

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

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The isomers

$\Delta(+)[Rh\{(-)chxn\}_3\lambda\lambda\lambda]^{3+}$ (lel_3), $\Delta(+)[Rh\{(-)chxn\}_3\lambda\lambda\lambda]^{3+}$ (ob_3), $\Delta(-)[Rh\{(+)chxn\}_3\delta\delta\delta]^{3+}$ (lel_3), and $\Delta(-)[Rh\{(+)chxn\}_3\delta\delta\delta]^{3+}$ (ob_3) ($chxn = trans$ -1,2-cyclohexanediamine) have been isolated as chlorides and nitrates and characterized by their electronic and circular dichroism spectra, their optical rotation, and by thermogravimetry. The lel_3 chlorides are white whereas the ob_3 chlorides are yellowish, the yellowish colour being caused by a big redshift of the ligand field bands of the solids compared to solution. A similar behaviour is observed for the corresponding cobalt complexes.

The formula $[Rh\{(\pm)chxn\}_3]^{3+}$ ($chxn = trans$ -1,2-cyclohexanediamine) represents eight isomers caused by (1) the conformations of the chelate rings and (2) the absolute configuration of the complex. This work is limited to the four isomers which arise when only one of the enantiomers of $chxn$ is bound to the central atom. *trans*-(-)-1(*R*),2(*R*)-Cyclohexanediamine, (-) $chxn$, has a λ and (+) $chxn$ a δ conformation (IUPAC 1968).¹ Each one forms two diastereoisomeric tris-complexes, e.g. $\Delta(+)[Rh\{(-)chxn\}_3\lambda\lambda\lambda]^{3+}$ and $\Delta(+)[Rh\{(-)chxn\}_3\lambda\lambda\lambda]^{3+}$ denoted² lel_3 and ob_3 , respectively, using an obvious extension of the original notation of Corey and Bailar³ by which tris-complexes containing both (-) $chxn$ and (+) $chxn$ will be characterized as lel_2ob and ob_2lel .

Tris(*trans*-1,2-cyclohexanediamine)rhodium(III) complexes were first prepared by Jaeger and Bijkerk^{4,5} by the reaction of sodium hexachlororhodate(III) dodecahydrate with the (resolved or racemic) amine followed by precipitation with sodium iodide giving a yield of 94–96 % of the iodide. Although they were aware of the possibility of the formation of isomers, their discussion of the isomerism is unfortunate as it is not based on the

absolute configurations but on the optical rotation of the ligand and the complexes in the visible region. Their experimental results, that both in the cobalt- and the rhodium-series only $(+)[M\{(-)chxn\}_3]^{3+}$ or $(-)[M\{(+)chxn\}_3]^{3+}$ is formed⁴⁻⁶ when the metal is reacted with the optically active diamine, are uninterpretable as these formulas each represent two isomers, *e.g.* both the lel_3 - and the ob_3 -isomers of the $tris\{(-)chxn\}$ rhodium(III) ion (*vide supra*) have a positive rotation in the visible region (Table 2).

In the procedure described here rhodium(III) chloride is reacted with $(+)chxn$ or $(-)chxn$ (*ca.* 20 % excess) in aqueous solution and the reaction mixture evaporated to dryness. The residue is an approximately 8 : 5 mixture of the lel_3 - and the ob_3 -isomers from which the lel_3 -isomer can be extracted with *ca.* 80 % ethanol in which the ob_3 -isomer is practically insoluble. It is difficult to remove coloured impurities from these two diastereoisomeric chlorides. The nitrates of both isomers are, however, slightly soluble in water, and are also easily prepared as colourless crystals, so we chose to purify *via* the nitrates. The conversion of chlorides into nitrates was performed by adding an excess of concentrated nitric acid to a boiling aqueous solution of the chloride, after which the mixture was refluxed until the evolution of nitrogen oxides had ceased. The nitrate was then filtered and converted into the chloride by dissolution in concentrated hydrochloric acid followed by evaporation to dryness. For further purification the residue was dissolved in water after which iron(II) chloride and ammonia were added and iron(III) hydroxide precipitated by passing a stream of air through the mixture. The iron(III) hydroxide was filtered and the filtrate boiled with active carbon before it was evaporated to dryness. The residue was finally recrystallized from boiling water by addition of concentrated hydrochloric acid. (The lel_3 -isomer has a solubility minimum in *ca.* 0.5 M, the ob_3 -isomer in *ca.* 3 M hydrochloric acid.)

