

$V = 453.9 (4) \text{ \AA}^3$
 $Z = 1$
 $D_x = 2.305 \text{ Mg m}^{-3}$

Crystal source: chemical
 synthesis

the electron density map and refined with a fixed temperature factor ($U_{\text{iso}} = 0.07 \text{ \AA}^2$). All calculations were performed on a MicroVAX using *SHELX76* (Sheldrick, 1976)

Data collection

Philips PW1100 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: empirical
 $T_{\text{min}} = 0.890$, $T_{\text{max}} = 0.995$
 4279 measured reflections
 4001 independent reflections

2435 observed reflections [$F > 12\sigma(F)$]
 $\theta_{\text{max}} = 25^\circ$
 $h = -13 \rightarrow 14$
 $k = -13 \rightarrow 13$
 $l = 0 \rightarrow 10$
 2 standard reflections monitored every 100 reflections
 intensity variation: none

Refinement

Refinement on F
 Final $R = 0.031$
 $wR = 0.031$
 $S = 0.777$

$w = 1$
 $(\Delta/\sigma)_{\text{max}} = 0.02$
 $\Delta\rho_{\text{max}} = 1.2 \text{ e \AA}^{-3}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

2435 reflections
 121 parameters
 Only coordinates of H atoms refined

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Pd	0.0	0.0	0.0	0.0255 (1)
Cl(1)	-0.1585 (1)	0.1833 (1)	0.2099 (2)	0.0357 (4)
Cl(2)	0.1108 (1)	0.1579 (1)	-0.2580 (2)	0.0417 (4)
N(1)	0.4893 (4)	0.1183 (4)	-0.2567 (6)	0.034 (1)
C(2)	0.6059 (4)	0.0570 (4)	-0.2453 (6)	0.032 (1)
N(3)	0.7499 (4)	0.1744 (4)	-0.2416 (6)	0.032 (1)
C(4)	0.7826 (4)	0.3370 (4)	-0.2489 (6)	0.029 (1)
C(5)	0.6573 (4)	0.3896 (4)	-0.2686 (6)	0.029 (1)
C(6)	0.5147 (4)	0.2776 (5)	-0.2725 (7)	0.033 (1)
O(2)	0.5860 (4)	-0.0862 (3)	-0.2390 (6)	0.047 (1)
N(4)	0.9248 (4)	0.4340 (5)	-0.2375 (7)	0.044 (2)
Br	0.69082 (6)	0.60824 (5)	-0.29450 (8)	0.0449 (2)

Table 2. Geometric parameters (\AA , $^\circ$)

Pd—Cl(1)	2.302 (2)	C(4)—C(5)	1.419 (7)
N(1)—C(2)	1.368 (7)	C(6)—N(1)	1.354 (6)
N(3)—C(4)	1.353 (5)	C(4)—N(4)	1.309 (5)
C(5)—C(6)	1.349 (5)		
C(2)—O(2)	1.205 (5)	N(1)···Cl(1) ⁱ	3.291 (4)
C(5)—Br	1.871 (4)	N(3)···Cl(2) ⁱⁱ	3.316 (4)
Pd—Cl(2)	2.304 (2)	N(4)···Cl(2) ⁱⁱⁱ	3.302 (5)
C(2)—N(3)	1.378 (5)	N(4)···Cl(1) ⁱⁱⁱ	3.287 (4)
Cl(1)—Pd—Cl(2)	90.3 (1)	N(1)—C(2)—N(3)	113.9 (3)
C(2)—N(3)—C(4)	126.3 (4)	N(3)—C(4)—C(5)	116.5 (4)
C(4)—C(5)—C(6)	118.6 (4)	C(5)—C(6)—N(1)	121.5 (4)
C(6)—N(1)—C(2)	123.1 (4)	N(1)—C(2)—O(2)	123.6 (4)
O(2)—C(2)—N(3)	122.5 (4)	N(3)—C(4)—N(4)	118.8 (4)
N(4)—C(4)—C(5)	124.7 (4)	C(4)—C(5)—Br	120.6 (3)
Br—C(5)—C(6)	120.9 (3)		

