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The Preparation, Separation, and Characterization of the lel_3- and ob_3-Isomers of Tris(*trans*-1,2-cyclohexanediamine)iridium(III) Complexes

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

The isomers $\Delta(+)[Ir\{(-)chxn\}_3\lambda\lambda\lambda]^{3+}$ (lel_3), $\Lambda(+)[Ir\{(-)chxn\}_3\lambda\lambda\lambda]^{3+}$ (ob_3), $\Lambda(-)[Ir\{(+)chxn\}_3\delta\delta\delta]^{3+}$ (lel_3), and $\Delta(-)[Ir\{(+)chxn\}_3\delta\delta\delta]^{3+}$ (ob_3) (chxn = *trans*-1,2-cyclohexanediamine) have been isolated as chlorides and nitrates, and characterized by their electronic and circular dichroism spectra and their optical rotation. The nitrates are isomorphous with the corresponding Cr, Co, and Rh compounds. The lel_3-isomers form sparingly soluble hexachloroiridate(III) salts which are isomorphous with the analogous Co and Rh hexachloroiridates.

The formula $[Ir\{(\pm)chxn\}_3]^{3+}$ (chxn = *trans*-1,2-cyclohexanediamine) represents eight isomers (four possible combinations for the chelate ring conformations within each of the absolute configurations Δ and Λ). The present work is confined to the two pairs of isomers which arise when three (−)chxn or three (+)chxn ligands are bound to the central atom. *trans*-(−)-1(*R*),2(*R*)-Cyclohexanediamine, (−)chxn, has the λ and (+)chxn the δ conformation (IUPAC 1968).[1] Each enantiomer of chxn forms two diastereoisomeric tris-complexes, *e.g.* $\Delta(+)[Ir\{(-)chxn\}_3\lambda\lambda\lambda]^{3+}$ and $\Lambda(+)[Ir\{(-)chxn\}_3\lambda\lambda\lambda]^{3+}$, denoted[2] lel_3 and ob_3, respectively, using an obvious extension of the original notation of Corey and Bailar[3] whereby the mixed tris-complexes containing both (−)chxn and (+)chxn would be described as lel_2ob and ob_2lel.

The attempt of Jaeger and Bijkerk[4] to prepare tris(*trans*-1,2-cyclohexanediamine)iridium(III) by a method analogous to that for the corresponding rhodium compound, *i.e.* from sodium hexachloroiridate(III) and (−)chxn in a water-ethanol mixture, was only partly successful. The reaction mixture precipitated a nearly colourless, poorly crystalline compound which on the basis of elemental analysis was assumed to be $(+)[Ir\{(-)chxn\}_3][IrCl_6]$.aq. In the present work the lel_3-isomer $\Delta(+)[Ir\{(-)chxn\}_3\lambda\lambda\lambda][IrCl_6]$.aq and the analogous Co- and Rh-hexachloroiridates have been precipitated from solutions of the constituent ions* and it seems very probable that the iridium-compound is identical to the precipitate obtained by Jaeger and Bijkerk. The latter authors' failure to induce this compound to react further is probably due to the low solubility of the compound and the kinetic inertness of iridium(III).

In the procedure described here an aqueous solution of (−)chxn or (+)chxn (*ca.* 25 % excess) is allowed to react with soluble iridium(III) chloride. Carbon dioxide appears to catalyze the reaction. To complete the reaction the mixture is kept at 170 °C for approx. 300 h and then evaporated to dryness. The residue is a mixture of the lel_3- and ob_3-isomers from which the lel_3-isomer can be extracted with *ca.* 80 % ethanol in which the ob_3-isomer is only slightly soluble. It is difficult to remove coloured impurities from these two diastereoisomeric chlorides but the nitrates of both

* The ob_3-isomers are not precipitated by $[IrCl_6]^{3-}$ under the same experimental conditions.

isomers have a rather high solubility temperature coefficient and a rather low solubility at room temperature, and are easily prepared as colourless crystals. Purification as the nitrate salts was therefore chosen.

