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Structure of (−)$_{589}$-Tris(3,3′-dimethyl-2,2′-bipyridine)rhodium(III) Triperchlorate Monohydrate

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Abstract. $[\mathrm{Rh(C_{12}H_{12}N_2)_3}]^{3+}.3\mathrm{ClO_4^-}.\mathrm{H_2O}$, $M_r = 971{\cdot}4$, orthorhombic, $P2_12_12_1$ (systematic absences $h00$, $h \neq 2n$, $0k0$, $k \neq 2n$, $00l$, $l \neq 2n$), $a = 17{\cdot}675$ (2), $b = 18{\cdot}151$ (2), $c = 12{\cdot}637$ (4) Å, $U = 4054$ (1) Å^3, $Z = 4$, $D_m = 1{\cdot}57$, $D_x = 1{\cdot}59$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu(\mathrm{Mo}\ K\alpha) = 0{\cdot}68$ mm^{-1}. The structure was solved by Patterson–Fourier methods and refined to a final R value of 0·045 for the 4742 observed reflections. The absolute configuration of the complex ion can be designated as $\Lambda(\delta\lambda\lambda)$.

Introduction. The structures of two bis(diamine) Co$^{\mathrm{III}}$ complexes with 3,3′-dimethyl-2,2′-bipyridine (dmbpy) have been reported (Sato & Saito, 1978; Ohba, Sato & Saito, 1979). Recently, tris(dmbpy) complexes of Co$^{\mathrm{III}}$ and Rh$^{\mathrm{III}}$ were prepared and resolved into optical isomers (Suzuki, 1979). Because of its stability, the Rh complex was selected and subjected to crystal structure analysis in order to establish the absolute configuration and to gain the conformational details. Colorless plate-like crystals of the title compound were kindly supplied by Dr Suzuki. The cell dimensions were refined by least squares on the basis of 15 2θ values of higher-order reflections (31° $< 2\theta <$ 38°) measured on a diffractometer with Mo $K\alpha$ radiation. Intensities were measured from a spherical crystal 0·5 mm in diameter on a Rigaku automated four-circle diffractometer. Data were collected by the θ–2θ scan mode to a maximum 2θ value of 55° with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) monochromated by a graphite plate. Of the 5153 measured unique reflections (the $+h+k+l$ set), 4742 with $|F_o| > 3\sigma(|F_o|)$ were considered as observed. The intensities were corrected for Lorentz and polarization factors, but an absorption correction was not applied. Approximate positions of the Rh and three Cl atoms were deduced from three-dimensional Patterson maps, and the positions of all non-hydrogen atoms were derived by the Fourier method. They were refined by block-diagonal least squares with anisotropic thermal parameters. With $R = 0{\cdot}055$ ($R = \sum|\Delta F|/\sum|F_o|$), all the H atoms were located from a difference synthesis except those of the water molecule. In the refinement the weight $w = [\sigma^2(|F_o|) + (0{\cdot}010|F_o|)^2]^{-1}$ was assigned. The final R was 0·045 and $R_2 = 0{\cdot}062$ $\{R_2 = [\sum w(\Delta F)^2/\sum w(F_o)^2]^{1/2}\}$ for 4742 reflections. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The calculations were carried out on a FACOM 230-48 computer of this Institute with a local version of *UNICS* (Ashida, 1967). The final atomic parameters are listed in Table 1.†

The absolute structure was determined by an anomalous-scattering technique. Eight hkl and $\bar{h}kl$ pairs, for which $|F_c(hkl)|$ and $|F_c(\bar{h}kl)|$ differed by more than 7%, were measured with Mo $K\alpha$ radiation. The observed and calculated intensity ratios are compared in Table 2. All the observed $|F|$'s were

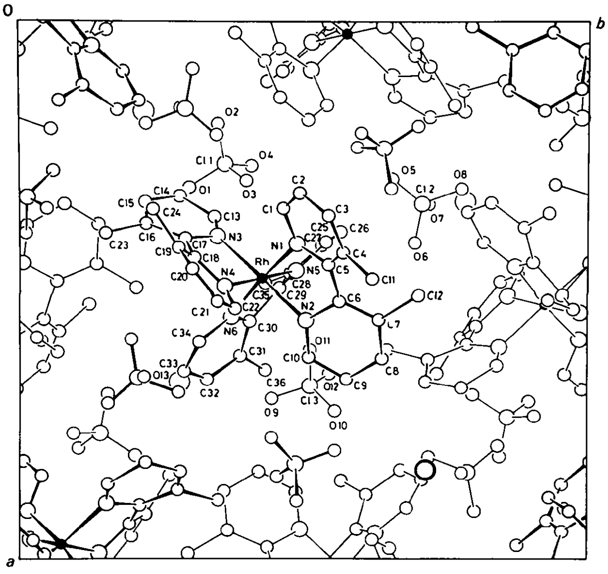

Fig. 1. A projection of the crystal structure along **c**.

