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The Phenomenon of Conglomerate Crystallization. XII. Spontaneous Resolution in Coordination Compounds. IX. The Structure of Racemic [*cis*-α-Rh(trien)$(NO_2)_2$]Cl

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Abstract

The title compound crystallizes in the monoclinic space group $P2_1/n$ with cell constants: $a = 9.212(7)$, $b = 14.250(13)$, $c = 10.117(3)$ Å and $\beta = 92.46(4)°$; $V = 1326.82$ Å^3 and D(calc., $Z = 4$) = 1.885 gm cm^{-3}. A total of 3407 data were collected over the range of $4° \leqslant 2\theta \leqslant 55°$; of these, 2786 (independent and with $I \geqslant 3\sigma(I)$) were used in the structural analysis. The final $R(F)$ and $R_w(F)$ residuals were, respectively 0.032 and 0.052.

The Rh–N(NO_2) distances are 2.030(1) and 2.026(1) Å, while the Rh–N(amine) distances, *trans* to the NO_2 nitrogens are 2.090(1) and 2.091(1) Å, values distinctly longer than the other two Rh–N distances (2.078(1) and 2.060(1) Å). The latter are the Rh–N distances to the terminal–NH_2 ligands which are *trans* to each other. Thus, we observe a *trans* effect, which is more pronounced in the Rh than the Co analogue.

Parallel with the increase in metal–N distances (going from Co to Rh) is an increase in the torsional angles C–N–C–N which, in the former case, are 42.6, −40.4 and 39.3° while in the Rh compound are −50.7, 41.2 and −48.2°. Interestingly, the metal–N–C, N–C–C and C–C–N angles are little altered.

The N–O distances are 1.214(1), 1.240(1), 1.236(1) and 1.212(1) Å, which are nearly identical with those found for the analogous Co isomer. The C–N are 1.485(2), 1.495(2), 1.507(2), 1.495(2), 1.488(2) and 1.494(2) Å, while the C–C bonds are 1.516(2), 1.528(2) and 1.515(2) Å. These values are also comparable with those obtained for the Co isomer and, in fact, the pattern of the bonds is nearly identical in both.

Given the above, it is revealing that the Rh compound crystallizes as a racemate. We attribute this difference to the weaker hydrogen bonding between the oxygens of the –NO_2 ligands and the terminal –NH_2 hydrogens, a situation created by the inherently longer Rh–N bonds. In fact, the shortest intramolecular H bond present is O3···H2, which is *ca.* 2.45 Å and for which the ⟨N1–H2···O3 is 111°, values that render this 'bond' meaningless. The shortest hydrogen bond is an intermolecular bond between O2 and H17 on an adjacent molecule (2.17 Å) and the ⟨N4–H17···O = 174°.

As was the case with the Co analogue, the Cl$^-$ anion is associated with the hydrogens of the secondary nitrogens (*trans* to the –NO_2) ligands, the Cl···H7 distance being 2.16(2) Å and the ⟨Cl···H7–N2 = 164°.

Introduction

Sometime ago [1] we demonstrated that [*cis*-α-Co(trien)$(NO_2)_2$]Cl·H_2O (hereafter, **II**) crystallizes from water solutions, in the temperature range 5 to 26 °C, as a conglomerate of pure optically active crystals (space group $P2_12_12_1$) and attributed this behaviour to the dissymmetry induced by the formation of relatively strong hydrogen bonds between the oxygens of the –NO_2 ligands and the terminal amino hydrogens of the trien ligands. In a subsequent series of papers [2–8] we demonstrated that this concept is viable and crystal structures of suitable derivatives were provided as proof. Moreover, it was shown [4, 5] that the presence of charge compensating anions having strong hydrogen bonding ability often interferes with the process and racemic material is obtained – an observation consistent with the above statements.

We have attempted to obtain racemic and optically active crystals of the same compound in order to document the differences and/or similarities in inter- and intramolecular interactions present in such lattices. Several attempts (at temperatures of *ca.* 5 and 26 °C) have failed to produce crystals, of both type, suitable for X-ray diffraction. For example, [*cis*-Co$(en)_2(NO_2)_2$](NO_3) (hereafter, **III**) crystallizes [9] in the racemic space group $P2_1/n$. If the cation is resolved and converted to the nitrate salt, the resulting crystals are of such poor quality one cannot even index the space group. Other substances we have tried behave similarly. Therefore, in order to obtain

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data (structural and spectroscopic, for example) on chiral and racemic materials of comparable crystalline quality, we decided to approach the problem in a slightly different manner.