EXPERIMENTAL

Materials. Rhodium(III) chloride trihydrate: Johnson, Matthey and Co. (2.6 mol H_2O/mol Rh as determined by thermogravimetry). Cyclohexanediamine: BASF (through Wolff and Kaaber). A dark brown liquid with a normality of 16.64 as determined by titration with HCl (methylorange). The mixture contains, among other basic components, *cis*- and *trans*-1,2-cyclohexanediamine.

Physical measurements. Absorption spectra were recorded on a Cary 14 spectrophotometer and diffuse reflectance spectra on a Spectronic 505 spectrophotometer provided with an ultraviolet reflectance attachment. Circular dichroism was measured on a Roussel-Jouan Dichrographe I. Thermogravimetric measurements were performed on the thermobalance described by Pedersen.⁷ X-Ray powder photographs were taken with $CuK\alpha$ radiation using a focussing Guinier type camera.

Preparations

Preparation and separation of the lel_3 - and ob_3 -isomers. In a 1 l flask equipped with a condenser, a stirrer and a dropping funnel 29.09 g of $(-)chxn$ (0.255 mol) was dissolved in 213 ml of water. The solution was heated to boiling, and a solution of 18.80 g of $RhCl_3 \cdot 3H_2O$ (0.0714 mol) in 213 ml of water was added during a period of 15 min with stirring but without further heating. The reaction mixture immediately turned yellow and at the end of the addition it was yellow-brown and milky. After the addition

of 71 ml of ethanol, the reaction mixture was refluxed for 1 h, and the yellow solution evaporated to dryness in a rotating vacuum evaporator (RVE). The yellow residue was extracted with a mixture of 113 ml of water and 595 ml of ethanol by reflux for 5 min and allowed to stand overnight. The mixture was filtered and the residue washed with a mixture of 21 ml of water and 121 ml of ethanol. (The filtrate and washings were reserved for the isolation of the lel_3 chloride.) The beige residue (ob_3 chloride) was extracted on the filter with as little boiling water as possible (285 ml), and the yellow filtrate transferred to a 1 l flask equipped with a condenser and heated to boiling. Under continued heating 100 ml of 14 M HNO_3 was carefully added in 10 ml portions. (To control the reaction it may be necessary to cool the solution occasionally.) After about 1 h reflux, the evolution of nitrogen oxides stopped, and the reaction mixture was left overnight. After filtering, the crude product was washed with three 15 ml portions of water and dried in air. Yield ca. 17 g of an almost white product (ob_3 nitrate).

The crude ob_3 nitrate was placed in a 1 l flask equipped with a condenser. A 200 ml portion of 12 M HCl was added and the mixture was heated as fast as possible to the boiling point. The heating was continued for 5 min after the nitrate had dissolved, and the mixture was then allowed to stand for 3/4 h before it was evaporated to dryness in an RVE. The almost white residue (ob_3 chloride) was dissolved in 400 ml of water, and the solution was filtered. To the filtrate 1 g of $FeCl_2 \cdot 4H_2O$ and 10 ml of 12 M NH_3 was added and air was then passed through the solution for 1 1/2 h. The mixture was left overnight before filtering. Active carbon was added to the pale yellow filtrate, and the mixture was boiled for 5 min before filtering. The almost colourless filtrate was evaporated to dryness in an RVE. The residue (ob_3 chloride) was almost white but had a pale yellow tinge. It was dissolved in as little boiling water as possible (280 ml), 95 ml of 12 M HCl was added, and the solution was left overnight for crystallization. Before filtering, it was cooled in ice. The residue was washed with three 15 ml portions of ice-cold 3 M HCl and dried in air. Yield 12.4 g of pale yellow $\Delta(+)[Rh((-)C_6H_{14}N_2)_3\lambda\lambda\lambda]Cl_3 \cdot aq.$ (Found: C : N : Cl, 5.93 : 2.01 : 1.00.)

