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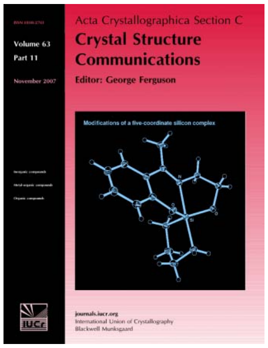

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Arrangement of Rh^{3+} ions in *fac*-triamminetrichloridorhodium from powder data and in *fac*-triamminetrinitratorhodium crystals twinned by merohedry

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The rhodium complexes $[RhCl_3(NH_3)_3]$, (I), and $[Rh(NO_3)_3(NH_3)_3]$, (II), are built from octahedral $RhX_3(NH_3)_3$ units; in (I) they are isolated units, while in (II) the units are stacked in columns with partially filled sites for the Rh atoms. The octahedra of monoclinic crystals of (I) are linked by N—H···Cl hydrogen bonds and the Rh^{3+} ions are located on the mirror planes. In the trigonal crystals of (II), the discontinuous 'columns' along the threefold axis are linked by N—H···O hydrogen bonds. The structure of (I) has been solved using laboratory powder diffraction data, the structure of (II) has been solved by single-crystal methods using data from a merohedrally twinned sample. Both compounds possess low solubility in water.

Keywords: crystal structure; powder diffraction; merohedral twinning; *fac*-triamminetrichloridorhodium; low solubility; *fac*-triamminetrinitratorhodium.

1. Introduction

Since the publication of the first work on the synthesis of triamminetrichloridorhodium(III) (Lebedinskij, 1935) there have been reports of the syntheses of only three related complexes, *viz*. $Rh(NO_2)_3(NH_3)_3$ (Lebedinskij & Shenderetskaya, 1940), $Rh(OH)_3(NH_3)_3$ and $RhCl_3(NH_3)_3$ (Pannetier *et al.*, 1969). The absence of reports on the synthesis and study of the properties of this triammine series of complexes with other acido ligands is surprising because they possess very low solubility and can potentially be used both in processes for refining platinum group metals and in the development of gravimetric methods for the determination of rhodium. The complexes that do not contain any halide ions and possess sufficiently high solubility may prove to be good precursors for the creation of catalytic compositions containing rhodium.

The $[RhX_3(NH_3)_3]$ compounds must exist as two geometric isomers, but the overall lack of structural studies of this class of compounds, except for two *fac*-$[Rh(NO_2)_3(NH_3)_3]$ modifications (Khranenko *et al.*, 2002; Gromilov *et al.*, 2005), does not allow us to judge the isomer composition of the complexes obtained previously. Khranenko *et al.* (2002) mistakenly indicated the space group $P2_1/m$ for the structure of the α-phase, while the true space group is $P2_1$. But all calculations and other descriptions were made in the correct space group. In addition, the absolute structure was not determined.

2. Experimental

2.1. Synthesis and crystallization

A light-yellow powder of *fac*-$[RhCl_3(NH_3)_3]$, (I), was prepared by heating *fac*-$[Rh(NO_2)_3(NH_3)_3]$ (0.103 g), synthesized according to the procedure of Khranenko *et al.* (2002), in HCl (25 ml, 1:1 aqueous solution) for 3 h followed by cooling to room temperature. The compound is poorly soluble in water and is stable when stored at ambient temperature; the yield of (I) was 91%. The composition of the powder was determined by thermal decomposition of the complex in a stream of H_2 with the capture of volatile products by an aqueous solution. The Rh content was determined gravimetrically by the solid residue and the Cl^- content was determined using titration with a Hg^{2+} solution using difenilkarbazone as an indicator; the content of NH_3 was determined by acidimetric titration using urotropin (hexamethylenetetramine).

fac-$[Rh(NO_2)_3(NH_3)_3]$ and *fac*-$[RhCl_3(NH_3)_3]$ were used as starting materials for the synthesis of *fac*-$[Rh(NO_3)_3(NH_3)_3]$, (II). On heating *fac*-$[Rh(NO_2)_3(NH_3)_3]$ (0.594 g) in HNO_3 (20 ml, 1:1 aqueous solution), the complex dissolved with separation of a colourless gas and the formation of a green–yellow solution. After a brief boiling and subsequent incubation of the solution at room temperature for 2 d, pale-yellow single crystals of (II) were extracted; the yield was 25–30%. The same complex was obtained by heating *fac*-$[RhCl_3(NH_3)_3]$ to boiling point in concentrated nitric acid followed by concentration of the resulting solution at room temperature. The same composition and crystal state were confirmed by X-ray phase analysis, CHN analysis and IR spectroscopy. The crystals are poorly soluble in water and are stable when stored in air.

The compositions of the synthesized complexes were set based on the CHN analyses. The analysis data for (I) are in good agreement with the formula: Rh 39.8, Cl 40.6, NH_3 19.7%; calculated: Rh 39.5, Cl 40.9, NH_3 19.6%. IR (cm^{-1}): 491 (ν Rh—N), 775, 821, 855 (ρ NH_3), 1279, 1302 (δ N—H), 1546, 1572, 1616 (δ N—H), 3181 and 3276 (ν N—H).

