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The Crystal Structure of $(+)_{589}$-Tris[*trans*-1(R),2(R)-diaminocyclohexane]rhodium(III) Nitrate Trihydrate

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Crystals of $(+)_{589}$-[Rh(R,R-chxn)$_3$](NO$_3$)$_3$.3H$_2$O are hexagonal, space group $P6_3$ with a = 13·008 (2), c = 10·150 (1) Å, Z = 2. Positional and anisotropic thermal parameters were refined by a full-matrix least-squares program. The final R value is 0·034 for 2954 independent reflexions collected by diffractometry. The complex cation has approximate D_3 symmetry. The mean Rh–N distance is 2·076 (4) Å, and the N–Rh–N angle is 83·61 (8)° in the chelate ring. All the bond lengths and angles are normal. The central C–C bond in the chelate ring is inclined at an angle of 3·1° with respect to the threefold axis; hence the complex cation takes the lel_3 conformation. The absolute configuration can be designated as $\Delta(\lambda\lambda\lambda)$. The residual electron density around the Rh atom accumulates on the threefold axis to form two peaks with heights of 0·29 e Å^{-3} at 0·51 Å from the Rh nucleus. The remaining residual electron density is mainly distributed on the equatorial plane, forming three peaks of 0·44 e Å^{-3} between the chelate rings at 0·53 Å from the Rh atom.

Introduction

There is a growing interest in the asphericity of the electron density of a transition-metal atom placed in a crystal field (Rees & Coppens, 1973; Iwata & Saito, 1973; Marumo, Isobe, Saito, Yagi & Akimoto, 1974; Maslen, Ridout & White, 1975; Shintani, Sato & Saito, 1975; Iwata, 1977). As part of a series of investigations into the residual electron densities of transition-metal atoms in complexes, the crystal structure of the title compound was determined. This compound was chosen to see whether it is possible to obtain any meaningful residual electron density around a transition metal in the fifth period of the periodic table.

Experimental

Crystals of $(+)_{589}$-[Rh(R,R-chxn)$_3$](NO$_3$)$_3$.3H$_2$O were kindly supplied by Dr Galsbøl of the H. C. Ørsted Institute. They are colourless, transparent hexagonal needles and are stable in air and under X-radiation. Unit-cell dimensions were determined from Weissenberg photographs. They were later refined by least-squares calculations on the basis of 33 2θ values of higher-order reflexions (40° < 2θ < 61°) measured on a diffractometer. Table 1 lists the crystal data together with those of the ob_3 analogue (Kuroda, Sasaki & Saito, 1974). The density of the crystal was determined by flotation in a mixture of chloroform and ethanol.

A crystal shaped into a sphere about 0·3 mm in diameter was used for the intensity measurement. The intensity data were collected on a Rigaku automated four-circle diffractometer. The experimental conditions (summarized in Table 2) were broadly similar to those described in a previous paper (Iwata & Saito, 1973). The measurement was repeated automatically until $\sigma(|F|)/|F|$ became less than 0·055 when $2\theta \leq 95°$, and 0·015 otherwise [$\sigma(|F|)$ is the standard deviation of $|F|$

Table 1. *Crystallographic data*

$(+)_{589}$-Tris[*trans*-1(R), 2(R)-diaminocyclohexane]rhodium(III) nitrate trihydrate, M_r = 685·5

	$(+)_{589}$-lel_3 Isomer	$(+)_{589}$-ob_3 Isomer*
Space group	$P6_3$	$P6_3$
a	13·008 (2) Å	13·339 (2) Å
c	10·150 (1)	9·848 (2)
U	1487 Å^3	1517 Å^3
μ(Mo $K\alpha$)	6·4 cm^{-1}	6·2 cm^{-1}
Z	2	2
d_m	1·524 g cm^{-3}	1·498 g cm^{-3}
d_x	1·534	1·500

* Kuroda, Sasaki & Saito (1974).

