ACTA CHEMICA SCANDINAVICA 27 (1973) 3973–3978

Correlation of the Absolute Configurations of Tris-(*trans*-1,2-cyclohexanediamine) Complexes of Cr(III), Co(III), Rh(III), and Ir(III) by Means of X-Ray Powder Photographs of Active Racemates

P. ANDERSEN, F. GALSBØL, S. E. HARNUNG and T. LAIER

Chemistry Department I (Inorganic Chemistry), H. C. Ørsted Institute, Universitetsparken 5, DK 2100 Copenhagen Ø, Denmark

Racemates and active compounds of [M $chxn_3$]Cl_3.aq and active racemates {[M′$chxn_3$][M″$chxn_3$]}Cl_6.aq have been prepared, where M is one of the metals Cr, Co, Rh, and Ir; M′ and M″ denote two different metals, and chxn = *trans*-1,2-cyclohexanediamine. From X-ray powder photographs of these compounds it has been possible to conclude that the isomers of $(-)_{589}$[Co(+)$chxn_3$]$^{3+}$, $(-)_{589}$[Cr(+)-$chxn_3$]$^{3+}$, (−)[Rh(+)$chxn_3$]$^{3+}$, and (−)[Ir(+)$chxn_3$]$^{3+}$ which have a positive rotational strength for the spin-allowed ligand field band with lowest energy have the same absolute configuration. This absolute configuration is *Λ* (from other considerations), and the ring conformation is *δ* (IUPAC 1968). A determination of the space groups by single crystal X-ray diffraction showed that the tetragonal cells of the racemates ($I\bar{4}2d$) differ only slightly from the orthorhombic cells of the active racemates ($I2_12_12_1$).

An earlier investigation[1] of the correlation of the absolute configurations of tris(diamine) complexes by means of X-ray powder photographs of active racemates included the tris(ethylenediamine) and tris(propylenediamine) complexes of chromium(III), cobalt(III), and rhodium(III). The tris-complexes were all of the lel_3 type[1] and the investigation led to a clear correlation of the absolute configurations within each of the two series. We concluded that the method is convenient for correlating the absolute configurations in such systems, and we present here a similar investigation of the lel_3 isomers of the tris(*trans*-1,2-cyclohexanediamine) complexes of chromium(III), cobalt(III), rhodium(III), and iridium(III).

We have prepared some of the active racemates, {*Δ*[M′ $chxn_3$; lel_3] *Λ*[M″ $chxn_3$; lel_3]}Cl_6.aq, M′ and M″ being two of the metals Cr, Co, Rh, and Ir, and compared their X-ray powder photographs with those of the ordinary racemates and active forms. In this way it has been possible to correlate the

Table 1. X-Ray powder data of racemates and active racemates. Unit cell dimensions and densities for some of the table.

