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The Phenomenon of Conglomerate Crystallization.
XV. Spontaneous Resolution in Coordination Compounds.
XIII. The Crystallization Behaviour and the Crystal and Molecular Structure of $\Delta(\lambda\delta)$-[*cis*-Rh(en)$_2$(NO$_2$)$_2$]Cl

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Abstract

The title compound, **I**, crystallizes in the monoclinic space group $P2_1$ with cell constants: $a = 6.599(3)$, $b = 11.121(2)$, $c = 8.375(1)$ Å and $\beta = 106.35(2)°$; $V = 589.74$ Å^3 and D(calc; $Z = 2$) = 1.974 g cm^{-3}. The compound is isomorphous and isostructural with its Co analogue. A total of 2982 data were collected over the range of $4° \leqslant 2\theta \leqslant 70°$; of these, 2537 (independent and with $I \geqslant 3\sigma(I)$) were used in the structural analysis. Data were corrected for absorption ($\mu = 16.6$ cm^{-1}) and the relative transmission coefficients ranged from 1.000 to 0.9504. Refinement was carried out for both enantiomeric configurations and the crystal used was found to contain cations with $\Delta(\lambda\delta)$ absolute configuration. The final $R(F)$ and $R_w(F)$ residuals were, respectively 0.0220 and 0.0239 for (– – –; *i.e.* $\Delta(\lambda\delta)$) and 0.0231 and 0.0317 for (+ + +; *i.e.* $\Lambda(\delta\lambda)$). Thus, the former was selected as correct for our specimen.

In the case of **I**, as well as in the Co derivative [*cis*-Co(en)$_2$(NO$_2$)$_2$]Cl (**II**), the conformation of one of the rings is opposite that expected for the lowest energy conformation, which in the current case should be $\Delta(\lambda\lambda)$.

The Rh–N(NO$_2$) distances are 2.020(2) and 2.010(2) Å, while the Rh–N(amine) distances, *trans* to the NO$_2$ ligands are 2.085(2) and 2.093(1) Å, values distinctly longer than the other two Rh–N distances (2.064(1) and 2.068(1) Å). The latter are the Rh–N distances to the terminal–NH$_2$ ligands located *trans* to each other. Thus, we observe a *trans* effect, which is more pronounced in **I** than in **II**, and which is of comparable magnitude to that observed in the case of the trien derivative, [*cis*-α-Rh(trien)(NO$_2$)$_2$]Cl (**III**).

Parallel with an increase in metal–N distances in going from [*cis*-α-Co(trien)(NO$_2$)$_2$]Cl·H$_2$O (**IV**) to **III** is an increase in the torsional angles of the outer rings (N–C–C–N) of about 10°. Comparison of these parameters in **I** and **II** reveal that this change is not so marked for this pair since in **I** they are –54.9° and 52.8° while in **II** they are 50.2° and –48.1°; *i.e.* a change of only 4°. This important difference between trien and en derivatives is caused by the presence of the central five-membered ring, which for compounds **III** and **IV** remains largely unchanged, except for the metal–N distances.

The N–O bond lengths are 1.244(3), 1.220(2), 1.237(2) and 1.211(2) Å, which are similar to those found for the analogous Co isomer. The C–N bond lengths are 1.492(3), 1.474(2), 1.486(2) and 1.475(2) Å, while the C–C bonds are 1.509(3) and 1.524(3) 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, including the common feature of having a longer C–C bond for the en ring with the conformation opposite that expected.

As was the case with the Co analogue, the Cl$^-$ anion is associated with the hydrogens of the secondary nitrogen (*trans* to the –NO$_2$) ligands, the Cl...H7 distance being 2.18(3) Å and the ⟨Cl...H7–N2 = 163°.