Table 2. *Information for data collection*

Crystal size	Radius 0·15 mm
External form	Sphere
φ axis	[001]
X-ray source	Mo $K\alpha$ radiation (λ = 0·7107 Å)
Monochromator	Graphite plate
Scanning method	ω–2θ
Scanning range	(1·2 + 0·45 tan θ)°
Scanning speed	2° min^{-1} in ω
Counter aperture	5·5 mm ϕ
Collimator	0·5 mm ϕ × 150 mm
$(\sin\theta/\lambda)_{\max}$	1·2 Å^{-1}
Number of independent $F(hkl)$'s measured	5710
Number of $\lvert F(hkl)\rvert$'s used for refinement [$\lvert F\rvert > 3\sigma(\lvert F\rvert)$]	2954

due to counting statistics]. The maximum number of repetitions was limited to four for $2\theta \leq 95°$ and to ten for $2\theta > 95°$. Reflexions with $h \geq 0$, $k \geq 0$ and $l \geq 0$ were measured up to $2\theta = 135°$. Some of the $\bar{h}kl$ reflexions were also measured in order to check accidental errors in the $F(hkl)$'s. 2954 independent reflexions with $|F| \geq 3\sigma(|F|)$ were classified as observed and used for the structure determination. All the reflexions beyond 110° in 2θ were excluded by this criterion. The intensities were corrected for Lorentz and polarization effects.

Structure determination

The structure was solved by the routine application of the heavy-atom method and was refined by the block-diagonal least-squares procedure, assuming anisotropic thermal parameters, based on 1920 reflexions with $2\theta \leq 70°$. The R value dropped to 0·045. At this stage a difference synthesis was calculated and the positions of all the H atoms except those of the water molecules could be located. Further cycles of the refinement reduced the R value to 0·031. The second difference synthesis revealed the positions of the remaining H atoms. The R value for the 1920 reflexions became 0·026. In the low-angle region, $\sin\theta/\lambda < 0{\cdot}13$ Å^{-1}, four strong reflexions (010, 011, 121 and 002) appeared to be seriously affected by secondary extinction, even though the crystal specimen was shaped into a sphere by the air-blow method (Bond, 1951) and a strong extinction effect was not, therefore, expected. When the refinement was carried out including an isotropic extinction parameter, the value of g became $0{\cdot}30 \times 10^4$ and the R value did not change at all. There were only ten reflexions with $y < 0{\cdot}98$. The values of F_o, F_c and y for these reflexions are listed in Table 3. When the refinement was performed excluding these four reflexions, g reduced to $0{\cdot}01 \times 10^4$ indicating practically no extinction effect. This remarkable change in g leads us to suspect that the discrepancy between F_o and F_c for these four reflexions could not be attributed solely to the extinction effect. According to our experience the crystal suffering from serious secondary extinction with g as large as $0{\cdot}30 \times 10^4$ generally had a number of reflexions with smaller y values; *i.e.* at least 40 reflexions with $y < 0{\cdot}98$ in the region of $\sin\theta/\lambda < 0{\cdot}70$

Table 3. *Contribution of aspherical* 4*d electrons of* Rh *to the structure amplitudes*

	Refinement with extinction correction*				Refinement including five peaks†		
h k l	F_o	F_c	F_o/F_c	y	F_o	F_c	F_o/F_c
0 1 0	82·3	92·5	0·890	0·898	90·7	97·4	0·931
1 1 0	71·0	73·2	0·970	0·959	75·6	78·7	0·960
1 2 0	75·9	76·2	0·996	0·970	80·4	79·3	1·014
0 1 1	88·0	95·2	0·924	0·924	95·6	101·6	0·940
1 2 1	144·5	165·5	0·873	0·889	159·9	169·8	0·942
0 0 2	148·3	172·0	0·862	0·853	167·6	173·1	0·968
1 2 2	93·0	97·3	0·956	0·964	98·8	97·0	1·019
2 3 2	88·0	87·8	1·002	0·979	92·8	90·1	1·031
0 0 4	101·6	103·1	0·986	0·969	107·7	105·9	1·016
2 2 4	94·7	97·2	0·974	0·978	99·9	100·5	0·994

* Scale factor for F_o: 0·3251; $g = 0{\cdot}296 \times 10^4$.

† Scale factor for F_o: 0·3356; the positional and thermal parameters of the five peaks were as follows: $x = 0{\cdot}3333$, $y = 0{\cdot}6667$, $z = \pm 0{\cdot}05$, $b_{11} = b_{22} = 0{\cdot}0079$, $b_{33} = 0{\cdot}0049$ and $b_{12} = 0{\cdot}0039$ Å^2 with a weight of $\frac{1}{4}$ for two peaks on the threefold axis, and $x = 0{\cdot}29$, $y = 0{\cdot}63$, $z = 0$ and $b = 3{\cdot}0$ Å^2 with a weight of $\frac{1}{3}$ for the remaining three peaks.