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† Lists of structure factors, thermal parameters and relevant interatomic distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34256 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters* ($\times 10^4$; *for* Rh *and* Cl $\times 10^5$; *for* H $\times 10^3$)

	x	y	z
Rh	47723 (2)	42539 (2)	39490 (3)
N(1)	4105 (3)	4865 (3)	4942 (4)
N(2)	5533 (3)	5047 (3)	4356 (4)
N(3)	3978 (3)	3465 (3)	3612 (4)
N(4)	4915 (3)	3589 (3)	5234 (4)
N(5)	4612 (3)	4859 (3)	2596 (4)
N(6)	5469 (3)	3720 (3)	2951 (4)
C(1)	3457 (4)	4623 (4)	5366 (6)
C(2)	3176 (4)	4929 (4)	6274 (7)
C(3)	3599 (5)	5423 (5)	6805 (6)
C(4)	4270 (4)	5690 (4)	6414 (5)
C(5)	4493 (4)	5427 (4)	5428 (5)
C(6)	5192 (4)	5632 (3)	4861 (5)
C(7)	5519 (5)	6341 (4)	4790 (6)
C(8)	6250 (5)	6392 (4)	4436 (6)
C(9)	6632 (4)	5766 (5)	4029 (6)
C(10)	6237 (4)	5113 (4)	3970 (5)
C(11)	4768 (6)	6210 (6)	7067 (7)
C(12)	5079 (6)	7029 (5)	4964 (9)
C(13)	3613 (4)	3420 (4)	2695 (5)
C(14)	3221 (5)	2792 (5)	2389 (7)
C(15)	3327 (5)	2175 (5)	3066 (7)
C(16)	3729 (4)	2206 (4)	3931 (7)
C(17)	4009 (4)	2891 (4)	4288 (5)
C(18)	4364 (4)	3063 (4)	5310 (5)
C(19)	4161 (4)	2782 (4)	6312 (5)
C(20)	4599 (5)	3028 (5)	7143 (6)
C(21)	5181 (5)	3470 (4)	7039 (5)
C(22)	5338 (4)	3785 (4)	6067 (5)
C(23)	3911 (6)	1486 (4)	4491 (9)
C(24)	3469 (5)	2356 (6)	6510 (7)
C(25)	4075 (4)	5383 (4)	2510 (6)
C(26)	3876 (4)	5652 (4)	1550 (6)
C(27)	4137 (4)	5301 (5)	675 (6)
C(28)	4672 (4)	4753 (4)	726 (5)
C(29)	4945 (3)	4566 (3)	1731 (5)
C(30)	5553 (4)	4042 (3)	1962 (5)
C(31)	6195 (4)	3887 (4)	1367 (5)
C(32)	6644 (4)	3292 (4)	1682 (6)
C(33)	6485 (5)	2901 (4)	2565 (7)
C(34)	5934 (4)	3167 (4)	3255 (6)
C(35)	4855 (5)	4314 (5)	−254 (5)
C(36)	6468 (4)	4325 (5)	458 (6)
Cl(1)	26491 (12)	35948 (13)	93232 (20)
Cl(2)	33815 (10)	70859 (10)	93122 (15)
Cl(3)	67562 (14)	51275 (14)	74513 (18)
O(1)	3075 (5)	2979 (6)	9231 (8)
O(2)	1906 (4)	3471 (5)	9498 (11)
O(3)	2955 (5)	3982 (8)	10140 (12)
O(4)	2671 (9)	4066 (12)	8501 (12)
O(5)	2904 (5)	6551 (5)	9549 (12)
O(6)	4122 (3)	6961 (3)	9687 (5)
O(7)	3400 (5)	7196 (7)	8217 (7)
O(8)	3110 (4)	7782 (5)	9656 (8)
O(9)	7006 (9)	4437 (7)	7320 (12)
O(10)	7248 (5)	5565 (6)	8028 (10)
O(11)	6081 (6)	5110 (7)	7985 (11)
O(12)	6540 (6)	5458 (8)	6519 (7)
O(13)	6671 (8)	2826 (7)	8952 (11)
H(C1)	310 (4)	417 (4)	526 (5)
H(C2)	265 (4)	470 (4)	663 (6)
H(C3)	344 (6)	553 (6)	726 (9)
H(C8)	649 (5)	682 (5)	445 (7)
H(C9)	703 (4)	578 (4)	356 (6)
H(C10)	644 (3)	464 (3)	366 (5)
H(C11)1	443 (5)	671 (5)	709 (7)
H(C11)2	476 (5)	592 (5)	795 (7)
H(C11)3	519 (6)	637 (5)	650 (8)
H(C12)1	510 (3)	735 (3)	442 (4)
H(C12)2	489 (5)	686 (5)	521 (7)
H(C12)3	507 (4)	746 (4)	525 (5)
H(C13)	363 (6)	380 (5)	224 (8)
H(C14)	291 (3)	276 (3)	172 (5)
H(C15)	302 (3)	170 (3)	280 (5)
H(C20)	448 (6)	284 (6)	788 (9)
H(C21)	530 (5)	355 (5)	745 (8)
H(C22)	585 (3)	406 (3)	578 (5)
H(C23)1	436 (4)	155 (4)	470 (6)
H(C23)2	388 (4)	103 (4)	413 (6)
H(C23)3	360 (4)	145 (4)	503 (6)
H(C24)1	323 (4)	260 (4)	706 (5)
H(C24)2	309 (6)	233 (6)	592 (9)
H(C24)3	360 (6)	184 (5)	669 (8)
H(C25)	391 (3)	573 (4)	328 (5)
H(C26)	357 (4)	590 (4)	140 (6)
H(C27)	401 (5)	542 (5)	15 (8)
H(C32)	716 (4)	321 (4)	129 (6)
H(C33)	675 (6)	247 (6)	278 (9)
H(C34)	593 (4)	301 (4)	394 (6)
H(C35)1	506 (4)	379 (4)	19 (5)
H(C35)2	502 (4)	478 (4)	−97 (5)
H(C35)3	445 (6)	424 (6)	−50 (9)
H(C36)1	611 (4)	405 (4)	−18 (6)
H(C36)2	629 (6)	484 (5)	55 (8)
H(C36)3	702 (6)	427 (6)	38 (8)