The results for (II) (N 23.51, H 2.84%) can be interpreted in two ways. The values of N 24.71% and H 2.65% correspond to the formula for (II), but the values of N 23.47% and H 3.07% correspond to (II)·H_2O. Despite the fact that the (II)·H_2O

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Table 1
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$[RhCl_3(NH_3)_3]$	$[Rh(NO_3)_3(NH_3)_3]$
M_r	260.36	340.04
Crystal system, space group	Monoclinic, $P2_1/m$	Trigonal, $P3$
Temperature (K)	300	296
a, b, c (Å)	6.7279 (3), 9.7888 (4), 5.4611 (2)	7.496 (1), 7.496 (1), 5.2560 (8)
α, β, γ (°)	90, 95.149 (2), 90	90, 90, 120
V (Å^3)	358.21 (2)	255.77 (7)
Z	2	1
Radiation type	Cu $K\alpha_1$, λ = 1.5406, 1.5444 Å	Mo $K\alpha$
μ (mm^{-1})	28.8	1.72
Specimen shape, size (mm)	Tablet, 20 × 20 × 0.6	0.40 × 0.15 × 0.15
Data collection		
Diffractometer	Bruker D8-ADVANCE diffractometer with a VANTEC linear detector	Bruker APEXII CCD area-detector diffractometer
Specimen mounting	Packing in a silicon single-crystal sample holder	–
Data collection mode	Reflection	–
Data collection method	Step	φ and ω scans
Absorption correction	–	Multi-scan (*SADABS*; Sheldrick, 2004)
T_{min}, T_{max}	–	0.546, 0.782
No. of measured, independent and observed reflections	–	3780, 879, 879
R_{int}	–	0.030
θ values (°)	$2\theta_{min} = 5$ $2\theta_{max} = 139.987$ $2\theta_{step} = 0.016$	$\theta_{max} = 33.0$, $\theta_{min} = 3.1$
Distance from source to specimen (mm)	217	320
Refinement		
R factors and goodness of fit	$R_p = 0.0422$, $R_{wp} = 0.0456$, $R_{exp} = 0.0154$, $R_{Bragg} = 0.0179$, $\chi^2 = 8.768$	$R[F^2 > 2\sigma(F^2)] = 0.019$, $wR(F^2) = 0.048$, $S = 1.12$
No. of reflections/data points	8436.68125	879
No. of parameters	78	54
No. of restraints	16	0
H-atom treatment	Only H-atom coordinates refined	H-atom parameters not defined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	–	1.11, −0.32
Absolute structure	–	Flack (1983), 230 Friedel pairs
Absolute structure parameter	–	−0.03 (9)

Computer programs: *XRD Wizard* (Bruker, 2007), *APEX2* (Bruker, 2008*a*), *TOPAS* (Bruker, 2008*b*), *SAINT* (Bruker, 2008*a*), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg & Putz, 2005).

formula best describes the analysis results, IR spectroscopy and XRD data did not confirm the existence of a hydrate or absorbed water in the compound. IR (cm^{-1}): 530 (ν Rh—N), 792, 835, 1009 (ρ NH_3), 1279 and 1508 (bands cleavage ν N—O), 1356 and 1723 (δ N—H), 3229 and 3301 (ν N—H). We believe that the difference between the results of nitrogen analysis and the theoretical calculation for (II) is the systematic error dependent standard analysis procedure.

The assignment of the solid phases to *fac*-isomers of the complexes was made under the assumption that the isomerization of (I) and (II) is absent in the synthesis process.

The nitrogen and hydrogen content in the crystal phase was determined by elemental CHN analysis with Euro EA 3000 equipment. The IR spectra were recorded with an IR SCIMITAR FTS 2000 spectrometer using tablets of KBr in the wavenumber range 400–4000 cm^{-1} in increments of 1 cm^{-1}.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. To determine the structure of (I), powder X-ray data were collected with an X-ray D8-ADVANCE (Bruker) diffractometer at 300 K. The experi-

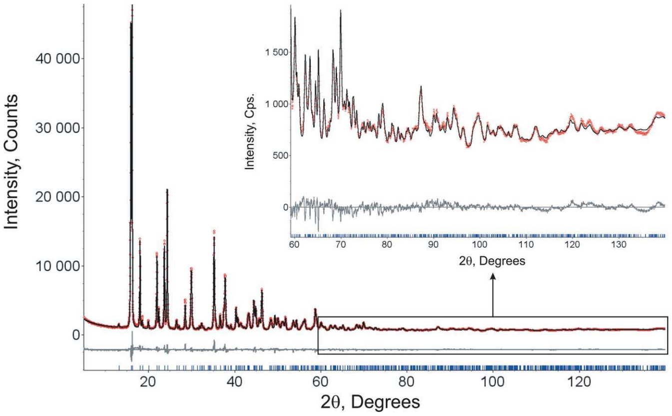

Figure 1
The results of Rietveld refinement of the $[RhCl_3(NH_3)_3]$ structure, showing experimental (red points), calculated (line) and difference (line below) powder patterns.

ment used the variable scan speed technique (VCT) and variable step size (VSS) (Madsen & Hill, 1992; Madsen & Hill, 1994; David, 1992). The exposure time increased with increasing 2θ angle, resulting in a significant improvement in the quality of the collected X-ray data. Typically, the peak half-width (FWHM) must contain 5–8 experimental points, but increasing the 2θ angle significantly broadens the peaks, so the step can be increased in areas with high angles to reduce the duration of the experiment.