It is known that the metal–ligand distances (metal = Co and Rh) differ by *ca.* 0.1 Å. Consequently, it was our hope that by enlarging the distance between $-NO_2$ oxygens and terminal $-NH_2$ hydrogens we would obtain the racemic form of the Rh analogue of **II**. The results of our successful efforts are herein reported.

Experimental

Preparations

(a) Preparation of triethylenetetramine tetrahydrochloride (trien·4HCl)

The procedure is an adaptation of that by Glerup *et al.* [10]. 50 ml technical grade (Aldrich) triethylenetetramine (trien) are dissolved in 100 ml absolute ethanol and cooled to 0 °C. Slowly add 50 ml 12 M HCl while keeping the temperature below 10 °C. A white precipitate is formed which is filtered. It contains a contaminant of trien – the hydrochloride of tris(2-aminoethyl)amine).

Cool the filtrate below 10 °C and slowly add 65 ml of 12 M HCl. A white precipitate of (trien·4HCl) is formed. This is filtered and recrystallized from water–ethanol. The precipitate is washed with absolute ethanol, followed by ether.

(b) Preparation of $[Rh(trien)Cl_2]Cl$

The procedure was an adaptation of that by Johnson and Basolo [11] and using the pH control precautions suggested by Gidney *et al.* [12].

0.745 g $RhCl_3 \cdot 3H_2O$ (2.83×10^{-3} mol) is placed in a reaction flask with 0.865 g (trien·4HCl) and 0.294 g KOH, dissolved in 60 ml water, is added to the mixture. Stirring and reflux begin, whereupon the mixture is cloudy and reddish brown in color.

When the solution clears up, the color changes to a deep orange (*ca.* 45 min) and, at this point, a solution of 0.371 g KOH in 5 ml water is slowly added in order to free the remaining trien. Remove the reflux condenser, allow to cool and check the pH. If necessary add KOH to adjust the pH to 8. Reflux for 15 more minutes. Evaporate 2/3 of the solvent and place the solution in the refrigerator to crystallize the product. A light yellow crystalline material appears, which is filtered off. This is $[Rh(trien)Cl_2]Cl$, which is used to prepare the dinitro derivative.

(c) Preparation of $[Rh(trien)(NO_2)_2]Cl$

0.352 g $[Rh(trien)Cl_2]Cl$ are dissolved in 20 ml of water and a five-fold excess (0.68 g) of $NaNO_2$ added. The mixture was refluxed for one hour, during which time the solution became colorless. One half of the solvent was evaporated and the solution placed in a refrigerator to crystallize.

The crystals thus obtained are a mixture, as shown by (a) the elemental analysis* (Calc.: N, 22.3; Cl, 9.4; H_2O, 8.73. Found: N, 18.35; Cl, 9.69; H_2O, 8.18%) and (b) X-ray data collected on a crystal from this batch which was of poor quality. This substance crystallized in space group *Pbcm*(No. 57) or $Pca2_1$-(No. 29) with cell constants of $a = 25.090(11)$, $b = 8.357(10)$ and $c = 13.850(3)$ Å, and though the intensity data easily gave a solution for the position of the Rh atom and one five membered ring, the rest of the cation was disordered (*R* factor in *Pbcm* = 19%). Equally poor crystallographic results were obtained using the space group $Pca2_1$.

Crystal Growth of a Useful Crystal

The crystal used in the successful X-ray determination of **I** was obtained as follows. All the crystalline material obtained above was redissolved in a solution of NaCl (estimated to be *ca.* 2 M) and placed in the refrigerator at *ca.* 2 °C. After several days, one large crystal appeared which was nearly cubic in shape and *ca.* 1 mm on edge. This crystal was placed in an Enraf-Nonius spherizer and ground into a nearly perfect sphere of about 0.5 mm diameter. It was this crystal which was used for data collection.

X-ray Data Collection

Data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification [13] of the SDP-Plus software package [14]. The crystal used was a prolate spheroid ground from a much larger one (see above). The crystal was centered with data in the $20° \leqslant 2\theta \leqslant 30°$ range and examination of the cell constants and Niggli matrix [15] clearly showed it to crystallize in a primitive, monoclinic lattice whose systematic absences showed it to belong to the space group $P2_1/n$. The intensity data set was corrected for absorption using empirical curves derived from Psi scans [13, 14] of six reflections. The scattering curves were taken from Cromer and Waber's compilation [16].