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

Intensities were corrected for Lp and for absorption (North Phillips & Mathews, 1968). The structure was solved by the heavy-atom method and final scale factors, atomic coordinates and anisotropic thermal parameters were obtained by full-matrix least-squares refinement. H-atom positions were obtained from

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and possible hydrogen bonds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55789 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1012]

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2-(η^2 -Dithioformato)-2-(triphenylphosphine)-1,7-dicarbonyl-2-rhoda-closo-dodecaborane(12)

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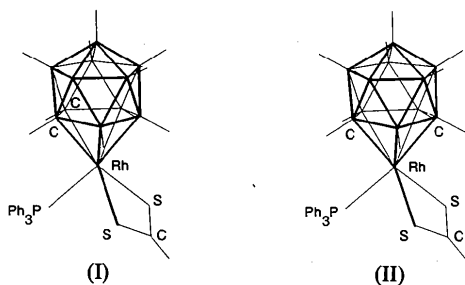
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Abstract

The asymmetric unit has two independent molecules which have very similar conformations. The dithioformato ligand is bonded asymmetrically with Rh—S distances of 2.355(1) and 2.432(1) \AA in one molecule and 2.347(1) and 2.423(1) \AA in the other; in each case, the shorter Rh—S bond is *trans* to a C atom and the longer one *trans* to a B atom. The Rh—P bond [2.314(1) and 2.320(1) \AA , respectively, in the two molecules] is *trans* to the second C atom in the C_2B_9 cage.

Comment

We have previously described the structure of 3-(η^2 -dithioformato)-3-(triphenylphosphine)-1,2-dicarba-3-rhoda-*closo*-dodecaborane(12) (I) (Ferguson *et al.*, 1990) and we now report the structure of the 1,7-dicarba-2-rhoda-RhC₂B₉ isomer (II). This was synthesized in low yield (3.3%) from the reaction between *closo*-[2,2-(PPh₃)₂-2-H-2,1,7-RhC₂B₉H₁₁] and excess CS₂ at reflux for 30 h. Under similar conditions, (I) was isolated in 31% yield. The X-ray analysis of (II) allows us to compare the effects of the different C₂B₉-cage ligands on the structural chemistry of the [Rh(PPh₃)(S₂CH)] unit.



There are two independent molecules [(IIa) and (IIb)] in the crystal asymmetric unit; analysis of the molecular parameters with *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) and *PLATON-91* (Spek, 1991) showed that the two molecules are unrelated by any crystal symmetry transformation. The molecules have very similar geometries and conformations; molecule (IIa) is shown in Fig. 1 [diagrams of (IIb) have been deposited] and selected dimensions are listed in Table 2.

As with the 1,2-dicarba-3-rhoda-RhC₂B₉ isomer (I), molecule (II) contains a 12-vertex closed RhC₂B₉ cage with *exo*-cage PPh₃ and η^2 -S₂CH ligands bonded to Rh.

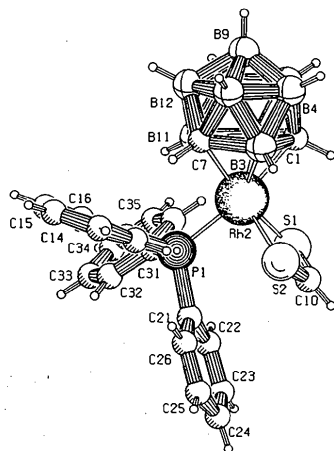


Fig. 1. A *PLUTON* drawing of (IIa) showing the chemical numbering scheme for the RhC₂B₉ cage; the Rh(2)—B(11) bond is hidden behind the Rh(2)—C(7) bond.

The angles made at Rh by the P and S atoms are close to 90° [P—Rh—S(1) 88.75(3), 87.90(3); P—Rh—S(2) 90.49(3), 89.37(3)°] while the angles P—Rh—C(1) and S(1)—Rh—C(7) are 167.86(8) and 165.7(1), 169.03(7) and 168.47(8)°, respectively. This suggests a pseudo-octahedral environment at Rh, modified by the small S—Rh—S angles [71.64(3) and 71.67(3)°] and the involvement of the Rh atom with the C₂B₉-cage ligand in multi-centre cluster bonds.