Introduction

Throughout the paper the compounds will be represented as follows: **I**, [*cis*-Rh(en)$_2$(NO$_2$)$_2$]Cl; **II**, [*cis*-Co(en)$_2$(NO$_2$)$_2$]Cl; **III**, [*cis*-α-Rh(trien)(NO$_2$)$_2$]Cl; **IV**, [*cis*-α-Co(trien)(NO$_2$)$_2$]Cl·H$_2$O; **V**, [*cis*-Co(en)$_2$(NO$_2$)$_2$](NO$_2$).

Sometime ago [1] we demonstrated that **II** and **IV** crystallize from water solutions, in the temperature range 4 to 26 °C, as conglomerates of pure optically active crystals (respective space groups $P2_1$ and $P2_12_12_1$) 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 –NH$_2$ hydrogens of the chelate rings. In a subsequent series of papers [2–8] we demonstrated that this concept is viable for a wider group of substances, and crystal structures

0020-1693/88/$3.50

of suitable derivatives were provided as proof. Moreover, it was also shown [4, 5] that the presence of charge compensating anions having strong hydrogen bonding ability often interferes with the process of conglomerate crystallization and racemic material is obtained with those salts – an observation consistent with the attribution of intramolecular hydrogen bonding to the origin of the phenomenon.

To test these ideas further, we synthesized the Rh complex **III** and found that it crystallizes as a racemate [9]. In analyzing the structural data for **III**, we noted that there is a major difference between the N–C–C–N torsional angles present in outer rings of this substance when compared with those present in its Co analogue **IV**. This difference is caused by the larger metal–N distances, which are approximately 0.1 Å longer in the former. Moreover, since the N–C and C–C distances, the M–N–C, N–C–C angles, and the N–C–C–N torsional angle of the central ring remain largely unchanged in **III** and **IV**, the torsional angle increase of the two outer rings is due to the need to span a larger ligand bite for the Rh species, while retaining the central ring largely invariant except for the lengths of the Rh–N distances.

A consequence of the above facts is that, in **III**, the terminal $-NH_2$ hydrogens are re-oriented such that they no longer can form hydrogen bonds as strong as is possible in the case of the Co complex **IV**. At this point we recalled that the ethylenediamine cation $[cis\text{-}Co(en)_2(NO_2)_2]^+$ has an interesting feature associated with the conformation of its rings: namely, in the form of the nitrite, **V**, which crystallizes as a racemate [10], the compounds has the expected, low energy, conformation of the Co(en) rings, *i.e.* $\Delta(\lambda\lambda)$ or $\Lambda(\delta\delta)$. In the conglomerate chloride, **III**, the substance has one ring oppositely conformed to that expected, *i.e.*, instead of being $\Delta(\lambda\lambda)$ or $\Lambda(\delta\delta)$, it is found to be $\Delta(\lambda\delta)$ or $\Lambda(\delta\lambda)$. Analysis of their structures reveals [1, 10] that whereas in **III** the chloride anion is interacting with the $-NH_2$ hydrogens *trans* to the NO_2 ligands, the nitrite anion forms strong hydrogen bonds with the axial $-NH_2$ hydrogens located *cis* to the $-NO_2$ ligands, thus effectively blocking the possibility of $-NO_2$ oxygens forming hydrogen bonds with the axial $-NH_2$ hydrogens.

We reasoned that if this explanation for the conformational differences described above is correct, then **I** should display a pair of oppositely conformed rings as well and probably would form a conglomerate. This, as we now realize is impossible for the Rh compound **III** since the strain on the central ring prevents the $-NO_2$ from coercing the outer $-NH-CH_2-CH_2-NH_2$ rings into the opposite conformation needed to strengthen hydrogen bonds, *i.e.* the barrier is too high in comparison with the gain associated with the improved hydrogen bonding situation. The results of investigating such stereochemical conjectures are given below.

Experimental

Synthesis

$[cis\text{-}Rh(en)_2Cl_2]Cl$ was made according to the procedure of Johnson and Basolo [11] and converted to the $[cis\text{-}Rh(en)_2(NO_2)_2]Cl$ by reaction with $NaNO_2$, as follows.