Table 4. *Positional parameters* ($\times 10^4$, *for* H $\times 10^3$), *with estimated standard deviations in parentheses*

The mean isotropic temperature factor of the H atoms is 3·2 (8) Å^2.

	x	y	z
Rh	3333	6667	0
N(1)	2178 (2)	5224 (2)	−1142 (2)
N(2)	3371 (2)	5384 (2)	1167 (2)
C(1)	2359 (3)	4216 (3)	−758 (4)
C(2)	2397 (3)	4207 (3)	731 (4)
C(3)	2561 (3)	3205 (2)	1235 (3)
C(4)	1576 (5)	2008 (4)	656 (6)
C(5)	1596 (5)	2045 (4)	−842 (5)
C(6)	1408 (2)	3040 (2)	−1319 (3)
N(3)	6017 (2)	5161 (2)	978 (3)
O(1)	5550 (2)	5288 (3)	1962 (3)
O(2)	5700 (2)	5292 (2)	−142 (3)
O(3)	6767 (2)	4851 (3)	1129 (3)
O(*W*)	7966 (3)	5044 (3)	−1385 (3)
H(N11)	232 (2)	534 (2)	−186 (3)
H(N12)	140 (2)	503 (2)	−98 (2)
H(N21)	320 (2)	545 (2)	198 (3)
H(N22)	397 (2)	537 (2)	113 (3)
H(C1)	307 (2)	436 (2)	−108 (2)
H(C2)	171 (2)	407 (2)	104 (3)
H(C31)	263 (3)	329 (3)	223 (3)
H(C32)	334 (2)	331 (2)	105 (3)
H(C41)	75 (4)	186 (4)	117 (5)
H(C42)	175 (5)	144 (5)	111 (6)
H(C51)	238 (3)	226 (3)	−116 (4)
H(C52)	106 (3)	134 (3)	−111 (4)
H(C61)	158 (3)	313 (3)	−225 (3)
H(C62)	64 (2)	291 (2)	−102 (2)
H(O1)	848 (2)	499 (4)	−115 (5)
H(O2)	759 (3)	506 (4)	−79 (3)

Table 5. *Determination of the absolute configuration*

h k l	$F_c(hkl)$	Observed relations	$F_c(hk\bar{l})$
4 0 1	44	>	42
5 0 1	55	<	57
1 3 1	74	>	71
1 5 1	43	<	47
1 5 2	29	>	26
1 7 2	49	>	44
2 1 2	50	<	57
2 3 2	92	>	86
2 4 2	58	<	63
5 0 3	57	<	60
1 6 4	22	<	24

Å^{-1}. It was then decided to carry out the subsequent refinements without an extinction correction. The refinement, including the higher-order reflexions, was carried out by the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970). The final R and R_w values were 0·034 and 0·022, respectively, for 2954 observed reflexions. At the final stage of the refinement all the parameter shifts, except for the H atoms, were less than a quarter of the corresponding standard deviations. The scattering factors for the Rh, C, N and O atoms were those listed in *International Tables for X-ray Crystallography* (1974) and that for the H atoms was from Stewart, Davidson & Simpson (1965). Atomic parameters are listed in Table 4.*

The absolute configuration of the complex cation was determined with reference to the known absolute configuration of $(-)_{589}$-(R,R-chxn) (Marumo, Utsumi & Saito, 1970), since the compound was synthesized from $(-)_{589}$-(R,R-chxn) (Galsbøl, Steenbøl & Sørensen, 1972). In order to confirm the absolute configuration, equi-inclination Weissenberg photographs were taken around the a axis with Cu $K\alpha$ radiation ($f' = -1{\cdot}1$, $f'' = 1{\cdot}2$). Some of the calculated differences and observed relations between hkl and $hk\bar{l}$ are compared in Table 5. The concordance in the table certainly indicates that the absolute configuration of $(+)_{589}$-[Rh(R,R-chxn)$_3$]$^{3+}$ can be designated as $\Delta(\lambda\lambda\lambda)$, in agreement with the assignment by the method of active racemates (Andersen, Galsbøl, Harnung & Laier, 1973).