averaged for the two equivalent reflections (*hkl* and $\bar{h}\bar{k}\bar{l}$). The concordance in Table 2 indicated that $(-)_{589}$-$[Rh(dmbpy)_3]^{3+}$ has the absolute configuration Λ (IUPAC, 1970) in agreement with the assignment based on the sign of the circular dichroism of the π–π^* exciton bands ($\nu = 29{\cdot}85 \times 10^2$ mm^{-1}, $\Delta\varepsilon = +19{\cdot}7$ and $\nu = 32{\cdot}68 \times 10^2$ mm^{-1}, $\Delta\varepsilon = -35{\cdot}6$: Suzuki, 1979).

Discussion. Fig. 1 shows a projection of the structure along **c**. A perspective drawing of the complex cation is given in Fig. 2, where the ion is viewed along the normal to the plane through the midpoints of the line joining the two N atoms of each ligand. Hereafter this line will be called the axis of the complex ion. The absolute configuration of the present complex ion is $\Lambda(\delta\lambda\lambda)$. Two of the C—C bonds in the chelate rings are inclined at a mean angle of 54·8° to the axis of the complex ion, while the remaining bond is at an angle of 25·2°. Thus the complex ion takes the '*ob*$_2$ *lel*' conformation. The inclination of the C—C bond in the *lel* ring is greater by about 10° than those of $[Co(diamine)_2(dmbpy)]^{3+}$ complexes (Sato & Saito, 1978; Ohba, Sato & Saito, 1979). The ion has an approximate twofold symmetry axis through the Rh and the midpoint of the C—C bond in the δ chelate ring.