The experimental diffractogram was divided into four parts: (i) $5 \leq 2\theta \leq 39.9^\circ$, with a step size of 0.016° and an exposure time of 3 s; (ii) $39.9 \leq 2\theta \leq 61.5^\circ$, with a step size of 0.024° and an exposure time of 9 s; (iii) $61.5 \leq 2\theta \leq 97.3^\circ$, with a step size of 0.032° and an exposure time of 15 s; (iv) $97.3 \leq 2\theta \leq 140^\circ$, with a step size of 0.040° and an exposure time of 30 s. The total exposure time for the experiment was approximately 19 h. Due to the detector (VANTEC), the total exposure time of any one point in the powder pattern was ~700 s. The partition of the experiment for VCT/VSS was executed with the *XRD Wizard* program (Bruker, 2007). Then the experimental data were converted to a conventional XYE-file containing the $2\theta_i$ coordinate, the intensity I_i and the standard deviation $\sigma(I_i)$ for each experimental point. Refinement with the Rietveld method, implemented in the program *TOPAS4.2* (Bruker, 2008*b*), takes into account the standard deviation of intensity at each point by the introduction into the least-squares treatment of the weight $w_i = \sigma(I_i)^{-2}$ for each point.

The powder diffraction pattern of $[RhCl_3(NH_3)_3]$ indicated monoclinic symmetry, with the space group $P2_1/m$ or $P2_1$. The unit-cell volume corresponds to 5–6 non-H atoms in the asymmetric part of the centrosymmetric space group $P2_1/m$ and hence it was selected. The structure was solved by modelling in direct space followed by phase annealing using *TOPAS4.2* (Bruker, 2008*b*). One Rh^{3+} ion, two Cl^- ions and two N atoms were generated and a dynamic population of positions was used for all atoms (Favre-Nicolin & Černý, 2002, 2004). The phase annealing gave a model of the structure which was refined using Rietveld refinement (*TOPAS4.2*). The VCT technique allowed the refinement of anisotropic atomic displacement parameters for rhodium. The isotropic displacement parameters of the remaining non-H atoms had reasonable values. At this stage, the difference synthesis showed several maxima corresponding to the H atoms of NH_3 groups. This information allowed the unambiguous assignment of all H atoms and the refinement of their positions with a soft restraint on the N—H bond lengths of 0.90 (5) Å, as well as on the tetrahedral angles Rh—N—H and H—N—H [109.4 (10)°]. The isotropic displacement parameters of the H

Table 2
Selected geometric parameters (Å, °) for (I).

Rh—N1	2.113 (5)	Rh1—Cl1	2.382 (4)
Rh1—N2	2.039 (4)	Rh1—Cl2	2.366 (2)
N2—Rh1—N2^i	96.81 (15)	N1—Rh1—Cl2	87.21 (12)
N2—Rh1—N1	92.22 (15)	Cl1—Rh1—Cl2	90.28 (8)
N2—Rh1—Cl1	90.15 (12)	Cl2—Rh1—Cl2^i	90.96 (8)
N2—Rh1—Cl2	86.11 (11)		

Symmetry code: (i) $x, -y + \frac{1}{2}, z$.

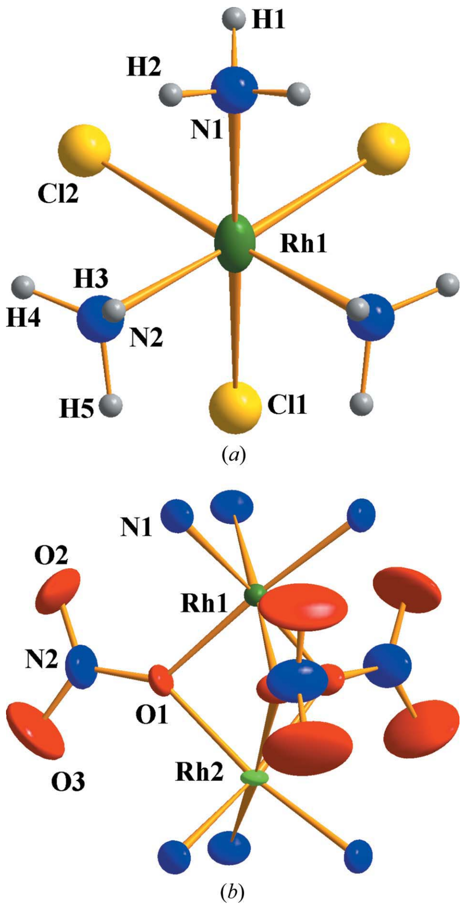

Figure 2
The building blocks of (I) and (II), showing the atom-numbering schemes (50% probability displacement ellipsoids). (*a*) The octahedral $[RhCl_3(NH_3)_3]$ complex and (*b*) the paired $[Rh(NO_3)_3(NH_3)_3]$ octahedra.