The structure was solved from the Patterson map, using the Rh atom as the heavy atom. After refinement of the scale factor and the positional parameters of the Rh, a difference Fourier map, produced most of the non-hydrogen atoms; the rest were found in the second difference map. Heavy atoms were refined isotropically till convergence, at which point the hydrogen atoms of the cation were added at idealized positions (N–H, C–H = 1.00 Å) and all atoms allowed to refine with hydrogen thermal parameters

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TABLE I. Summary of Data Collection and Processing Parameters for Racemic [*cis*-α-Rh(trien)(NO$_2$)$_2$]Cl

Space group	$P2_1/n$
Cell constants	$a = 9.212(7)$ Å $b = 14.250(13)$ Å $c = 10.117(3)$ Å $\beta = 92.46(4)°$
Cell volume	$V = 1326.82$ Å^3
Molecular formula	$C_6H_{18}N_6O_4RhCl$
Molecular weight	376.61 gm mol^{-1}
Density (calc., $Z = 4$ mol/cell)	1.885 gm cm^{-1}
Radiation employed	Mo Kα (λ = 0.71073 Å)
Absorption coefficient	$\mu = 14.864$ cm^{-1}
Transmission coefficients	1.00 to 0.944
Data collection range	$4° \leqslant 2\theta \leqslant 40°$
Scan width	$\Delta\theta = 0.90 + 0.35 \tan\theta$
Total data collected	3407
Data used in refinement[a]	2786
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.032
$R_w = [\Sigma w^2(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.052
Weights used	$w = [\sigma(F_o)]^{-2}$

[a] The difference between this number and the total is due to subtraction of 621 data which either were systematically absent (but collected for verification of space group), were symmetry related, standards or did not meet the criterion that $I \geqslant 3\sigma(I)$.

fixed at 5.0 Å^2). Conversion of the heavy atoms to anisotropic motion and allowing the hydrogens to refine with fixed, isotropic (5.0 Å^2) thermal parameters resulted in refinement of the overall structure to final $R(F)$ and $R_w(F)$ factors of 0.033 and 0.055, respectively. Details of data collection and processing are summarized in Table I.

Figure 1 gives a labelled view of the molecule; Fig. 2 gives a stereo representation of which, the righthand side is identical with Fig. 1.

Final positional and equivalent-isotropic thermal parameters are given in Table II. Bond lengths, angles and torsional angles are given in Table III.

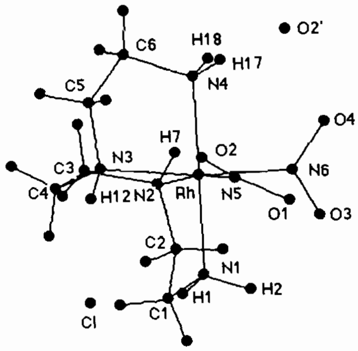

Fig. 1. Labelled view of the molecule. Note that the Cl$^-$ anion forms a hydrogen bond to H12 of 2.296 Å, while O2', which is part of an adjacent cation, forms an interionic hydrogen bond with H17 of 2.17 Å. The N4–H17···O2' angle is 174°. There is no intramolecular NO···H–N hydrogen bond of comparable strength, the shortest one being H2···O3 > 2.45 Å and the angle N1–H2···O3 = 111°, which renders this 'hydrogen bond' meaningless.

Discussion and Conclusions

(A) Mode of Crystallization of I

As we had hoped, the crystal of **I** was a racemate ($P2_1/n$); thus, even though a change of metals was necessary to achieve the desired goal, we are provided with an opportunity of comparing intra- and intermolecular interactions in two closely related compounds, one as a racemate and the other as an enantiomorph.

(B) Molecular Parameters in I and Comparison to II

There are no known structures of Rh derivatives of ethylenediamines or triens; therefore, inasmuch as the refinement is very satisfactory and the standard deviations small and uniform, we will assume they are typical of well behaved Rh compounds of this class.