Table 2. *Determination of the absolute configuration*

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$\frac{\lvert F_o(hkl)\rvert}{\lvert F_o(\bar{h}kl)\rvert}$	$\frac{\lvert F_c(hkl)\rvert}{\lvert F_c(\bar{h}kl)\rvert}$
5	4	1	12·9	12·8	1·48	1·51
$\bar{5}$	4	1	8·7	8·5		
12	6	1	37·9	36·7	1·08	1·08
$\overline{12}$	6	1	35·0	34·1		
1	7	1	38·0	36·1	1·09	1·09
$\bar{1}$	7	1	34·9	33·1		
8	14	1	18·0	17·6	1·08	1·07
$\bar{8}$	14	1	16·6	16·4		
5	14	3	20·8	20·6	1·11	1·09
$\bar{5}$	14	3	18·7	18·9		
7	2	4	14·3	14·7	0·85	0·86
$\bar{7}$	2	4	16·9	17·1		
5	1	10	13·8	14·7	0·85	0·87
$\bar{5}$	1	10	16·2	16·9		
6	2	11	16·2	17·5	1·11	1·11
$\bar{6}$	2	11	14·6	15·8		

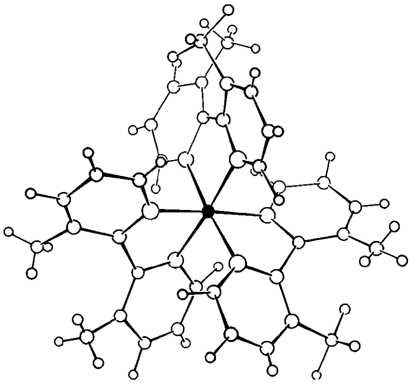

Fig. 2. A perspective drawing of the complex ion, $(-)_{589}[Rh(dmbpy)_3]^{3+}$.

Mean values of the interatomic distances and bond angles within the chelate rings are indicated in Fig. 3. There are no significant differences between the δ and λ chelate rings. The average values are: Rh—N 2·039 (5), N—C 1·368 (8), C—C 1·470 (9) Å; N—Rh—N 80·4 (2), Rh—N—C 113·1 (4), N—C—C 113·3 (6)°. Each chelate ring takes an unsymmetrical skew conformation as shown in Fig. 4. The dihedral angles about the C—C bond of the chelate rings are 25·0 (7) and 31·9 (8)° for the δ and λ rings respectively.

Two pyridine moieties of dmbpy are twisted owing to the interaction between bulky methyl groups, and are inclined at mean angles of 15·8 and 21·0° to the coordination plane, for δ-dmbpy and λ-dmbpy respectively. The twist angles of both pyridine rings for the δ and λ chelate rings are 29·0 and 36·7° respectively. Accordingly, the C···C distance between the two methyl groups is 0·11 Å longer in the λ ring than the value of 2·989 (11) Å in the δ ring. The mean tilt angle of the C—CH_3 bond to the appropriate pyridine ring is 10·5°. Non-bonded H···H contacts less than 3·00 Å do not occur in the complex ion, except for those between the methyl groups.

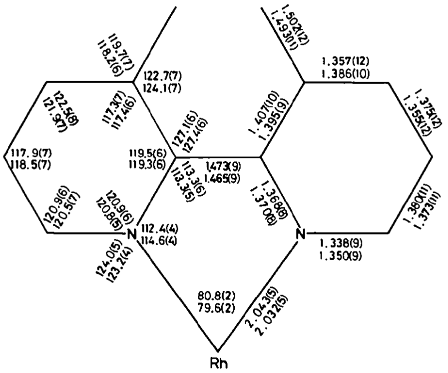

Fig. 3. Mean bond lengths (Å) and angles (°) within the complex ion. The upper values refer to the δ chelate ring and the lower to the λ ring.

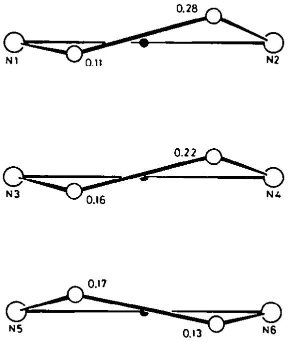

Fig. 4. Conformations of the chelate rings. Figures next to each C atom indicate the deviations (Å) from the coordination plane; the average e.s.d. is 0·01 Å.

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