	[Cr chxn$_3$]Cl$_3$.aq rac, lel$_3$			[Co chxn$_3$]Cl$_3$.aq rac, lel$_3$			[Rh chxn$_3$]Cl$_3$.aq rac, lel$_3$			[Ir chxn$_3$]Cl$_3$a.q rac, lel$_3$		
h k l	I_{obs}	d_{obs}(Å)	d_{calc}(Å)	I_{obs}	d_{obs}(Å)	d_{calc}(Å)	I_{obs}	d_{obs}(Å)	d_{calc}(Å)	I_{obs}	d_{obs}(Å)	d_{calc}(Å)
1 1 0												
1 0 1 / 0 1 1	s	11.27	11.26	s	11.00	11.01	s	11.26	11.27	s	11.31	11.31
2 0 0 / 0 2 0	s	9.599	9.604	s	9.636	9.624	s	9.599	9.603	ms	9.577	9.582
2 1 1 / 1 2 1	vs	7.310	7.307	vs	7.252	7.246	vs	7.307	7.307	vs	7.307	7.310
1 1 2	m	6.192	6.190	ms	6.024	6.014	s	6.184	6.192	s	6.216	6.222
3 1 0 / 1 3 0	ms	6.076	6.074	ms	6.083	6.087	s	6.072	6.074	ms	6.059	6.061
3 0 1 / 0 3 1	vw	5.825	5.816	vvw	5.788	5.788						
2 0 2 / 0 2 2	vvw	5.643	5.632				vw	5.634	5.634	w	5.654	5.654
3 2 1 / 2 3 1	vw	4.972	4.975	vw	4.960	4.961	mw	4.975	4.975	ms	4.970	4.970
3 1 2 / 1 3 2	w	4.578	4.574	w	4.508	4.507	w	4.579	4.575	w	4.583	4.584
1 0 3 / 0 1 3	w	4.508	4.507	w	4.354	4.354	vw	4.506	4.508			
4 1 1 / 1 4 1	mw	4.419	4.417	w	4.411	4.409	vw	4.422	4.417	vvw	4.412	4.411
2 1 3 / 1 2 3	vvw	4.081	4.080				vw	4.082	4.081	w	4.101	4.101
4 0 2 / 0 4 2	vs	3.951	3.951	s	3.910	3.910	s	3.953	3.951	s	3.954	3.955
3 3 2	vw	3.792	3.794	vw	3.758	3.757	w	3.795	3.794	w	3.797	3.796
5 1 0 / 1 5 0							w	3.768	3.766	w	3.760	3.758
3 0 3 / 0 3 3	vvw	3.757	3.755	vvw	3.667	3.668						
4 3 1 / 3 4 1	w	3.703	3.703	vw	3.701	3.700	w	3.700	3.702	vw	3.697	3.697
4 2 2 / 2 4 2	m	3.653	3.654	s	3.622	3.622	ms	3.653	3.654	m	3.656	3.655
3 2 3 / 2 3 3	mw	3.495	3.497	mw	3.428	3.427	ms	3.500	3.498	ms	3.509	3.508
0 0 4				vvw	3.352	3.354	w	3.475	3.478			
5 2 1 / 2 5 1	w	3.457	3.455	w	3.451	3.453	m	3.455	3.454	mw	3.449	3.449
4 4 0							vvw	3.397	3.395	w	3.387	3.388
5 3 0 / 3 5 0				vvw	3.299	3.301						
4 1 3 / 1 4 3	mw	3.287	3.286	mw	3.230	3.229	w	3.287	3.286	mw	3.293	3.294
	$a=b=19.20_8$ Å $c=13.90_8$ Å $\alpha=\beta=\gamma=90.0°$			$a=b=19.24_8$ Å $c=13.42_0$ Å $\alpha=\beta=\gamma=90.0°$ Density: exp.: 1.411 g/ml calc.: 1.405 g/ml[d]			$a=b=19.20_6$ Å $c=13.91_3$ Å $\alpha=\beta=\gamma=90.0°$			$a=b=19.16_4$ Å $c=14.00_9$ Å $\alpha=\beta=\gamma=90.0°$		

[a], [b], [c] Refer to observed diffraction lines which are given twice in the table. [d] The densities are calculated on *per* metal atom (the average found for these compounds by thermogravimetric analysis).

the compounds (measured by flotation in carbon tetrachloride/toluene mixtures) are given at the bottom of