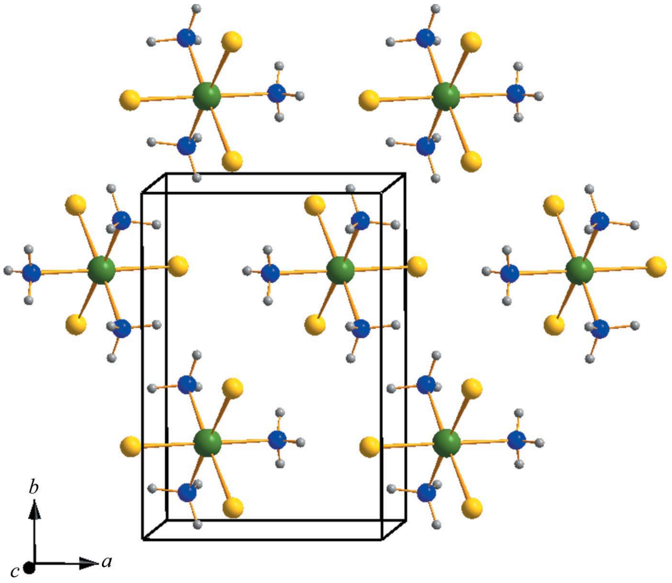

Figure 3
The packing of building blocks in the $[RhCl_3(NH_3)_3]$ crystal, (I).

Table 3
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl1^{ii}	0.97 (5)	2.35 (5)	3.297 (7)	166 (4)
N1—H2···Cl2^{iii}	0.89 (3)	2.68 (3)	3.405 (4)	140 (3)
N2—H3···Cl2^{iv}	0.91 (3)	2.51 (3)	3.340 (5)	152 (3)
N2—H4···Cl1^{v}	0.98 (4)	2.56 (4)	3.392 (3)	143 (3)
N2—H5···Cl2^{vi}	0.99 (4)	2.79 (4)	3.550 (5)	134 (3)

Symmetry codes: (ii) $x+1, y, z$; (iii) $-x+1, -y, -z+1$; (iv) $x, y, z-1$; (v) $-x, y-\frac{1}{2}, -z+1$; (vi) $-x, -y, -z+1$.

atoms were fixed at 0.038 Å^2. The agreement between the observed and calculated patterns is shown in Fig. 1. A check of the structure using *PLATON* (Spek, 2009) did not reveal any unreported features..

Crystals of (II) possess a perfect cleavage and, as a result, the powder samples showed strong texturing, making the structural study difficult. Therefore, due to the presence of single crystals, the single-crystal diffraction technique was used at 296 K by employing a Bruker SMART APEXII diffractometer. Initial characteristics of the experiment and the results of automatic detection of symmetry indicated possible merohedral twinning of the crystal. Thus, the $\langle|E^2-1|\rangle$ value was extremely low (0.316), $R_{\rm sym}$ for 15 space groups had values of 0.016–0.019, while the best value of the combined quality criteria (CFOM) was very high (32.5). The simplest possible space group, $P3$, was chosen and was confirmed by a refinement. Direct methods allowed the determination of the rhodium coordinates, but the difference electron-density maps did not help to solve the structure completely, although the octahedral environment of the Rh atom was recognizable. At this stage, the twin law (010, 100, 00$\bar{1}$) was introduced and the absolute structure was determined. All non-H atoms were clearly located at the same time and refined in the anisotropic approximation. The Rh atom is disordered over two unequally occupied positions [Rh1 is the major occupied position with an occupation factor of 0.8039 (18)] on the threefold axis and due to this fact the H atoms were not located.

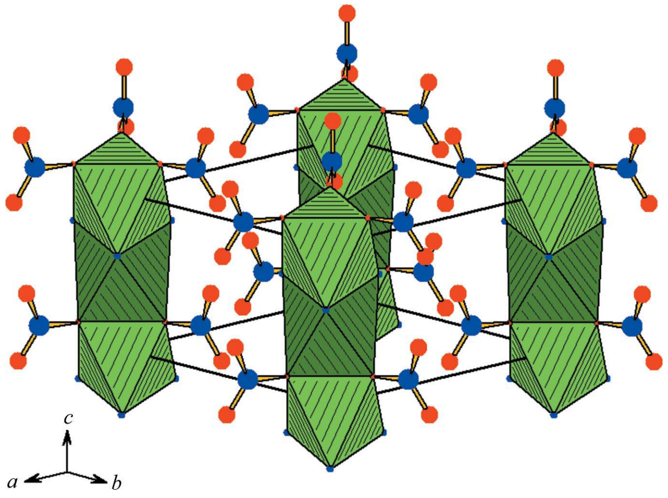

Figure 4
The columnar packing in the $[Rh(NO_3)_3(NH_3)_3]$ structure, (II), with darker octahedra shown around atom Rh1.