Description of the structure and discussion

A partial projection of the structure is presented in Fig. 1. The structure is isotypic with the ob_3 analogue (Kuroda *et al.*, 1974), except for the conformation of the complex cation. In fact, the cell dimensions are very similar (see Table 1). The structure is composed of complex cations, nitrate ions and water molecules. The complex cation has rigorous C_3 symmetry and is very similar to that of the Co analogue (Marumo *et al.*, 1970), so the structure of the complex cation will not be described in detail. The bond distances and angles within the complex ion are given in Table 6. The Rh–N distances of 2·075 (2) and 2·067 (2) Å are slightly longer than those of 2·067 (6) and 2·056 (7) Å observed for (±)-[Rh(en)$_3$]Cl$_3$.3H$_2$O (Whuler, Brouty, Spinat & Herpin, 1976). The N–Rh–N angle of 83·61 (8)° in the chelate rings, which is similar to the 83·6 (2)° in [Rh(en)$_3$]$^{3+}$, is larger than that of the ob_3 isomer by 0·9°, but it is smaller than the 86·7 (9)° in the Co analogue. The octahedron formed by the six N atoms is slightly distorted. The upper triangle formed by the three N atoms is rotated clockwise by about 9·4°, with respect to the lower triangle of the three remaining N atoms, from the position expected for a regular octahedron. The Rh–N bond is inclined at an average angle of 55·5° with respect to the threefold axis. This angle should be 54·75° for a regular octahedron. The RhN$_6$ chromophore is slightly compressed.

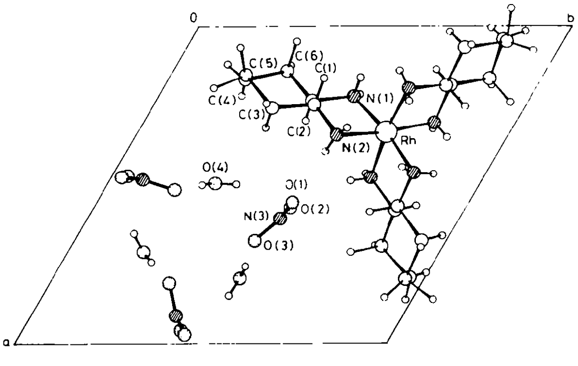

Fig. 1. Partial projection of the crystal structure along the c axis.

Table 6. *Bond distances* (Å) *and angles* (°) *within the complex ion*

Rh···N(1)	2·075 (2)	N(1)···Rh···N(2)	83·61 (8)
Rh···N(2)	2·067 (2)	Rh···N(1)–C(1)	106·7 (2)
N(1)–C(1)	1·495 (5)	Rh···N(2)–C(2)	108·1 (2)
N(2)–C(2)	1·485 (3)	N(1)–C(1)–C(2)	106·8 (3)
C(1)–C(2)	1·512 (5)	N(1)–C(1)–C(6)	112·3 (3)
C(2)–C(3)	1·510 (6)	N(2)–C(2)–C(1)	107·7 (3)
C(3)–C(4)	1·554 (5)	N(2)–C(2)–C(3)	111·9 (3)
C(4)–C(5)	1·521 (8)	C(2)–C(1)–C(6)	112·4 (3)
C(5)–C(6)	1·512 (7)	C(1)–C(2)–C(3)	111·5 (3)
C(6)–C(1)	1·518 (4)	C(2)–C(3)–C(4)	109·6 (3)
N(3)–O(1)	1·221 (4)	C(3)–C(4)–C(5)	110·8 (4)
N(3)–O(2)	1·250 (4)	C(4)–C(5)–C(6)	109·9 (4)
N(3)–O(3)	1·237 (5)	C(1)–C(6)–C(5)	110·1 (3)
		O(1)–N(3)–O(2)	120·3 (3)
		O(1)–N(3)–O(3)	118·0 (3)
		O(2)–N(3)–O(3)	121·6 (3)

Table 7. *Interatomic distances* (Å) *less than* 3·5 Å *outside the complex ions*