CrCo chxn$_6$ Cl$_6$.aq act rac, lel$_3$			CoRh chxn$_6$ Cl$_6$.aq act rac, lel$_3$			CoIr chxn$_6$ Cl$_6$.aq act rac, lel$_3$			
I_{obs}	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	d_{obs} (Å)	d_{calc} (Å)	$h\ k\ l$
						w	13.61	13.59	1 1 0
ms	11.08	11.12 11.06	vs	11.17	11.16 11.12	m (br.)	11.19	11.21 11.14	1 0 1 0 1 1
m	9.697	9.695	ms	9.704	9.682	mw	9.704	9.704	2 0 0
mw	9.547	9.547	ms	9.577	9.547	ms	9.533	9.526	0 2 0
ms	7.278	7.291	ms	7.314	7.300	s	7.307	7.317	2 1 1
m	7.240	7.242	ms	7.268	7.255	ms	7.255	7.255	1 2 1
m	6.055[a]	6.068	s	6.106	6.106	s	6.129	6.125	1 1 2
mw	6.116	6.122	(br.)		6.114	(br.)		6.127	3 1 0
m	6.055[a]	6.047	mw	6.051	6.046	mw	6.036	6.034	1 3 0
vvw	5.841	5.834							3 0 1
vvw	5.778	5.762							0 3 1
									2 0 2
			vvw	5.556	5.557	w	5.564	5.566	0 2 2
vvw	4.969	4.978	vw	4.971	4.979	w	4.984	4.987	3 2 1
(br.)		4.954	(br.)		4.957	w	4.954	4.955	2 3 1
vw	4.544	4.544							3 1 2
vvw	4.510	4.513	mw	4.525	4.529	w	4.529	4.531	1 3 2
w	4.399[b]	4.403	vw	4.432	4.435			4.452	1 0 3
		4.400	(br.)		4.432	vw	4.449	4.447	0 1 3
vw	4.438	4.439			4.438			4.449	4 1 1
w	4.399[b]	4.386							1 4 1
									2 1 3
									1 2 3
m	3.943	3.943	vs	3.953	3.950	m	3.963	3.962	4 0 2
m	3.906	3.904	vs	3.912	3.914	mw	3.911	3.912	0 4 2
vvw	3.768	3.770	mw	3.778	3.777	vw	3.779	3.782	3 3 2
									5 1 0
						vw	3.738	3.738	1 5 0
									3 0 3
									0 3 3
vvw	3.702	3.709							4 3 1
(br.)		3.695							3 4 1
mw	3.646	3.645	s	3.650	3.650	mw	3.659	3.658	4 2 2
mw	3.620	3.622	s	3.629	3.628	w	3.628	3.628	2 4 2
mw	3.447[c]	3.453	w	3.469[a]	3.468	mw	3.476[a]	3.477	3 2 3
(br.)		3.446	ms	3.459	3.460	mw	3.465	3.466	2 3 3
vvw	3.385	3.390	w	3.408[b]	3.418				0 0 4
vw	3.473	3.473	w	3.469[a]	3.471	mw	3.476[a]	3.478	5 2 1
mw	3.447[c]	3.437	m	3.441	3.438	mw	3.434	3.433	2 5 1
(br.)			w	3.408[b]	3.399				4 4 0
vvw	3.310	3.312							5 3 0
			vw	3.286	3.286				3 5 0
vw	3.263	3.258	mw	3.270	3.269	w	3.281	3.279	4 1 3
vw	3.235	3.236	mw	3.252	3.249	vw	3.252	3.252	1 4 3

$a = 19.39_0$ Å
$b = 19.09_5$ Å
$c = 13.56_3$ Å
$\alpha = \beta = \gamma = 90.0°$

$a = 19.36_3$ Å
$b = 19.09_4$ Å
$c = 13.67_0$ Å
$\alpha = \beta = \gamma = 90.0°$

$a = 19.41_2$ Å
$b = 19.04_8$ Å
$c = 13.72_0$ Å
$\alpha = \beta = \gamma = 90.0°$

Density:
exp.: 1.456 g/ml
calc.: 1.440 g/ml[d]

the basis of eight metal atoms *per* unit cell and on the assumption that there is one water of crystallization

absolute configurations of the ions act[M chxn$_3$; lel$_3$]$^{3+}$, M being Cr, Co, Rh, or Ir. The space groups have been determined for the racemates as well as for the active racemates from single crystal X-ray diffraction data.

EXPERIMENTAL

X-Ray powder photographs were taken at 25°C with Cu$K\alpha$ radiation using a focussing camera of the Guinier type, calibrated with silicon.