Table 4
Selected geometric parameters (Å, °) for (II).

Rh1—N1	2.106 (9)	N2—O3	1.242 (7)
Rh1—O1^{i}	2.030 (8)	N2—O2	1.220 (10)
O1—N2	1.292 (8)		
N1—Rh1—N1^{ii}	87.5 (4)	O1^{ii}—Rh2—O1	77.1 (3)
N1—Rh1—O1^{i}	175.3 (5)	O1^{ii}—Rh2—N1^{iii}	95.8 (5)
N1^{ii}—Rh1—O1^{i}	96.0 (6)	O1—Rh2—N1^{iii}	171.0 (5)
N1^{i}—Rh1—O1^{i}	95.8 (6)	O1^{i}—Rh2—N1^{iii}	96.0 (6)
O1^{i}—Rh1—O1	80.6 (3)	N1^{iii}—Rh2—N1^{iv}	90.4 (4)

Symmetry codes: (i) $-x+y, -x, z$; (ii) $-y, x-y, z$; (iii) $-y, x-y, z-1$; (iv) $-x+y, -x, z-1$.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, FRG, 76344 Eggenstein-Leopoldshafen. (Fax: +49–7247–808–666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the deposition number CSD-426435 for (I) and CSD-426436 for (II).

3. Results and discussion

Both crystal structures are constructed from the neutral complexes $[RhX_3(NH_3)_3]$ (X = NO_3 and Cl), which are *fac*-isomers. The structures of the complexes and the atom-numbering schemes are shown in Fig. 2.

In (I), the $[RhCl_3(NH_3)_3]$ complex has an octahedral structure and the Rh1, Cl1, N1 and H1 atoms are arranged on a mirror plane. Rh—Cl and Rh—N bond lengths (Table 2), lying on the mirror plane, are 0.016 (4) and 0.074 (6) Å longer than the others. Deviations of valence *cis* angles on the Rh^{III} atom from the ideal value of 90° do not exceed 6.8°. The octahedral complexes are connected by N—H···Cl hydrogen bonds in the crystal (Table 3); the packing of the octahedra is shown in Fig. 3. It should be noted that, as in the crystals of the α- and β-phase of $[Rh(NH_3)_3(NO_2)_3]$ (Khranenko *et al.*, 2002; Gromilov *et al.*, 2005), in this case the Rh^{III} atoms (and with them the octahedra) are arranged in essentially flat hexagonal grids; the a and c axes have been swapped in the present case to allow easy comparison with the α- and β-phases. The grids are oriented perpendicular to the c axis and with a repeat distance equal to c (Fig. 3). The deviations of the Rh^{III} atoms

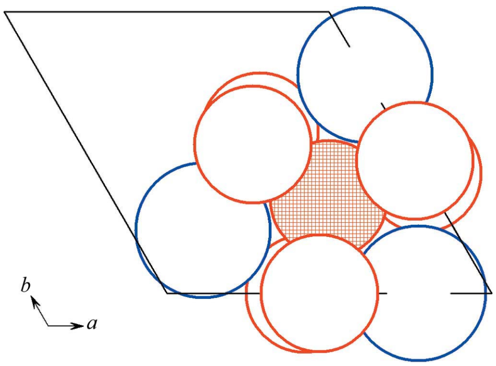

Figure 5
A cavity between $[Rh(NO_3)_3(NH_3)_3]$ columns in (II), with the water O atom shown as a hatched circle. The atomic radii correspond to van der Waals radii.

out of the grid do not exceed 0.114 Å and the distances between atoms in a grid are in the range 5.7284 (12)–6.7279 (13) Å (the latter value is the length of the *a* axis).