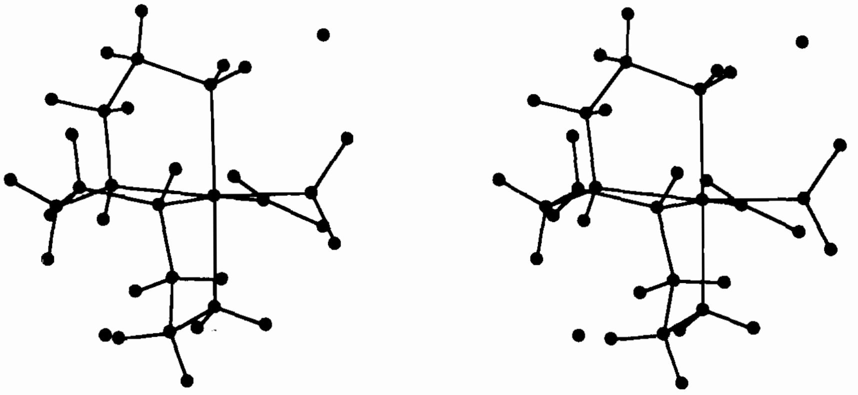

Fig. 2. Stereo pair of which the righthand view is identical with that appearing in Fig. 1.

TABLE II. Positional Parameters

Atom	x	y	z	B (Å^2)^a
Rh	0.25084(3)	0.09735(2)	0.15623(3)	1.434(6)
Cl	0.3065(2)	0.37523(8)	0.0963(1)	3.41(3)
O1	0.2497(4)	−0.0512(2)	−0.0322(4)	3.61(7)
O2	0.4235(4)	−0.0658(2)	0.1089(4)	3.39(7)
O3	0.0318(3)	0.1445(3)	−0.0419(3)	3.52(7)
O4	0.2455(4)	0.1633(3)	−0.1071(4)	3.92(8)
N1	0.0553(4)	0.0334(3)	0.1978(4)	2.15(7)
N2	0.1657(4)	0.2091(3)	0.2621(4)	2.25(7)
N3	0.3600(4)	0.0648(3)	0.3358(4)	2.43(7)
N4	0.4432(4)	0.1643(2)	0.1194(4)	2.22(7)
N5	0.3167(4)	−0.0210(2)	0.0646(4)	2.15(7)
N6	0.1648(4)	0.1420(3)	−0.0204(4)	2.13(7)
C1	−0.0253(5)	0.0909(3)	0.2927(5)	2.9(1)
C2	0.0055(5)	0.1936(3)	0.2662(5)	2.95(9)
C3	0.2435(5)	0.2170(3)	0.3957(5)	2.91(9)
C4	0.2979(6)	0.1212(3)	0.4444(5)	2.9(1)
C5	0.5183(5)	0.0793(4)	0.3203(5)	3.5(1)
C6	0.5426(5)	0.1672(4)	0.2399(5)	3.1(1)
H1	0.051(5)	−0.032(4)	0.238(5)	5.0*
H2	−0.004(5)	0.025(4)	0.131(5)	5.0*
H3	0.014(5)	0.068(4)	0.378(5)	5.0*
H4	−0.137(6)	0.078(4)	0.291(5)	5.0*
H5	−0.038(5)	0.239(4)	0.333(5)	5.0*
H6	−0.041(5)	0.200(4)	0.190(5)	5.0*
H7	0.197(5)	0.273(4)	0.215(5)	5.0*
H8	0.175(5)	0.241(4)	0.459(5)	5.0*
H9	0.332(5)	0.257(4)	0.385(5)	5.0*
H10	0.230(6)	0.089(3)	0.471(6)	5.0*
H11	0.380(6)	0.124(4)	0.538(5)	5.0*
H12	0.374(5)	0.008(4)	0.348(5)	5.0*
H13	0.569(5)	0.022(4)	0.277(5)	5.0*
H14	0.578(6)	0.070(4)	0.406(5)	5.0*
H15	0.652(5)	0.180(4)	0.216(5)	5.0*
H16	0.540(5)	0.227(4)	0.290(5)	5.0*
H17	0.484(5)	0.134(4)	0.060(5)	5.0*
H18	0.432(5)	0.227(4)	0.101(5)	5.0*

e.s.d.s are given in parentheses. [a]Starred atoms were refined isotropically, Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

TABLE III. Distances (Å) and Angles (°)