The ethanolic solution of lel_3 chloride (from the separation of the diastereoisomers) was evaporated to dryness in an RVE. The residue was transferred to a 1 l flask equipped with a condenser and dissolved in 235 ml of boiling water. Under continued heating 100 ml of 14 M HNO_3 was added in 10 ml portions. After 1 1/2 h reflux (some nitrogen oxides still appeared), the mixture was left overnight. After filtering, the crude product was washed with three 20 ml portions of water and dried in air. Yield ca. 27 g of a pale red product (lel_3 -nitrate). The crude lel_3 nitrate was converted into the chloride just as the ob_3 nitrate using 500 ml of 12 M HCl to produce the crude chloride which was dissolved in 450 ml of water. After treatment with iron(II) chloride and active carbon and evaporation to dryness, the lel_3 chloride was almost white. The product was dissolved in as little boiling water as possible (150 ml), 6.5 ml of 12 M HCl was added, and the solution was left overnight. After cooling in ice, filtration and washing with 0.5 M HCl, the product was dried in air. Yield 21.0 g of white $\Delta(+)[Rh((-)C_6H_{14}N_2)_3\lambda\lambda\lambda]Cl_3 \cdot aq.$ (Found: C : N : Cl, 5.97 : 2.02 : 1.00.)

In order to obtain a nearly quantitative use of the rhodium the corresponding nitrates were isolated from the mother liquors by the addition of enough 14 M HNO_3 to make the solution four molar with respect to nitric acid. The precipitated white nitrates were filtered and recrystallized from water. Yield 0.72 g of ob_3 nitrate (Found: C 31.4; N 18.5; H 7.0), and 4.2 g of lel_3 nitrate (Found: C 31.5; N 18.6; H 7.0. Calc. for $[Rh((-)C_6H_{14}N_2)_3](NO_3)_3 \cdot 3H_2O$: C 31.5; N 18.4; H 7.1).

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

Resolution of trans-1,2-cyclohexanediamine was performed by a modification of the method of Jaeger and Bijkerk.^{5,8} In a 1 l beaker 240 ml of the crude amine mixture (4 equiv. of base) was dissolved in 400 ml of water. The solution was heated to 90°C and first 150 g (1 mol) of (+)-tartaric acid, then 100 ml (1.7 mol) of glacial acetic acid was added in small portions with stirring (pH approx. 6). The mixture was cooled in ice with continued stirring. The precipitate was filtered in a basket centrifuge, washed, first with 80 ml of icecold water, then with 200 ml of ethanol and dried in air. Yield: 115 g of white, crystalline $\{(-)chxnH_2\} \{(+)\text{tart}\}$. (Found: C 45.49; H 7.74; N 10.74. Calc.: C 45.45; H 7.63; N 10.60.) $[\alpha_D]^{20} = 12.2^\circ$ (1% aqueous solution), 11.6° after recrystallization from water.

The mother liquor was heated to 80°C, 375 g (2.5 mol) of (+)-tartaric acid was added with stirring and the solution allowed to stand overnight at room temperature with continued stirring. The precipitate was filtered in a basket centrifuge, washed, first with 40 ml of icecold water, then with 200 ml of ethanol, and dried in air. Yield: 177 g of white, crystalline $\{(+)\text{chxnH}_2\}\{\text{H}(+)\text{tart}\}_2\cdot\text{H}_2\text{O}$. (Found: C 38.85; H 6.54; N 6.51. Calc.: C 38.89; H 6.53; N 6.48). $[\alpha_D]^{20} = 25.8^\circ$ (1% aqueous solution).