A two-fold excess of $NaNO_2$ was added to a water solution of the *cis*-dichloro derivative and refluxed for one hour. The solution volume was reduced to one third the original. Excess NaCl was added to the solution which was then placed in the refrigerator. Long needles of the compound appeared, from the thickest of which a suitable crystal was cut.

X-ray Data Collection

Data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification [12] of the SDP-Plus software package [13]. The crystal was centered with data in the $18° \leqslant 2\theta \leqslant 25°$ range and examination of the cell constants and Niggli matrix [14] clearly showed it to crystallize in a primitive, monoclinic lattice whose systematic absences showed it to belong to the space groups $P2_1$ or $P2_1/m$; however, since $Z = 2$, the second choice would require the cation to sit at a mirror plane – impossible for the *cis*-derivative. Moreover, the cell constants were essentially identical with those of the Co analogue **III**; thus, the former space group was assumed to be the correct one. The intensity data set was corrected for absorption using empirical curves derived from Psi scans [12, 13] of six reflections. The scattering curves were taken from Cromer and Waber's compilation [15].

The structure was solved from the Patterson map, using the Rh atom as the heavy atom. This verified that it and **III** are isomorphous and isostructural. 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 fixed at 5.0 $Å^2$. Conversion of the heavy atoms to anisotropic motion and allowing the hydrogens to refine with fixed, isotropic (4.0 $Å^2$) thermal parameters resulted in refinement of the overall structure to final $R(F)$ and $R_w(F)$ factors of 0.0220 and 0.0239, respectively. Refinement of the enantiomorph gave $R(F)$ and $R_w(F)$ values of 0.0231 and 0.0249. Thus, the absolute configuration

TABLE I. Summary of Data Collection and Processing Parameters for $\Delta(\lambda\delta)$-[*cis*-Rh(en)$_2$(NO$_2$)$_2$]Cl

Space group	$P2_1$
Cell constants	$a = 6.599(3)$ Å $b = 11.121(2)$ Å $c = 8.375(1)$ Å $\beta = 106.35(2)°$
Cell volume	$V = 589.74$ Å^3
Molecular formula	$C_4H_{16}N_6O_4RhCl$
Molecular weight	345.57 g mol^{-1}
Density (cal; Z = 2 mol/cell)	1.974 g cm^{-1}
Radiation employed	Mo Kα (λ = 0.71073 Å)
Absorption coefficient	$\mu = 16.6$ cm^{-1}
Relative transmission coefficients	1.000 to 0.9504
Data collection range	$4° \leqslant 2\theta \leqslant 70°$
Scan width	$\Delta\theta = 1.2 + 0.35\tan\theta$
Total data collected	2982
Data used in refinement[a]	2537
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.022
$R_w = [\Sigma w^2(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.024
Weights used	$w = [\sigma(F_o)]^{-2}$

[a] The difference between this number and the total is due to subtraction of 445 data which either were systematically absent (but collected for verification of space group), were symmetry related, standards or did not meet the criterion that $I \geqslant 3\sigma(I)$.

was determined to be $\Delta(\lambda\delta)$ for the crystal used in this study. Details of data collection and processing are summarized in Table I.

Figure 1 gives a labelled stereoview of the molecule; Fig. 2 depicts in stereo the packing of the ions in the unit cell. Final positional and equivalent isotropic thermal parameters are given in Table II. Bond lengths, angles and torsional angles are given in Table III.

Discussion

Mode of Crystallization of I

As we had hoped, **I** crystallizes as a conglomerate ($P2_1$); thus, even though the Co and Rh trien derivatives ((**III**) and (**IV**)) differ in their crystallization behaviour, **I** and **II** do not, as per expectations (*vide supra*).

Molecular Parameters in I and Comparison to II

There are no known structures of Rh derivatives of *cis*-bis-ethylenediamines or [*cis*-α or β-triens] other than that we reported recently [9]; 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.

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.