(a) Distances			
Rh–N1	2.078(1)	N1–C1	1.485(2)
Rh–N2	2.090(1)	C1–C2	1.516(2)
Rh–N3	2.091(1)	C2–N2	1.495(2)
Rh–N4	2.060(1)	N2–C3	1.507(2)
Rh–N5	2.030(1)	C3–C4	1.528(2)
Rh–N6	2.026(1)	C4–N3	1.495(2)
N5–O1	1.214(1)	N3–C5	1.488(2)
N5–O2	1.240(1)	C5–C6	1.515(2)
N6–O3	1.236(1)	C6–N4	1.494(2)
N6–O4	1.212(1)		
Hydrogen contacts less than 2.40 Å			
H17–O2	2.17 O2 at $1-x, -y, -z$		
(b) Angles			
N1–Rh–N2	83.26(4)	Rh–N1–C1	110.53(8)
N1–Rh–N3	96.64(4)	Rh–N2–C2	107.13(7)
N1–Rh–N4	178.07(4)	Rh–N2–C3	110.03(7)
N1–Rh–N5	90.40(4)	Rh–N3–C4	109.53(8)
N1–Rh–N6	90.36(4)	Rh–N3–C5	108.31(9)
N2–Rh–N3	84.30(4)	Rh–N4–C6	111.54(9)
N2–Rh–N4	94.84(4)	Rh–N5–O1	120.77(8)
N2–Rh–N5	173.20(4)	Rh–N5–O2	120.70(8)
N2–Rh–N6	94.13(4)	Rh–N6–O3	120.76(8)
N3–Rh–N4	82.81(4)	Rh–N6–O4	119.20(8)
N3–Rh–N5	94.04(4)	N1–C1–C2	108.4(1)
N3–Rh–N6	172.58(4)	C1–C2–N2	109.9(1)
N4–Rh–N5	91.48(4)	C2–N2–C3	114.7(1)
N4–Rh–N6	90.12(4)	N2–C3–C4	111.0(1)
N5–Rh–N6	88.34(4)	C3–C4–N3	112.0(1)
O1–N5–O2	118.5(1)	C4–N3–C5	114.2(1)
O3–N6–O4	120.0(1)	N3–C5–C6	109.9(1)
		C5–C6–N4	108.4(1)
(c) Torsional angles			
N2–Rh–N1–C1	−8.7	N2–Rh–N5–O1	82.5
N3–Rh–N1–C1	74.7	N2–Rh–N5–O2	−95.0
N4–Rh–N1–C1	1.6	N3–Rh–N5–O1	158.1
N5–Rh–N1–C1	168.9	N3–Rh–N5–O2	−19.4
N6–Rh–N1–C1	−102.8	N4–Rh–N5–O1	−119.0
N1–Rh–N2–C2	−18.2	N4–Rh–N5–O2	63.5
N1–Rh–N2–C3	107.1	N6–Rh–N5–O1	−28.9
N3–Rh–N2–C2	−115.6	N6–Rh–N5–O2	153.5
N3–Rh–N2–C3	9.7	N1–Rh–N6–O3	18.1
N4–Rh–N2–C2	162.1	N1–Rh–N6–O4	−159.4
N4–Rh–N2–C3	−72.5	N2–Rh–N6–O3	−65.1
N5–Rh–N2–C2	−39.5	N2–Rh–N6–O4	117.3
N5–Rh–N2–C3	85.8	N3–Rh–N6–O3	−142.6
N6–Rh–N2–C2	71.7	N3–Rh–N6–O4	39.8
N6–Rh–N2–C3	−163.0	N4–Rh–N6–O3	−160.0
N1–Rh–N3–C4	−70.4	N4–Rh–N6–O4	22.5
N1–Rh–N3–C5	164.4	N5–Rh–N6–O3	108.5
N2–Rh–N3–C4	12.1	N5–Rh–N6–O4	−69.0
N2–Rh–N3–C5	−113.1	Rh–N1–C1–C2	33.6
N4–Rh–N3–C4	107.7	Rh–N2–C2–C1	42.1
N4–Rh–N3–C5	−17.5	C3–N2–C2–C1	−80.4
N5–Rh–N3–C4	−161.3	Rh–N2–C3–C4	−29.5
N5–Rh–N3–C5	73.5	C2–N2–C3–C4	91.3

(continued)

In order to ascertain if there is a molecular basis for the differences in crystallization behaviour between **I** and **II**, we will now compare their molecular parameters, which qualitatively are very similar in that

(a) in both, metal–N(NO_2) bonds are shorter than metal–N(amine);

(b) in both, metal–N(secondary NH) are longer than metal–N(NH_2) bonds; this is the result of the *trans* effect, which is more pronounced in the Rh complex;