EXPERIMENTAL

Materials. Iridium(III) chloride hydrate (52.39 % Ir, *i.e.* 3.8 mol H_2O/mol Ir) was obtained from Johnson, Matthey and Co. *trans*-Cyclohexanediamine was purified and resolved as described earlier.[5]

Physical measurements. Absorption spectra were recorded on a Cary 118C spectrophotometer and circular dichroism on a Roussel-Jouan Dichrographe II. Optical rotation was measured using a Perkin-Elmer polarimeter 141 and thermogravimetric measurements were performed with the thermobalance described by Pedersen.[6] X-Ray powder photographs were taken using a focussing Guinier type camera and Cu$K\alpha$ radiation.

Preparation and separation of the lel_3- and ob_3-isomers. A 6.28 g sample of (−)chxn (55.0 mmol, *ca.* 25 % excess) was dissolved in 6.5 ml of water in a test tube, and carbon dioxide was bubbled through the solution until a slight amount of white precipitate had formed (*ca.* 1 min). 5.35 g of $IrCl_3$.aq (14.5 mmol) were then added. (It is sometimes necessary to moderate the reaction by cooling the tube under the water tap). After 5 min the mixture was carefully heated to boiling and then boiled until an orange-brown solution containing a small amount of fine precipitate had formed. The test tube was sealed, placed in an autoclave containing a little water, and the autoclave was kept in an oven at 170 °C for approx. 300 h and then allowed to cool to room temperature. At this point the reaction mixture consisted of large colourless crystals in a light yellow solution. After opening the tube the content was dissolved in water and the solution was filtered (Whatman No. 50). The filtrate was evaporated to dryness on a rotating vacuum evaporator (RVE) using a final water-bath temperature of 90 °C. The resulting beige solid was extracted using a mixture of 193 ml of ethanol and 34 ml of water by heating the mixture under reflux for 5 min and then leaving it to stand overnight. The mixture was filtered and the residue was washed with a mixture of 50 ml of ethanol and 5 ml of water. (The filtrate and washings were reserved for the isolation of the lel_3-isomer).

The almost white residue (ob_3-chloride) was dissolved in the minimum necessary volume of boiling water (*ca.* 40 ml) and 18 ml of 14 M HNO_3 were added. The mixture was heated under reflux for 1 h and then allowed to stand overnight. The white precipitate was filtered off, washed with water and dissolved in the minimum necessary volume of boiling water (*ca.* 125 ml). After filtering the solution, the filtrate was heated to boiling, 50 ml of 14 M HNO_3 were added, and the mixture was allowed to stand overnight. The white precipitate was then filtered off, washed with water and dried in air. Yield 2.8 g (25 %) of $\Lambda(+)[Ir\{(-)C_6H_{14}N_2\}_3\text{-}\lambda\lambda\lambda](NO_3)_3.3H_2O$. (Found: C 27.79; N 16.34; H 6.20. Calc: C 27.90; N 16.27; H 6.24).

The ob_3-nitrate was dissolved in 90 ml of 12 M HCl by heating to boiling and the solution was heated under reflux for 5 min. It was then allowed to stand for 30 min before being evaporated to dryness on an RVE. The white residue was dissolved in the minimum necessary volume of boiling water (*ca.* 35 ml), 12 ml of 12 M HCl were added and the solution was then left to stand overnight. The resulting crystals of ob_3-chloride were isolated by filtration, washed, first with two 1 ml portions of 4 M HCl, then with 1 ml of water, and dried in air. Yield 2.2 g of $\Lambda(+)[Ir\{(-)C_6H_{14}N_2\}_3\lambda\lambda\lambda]Cl_3$.aq.* (Found: C:N:Cl, 18.00:6.033:3.000).

The ethanolic solution of lel_3-chloride (remaining from the separation of the diastereoisomers) was evaporated to dryness on an RVE. The light brown residue was dissolved in the minimum necessary volume of boiling water (*ca.* 32 ml) and 15 ml of 14 M HNO_3 were added. The mixture was heated under reflux for 1 h and then allowed to stand overnight. The resulting light brown precipitate was filtered off, washed with water and extracted with 450 ml of water under reflux. The mixture was then filtered to remove a brown voluminous impurity. The filtrate was heated to boiling after which 180 ml of 14 M HNO_3 were added and the mixture left to stand overnight. The white precipitate was isolated by filtration, washed with water and dried in air. Yield 6.5 g (57 %) of $\Delta(+)[Ir\{(-)C_6H_{14}N_2\}_3\text{-}\lambda\lambda\lambda](NO_3)_3.3H_2O$. (Found: C 27.82; N 16.34; H 5.97. Calc: C 27.90; N 16.27; H 6.24).