(a) In both, metal–N(NO$_2$) bonds are shorter than metal–N(amine). Table IV shows they follow a common pattern of having Co–N bonds shorter by *ca.* 0.1 Å. Moreover, both have M–N(NO$_2$) which differ by 0.01 Å, the shorter one being associated with the hydrogen bond to the ring with the high energy conformation.

(b) In both, metal–N (secondary NH$_2$) *trans* to –NO$_2$ are longer than metal–N(NH$_2$) bonds *trans* to –NH$_2$. This is the result of the *trans* effect, which is a little more pronounced in the Rh complex.

(c) For both, the M–NH$_2$ differ, the longer one is associated with the ill conformed ring.

(d) C–N distances and C–C distances follow the same pattern which is as follows: the average value of the C–N distances for the well conformed ring are longer than the average for the ill conformed

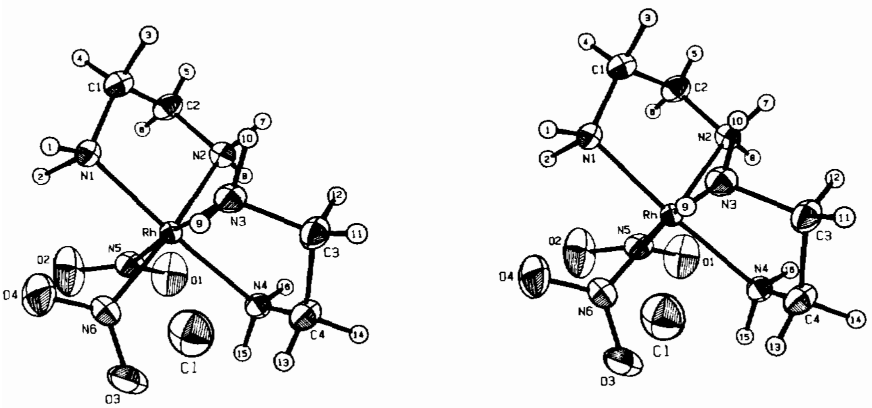

Fig. 1. Stereo view of the cation. Note that the absolute configuration is $\Delta(\lambda\delta)$ and that the ring with high energy conformation is that defined by N3–C3–C4–N4, which is δ. Note also the position of the Cl anion, whose closest contact is H7 (2.16 Å; 10 I. Bernal, S. Berhane and J. Cetrullo, to be published.

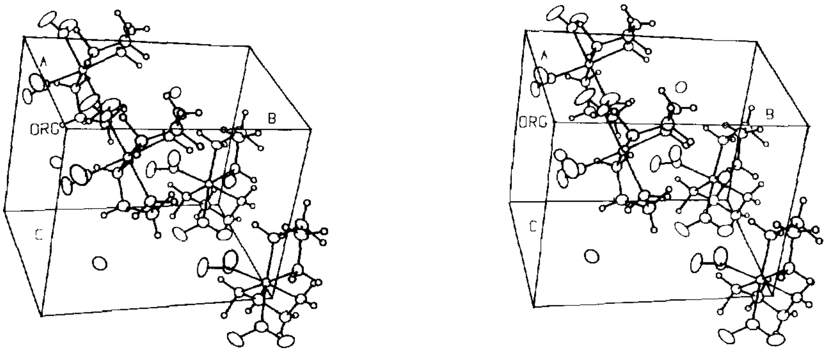

Fig. 2. Stereo view of the packing of cations and anions in the unit cell.