The main and unique feature of crystalline complex (II) is its columnar structure. The columns are constructed from the distorted [Rh(NO$_3$)$_3$(NH$_3$)$_3$] octahedra lying on a threefold axis (Fig. 4). The Rh atom occupies two positions on the axis with different degrees of occupation: the position with coordinates (0, $\frac{1}{2}$, 0), Rh1, has a site-occupation factor (sof) of 0.8039 (18), while for the second, Rh2, the sof is 0.1961 (18). So, these 'columns' are not continuous but consist of the isolated Rh1 and Rh2 octahedra and of the Rh1+Rh2 octahedral pairs connected *via* a common face of the O-type (Fig. 2*b*); the Rh1···Rh2 distance is 2.8129 (18) Å. The Rh2 atom is not in the top of the cell, and although the Rh1 atom has $z = 0.5$ it is not in the middle between the nearest Rh2 atoms, and the second distance is between the positions is 2.4431 (18) Å; hereupon the octahedral parameters for Rh1 and Rh2 are different (Table 4). If the Rh1 atom is closer to the octahedral O-face, the Rh2 is closer to the N-face. The maximal deviation of the bond angles from 90° in the octahedra is 12.9° (Table 4). The anisotropic atomic dispacement parameters show librational vibrations of the octahedra around the threefold axis parallel with unit-cell axis *c*. The columns form channels along the threefold axes which could accomodate water molecules in the cavities (Fig. 5); the distances between the water molecule and the nearest atoms would be O···O = 2.83 Å and O···N = 2.99 Å. If we take into account the gaps between the octahedra in the columns, then crystallization under different conditions might allow water molecules to occupy the denoted positions. In (II), the Rh^{III} atoms are arranged strictly in hexagonal grids. The grids lie parallel to the *ab* unit-cell plane with the Rh···Rh distances equal to the *a* cell parameter.

An important feature of the structure is that octahedra with empty metal-atom positions cannot be located side-by-side; the monoatomic face cannot be placed separately. But if the metal atom is present in one polyhedron, say Rh1, and not in the other with a common N-face, Rh2, then the H atoms of the NH$_3$ groups create N—H···O hydrogen bonds between the columns. The arrangement of H atoms in the presence of Rh2 and the absence of Rh1 is different, as is the arrangement of hydrogen bonds. In connection with the mentioned disorder of H atoms, they were not located, but N···O distances (2.92–3.09 Å) between columns indicate the presence of hydrogen bonds.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3133). Services for accessing these data are described at the back of the journal.

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supplementary materials

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Computing details

Data collection: XRD Wizard (Bruker, 2007) for (I); *APEX2* (Bruker, 2008*a*) for (II). Cell refinement: TOPAS Rietveld (Bruker, 2008*b*) for (I); *APEX2* (Bruker, 2008*a*) for (II). Data reduction: XRD Wizard (Bruker, 2007) for (I); *SAINT* (Bruker, 2008*a*) for (II). Program(s) used to solve structure: TOPAS Phase annealing (Bruker, 2008*b*) for (I); *SHELXS97* (Sheldrick, 2008) for (II). Program(s) used to refine structure: TOPAS Rietveld (Bruker, 2008*b*) for (I); *SHELXL97* (Sheldrick, 2008) for (II). Molecular graphics: *SHELXTL* (Sheldrick, 2008) for (II). Software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) for (II).

(I) *fac*-Triamminetrichloridorhodium(III)

Crystal data

$[RhCl_3(NH_3)_3]$	V = 358.21 (2) Å^3
M_r = 260.36	Z = 2
Monoclinic, $P2_1/m$	D_x = 2.414 Mg m^{-3}
Hall symbol: -P 2yb	Cu $K\alpha_1$ radiation, λ = 1.5406, 1.5444 Å
a = 6.7279 (3) Å	T = 300 K
b = 9.7888 (4) Å	yellow
c = 5.4611 (2) Å	?, ? × ? × ? mm
β = 95.149 (2)°	

Data collection

VANTEC linear detector diffractometer	Data collection mode: reflection
	Scan method: step
None monochromator	$2\theta_{min}$ = 5°, $2\theta_{max}$ = 139.987°, $2\theta_{step}$ = 0.016°

Refinement

R_p = 4.215	78 parameters
R_{wp} = 4.555	16 restraints
R_{exp} = 1.538	Only H-atom coordinates refined
R_{Bragg} = 1.790	$(\Delta/\sigma)_{max}$ = 0.010
χ^2 = 8.768	Preferred orientation correction: PO-March Dollase - 1 Dir (0 0 1)
8436.68125 data points	
Profile function: PearsonVII	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Rh	0.2195 (2)	0.25	0.4826 (2)	0.0318 (7)
N1	0.4960 (9)	0.25	0.327 (1)	0.040 (4)*
N2	0.1122 (6)	0.0942 (3)	0.2608 (7)	0.033 (3)*
Cl1	−0.0810 (5)	0.25	0.6825 (6)	0.038 (2)*
Cl2	0.3532 (4)	0.0777 (2)	0.7530 (4)	0.035 (1)*
H1	0.606 (8)	0.25	0.454 (9)	0.06*
H2	0.498 (5)	0.176 (3)	0.232 (6)	0.06*
H3	0.141 (5)	0.110 (3)	0.104 (6)	0.05*
H4	0.161 (6)	0.006 (4)	0.323 (5)	0.05*
H5	−0.035 (6)	0.106 (3)	0.253 (6)	0.05*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rh	0.0490 (15)	0.0229 (12)	0.0229 (11)	0	0.0003 (6)	0

Geometric parameters (Å, º)