The lel_3-nitrate was dissolved in 150 ml of 12 M HCl by heating under reflux for 5 min. The solution was then allowed to stand for 30 min before being evaporated to dryness on an RVE. The white residue was dissolved in the minimum necessary volume of boiling water (*ca.* 30 ml), 1.3 ml of 12 M HCl were added and the solution was left to stand overnight. The crystals of lel_3-chloride were filtered off, washed, first with two 1.5 ml portions of 0.5 M HCl, then with 1.5 ml of water, and dried in air. Yield 4.8 g of $\Delta(+)[Ir\{(-)C_6H_{14}N_2\}_3\lambda\lambda\lambda]$-

* The content of water of crystallization is somewhat variable. Between 0.5 and 1.2 mol H_2O/mol Ir were found by thermogravimetry.

Cl_3.aq.* (Found: C:N:Cl, 18.00:6.008:3.013).

The catoptromeric lel_3- and ob_3-complexes were prepared in an identical manner and with identical yields using (+)chxn.

Preparation of hexachloroiridate(III) salts. A solution of $[IrCl_6]^{3-}$ was prepared as follows: 0.373 g of $IrCl_3$.aq (1.02 mmol) was dissolved in 10 ml of boiling water. After the addition of 20 ml of 12 M HCl and a few crystals of ascorbic acid, the solution was heated to boiling and then allowed to cool. 6 ml portions of this solution were then added to solutions containing *ca.* 0.2 mmol of $[M(chxn)_3]Cl_3$.aq (M = Co, Rh, and Ir) in 2 ml of water, *i.e.* the mixtures from which the hexachloroiridates were precipitated were *ca.* 6 M in HCl and *ca.* 0.025 M in $[M(chxn)_3]^{3+}$ and $[IrCl_6]^{3-}$.

1. $\Delta(+)_{589}[Co\{(-)C_6H_{14}N_2\}_3\lambda\lambda\lambda][IrCl_6]$.aq. 0.117 g of $\Delta(+)_{589}[Co\{(-)chxn\}_3\lambda\lambda\lambda]Cl_3.4H_2O$ (0.202 mmol) was dissolved in 2 ml of water. On adding the 6 ml of hexachloroiridate(III) solution (0.203 mmol) a voluminous precipitate immediately formed. After 2 h the mixture was heated to boiling and allowed to cool. After a further 2 h a few crystals of ascorbic acid were added and the mixture was heated to boiling and then allowed to stand overnight. This heat treatment facilitated the settling of the precipitate. The product was filtered off, washed, first with two 1 ml portions of 6 M HCl, then with two 1 ml portions of water, and dried in air. Yield 0.16 g. (Found: C 25.52; N 9.90; H 5.63; Cl 23.83, *i.e.* C:N:H:Cl, 18.00:5.99:47.3:5.69).

2. $\Delta(+)[Rh\{(-)C_6H_{14}N_2\}_3\lambda\lambda\lambda][IrCl_6]$.aq was prepared in an analogous manner from 0.127 g of $\Delta(+)[Rh\{(-)chxn\}_3\lambda\lambda\lambda]Cl_3.4H_2O$ (0.203 mmol). Yield 0.13 g (Found: C 24.12; N 9.50; H 5.19; Cl 24.22, *i.e.* C:N:H:Cl, 18.00:6.08:46.2:6.12).

3. $\Delta(+)[Ir\{(-)C_6H_{14}N_2\}_3\lambda\lambda\lambda][IrCl_6]$.aq was prepared in an analogous way using 0.142 g of $\Delta(+)[Ir\{(-)chxn\}_3\lambda\lambda\lambda]Cl_3.3\frac{1}{2}H_2O$ (0.202 mmol). Yield 0.18 g (Found: C 22.14; N 8.65; H 4.68; Cl 21.76; Ir 39.32, *i.e.* C:N:H:Cl:Ir, 18.00:6.03:45.3:5.99:2.00. Thermogravimetry: 2.5 H_2O).