TABLE II. Positional Parameters[a]

Atom	x	y	z	B (Å^2)[b]
Rh	0.3086(3)	0.3283(–)	0.3121(1)	1.157(3)
Cl	−0.0256(2)	0.1934(1)	0.7002(1)	2.70(2)
O1	0.6873(4)	0.3215(6)	0.2179(4)	4.10(7)
O2	0.4778(6)	0.1806(4)	0.1013(5)	4.80(8)
O3	0.3904(5)	0.1168(3)	0.5127(4)	3.25(7)
O4	0.1255(6)	0.0978(4)	0.3055(5)	3.86(8)
N1	0.0654(4)	0.3086(3)	0.0961(3)	1.66(5)
N2	0.3335(5)	0.4971(3)	0.2108(4)	1.70(5)
N3	0.1128(4)	0.3964(3)	0.4487(4)	1.75(5)
N4	0.5433(4)	0.3597(3)	0.5307(4)	1.65(5)
N5	0.5168(5)	0.2672(3)	0.1945(4)	2.08(6)
N6	0.2663(5)	0.1608(3)	0.3873(4)	1.87(5)
C1	0.0181(6)	0.4268(4)	0.0090(5)	2.15(6)
C2	0.2259(6)	0.4907(4)	0.0311(4)	2.08(6)
C3	0.2474(6)	0.4558(4)	0.6006(4)	2.06(6)
C4	0.4459(6)	0.3802(4)	0.6668(4)	2.13(7)
H1	−0.068(8)	0.259(5)	0.098(6)	4.00*
H2	0.132(8)	0.238(6)	0.008(6)	4.00*
H3	−0.104(8)	0.497(6)	0.037(6)	4.00*
H4	−0.042(8)	0.414(6)	−0.104(6)	4.00*
H5	0.184(8)	0.557(6)	0.003(6)	4.00*
H6	0.411(8)	0.440(6)	−0.062(7)	4.00*
H7	0.261(8)	0.571(6)	0.252(6)	4.00*
H8	0.450(8)	0.515(6)	0.246(7)	4.00*
H9	0.040(7)	0.325(8)	0.485(5)	4.00*
H10	0.018(8)	0.469(5)	0.402(6)	4.00*
H11	0.191(7)	0.478(6)	0.691(6)	4.00*
H12	0.318(8)	0.543(6)	0.535(6)	4.00*
H13	0.448(8)	0.303(6)	0.716(6)	4.00*
H14	0.563(8)	0.428(6)	0.753(6)	4.00*
H15	0.657(7)	0.296(5)	0.558(6)	4.00*
H16	0.628(7)	0.428(6)	0.508(6)	4.00*

[a] e.s.d.s given in parentheses. [b] 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. Bond Lengths, Angles and Torsional Angles

Distances (Å)			
Rh–N1	2.064(1)	N1–C1	1.492(3)
Rh–N2	2.085(2)	C1–C2	1.509(3)
Rh–N3	2.093(1)	C2–N2	1.474(2)
Rh–N4	2.068(1)	N3–C3	1.486(2)
Rh–N5	2.020(2)	C3–C4	1.524(3)
Rh–N6	2.010(2)	C4–N4	1.475(2)
N5–O1	1.244(3)		
N5–O2	1.220(2)		
N6–O3	1.237(2)		
N6–O4	1.211(2)		
Hydrogen contacts less than 2.40 Å			
O1–H1	2.24	O2–H2	2.29
O3–H8	2.30 H8 at 1 − x, −0.5 + y, 0.5 − z		
O3–H12	2.22 H12 at 1 − x, −0.5 + y, 0.5 − z		
O3–H16	2.11 H16 at 1 − x, −0.5 + y, 0.5 − z		
Cl–H7	2.18 H7 at 1 − x, −0.5 + y, 0.5 − z		
Angles			
N1–Rh–N2	82.53(6)	O1–N5–O2	120.2(2)
N1–Rh–N3	93.99(6)	O3–N6–O4	118.1(2)
N1–Rh–N4	175.95(6)	Rh–N1–C1	109.8(1)
N1–Rh–N5	90.30(6)	Rh–N2–C2	107.5(1)
N1–Rh–N6	91.95(6)	Rh–N3–C3	108.4(1)
N2–Rh–N3	91.61(6)	Rh–N4–C4	109.2(1)
N2–Rh–N4	94.74(6)	Rh–N5–O1	118.0(2)
N2–Rh–N5	87.84(7)	Rh–N5–O2	121.8(1)
N2–Rh–N6	174.31(6)	Rh–N6–O3	121.0(1)
N3–Rh–N4	83.06(6)	Rh–N6–O4	120.7(1)
N3–Rh–N5	175.57(6)	N1–C1–C2	107.3(2)
N3–Rh–N6	90.14(6)	C1–C2–N2	107.9(2)
N4–Rh–N5	92.60(6)	N3–C3–C4	108.2(2)
N4–Rh–N6	90.84(6)	C3–C4–N4	108.7(1)
N5–Rh–N6	90.83(7)		
Torsion angles			
N2–Rh–N1–Cl	−10.4		
N3–Rh–N5–O1	−29.6		
N3–Rh–N5–O2	151.2		