Symmetry code

(i) x, y, z

(ii) $1 + x + y$, $x + y$, z

(iii) $1 - x + y$, $1 - x - y$, z

(iv) $1 - x + y$, $1 - x - y$, $\frac{1}{2} + z$

(v) $1 - x + y$, $1 - x - y$, $-\frac{1}{2} + z$

N(1$^{\text{i}}$)–O(2$^{\text{iii}}$)	3·122 (4)*	C(1$^{\text{i}}$)–O(1$^{\text{v}}$)	3·379 (5)
N(1$^{\text{i}}$)–C(1$^{\text{iii}}$)	3·394 (4)	C(1$^{\text{i}}$)–O(3$^{\text{v}}$)	3·372 (4)
N(2$^{\text{i}}$)–O(2$^{\text{i}}$)	3·365 (4)	O(1$^{\text{i}}$)–O(2$^{\text{iv}}$)	3·260 (4)
N(2$^{\text{i}}$)–O(W^{iv})	2·922 (4)*	O(2$^{\text{i}}$)–O(W^{i})	3·367 (5)
C(2$^{\text{i}}$)–O(W^{iv})	3·195 (5)	O(3$^{\text{i}}$)–N(1$^{\text{iv}}$)	3·115 (4)*
		O(3$^{\text{i}}$)–O(W^{i})	2·935 (4)*

* Hydrogen bonding.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32694 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The central C—C bond in the chelate ring makes an angle of 3·1° with respect to the threefold axis of the complex ion.

The nitrate ion is almost planar. The average N—O distance is 1·236 (4) Å and the average O—N—O angle is 120·0 (3)°. The nitrate ions and the water molecules are arranged with their molecular planes parallel to the threefold axis (Fig. 1). Table 7 lists the pertinent short contacts. The amino atom N(2) forms an N—H···O hydrogen bond of 3·010 (4) Å with the atom O(1) of the nitrate ion. N(1) forms two longer hydrogen bonds with the O atoms of the nitrate ion [O(2) and O(3′); 3·122 (4) and 3·115 (4) Å respectively]. The water molecules form an O—H···O hydrogen bond with the O atom of the nitrate ion [2·936 (4) Å].

The number of electrons around the Rh atom

The number of electrons in a sphere centred at the Rh atom with an appropriate radius can be calculated on the basis of observed structure amplitudes by a method described earlier (Kobayashi, Marumo & Saito, 1972). In the case of $[Co(NH_3)_6][Co(CN)_6]$, the radius was taken to be equal to the covalent radius of the Co atom and it was shown that the central metal atom is largely neutralized (Iwata & Saito, 1973). The term 'covalent radius' has, however, no precise physical significance, since the observed electron density does not fall abruptly to zero at a particular distance from the centre of the atom. If the covalent radius is replaced by the distance from the atomic centre to the bonding-electron-density peak, the concept of 'charge density of the central metal atom' will become clearer. In $[Rh(R,R\text{-chxn})_3]^{3+}$, the residual electron-density peak appears at 1·52 Å from Rh (see below). In Table 8, the number of electrons within a sphere of radius equal to the distance from the atomic centre to the bonding-electron peak is listed. The number of electrons in a sphere of radius 1·52 Å is 44·8 (2), indicating that the central Rh atom is neutralized to a great extent by the donation of electron pairs from the ligating atoms. The result agrees with that of molecular-orbital calculations (Mehrotra & Manoharan, 1976). The results obtained for $[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$ are also listed for comparison. As can be seen from the table, all the central metal atoms are largely neutralized, the effective charge at the metal atoms being about +0·5 e. Thus, Pauling's electroneutrality principle can be stated for the metal complexes as follows: the number of electrons within a sphere of radius equal to the distance from the atomic centre to the centre of the bonding-electron peak is nearly equal to the atomic number of the central metal atom. The distance depends on the central metal atom and the ligating atoms. It should be noted that the distances in Table 8 roughly correspond to the maximum of the radial density distribution of the 4*s* and 5*s* electrons for Co and Rh respectively (Fischer, 1968).