Rh—N1	2.113 (5)	N1—H2	0.89 (3)
Rh1—N2	2.039 (4)	N2—H3	0.91 (3)
Rh1—Cl1	2.382 (4)	N2—H4	0.98 (4)
Rh1—Cl2	2.366 (2)	N2—H5	0.99 (4)
N1—H1	0.96 (5)		
N2—Rh1—N2^{i}	96.81 (15)	N1—Rh1—Cl2	87.21 (12)
N2—Rh1—N1	92.22 (15)	Cl1—Rh1—Cl2	90.28 (8)
N2—Rh1—Cl1	90.15 (12)	Cl2—Rh1—Cl2^{i}	90.96 (8)
N2—Rh1—Cl2	86.11 (11)		

Symmetry code: (i) *x*, −*y*+1/2, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1^{ii}	0.97 (5)	2.35 (5)	3.297 (7)	166 (4)
N1—H2···Cl2^{iii}	0.89 (3)	2.68 (3)	3.405 (4)	140 (3)
N2—H3···Cl2^{iv}	0.91 (3)	2.51 (3)	3.340 (5)	152 (3)
N2—H4···Cl1^{v}	0.98 (4)	2.56 (4)	3.392 (3)	143 (3)
N2—H5···Cl2^{vi}	0.99 (4)	2.79 (4)	3.550 (5)	134 (3)

Symmetry codes: (ii) *x*+1, *y*, *z*; (iii) −*x*+1, −*y*, −*z*+1; (iv) *x*, *y*, *z*−1; (v) −*x*, *y*−1/2, −*z*+1; (vi) −*x*, −*y*, −*z*+1.

(II) *fac*-Triamminetrinitratorhodium(III)

Crystal data

$[Rh(NO_3)_3(NH_3)_3]$	*a* = 7.496 (1) Å
M_r = 340.04	*c* = 5.2560 (8) Å
Trigonal, *P*3	*V* = 255.77 (7) $Å^3$
Hall symbol: P 3	*Z* = 1

$F(000) = 168$	$\mu = 1.72$ mm^{-1}
$D_x = 2.208$ Mg m^{-3}	$T = 296$ K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å	Needle, yellow
Cell parameters from 3627 reflections	0.40 × 0.15 × 0.15 mm
$\theta = 3.1$–32.9°	

Data collection

Bruker APEXII CCD area-detector diffractometer	3780 measured reflections
Radiation source: fine-focus sealed tube	879 independent reflections
Graphite monochromator	879 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{\text{int}} = 0.030$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)	$\theta_{\text{max}} = 33.0°$, $\theta_{\text{min}} = 3.1°$
	$h = -11\rightarrow11$
	$k = -11\rightarrow11$
$T_{\text{min}} = 0.546$, $T_{\text{max}} = 0.782$	$l = -8\rightarrow3$

Refinement

Refinement on F^2	H-atom parameters not defined
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.019$	
$wR(F^2) = 0.048$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.12$	$\Delta\rho_{\text{max}} = 1.11$ e Å^{-3}
879 reflections	$\Delta\rho_{\text{min}} = -0.32$ e Å^{-3}
54 parameters	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
0 restraints	
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.035 (8)
Secondary atom site location: difference Fourier map	Absolute structure: Flack (1983), 230 Friedel pairs
	Absolute structure parameter: −0.03 (9)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Rh1	0.0000	0.0000	0.5000	0.01434 (9)	0.8039 (18)
Rh2	0.0000	0.0000	−0.0352 (3)	0.0161 (7)	0.1961 (18)
O1	0.2025 (13)	0.001 (2)	0.2430 (16)	0.0300 (10)	
N1	0.2245 (15)	0.2239 (16)	0.741 (2)	0.0311 (12)	
N2	0.3732 (7)	0.0006 (9)	0.2773 (9)	0.0574 (15)	
O2	0.4248 (16)	−0.001 (3)	0.4969 (19)	0.101 (2)	
O3	0.4708 (14)	0.0001 (19)	0.0867 (13)	0.125 (3)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rh1	0.01485 (9)	0.01485 (9)	0.01332 (17)	0.00742 (5)	0.000	0.000
Rh2	0.0208 (5)	0.0208 (5)	0.0068 (16)	0.0104 (2)	0.000	0.000
O1	0.0222 (19)	0.050 (2)	0.0254 (15)	0.0237 (18)	0.0049 (17)	0.0002 (14)
N1	0.021 (2)	0.027 (3)	0.0293 (18)	0.0006 (17)	0.0005 (18)	0.001 (2)
N2	0.041 (2)	0.101 (4)	0.050 (3)	0.050 (3)	0.0028 (19)	0.000 (3)
O2	0.081 (6)	0.212 (7)	0.055 (3)	0.106 (6)	−0.023 (3)	0.000 (3)
O3	0.110 (7)	0.215 (9)	0.082 (5)	0.105 (7)	0.048 (5)	0.000 (6)

Geometric parameters (Å, º)