4. An attempt to prepare a hexachloroiridate(III) salt of an ob_3-isomer using the same procedure as described above but starting with a solution of 0.109 g of $\Lambda(+)[Rh\{(-)chxn\}_3\lambda\lambda\lambda]Cl_3.\frac{1}{2}H_2O$ (0.194 mmol) in 3 ml of water resulted in the formation of a white precipitate – denser than the previous ones – which shrank considerably on washing with water. The residue (0.05 g) was identified by its X-ray powder photograph as the ob_3-chloride.

* The content of water of crystallization is somewhat variable. Between 3.3 and 4.5 mol H_2O/mol Ir were found by thermogravimetry.

RESULTS

The absolute configurations of the iridium complexes have been assigned by correlation of the lel_3-isomers to $\Lambda(-)_{589}[Co\{(+)chxn\}_3\delta\delta\delta]Cl_3.5H_2O$, using the method of active racemates.[7]

The specific and molar rotations of the chlorides and nitrates are given in Table 1 and the electronic and circular dichroism spectra of the chlorides are shown in Fig. 1 (allowance has to be made for the variable content of water of crystallization of the weighed samples). Fig. 2 shows the spectra of the nitrates. It is noteworthy that the CD curve for the ob_3-isomer is all positive in the $d-d$ transition region and that $\Delta\varepsilon_{max}$ for the main band of the ob_3-isomer is numerically *ca.* four and a half times $\Delta\varepsilon_{max}$ for the main band of the lel_3-isomer (for the

Table 1. Specific rotations, [α], and molar rotations, [M], of the $\Delta(+)[Ir\{(-)chxn\}_3\lambda\lambda\lambda]^{3+}$ (lel_3) and $\Lambda(+)[Ir\{(-)chxn\}_3\lambda\lambda\lambda]^{3+}$ (ob_3) chlorides and nitrates in aqueous solution at 25 °C. Conc. *ca.* 1.6 mmol/l. [M] = [α]M/100 ([α] in deg. ml g^{-1} dm^{-1}; M = molecular weight).

		313 nm	364 nm	436 nm	546 nm	578 nm	589 nm
$\Delta(+)[Ir\{(-)chxn\}_3\lambda\lambda\lambda]Cl_3.3\frac{1}{2}H_2O$	[α]	915	640	412	243	214	205
	[M]	6440	4510	2900	1710	1510	1440
$\Lambda(+)[Ir\{(-)chxn\}_3\lambda\lambda\lambda]Cl_3.\frac{1}{2}H_2O$	[α]	392	278	102	45	38	35
	[M]	2550	1810	665	290	250	230
$\Delta(+)[Ir\{(-)chxn\}_3\lambda\lambda\lambda](NO_3)_3.3H_2O$	[α]	818	586	377	222	196	186
	[M]	6340	4540	2920	1720	1520	1440
$\Lambda(+)[Ir\{(-)chxn\}_3\lambda\lambda\lambda](NO_3)_3.3H_2O$	[α]	322	230	83.2	36	31	30
	[M]	2500	1780	645	280	240	230

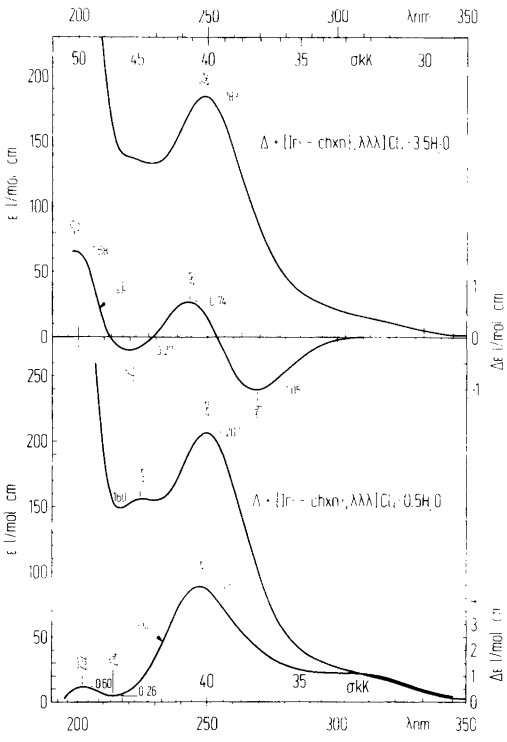

Fig. 1. Absorption and circular dichroism spectra of $\Delta(+)[Ir\{(-)chxn\}_3\lambda\lambda\lambda]Cl_3.aq$ (lel_3) and $\Lambda(+)[Ir\{(-)chxn\}_3\lambda\lambda\lambda]Cl_3.aq$ (ob_3).