Residual electron-density

At the final stage of the refinement, a three-dimensional difference synthesis was calculated including all the atoms. The standard deviation of the electron density at the general position is 0·07 e Å^{-3} [calculated on the basis of the observed $\sigma(|F|)$'s]. Fig. 2 shows a section through the Rh atom perpendicular to the threefold axis

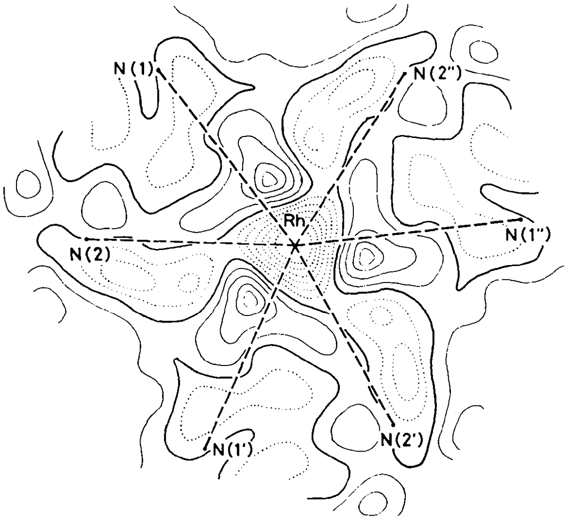

Fig. 2. Difference Fourier synthesis in the *ab* plane around the Rh atom. The contours are at intervals of 0·1 e Å^{-3}; negative contours are represented by dotted and zero contours by heavy lines.

Table 8. *The charge on the central metal atoms*

Complex ion	Z	Radius of sphere†	Number of electrons	Effective charge of the central metal atom	M—L bond length
$[Rh(R,R\text{-chxn})_3]^{3+}$	45	1·52 Å	44·6 (2)	+0·4 e	2·071 Å
$^*[Co(NH_3)_6]^{3+}$	27	1·21	26·2 (1)	+0·8	1·972
$^*[Co(CN)_6]^{3}$	27	1·17	26·4 (2)	+0·6	1·894

* Estimated from the data by Iwata & Saito (1973).

† The distance from the central metal atom to the centre of the peak due to bonding electrons.

of the complex ion. Fig. 3 (*a*) and (*b*) represents two sections of the residual electron density containing the threefold axis and both the two crystallographically independent Rh—N bonds. The distribution of the residual electron density has threefold symmetry owing to the requirement of the space group. There are five prominent peaks: two are on the threefold axis at 0·51 Å from the Rh nucleus with heights of 0·29 e $Å^{-3}$, and the remaining three are on the equatorial plane; they are located between the two adjacent chelate rings with peak heights of 0·44 e $Å^{-3}$ at 0·53 Å from the Rh nucleus. It turned out that the two peaks on the threefold axis were entirely due to the contribution of four strong reflexions: 010, 011, 121 and 002. If these four reflexions were excluded, the peak heights diminished drastically. When these five prominent peaks on the difference maps were included in the calculation of the structure factors, by assuming appropriate scattering factors for them, the agreement between F_o and F_c was improved, as listed in the second column of Table 3. For the scattering factors of these peaks, the scattering factor of an H atom (Stewart *et al.*, 1965) was used with the following slight modifications: a weight of $\frac{1}{4}$ for the peaks on (00*z*) with anisotropic thermal factors and a weight of $\frac{1}{3}$ for those on (*xy*0) with isotropic thermal factors. These parameters are also listed in Table 3. For the scattering factor of the Rh atom the average scattering factor of Rh^0 and Rh^{3+} was used to keep the number of electrons around Rh at 45. Phase refinement including the contributions of the five peaks gave more reasonable structural features, although the *R* value did not improve. For instance, the Rh—N distances of 2·075 (2) and 2·067 (2) Å, which are chemically equivalent but crystallographically independent, became closer to each other after phase refinement: 2·074 (4) and 2·077 (4) Å. Some important information on the aspherical distribution of the electron density may be lost by indiscriminate application of the extinction correction. Moreover, the peaks due to bonding electrons between Rh and N were clearer (Fig. 3). The peak height is 0·15 e $Å^{-3}$. The positions are (0·265,0·575,–0·095) and (0·335,0·575,0·095). The peak is located at 0·6 Å from the N atom (at 1·52 Å from Rh), slightly off the line joining the Rh atom and each of the two crystallographically independent N atoms. The peak–Rh–peak angle is 91°. This feature may indicate that the 'lone-pair' orbital of the N atom is not directed exactly towards the Rh atom. A similar feature was also observed in the residual electron density of $(+)_{589}$-[Co(*R*,*R*-chxn)$_3$]Cl$_3$.H$_2$O (Kobayashi, Marumo & Saito, 1972).