(continued)

TABLE III. *(continued)*

N4–Rh–N5–O1	-41.3
N3–Rh–N1–C1	80.7
N4–Rh–N5–O2	139.5
N6–Rh–N5–O1	-132.2
N6–Rh–N5–O2	48.6
N4–Rh–N1–C1	37.6
N1–Rh–N6–O3	173.2
N1–Rh–N6–O4	-2.4
N2–Rh–N6–O3	159.3
N5–Rh–N1–C1	-98.1
N2–Rh–N6–O4	-16.3
N3–Rh–N6–O3	-92.8
N3–Rh–N6–O4	91.6
N6–Rh–N1–C1	171.0
N4–Rh–N6–O3	-9.7
N4–Rh–N6–O4	174.6
N5–Rh–N6–O3	82.9
N1–Rh–N2–C2	-19.2
N5–Rh–N6–O4	-92.8
Rh–N1–C1–C2	37.4
N3–Rh–N2–C2	-113.0
N4–Rh–N2–C2	163.8
N5–Rh–N2–C2	71.4
Rh–N2–C2–C1	45.2
N6–Rh–N2–C2	-5.2
N1–Rh–N3–C3	-163.1
Rh–N3–C3–C4	-39.1
N2–Rh–N3–C3	-80.4
N4–Rh–N3–C3	14.2
N5–Rh–N3–C3	2.4
Rh–N4–C4–C3	-39.7
N6–Rh–N3–C3	105.0
N1–Rh–N4–C4	57.7
N2–Rh–N4–C4	105.4
N1–C1–C2–N2	-54.9
N3–Rh–N4–C4	14.3
N5–Rh–N4–C4	-166.6
N3–C3–C4–N4	52.8
N6–Rh–N4–C4	-75.7
N1–Rh–N5–O1	135.9
N1–Rh–N5–O2	-43.3
N2–Rh–N5–O1	53.3
N2–Rh–N5–O2	-125.8

ring; however, the C–C distance of the latter is longer by about 0.13 Å.

(e) The various angles are closely related in both (see Table III and Ref. 1).

However, since the Rh–N distances are longer (see Table IV) and the en ligands retain nearly constant values of bond lengths and angles, the torsional angles of the N–C–C–N fragment must change in order to span the larger distance across the edge of the Rh octahedron.

Note that:

(a) The torsional angles being compared belong to species oppositely configurated, the Co species being $\Lambda(\delta\lambda)$ while the Rh one is $\Delta(\lambda\delta)$.

TABLE IV. Bond Distances and Torsion Angles

Co–N1	1.953(4)	Rh–N1	2.064(1)
Co–N2	1.963(4)	Rh–N2	2.085(2)
Co–N3	1.965(3)	Rh–N3	2.093(1)
Co–N4	1.967(4)	Rh–N4	2.068(1)
Co–N5	1.926(4)	Rh–N5	2.020(2)
Co–N6	1.914(4)	Rh–N6	2.010(2)
N1–Co–N5–O1	-137.3	N1–Rh–N5–O1	135.9
N1–Co–N5–O2	39.9	N1–Rh–N5–O2	-43.3
N1–Co–N6–O3	-165.5	N1–Rh–N6–O3	173.2
N1–Co–N6–O4	15.9	N1–Rh–N6–O4	-2.4
N5–Co–N1–H1	-22.1	N5–Rh–N1–H1	126.7
N5–Co–N1–H2	-141.8	N5–Rh–N1–H2	19.2
N5–Co–N4–H15	44.4	N5–Rh–N4–H15	-39.0
N5–Co–N4–H16	-75.4	N5–Co–N4–H16	69.1