(c) for both, one of the M–NH_2 (terminal) distances is longer than the other;

TABLE III. *(continued)*

N6–Rh–N3–C4	90.2	Rh–N3–C4–C3	–31.9
N6–Rh–N3–C5	–35.0	C5–N3–C4–C3	89.8
N1–Rh–N4–C6	64.8	Rh–N3–C5–C6	40.4
N2–Rh–N4–C6	75.0	C4–N3–C5–C6	–82.0
N3–Rh–N4–C6	–8.6	Rh–N4–C6–C5	32.6
N5–Rh–N4–C6	–102.5	N1–C1–C2–N2	–50.7
N6–Rh–N4–C6	169.2	N2–C3–C4–N3	41.2
N1–Rh–N5–O1	61.4	N3–C5–C6–N4	–48.2
N1–Rh–N5–O2	–116.1		

(d) C–N distances and C–C distances follow the same pattern;

(e) the various angles are closely related in both.

However, since the Rh–N distances are longer (see below) and the trien chain retains nearly constant values of bond lengths and angles, the torsional angles of the N–C–C–N fragment must change, as shown in Scheme 1.

(1)	Co–N1	1.953(4)	Rh–N1	2.078(1)
	Co–N2	1.963(4)	Rh–N2	2.090(1)
	Co–N3	1.965(3)	Rh–N3	2.091(1)
	Co–N4	1.967(4)	Rh–N4	2.060(1)
	Co–N5	1.926(4)	Rh–N5	2.030(1)
	Co–N6	1.914(4)	Rh–N6	2.026(1)

(2)	N1–Co–N5–O1	–143.10	N1–Rh–N5–O1	61.4
	N1–Co–N5–O2	39.42	N1–Rh–N5–O2	–116.1
	N1–Co–N6–O3	–144.91	N1–Rh–N6–O3	18.1
	N1–Co–N6–O4	33.30	N1–Rh–N6–O4	–159.4
	N5–Co–N1–H1	–29.7	N5–Rh–N1–H1	48.5
	N5–Co–N1–H2	–148.7	N5–Rh–N1–H2	–71.5
	N5–Co–N4–H17	66.2	N5–Rh–N4–H17	16.6
	N5–Co–N4–H18	–53.0	N5–Co–N4–H18	143.6

Scheme 1.

Note that:

(a) The torsional angle of the central ring remains largely invariant (*i.e.* ⟨N2–C3–C4–N3 for **I** is 41.2° while for **II** is –40.4°).

(b) The average value of the N5–N1, N5–N4, N6–N1, N6–N4 distances in **I** and **II** are, respectively, 2.912 and 2.741 Å.

(c) In order to accommodate the increased bite across the octahedron, the outer rings, bearing the terminal –NH$_2$ hydrogens needed to form [1–8] hydrogen bonds with the –NO$_2$ oxygens, increase the N–C–C–N torsional angles of I by about 10°, each.

(d) This causes a fatal problem for the intramolecular hydrogen bonds needed [1–8] to anchor the clavic –NO$_2$ ligands in the needed dissymmetric orientation found in **II**. For example, the shortest intramolecular distances found for **II** and **I** are, respectively:

Compound II		Compound I	
N1–H1···O2	2.11 Å	N1–H1–O1	2.46
N4–H17–O3	2.24		

all other intramolecular hydrogens bond in **I** are larger than 2.50 Å. In fact, unlike **II**, where the Cl···H contacts are longer (shortest is Cl···H7 = 2.42 Å) than the intramolecular H···O bonds, in **I** the shortest Cl···H contact is Cl···H7 = 2.16 Å (*i.e.* it is shorter than any intramolecular hydrogen bond).

(e) Since the torsional angles differ so much in the two compounds, the nitro oxygens of **II** are no longer being directed as effectively by the terminal –NH$_2$ as they are in **I**. We have demonstrated how effective is this ability of –NH$_2$ hydrogens to control the stereochemistry of the –NO$_2$ ligands [1–8].

We know from previous experience [1–8], that for a given central ion, the trien skeleton is largely invariant to the nature of the metal complex. We demonstrated this very clearly in previous papers [1, 6]. Consequently, while leaving the Rh(trien) skeleton invariant, let us investigate torsional angular changes of the –NO$_2$ groups which lead to increases in the hydrogen bond strengths of **I**. The changes needed, and the consequences of those changes are:

(1) If the N5–O1–O1 ligand is rotated (*ca.* 20° counterclockwise) such that the N1–Rh–N5–O2 angle is 41.49°, the hydrogen bond O1···H2 is the shortest it can be, *i.e.* 2.39 Å.