Rh1—N1	2.106 (9)	Rh2—O1^{ii}	2.106 (7)
Rh1—N1^{i}	2.106 (9)	Rh2—N1^{iv}	2.051 (9)
Rh1—N1^{ii}	2.106 (9)	Rh2—N1^{v}	2.051 (9)
Rh1—O1^{ii}	2.030 (8)	Rh2—N1^{vi}	2.051 (9)
Rh1—O1	2.030 (7)	Rh2—Rh1^{vi}	2.4431 (18)
Rh1—O1^{i}	2.030 (7)	O1—N2	1.292 (8)
Rh1—Rh2^{iii}	2.4431 (18)	N1—Rh2^{iii}	2.051 (9)
Rh1—Rh2	2.8129 (18)	N2—O3	1.242 (7)
Rh2—O1^{i}	2.106 (7)	N2—O2	1.220 (10)
Rh2—O1	2.106 (7)		

N1—Rh1—N1^{i}	87.5 (4)	O1—Rh2—N1^{iv}	171.0 (5)
N1—Rh1—N1^{ii}	87.5 (4)	O1^{ii}—Rh2—N1^{iv}	96.0 (6)
N1^{i}—Rh1—N1^{ii}	87.5 (4)	O1^{i}—Rh2—N1^{v}	171.0 (5)
N1—Rh1—O1^{ii}	175.3 (5)	O1—Rh2—N1^{v}	96.0 (6)
N1^{i}—Rh1—O1^{ii}	96.0 (6)	O1^{ii}—Rh2—N1^{v}	95.8 (5)
N1^{ii}—Rh1—O1^{ii}	95.8 (6)	N1^{iv}—Rh2—N1^{v}	90.4 (4)
N1—Rh1—O1	95.8 (6)	O1^{i}—Rh2—N1^{vi}	96.0 (6)
N1^{i}—Rh1—O1	175.3 (4)	O1—Rh2—N1^{vi}	95.8 (5)
N1^{ii}—Rh1—O1	96.0 (6)	O1^{ii}—Rh2—N1^{vi}	171.0 (5)
O1^{ii}—Rh1—O1	80.6 (3)	N1^{iv}—Rh2—N1^{vi}	90.4 (4)
N1—Rh1—O1^{i}	96.0 (6)	N1^{v}—Rh2—N1^{vi}	90.4 (4)
N1^{i}—Rh1—O1^{i}	95.8 (6)	O1^{i}—Rh2—Rh1^{vi}	134.0 (2)
N1^{ii}—Rh1—O1^{i}	175.3 (4)	O1—Rh2—Rh1^{vi}	134.0 (2)
O1^{ii}—Rh1—O1^{i}	80.6 (3)	O1^{ii}—Rh2—Rh1^{vi}	134.0 (2)
O1—Rh1—O1^{i}	80.6 (3)	N1^{iv}—Rh2—Rh1^{vi}	55.0 (3)
N1—Rh1—Rh2^{iii}	53.0 (3)	N1^{v}—Rh2—Rh1^{vi}	55.0 (3)
N1^{i}—Rh1—Rh2^{iii}	53.0 (3)	N1^{vi}—Rh2—Rh1^{vi}	55.0 (3)
N1^{ii}—Rh1—Rh2^{iii}	53.0 (3)	O1^{i}—Rh2—Rh1	46.0 (2)
O1^{ii}—Rh1—Rh2^{iii}	131.7 (2)	O1—Rh2—Rh1	46.0 (2)
O1—Rh1—Rh2^{iii}	131.7 (2)	O1^{ii}—Rh2—Rh1	46.0 (2)
O1^{i}—Rh1—Rh2^{iii}	131.7 (2)	N1^{iv}—Rh2—Rh1	125.0 (3)
N1—Rh1—Rh2	127.0 (3)	N1^{v}—Rh2—Rh1	125.0 (3)
N1^{i}—Rh1—Rh2	127.0 (3)	N1^{vi}—Rh2—Rh1	125.0 (3)
N1^{ii}—Rh1—Rh2	127.0 (3)	Rh1^{vi}—Rh2—Rh1	180.0
O1^{ii}—Rh1—Rh2	48.3 (2)	N2—O1—Rh1	130.3 (6)
O1—Rh1—Rh2	48.3 (2)	N2—O1—Rh2	144.0 (6)

O1^{i}—Rh1—Rh2	48.3 (2)	Rh1—O1—Rh2	85.7 (2)
Rh2^{iii}—Rh1—Rh2	180.000 (1)	Rh1—N1—Rh2^{iii}	72.0 (2)
O1^{i}—Rh2—O1	77.1 (3)	O3—N2—O2	124.9 (6)
O1^{i}—Rh2—O1^{ii}	77.1 (3)	O3—N2—O1	118.2 (6)
O1—Rh2—O1^{ii}	77.1 (3)	O2—N2—O1	116.9 (6)
O1^{i}—Rh2—N1^{iv}	95.8 (5)		

Symmetry codes: (i) $-y, x-y, z$; (ii) $-x+y, -x, z$; (iii) $x, y, z+1$; (iv) $-y, x-y, z-1$; (v) $-x+y, -x, z-1$; (vi) $x, y, z-1$.