Liberation of (-)chxn. $\{(-)\text{chxnH}_2\}\{(+)\text{tart}\}$, 115 g (0.44 mol) was placed in a 1 l separating funnel. A solution of 100 g of KOH (1.8 mol) in 70 ml of water was added and the mixture shaken carefully. The amine layer was separated as rapidly as possible (*i.e.* before $\text{K}_2(+)\text{tart}$ started to precipitate), placed in a 1 l flask provided with a reflux condenser fitted with a KOH-tube, and diluted with 250 ml of ether. Sodium was added in excess, and the mixture was left overnight. The amine phase was then decanted, fresh sodium was added, and the mixture left overnight. The amine phase was decanted, treated with active carbon, and filtered under nitrogen. The yellowish solution was placed in a 500 ml flat flange flask which was placed in a water bath of room temperature, and the ether was evaporated by suction until the amine precipitated. The mixture was then cooled to -20°C before the precipitate was filtered, washed with ether (-20°C), and dried over potassium hydroxide. Yield: 34 g (68%). Another crop of crystals (7 g; 14%) was obtained by further evaporation of the filtrate and washings.

Liberation of (+)chxn was performed in the same way using 177 g (0.41 mol) of $\{(+)\text{chxnH}_2\}\{\text{H}(+)\text{tart}\}_2\cdot\text{H}_2\text{O}$, 100 g (1.8 mol) of KOH in 50 ml of water, and 250 ml of ether. Yield: 31+10 g (88%).

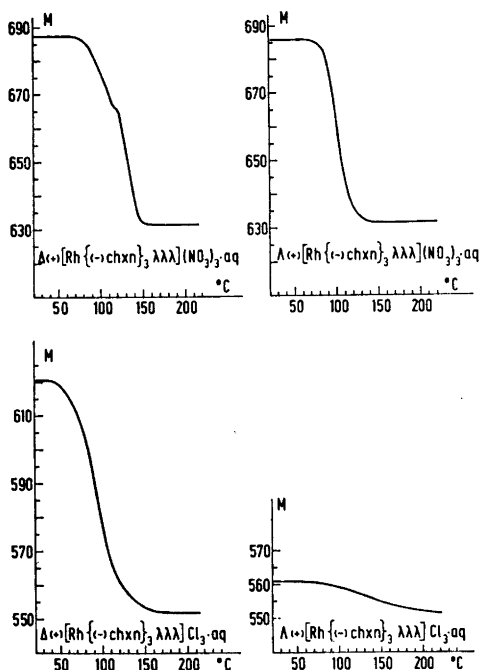


Fig. 1. Thermogravimetric analysis of the water content of the $[\text{Rh}\{(-)\text{chxn}\}_3\text{lel}_3]$ and $[\text{Rh}\{(-)\text{chxn}\}_3\text{ob}_3]$ chlorides and nitrates in air. The ordinate gives a number which is proportional to the sample weight, so that the starting value equals the molecular weight (corresponding to one rhodium atom) of the starting material.

RESULTS

The absolute configurations of the rhodium complexes have been assigned by correlation of the lel_3 -isomers to $\Delta(-)_{589}[\text{Co}\{(+)\text{chxn}\}_3\delta\delta\delta]\text{Cl}_3\cdot 5\text{H}_2\text{O}$ using the method of active racemates.² The racemates $\{\Delta(+)\}_{589}[\text{Co}$

$\{(-)chxn\}_3\lambda\lambda\lambda\}$ $\Delta(-)_{589}[Co\{(+)chxn\}_3\delta\delta\delta]Cl_6.aq$ and $\{\Delta(+)[Rh\{(-)chxn\}_3-\lambda\lambda\lambda] \Delta(-)[Rh\{(+)chxn\}_3\delta\delta\delta]Cl_6.aq$ and the active racemate $\{\Delta(+)[Rh\{(-)chxn\}_3\lambda\lambda\lambda] \Delta(-)_{589}[Co\{(+)chxn\}_3\delta\delta\delta]Cl_6.aq$ have almost identical X-ray powder photographs, differing from those of the optically active compounds.* A consideration of this together with other experimental data leads us to conclude that $\Delta(-)_{589}[Co\{(+)chxn\}_3\delta\delta\delta]^{3+}$ and $\Delta(-)-[Rh\{(+)chxn\}_3\delta\delta\delta]^{3+}$ have the same chirality. The absolute configuration of the cobalt-containing constituent of the active racemate has been determined ** by X-ray single crystal methods⁹ to be Δ and therefore the rhodium-containing constituent must have the absolute configuration Δ .