Single crystal X-ray diffraction has been carried out on rac[Co chxn$_3$; lel$_3$]Cl$_3$.aq and act rac{Λ[Co chxn$_3$; lel$_3$] Δ[Rh chxn$_3$; lel$_3$]}Cl$_6$.aq. Using Cu$K\alpha$ radiation, equiinclination Weissenberg and precession photographs were obtained of crystals of dimensions 0.05, 0.05, and 0.3 mm in the *a*, *b*, and *c* direction, respectively, the *c*-axis being the axis of rotation.

Optically active complexes were prepared as described elsewhere: act[Cr chxn$_3$; lel$_3$]-Cl$_3$.aq,[2] act[Co chxn$_3$; lel$_3$]Cl$_3$.aq,[3] act[Rh chxn$_3$; lel$_3$]Cl$_3$.aq,[4] and act[Ir chxn$_3$; lel$_3$]Cl$_3$.aq.[5]

Racemic complexes. 0.25 g of rac[Cr chxn$_3$; lel$_3$]Cl$_3$.aq[2] was recrystallized from 7.0 ml of water at 47°C. After 1 h at 0°C 0.19 g was obtained. Recrystallization was repeated using 5.5 ml of water; yield 0.11 g.

rac[Co chxn$_3$; lel$_3$]Cl$_3$.aq was prepared from a solution of 1.0 g of Λ[Co chxn$_3$; lel$_3$]Cl$_3$.4H$_2$O in 13 ml of water and a solution of 1.0 g of Δ[Co chxn$_3$; lel$_3$]Cl$_3$.4H$_2$O in 13 ml of water. The two solutions were heated to boiling and were rapidly mixed, and precipitation soon commenced. After cooling to room temperature the precipitate was filtered off, washed with 40 % ethanol, and dried in air; yield 0.95 g. Another crop was obtained by heating the mother liquor to boiling and adding 12 M hydrochloric acid to make the solution 0.5 M with respect to HCl. After cooling, the crystals were filtered off, washed with water, and dried in air; yield 0.49 g. The two fractions had identical X-ray powder photographs.

rac[Rh chxn$_3$; lel$_3$]Cl$_3$.aq (yield 0.79 + 0.78 g) was prepared in an analogous manner from 1.0 g of Δ[Rh chxn$_3$; lel$_3$]Cl$_3$.4H$_2$O in 16 ml of water and 1.0 g of Λ[Rh chxn$_3$; lel$_3$]Cl$_3$.4H$_2$O in 22 ml of water.

Similarly rac[Ir chxn$_3$; lel$_3$]Cl$_3$.aq (yield 0.57 + 0.24 g) was prepared from 0.51 g of Δ[Ir chxn$_3$; lel$_3$]Cl$_3$. 3.5H$_2$O in 7 ml of water and 0.51 g of Λ[Ir chxn$_3$; lel$_3$]Cl$_3$. 3.5H$_2$O in 7 ml of water.

Active racemates. act rac{Δ[Cr chxn$_3$; lel$_3$]Λ[Co chxn$_3$; lel$_3$]}Cl$_6$.aq: 0.46 g of Δ[Cr chxn$_3$; lel$_3$]Cl$_3$.aq was dissolved in 6.4 ml of water at 65°C. This solution was rapidly mixed with a solution of 0.46 g of Λ[Co chxn$_3$; lel$_3$]Cl$_3$.aq in 3.2 ml of water at 65°C. The precipitate, 0.39 g, formed at 0°C, was recrystallized twice from water and the fractions had identical CD-spectra. In the last recrystallization 0.21 g of the active racemate was dissolved in 3.2 ml of water at 50°C. This solution was left for 1 h at 0°C to yield 0.12 g.

