrL^3Cl_2]^+$ and excess of $NaNO_2$

at 150 °C for 18 h. Attempts to generate isomerization by substituting *cis*-[IrL^{3}Cl$_2$]$^+$ with other anions were unsuccessful. In the case of NaN$_3$ only a very small quantity of the *trans* product was isolated. Isomerization did not occur even in the presence of base, such as NaOH or 2,4,6-trimethylpyridine, at 150 °C for 4 d. The mechanism for the NO$_2^-$-induced isomerization is not known. All other *trans*-L^3 complexes were then prepared from *trans*-[IrL^3(NO$_2$)$_2$]$^+$.

All the new complexes are light yellow or yellowish brown in colour and give well formed crystals which appear stable indefinitely in the solid state and in acidic solutions. The isomeric purity of each complex was confirmed by the observation that their i.r. and electronic absorption spectra were unaffected by repeated preparation and recrystallization. In some cases, this was further confirmed by chromatography as described previously.[2] All these complexes are diamagnetic, monomeric species.

The geometric configuration of the complexes was assigned on the basis of i.r. spectroscopy. It has been demonstrated [2,3,5,18,19] that the i.r. spectrum in the 780—950 cm^{-1} region is most useful in differentiating between *cis* and *trans* isomers of most tetra-amine complexes. The i.r. spectra in the 3 000—3 400 and 780—960 cm^{-1} regions for corresponding pairs of [RuLCl$_2$]$^+$ and [IrLCl$_2$]$^+$ (L = L^3—L^6) are shown in the Figure. It is clear that the i.r. spectra of the new [IrLCl$_2$]$^+$ complexes are very similar to those of the corresponding *cis*-

Table 2. Metal–halide vibrational and u.v. absorption spectra of some iridium(III) tetra-amine complexes in aqueous solution

Complex	$\tilde{\nu}$(Ir–X) [a]/cm^{-1}	U.v. absorption bands	
		λ [a,b] $_{max.}$/nm	Excited state [c]
cis-[IrL^{1}Cl$_2$]ClO$_4$ [d,e]	311s, 295s (sh)	*ca.* 320 (sh) (100)	$^1B_1$
		292 (145)	$^1A_2$, $^1B_2$ ($^1T_{1g}$)
		ca. 254 (sh) (162)	$^1A_2$, $^1B_2$ ($^1T_{2g}$)
cis-[IrL^{3}Cl$_2$]ClO$_4$	310s, 285s (sh)	*ca.* 285br (sh) (550)	$^1A_2$, $^1B_2$ ($^1T_{1g}$)
		250br (sh) (820)	$^1A_2$, $^1B_2$ ($^1T_{2g}$)
		207 (2 480)	π-c.t.t.m.
cis-[IrL^3(Cl)Br]Br	300s,[f] *ca.* 210m [g]	*ca.* 324br (145)	$^1B_1$
		294br (sh) (178)	$^1A_2$, $^1B_2$ ($^1T_{1g}$)
		ca. 257 (sh) (385)	$^1A_2$, $^1B_2$ ($^1T_{2g}$)
		208 (5 140)	π-c.t.t.m.
cis-[IrL^{3}Br$_2$]Br	*ca.* 210m	*ca.* 325br (sh) (165)	$^1B_1$
		298br (189)	$^1A_2$, $^1B_2$ ($^1T_{1g}$)
		ca. 260 (sh) (393)	$^1A_2$, $^1B_2$ ($^1T_{2g}$)
		212 (3 020)	π-c.t.t.m.
trans-[IrL^{1}Cl$_2$]ClO$_4$ [d,e]	321m,br	345 (45.9)	^1E_g
		ca. 275 (sh) (30)	$^1B_{2g}$
trans-[IrL^{1}Br$_2$]ClO$_4$ [d,h]	218s,br	362 (68)	^1E_g
		289 (30)	$^1B_{2g}$
		230 (3 280)	π-c.t.t.m.
trans-[IrL^{3}Cl$_2$]ClO$_4$	320s, 305s	334br (110)	^1E_g
		ca. 285 (sh) (220)	$^1B_{2g}$
		264 (285)	$^1A_{2g}$
		208 (4 130)	π-c.t.t.m.
trans-[IrL^3(NO$_2$)$_2$]ClO$_4$		*ca.* 283br (sh) (1 240)	^1E_g + $^1B_{2g}$
		255 (1 890)	$^1A_{2g}$
		221 (3 270)	π-c.t.t.m.
trans-[IrL^{4}Cl$_2$]ClO$_4$	325s, 305s	*ca.* 350br (sh) (227)	^1E_g
		ca. 270br (sh) (850)	$^1B_{2g}$
		ca. 245br (sh) (1 020)	$^1A_{2g}$
		205 (2 775)	π-c.t.t.m.
trans-[IrL^4(Cl)Br]ClO$_4$	325s,[f] 305s,[f] 220m,br [g]	*ca.* 340 (sh) (150)	^1E_g
		ca. 270 (sh) (640)	$^1B_{2g}$
		ca. 240 (sh) (1 140)	$^1A_{2g}$
		210 (5 060)	π-c.t.t.m.
trans-[IrL^{4}Br$_2$]ClO$_4$	220s	*ca.* 362br (sh) (224)	^1E_g
		ca. 234br (sh) (2 900)	$^1A_{2g}$
		217 (5 480)	π-c.t.t.m.
trans-[IrL^{5}Cl$_2$]ClO$_4$	330s, 300s	*ca.* 336br (sh) (132)	^1E_g
		265 (410)	$^1A_{2g}$
		209 (2 750)	π-c.t.t.m.
trans-[IrL^5(Cl)Br]ClO$_4$	320s,[f] 298s,[f] 230m [g]	350br (85)	^1E_g
		ca. 298br (sh) (150)	$^1B_{2g}$
		ca. 240 (sh) (1 050)	$^1A_{2g}$
		214 (5 730)	π-c.t.t.m.
trans-[IrL^{5}Br$_2$]ClO$_4$	220s,br	365br (79)	^1E_g
		ca. 296 (sh) (170)	$^1B_{2g}$
		240 (1 950)	$^1A_{2g}$
		219 (3 900)	π-c.t.t.m.
trans-[IrL^{6}Cl$_2$]ClO$_4$	320s, 300s	*ca.* 335 (sh) (70)	^1E_g
		ca. 258br (sh) (240)	$^1A_{2g}$
		212 (2 100)	π-c.t.t.m.