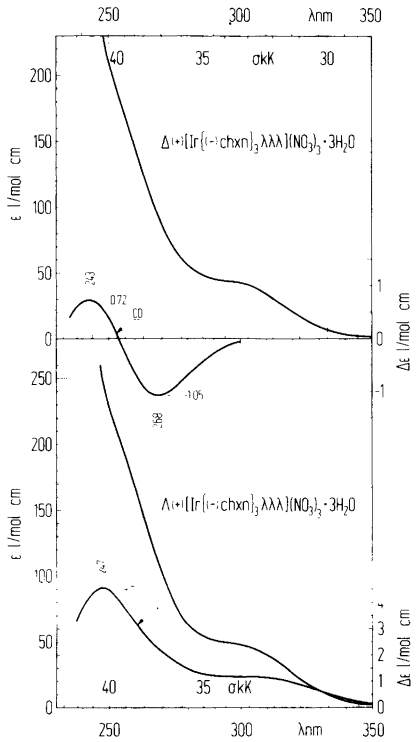

Fig. 2. Absorption and circular dichroism spectra of $\Delta(+)[Ir\{(-)chxn\}_3\lambda\lambda\lambda](NO_3)_3.3H_2O$ (lel_3) and $\Lambda(+)[Ir\{(-)chxn\}_3\lambda\lambda\lambda](NO_3)_3.3H_2O$ (ob_3).

analogous Cr, Co, and Rh compounds this ratio is *ca.* 1.6, 1.8, and 2.2, respectively). Apart from this the spectra show features similar to those of the corresponding Cr,[8] Co,[9] and Rh [5] complexes except for a triplet in $\Lambda(+)[Ir\{(-)chxn\}_3\lambda\lambda\lambda]^{3+}$ giving rise to some CD-intensity on the low energy side of the first spin allowed absorption band. The triplet can just be seen in the absorption spectra of both the lel_3- and ob_3-chlorides of iridium (Fig. 1). In the absorption spectra of the nitrates (Fig. 2) a combination of the absorption of this triplet and that of the nitrate ion which has an absorption band at *ca.* 300 nm ($\varepsilon_{max} = 7.2$ l mol^{-1} cm^{-1}) results in a plateau around *ca.* 295 nm.

X-Ray powder photographs show that the three compounds of the lel_3-series $\Delta[M\{(-)chxn\}_3\lambda\lambda\lambda](NO_3)_3.aq$ (M = Cr, Co, Rh, and Ir) are isomorphous, as are the members of the ob_3-series [10] $\Lambda[M\{(-)chxn\}_3\lambda\lambda\lambda](NO_3)_3.aq$. Saito *et al.* have determined the structure of one member of each series, *viz.* $\Lambda(+)[Rh\{(-)chxn\}_3\lambda\lambda\lambda](NO_3)_3.3H_2O$ [11] and $\Delta(+)[Rh\{(-)chxn\}_3\lambda\lambda\lambda](NO_3)_3.3H_2O$.[12] The analogous Cr- and Rh-compounds of both the lel_3- and ob_3-series have been syncrystallized and the chromium ESR spectra recorded.[13] The powder photographs also indicate great structural similarities between these two series, in accordance with the fact that both series belong to the hexagonal space group $P6_3$ ($Z = 2$). Both types of complex ions have rigorous threefold symmetry and are oriented with the C_3-axis parallel to the *c*-axis of the crystal.[11,12]

X-Ray powder photographs also show that the three complexes in the lel_3-series $\Delta[M\{(-)chxn\}_3\lambda\lambda\lambda][IrCl_6].aq$ (M = Co, Rh, and Ir) are isomorphous. A similar series of hexachlororhodate(III) salts can be prepared in an analogous fashion but the latter have been found to be non-isomorphous.

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