act rac{Λ[Co chxn$_3$; lel$_3$]Δ[Rh chxn$_3$; lel$_3$]}Cl$_6$.aq was prepared from a solution of 1.0 g of Δ[Rh chxn$_3$; lel$_3$]Cl$_3$.4H$_2$O in 16 ml of water and a solution of 1.0 g of Λ[Co chxn$_3$; lel$_3$]Cl$_3$.4H$_2$O in 13 ml of water. The two solutions were heated to boiling and rapidly mixed, and precipitation soon commenced. After cooling to room temperature the precipitate was filtered off, washed with 40 % ethanol and dried in air; yield 0.96 g. Another crop was obtained by heating the mother liquor to boiling and adding 12 M hydrochloric acid to make the solution 0.5 M with respect to HCl. After cooling the crystals were filtered off, washed with water, and dried in air; yield 0.60 g. The two fractions had identical X-ray powder photographs.

act rac{Λ[Co chxn$_3$; lel$_3$]Δ[Ir chxn$_3$; lel$_3$]}Cl$_6$.aq (yield 0.58 + 0.38 g) was prepared in an analogous way from 0.66 g of Δ[Ir chxn$_3$; lel$_3$]Cl$_3$.3.5H$_2$O in 9 ml of water and 0.59 g of Λ[Co chxn$_3$; lel$_3$]Cl$_3$.4H$_2$O in 8 ml of water.

RESULTS AND CONCLUSION

The powder photographs of the racemates and active racemates have been indexed assuming tetragonal and orthorhombic unit cells, respectively. Observed and calculated *d*-spacings and relative intensities of the diffraction

lines are given in Table 1. The unit cell dimensions and densities are given at the bottom of the table.

Table 1 shows that all the powder photographs have similar patterns and correspondingly the indexing has a general resemblance for all the compounds. The powder diagrams of the racemates have been indexed on the basis of tetragonal unit cells, the active racemates on the basis of orthorhombic unit cells, and there are only small, variations in the unit cell dimensions from one compound to another. A comparison of the photographs of the racemates with those of the active racemates shows that many lines on the racemate diagrams appear to be split into two lines on the active racemate diagrams. In most cases two such lines have nearly equal intensities. As mentioned previously,[1] racemates and active racemates cannot be expected to belong to the same crystal system, because any symmetry element which might connect the catoptromers in the racemates must be absent in the active racemates. However, for the ethylenediamine and propylenediamine complexes it was found [1] that the racemates as well as the active racemates belong to the hexagonal system. In the present case of cyclohexanediamine complexes it is observed that the racemates belong to the tetragonal system, whereas the active racemates belong to the orthorhombic system. Here, the two tetragonal axes of equal length in the racemates correspond to two axes of slightly different lengths in the active racemates, giving rise to the observed splitting of diffraction lines with $h \neq k$.

The resemblance between all the powder photographs in Table 1, which is also reflected in the indexing, shows that the structures of the crystals involved are very much alike, from which we conclude that $(-)_{589}$[Co(+)-chxn$_3$]$^{3+}$, $(-)_{589}$[Cr(+)chxn$_3$]$^{3+}$, $(-)$[Rh(+)chxn$_3$]$^{3+}$, and $(-)$[Ir(+)chxn$_3$]$^{3+}$ (series I)* all have the same absolute configuration. From a single crystal structure analysis on $(-)_{589}$[Co(+)chxn$_3$]Cl$_3$.5H$_2$O [6] it is known that the configuration of this complex is Λ,lel$_3$. This salt is one of the starting materials in our preparation of the active racemates. Thus all the tris(cyclohexanediamine) complexes in series I are of the Λ,lel$_3$ type, *i.e.* the configuration is $\Lambda\delta\delta\delta$ (IUPAC 1968).[7]

It is noted that all the complexes of series I have positive circular dichroism for the major component under the spin-allowed ligand field band with lowest energy.

X-Ray powder photographs have been taken of all act[M chxn$_3$; lel$_3$]-Cl$_3$.aq (M being Cr, Co, Rh, or Ir). These compounds show similar diffraction patterns (hexagonal [6]), which are different from those of the racemates. The absolute configuration of the lel$_3$ complexes follows as Λ from the stereospecific coordination of the active (+)cyclohexanediamine,[8,9] and it is seen that there is agreement between this assignment and the correlation found by the active racemate method.