The water of crystallization of the complexes was determined by thermo gravimetry. Fig. 1 shows typical curves. Determined in this way the water content of the le_3 chlorides varies between 1.95 and 3.88 mol H_2O/mol Rh. For the ob_3 chlorides 0.5 mol H_2O/mol Rh is found, but here – as the curve shows – the water content is much less accurately determined. For the nitrates 3.10 mol H_2O/mol Rh for the le_3 -isomers and 3.00 mol H_2O/mol Rh for the ob_3 -isomers are found.

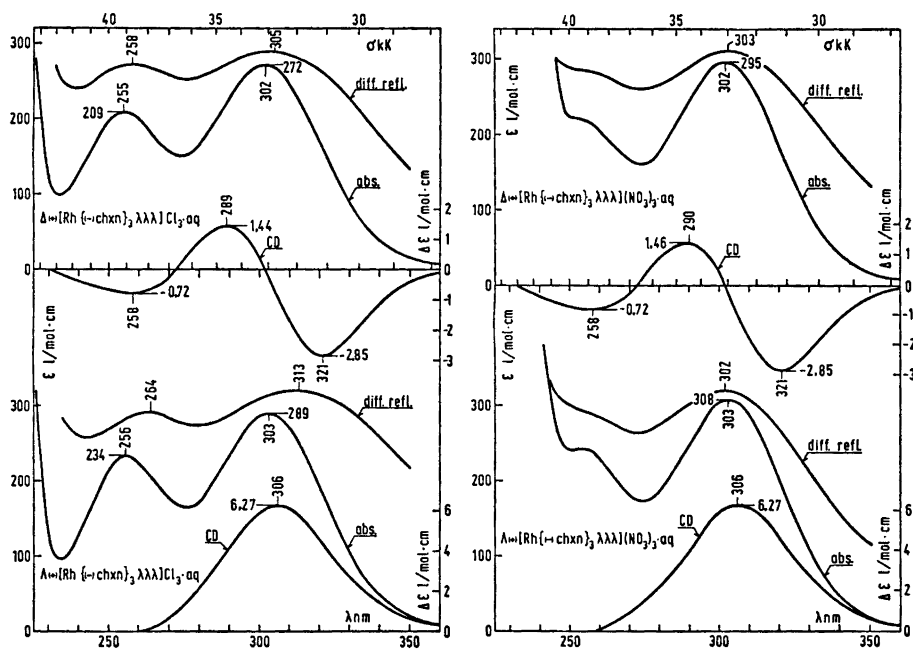


Fig. 2. Absorption, diffuse reflectance (on an arbitrary scale), and circular dichroism spectra of the $[Rh\{(-)chxn\}_3le_3]$ and $[Rh\{(-)chxn\}_3ob_3]$ chlorides and nitrates.

* The powder photographs show that optically active $[Rh\{chxn\}_3le_3]Cl_3.aq$ crystallizes in at least two modifications of which one has a powder photograph which is very like that of the corresponding cobalt compounds.

** The CD spectra showed that the cobalt-containing constituent of the active racemate was identical with $\Delta(-)_{589}[Co\{(+)chxn\}_3\delta\delta\delta]^{3+}$.

Table 1. The redshift, $\sigma_a - \sigma_r$, and the distance, $\sigma_{II} - \sigma_I$, between the ligand field bands I and II (${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$, respectively, with assignments corresponding to octahedral symmetry) for some tris((-)chxn) complexes of Rh(III) and Co(III) together with the octahedral ligand field parameter, $\Delta = E(e_g) - E(t_{2g})$, the Racah parameter, B , and the field strength parameter, $\Sigma = \Delta/B$, calculated from the energy matrices for d^6 in octahedral symmetry with $C/B = 4$.