(b) The average value of the N5–N1, N5–N4, N6–N4 distances in **I** is 2.922 Å, which is about 0.20 Å longer than in **II**.

(c) In order to accommodate the increased bite across the octahedron, the en 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** with respect to **II**) by about 4°. In the trien case (compounds **III** and **IV**) the increase of the outer torsional angles was about 10°, each.

(d) While the torsional motion of the $-NH_2$ moieties in **I**, compared with **II**, is smaller than in the trien case, the intramolecular hydrogen bonds needed [1–8] to anchor the clavic–NO_2 ligands in the dissymmetric orientation are still unfavourably affected. For example, the shortest intramolecular distances found for **II** and **I** are N1–H1...O2, 2.11 Å and N4–H17...O3, 2.24 Å for **II**; N1–H1...O1, 2.46 Å for **I**.

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, suggesting that for the Rh derivative (**I**) hydrogen bonded anchoring of the $-NO_2$ oxygens may be at the verge of losing significance. The Ir(III) analogue may be an interesting test case of this suggestion inasmuch as the radius of octahedral Ir(III) is about 0.06 Å longer than that of octahedral Rh(III).

(e) Since the torsional angles differ sufficiently in compounds **I** and **II**, the nitro oxygens of the former are no longer being directed as effectively by the terminal $-NH_2$ as they are in **II**. We have demonstrated how effective is this ability of $-NH_2$ hydrogens to control the stereochemistry of the $-NO_2$ ligands in the case of Co(III) compounds [1–8]. Therefore, we expect the same is true for the Rh analogues.

Conclusions

(i) In the case of the en derivatives, **I** and **II**, both crystallize as conglomerates. In both cases the cations contain one normal and one ill conformed ring, having configuration and conformation symbols Δ(λδ) or Λ(δλ). We attribute this behaviour to the improved hydrogen bonding derived from coercing one of the rings into a higher energy conformation.

(ii) Unlike the case of the en derivatives, **I** and **II**, which crystallize as conglomerates, the trien derivatives, **III** and **IV**, differ in their crystallization mode – the former is a racemate while the latter is a conglomerate. We attribute the opposite behaviour of the latter pair to the fact that the central ring of the trien retains its C–N, C–C, metal–N–C and N–C–C parametes largely unchanged in going from **IV** and **III**. The result is that the two outer rings of **III** must pay the penalty of spanning a larger octahedron edge by opening their N–C–C–N torsional angle by *ca.* 10°, compared with those present in **IV**. Moreover, the trien skeleton is, apparently, too rigid to be coerced into a Λ(λλδ) or a Δ(δδλ) conformation by the possibility of more favorable bonding between terminal $-NH_2$ hydrogens and the oxygens of the *cis*-NO_2 pair. Thus, the anchoring needed for stabilization of the desirable, dissymmetric conformation observed in **IV** is not available to **III** as a result of the large (10°) change in torsional angle required by the trien ligand to span the edge of the Rh octahedron. This torsional angle change results in a twisting of the $-NH_2$ moiety such that its hydrogens are less favourably positioned for hydrogen bonds.

(iii) The difference in the barrier to torsional inversion between the en rings and the outer rings of the trien derivatives puts a bracket to the value of the stabilization energy derived by $-NH_2...O-NO$ hydrogen bonding in these compounds. The barrier is small enough in the en drivatives to allow such torsional change to occur; however, the barrier to inversion of the trien outer rings is too large for the same process to occur there.

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