The unit cell dimensions indicate similar metal-ligand distances for Cr(III),

* Attention is drawn to the fact that for Rh and Ir [4,5] there are two isomers with the formula $(-)$[M(+)chxn$_3$]$^{3+}$, namely the lel$_3$-isomer and the ob$_3$-isomer.[1] This investigation concerns only the lel$_3$-isomers as revealed in the arguments to follow.

Rh(III), and Ir(III), and somewhat shorter distances for Co(III). This is as found earlier [1,10] for complexes of other diamines.

The single crystal work on rac[Co chxn$_3$; lel$_3$]Cl$_3$.aq shows that the space group of this salt is $I\bar{4}2d$ (No. 122, *Intern. Tables*). This result is based on the systematic absence of reflexions ($h+k+l\neq 2n$ for hkl, and $2h+l\neq 4n$ for hhl), on diffraction symmetry, and on the condition that in the unit cell there are eight metal atoms (Table 1) which cannot be placed at mirror planes or at centers of inversion.

The space group of act rac{Λ[Co chxn$_3$; lel$_3$]Δ[Rh chxn$_3$; lel$_3$]}Cl$_6$.aq has in the same way (absent reflexions: $h+k+l\neq 2n$ for hkl, and 2×4 metal atoms in the unit cell) been determined to be either $I222$ (No. 23, *Intern. Tables*) or $I2_12_12_1$ (No. 24, *Intern. Tables*). In the racemate the cobalt atoms must be placed at special positions, namely on 2-fold axes perpendicular to the 4-fold inversion axis. The 2-fold axes containing the one catoptromer are perpendicular to the 2-fold axes containing the other catoptromer. The choice of possible positions for the large complex molecules is thus highly restricted. When the metal of one of the catoptromers in the cobalt racemate is replaced by rhodium as in the active racemate, then the 4-fold inversion axes become 2-fold axes, the "diamond" glide planes vanish, and the a-axis need no longer be equal in length to the b-axis. If all other symmetry elements from $I\bar{4}2d$ are maintained and we still have $\alpha=\beta=\gamma=90°$, then just the orthorhombic subgroup of $I\bar{4}2d$, $I2_12_12_1$, is obtained. Thus $I222$ can be disregarded. This is supported by the fact that it seems impossible to place eight complex molecules in a unit cell of the dimensions found if the space group is $I222$.

REFERENCES

1. Andersen, P., Galsbøl, F. and Harnung, S. E. *Acta Chem. Scand.* **23** (1969) 3027.
2. Harnung, S. E. and Laier, T. *Acta Chem. Scand. To be submitted.*
3. Harnung, S. E., Sørensen, B. S., Creaser (Olsen), I., Maegaard, H., Pfenninger, U. and Schäffer, C. E. *Acta Chem. Scand. To be submitted.*
4. Galsbøl, F., Steenbøl, P. and Sørensen, B. S. *Acta Chem. Scand.* **26** (1972) 3605.
5. Galsbøl, F. *Acta Chem. Scand. To be submitted.*
6. Marumo, F., Utsumi, Y. and Saito, Y. *Acta Cryst.* **B 26** (1970) 1492.
7. IUPAC, *Information Bulletin* No. 33 (1968) 68; *Inorg. Chem.* **9** (1970) 1; IUPAC, *Nomenclature of Inorganic Chemistry*, 2nd Ed., Definitive rules 1970, Butterworths, London 1971, p. 75.
8. Corey, E. J. and Bailar, J. C., Jr. *J. Am. Chem. Soc.* **81** (1959) 2620.
9. Sargeson, A. M. In Carlin, R. L., Ed., *Transition Metal Chemistry*, Marcel Dekker, New York 1966, Vol. 3, p. 303.
10. Andersen, P. and Josephsen, J. *Acta Chem. Scand.* **25** (1971) 3255.

Received June 22, 1973.