[a] s = Strong, m = medium, br = broad, sh = shoulder. [b] Molar absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [c] The octahedral parentage excited states are given in parentheses. [d] Ref. 14. [e] Ref. 15. [f] ν(Ir–Cl) stretch. [g] ν(Ir–Br) stretch. [h] Ref. 20.

and *trans*-[RuLCl$_2$]$^+$ complexes, hence the assignment of the appropriate geometrical configuration to these iridium(III) complexes. It should be noted that, as expected, *cis* complexes give distinct splitting of the ν(N–H) stretch while *trans* complexes give only one band at *ca.* 3 200 cm^{-1}. The small splitting observed for *trans*-[IrL^{5}Cl$_2$]ClO$_4$ could arise from crystal-packing effects. The i.r. spectra of dibromo- and bromochloro-complexes in these regions are also very similar to their corresponding dichloro-analogues. The far-i.r. spectra are, however, less useful in differentiating between geometrical isomers of these iridium(III) complexes. A comparison between the far-i.r. spectra of corresponding pairs of dichloro- and dibromo-complexes enabled the assignment of ν(Ir–X) (X = Cl or Br) stretches. These vibrations are collected in Table 2. Both *cis*- and *trans*-[IrLCl$_2$]$^+$ give two ν(Ir–Cl) vibrations. For the [IrLBr$_2$]$^+$ complexes, it is not certain whether ν(Ir–Br) stretches also showed any splitting since they occur near our instrumental limit of 200 cm^{-1}.

The electronic absorption spectra of the iridium(III) complexes (Table 2) are typical of those of diamagnetic d^6 complexes of the tetra-amine type.[15,20] For the *trans* series of complexes, the lowest-energy transitions with molar absorption coefficients in the order of 10^2 dm^3 mol^{-1} cm^{-1} are undoubtedly assignable to the $^1A_{1g} \rightarrow {}^1E_g$ transition. Blanchard and Mason [20] noted that the second bands observed for *trans*-[IrL^{1}X$_2$]$^+$ (X = Cl or Br) lie lower in energy than the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition in [Ir(L^1)$_{3/2}$]$^{3+}$ and they could not assign these bands with confidence. The assignment of $^1A_{2g}$ implies that this state is substantially lower in energy than the $^1T_{1g}$ state in [Ir(L^1)$_{3/2}$]$^{3+}$. Such a situation is difficult to rationalize in terms of ligand-field or simple molecular-orbital theory.[21,22] The alternative assignment of these bands as one or more transitions to spin-forbidden ligand-field states is not satisfactory either. This uncertainty was very recently resolved by the calculations of Galsbøl and Rasmussen.[15] They showed that the $^1B_{2g}$ state arising from the octahedral $^1T_{2g}$ state actually lies lower than the $^1A_{2g}$ state and hence all these second bands could be assigned as $^1A_{1g} \rightarrow {}^1B_{2g}$ and the third bands as $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions. The bands below 230 nm with molar absorption coefficients in the order of 10^3 dm^3 mol^{-1} cm^{-1} are clearly charge-transfer-to-metal (c.t.t.m.) transitions. Probably they arise from the occupied π orbitals of X, *i.e.* π-c.t.t.m. The σ-c.t.t.m. transitions which arise from the occupied σ orbitals of X would be expected to lie at higher energy and have much higher intensity. For the *cis* series of complexes, the assignments of ligand-field bands (Table 2) also followed those of Galsbøl and Rasmussen.[15]

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