(2) If the N6–O3–O4 group is rotated 42°, counterclockwise, O4···H17 reaches its smallest value (2.46 Å).

(3) Neither of those two hydrogen bonds is as strong as the interionic bond (see Table III) between O2′ and H, 2.17 Å.

(4) Those torsional motions lead to a O1–O3 contact across nitro groups of 2.92 Å – a value which is impossibly low since, as pointed out earlier [17], this distance should be about 3.2 Å.

On the assumption the excess chloride had nothing to do with the racemic crystallization mode of **I**, two important, and mutually coupled, stereochemical factors seem to be at play here: (a) The longer metal–N distances keep the NH$_2$ hydrogens and the NO$_2$ oxygens farther apart and (b) in order for the –HN–CH$_2$–CH$_2$–NH$_2$ rings to span the longer ligand bite distances required by Rh, a larger torsional angle, N–C–C–N, is required, as shown above (2). A model of this molecule readily reveals that this increase in torsional angle has the added effect of twisting the –NH$_2$ hydrogens even farther from the reach of the –NO$_2$ oxygens.

Consequently, the fact that **I** has the stereochemistry described is fully consistent with its not forming a conglomerate.

(C) Implications of this Structural Study for Conglomerate Crystallization

(a) The structure of **I** can be used as a model of what **II** should look like were the latter to crystallize as an anhydrous racemate. That is, the structure we have described for **I** has all of the characteristics we could preview from our experiences with racemates and conglomerates of these substances, *i.e.*

(1) The intramolecular N–H···O–N hydrogen bonds are no longer the strongest ones.

(2) The strongest hydrogen bonds are, interestingly, interionic – a surprising result since it involves hydrogen bonds between two cations.

(3) The two cations in question consist of a racemic pair related to one another by an inversion center (see above, specially the footnote of Fig. 1). Thus, this pair bears a relationship to one another similar to that racemic and enantiomeric amino acids display in the solid, *i.e.* the racemic species form centrosymmetric pairs related to one another by inversion centers, as in the case of solid acetic acid. The enantiomeric, solid amino acids cannot be thus related without disorder. Instead, those crystallizing in ordered structures form extensive hydrogen bonded ensembles of various types [18b].

(b) While we have not succeeded in crystallizing racemic and an enantiomorphic crystal of the exact same substance, **I** and **II** are an interesting pair of compounds because the former can be viewed as a derivative of **II** in which the hydrogen bonding was, by a small chemical trick, weakened. If such a concept is valid, then we can safely predict that [*cis*-a-Ir(trien)$(NO_2)_2$]Cl should also be a racemate. This substance is, thus far, unknown.

(c) In the 'Introduction', we indicated we hoped that the lengthening of the metal–N bonds in **I** with respect to **II** would result in crystallization of the former as a racemate, and we appear to have succeeded. However, the possibility that the addition of large amounts of chloride to the solution of **I** causes a phase change cannot be ruled out at the moment and this point is currently under investigation at our laboratory. In that regard, we note that

(1) Hydration polymorphism affecting the outcome of conglomerate *versus* racemic crystallization has been known since Pasteur's experiment [18a] which showed that the salt $Na(NH_4)(tart)\cdot 4H_2O$ crystallizes as a conglomerate, whereas $Na(NH_4)(tart)\cdot H_2O$ crystallizes as a racemate. Temperature causes the phase change in this instance.

(2) One of us demonstrated [6] that crystallization of [*cis*-b-Co(trien)Cl_2]Cl from solutions of varying amounts of HCl result in the isolation of two different hydrates – a trihydrate and a dihydrate, the latter crystallizing from the more concentrated HCl solutions. Both phases were racemic.

(3) We now know [19] that **II** crystallizes as a conglomerate from pure water (0 to 21 °C), from NaCl solutions (up to 3 M and from 0 to 21 °C) and from LiCl (up to 8 M and 0 to 21 °C); however, the two systems may differ in crystallization behaviour and the possibility that **I** crystallized as an anhydrous racemate as a result of the high chloride concentration cannot be ruled out at the moment and is currently under investigation here.

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