		σ_I cm ⁻¹	$(\sigma_a - \sigma_r)_I$ cm ⁻¹	σ_{II} cm ⁻¹	$(\sigma_a - \sigma_r)_{II}$ cm ⁻¹	$\sigma_{II} - \sigma_I$ cm ⁻¹	Δ cm ⁻¹	B cm ⁻¹	Σ
$\Delta[\text{Rh}\{\text{chxn}\}_3\lambda\lambda\lambda]\text{Cl}_3\cdot\text{aq}$	abs.	33 110		39 120		6010	34 500	401	85.9
	refl.	32 830	280	38 680	440	5850	34 200	390	87.6
$\Delta[\text{Rh}\{\text{chxn}\}_3\lambda\lambda\lambda]\text{Cl}_3\cdot\text{aq}$	abs.	32 990		39 000		6010	34 300	401	85.5
	refl.	31 920	1070	37 950	1050	6030	33 200	404	82.3
$\Delta[\text{Co}\{\text{chxn}\}_3\lambda\lambda\lambda]\text{Cl}_3\cdot\text{aq}$	abs.	21 140		29 240		8100	22 800	594	38.5
	refl.	20 940	200	28 900	340	7960	22 600	583	38.8
$\Delta[\text{Co}\{\text{chxn}\}_3\lambda\lambda\lambda]\text{Cl}_3\cdot\text{aq}$	abs.	21 140		29 240		8100	22 800	594	38.5
	refl.	20 370	770	28 330	910	7960	22 000	587	37.6

In Fig. 2 the electronic and circular dichroism spectra of the complexes are shown. Four further recrystallizations had no effect either on the absorption spectra (the extinction coefficients in the maxima varying less than 0.5 % from the average) or on the CD spectra ($\Delta\varepsilon$ in the maxima varying less than 3 % from the average) when allowance was made for variable water content of the weighed samples. After the purification described in the experimental section, the lel_3 chloride is white whereas the ob_3 chloride is yellowish, but their ligand field spectra in solution (Fig. 2) are nearly identical. We therefore measured the diffuse reflectance spectra (Fig. 2) which show that the yellowish colour of the ob_3 chloride is caused by a large redshift of the ligand field bands of the solid compared to the solution. The nitrates are both white in the solid state, and their ligand field bands are only slightly shifted (Fig. 2).

A similar behaviour is observed for the corresponding cobalt chlorides. The energy differences are given in Table 1. It is seen that going from solution spectra to diffuse reflectance spectra, the ligand field parameter Δ is shifted approximately four times as much for the ob_3 -isomer as for the lel_3 -isomer.

Table 2. Molar rotations, $[\text{M}]$, of the $[\text{Rh}\{(-)\text{chxn}\}_3\text{lel}_3]$ and $[\text{Rh}\{(-)\text{chxn}\}_3\text{ob}_3]$ chlorides and nitrates in aqueous solution at 25°C. Conc. ca. 0.077 g/50 ml. $[\text{M}] = [\alpha] \text{ M}/100$; $[\alpha]$ in deg. ml g⁻¹ dm⁻¹.

	313 nm	364 nm	436 nm	546 nm	578 nm	589 nm
$\Delta(+)[\text{Rh}\{(-)\text{chxn}\}_3\lambda\lambda\lambda]\text{Cl}_3\cdot\text{aq}$	4440	4460	3450	2040	1800	1710
$\Delta(+)[\text{Rh}\{(-)\text{chxn}\}_3\lambda\lambda\lambda]\text{Cl}_3\cdot\text{aq}$	4000	3950	1150	435	362	336
$\Delta(+)[\text{Rh}\{(-)\text{chxn}\}_3\lambda\lambda\lambda](\text{NO}_3)_3\cdot\text{aq}$	4480	4500	3480	2050	1810	1730
$\Delta(+)[\text{Rh}\{(-)\text{chxn}\}_3\lambda\lambda\lambda](\text{NO}_3)_3\cdot\text{aq}$	4010	3920	1140	424	357	325

On the other hand the effect on the Racah parameter B is larger for the lel_3 -isomer than for the ob_3 -isomer.

In Table 2 the molar rotations of the rhodium complexes are given. The values published by Jaeger and Bijkerk^{4,5} for the chlorides are approximately the averages of our values for the lel_3 - and the ob_3 -isomers.

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