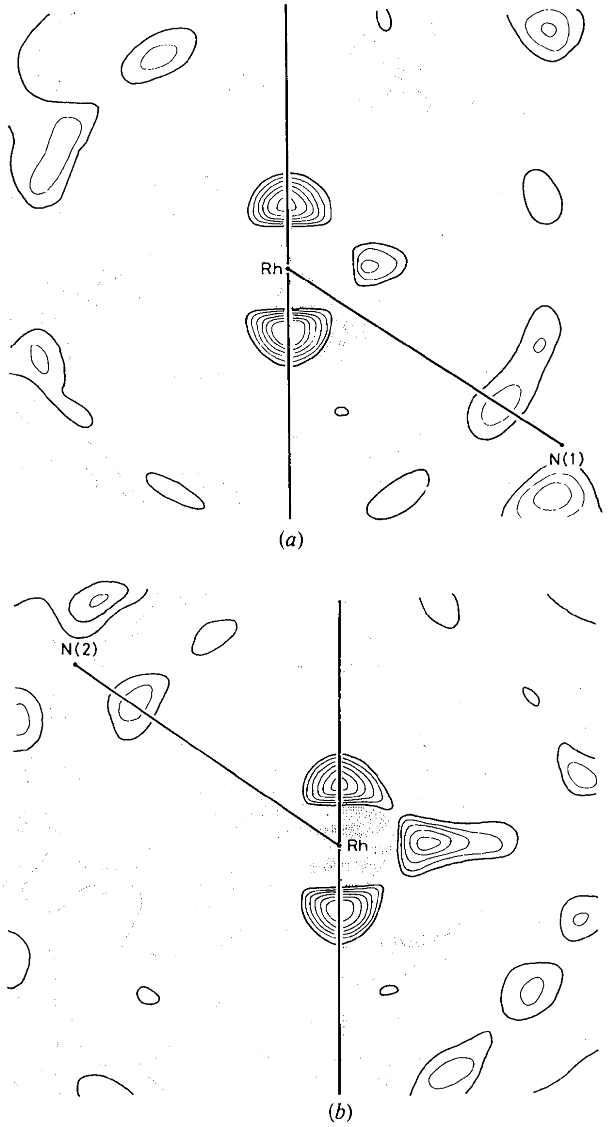

Fig. 3. Difference Fourier synthesis in the plane through a Rh—N bond and the threefold axis. The contours are at intervals of 0·05 e $Å^{-3}$. (*a*) Through the Rh—N(1) bond and (*b*) through the Rh—N(2) bond.

A remarkable feature of the distribution of the five residual electron-density peaks is that they have a tendency to avoid the regions of high field due to chelating ligands.

Such an observed distribution of the residual electron density around the Rh atom may be reasonably accounted for by the real space distribution of the 4*d* orbitals. Let us take the Cartesian coordinate system and consider the following combinations of the real *d* orbitals in an octahedral environment, where the *z* axis is taken as the axis of quantization:

$$t_{2g}\left\{\begin{aligned}\sqrt{2/3}\,d(x^2-y^2)-\sqrt{1/3}\,d(zx)&=t_{2g}^{+}\\ \sqrt{2/3}\,d(xy)+\sqrt{1/3}\,d(yz)&=t_{2g}^{-}\\ d(z^2)\qquad\qquad&=t_{2g}^{0}\end{aligned}\right.$$

$$e_g\left\{\begin{aligned}\sqrt{1/3}\,d(x^2-y^2)+\sqrt{2/3}\,d(zx)&=e_g^{+}\\ \sqrt{1/3}\,d(xy)-\sqrt{2/3}\,d(yz)&=e_g^{-}.\end{aligned}\right.$$

In the present case, the trigonal field exerted by the ligands further scrambles the t_{2g} and e_g orbitals (Balhausen, 1962). Threefold degenerate t_{2g} orbitals of O_h parentage will split into one single degenerate orbital (a_1) and one twofold degenerate orbital (e). The repulsion exerted by the bonding electron will stabilize the a_1 orbital [$d(z^2)$] the most. Accordingly there remains appreciable residual electron density on the threefold axis. Three peaks on the equatorial plane must have large components of $d(x^2-y^2)$ and $d(xy)$.

Further detailed analysis of the distribution of the residual electron density around the Rh atom in the present complex will be reported later, together with an analysis of the ob_3 isomer.

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