The Rh—S distances in (II) show a pronounced *trans* effect with Rh(2)—S(1) *trans* to C(7) being shorter than Rh(2)—S(2) *trans* to B(11) [mean values 2.351(1) and 2.428(1) Å, respectively]. There is also an effect on the C—S bond lengths, the longer C—S bonds being associated with the shorter Rh—S bonds and *vice versa* [*cf.* C(10)—S(1) mean value 1.670(3) Å; C(10)—S(2) mean value 1.650(4) Å]. In molecule (I) where both S atoms are *trans* to C atoms, the Rh—S distances are similar [mean value 2.354(1) Å] and the S—C distances do not differ from their mean value [1.652(3) Å]. The Rh—P bonds in (II) are *trans* to C(1) and the mean Rh—P value [2.317(1) Å] is shorter than in (I) where the Rh—P bond [2.374(1) Å] is *trans* to a B atom.

Trans effects are also seen in the Rh—C distances with the Rh(2)—C(1) bonds *trans* to P [mean value 2.205(3) Å] being shorter than Rh—C(7) bonds *trans* to S(1) [mean value 2.238(3) Å]. No Rh—B bond differs significantly from the mean value of 2.187(3) Å. In (I), there were significant differences between the Rh—B bond lengths [2.204(3) to 2.239(3) Å] but not the Rh—C distances [2.195(3) and 2.201(3) Å].

Within the C₂B₉ cage, the B—B distances vary from 1.747(8) to 1.836(5) Å and the C—B bonds from 1.667(5) to 1.722(5) Å; these ranges are typical of metallocarboranes in general. The dimensions of the PPh₃ moieties in the two molecules are normal.

An analysis of the form of the frontier molecular orbital interactions of the C₂B₉ ligand and the [RhL₂X] unit (Mingos, Forsyth & Welch, 1978; Faridoun *et al.*, 1988) suggests that there are several possible conformations of an Rh(L)(η^2 -L') unit above a C₂B₃ face to which it is attached. Each conformation would be expected to have one Rh—ligand vector parallel to the line joining the centres of the two C atoms (when projected onto the plane containing the C₂B₃ face). Two of the six possible conformations for a generalized Rh(L)(η^2 -L')-containing complex are illustrated in Fig. 2; Fig. 2(a) has the projected Rh—L vector parallel to the line joining the C atoms and Fig. 2(b) one of the projected Rh—L' bond vectors parallel. Both molecules of (II) have the same conformation about Rh and that for (IIa) is shown in Fig. 2(c); the corresponding diagram for (IIb) is essentially identical and has been deposited. The observed conformation is strongly affected by the fact that the mean S—Rh—S angle is 71.66(3)°. Thus, while one projected Rh—L' vector [*i.e.* Rh—S(1) in Fig. 2(c)] is almost 'parallel' to the line joining the C

atoms of the C_2B_3 face, the other [Rh—S(2)] is almost at right angles to this line. The Rh—S(2) orientation leads exactly to the alternative conformation which would be expected in complexes of the 7,8- C_2B_9 -based carborane* ligand with a projected Rh— L' vector at right angles to the line joining the C atoms of the C_2B_3 moiety (Mingos, Forsyth & Welch, 1978). The overall effect in the title compound is to produce an observed conformation which is not that expected in either 7,9- or 7,8- C_2B_9 -based compounds. Finally, it is unclear why the observed conformation does not have the projected Rh—P vector parallel to the line through the C atoms. This would remove the possibility of the alternative conformations discussed above.

* The 7,8- and 7,9-carborane nomenclature refers to the proper IUPAC names of the carboranes before the addition of the metal, *i.e.* while they are *nido* carborane units. After reaction with the metal substrate, the compounds become the *closo* species with the numbering scheme indicated in Fig. 1.

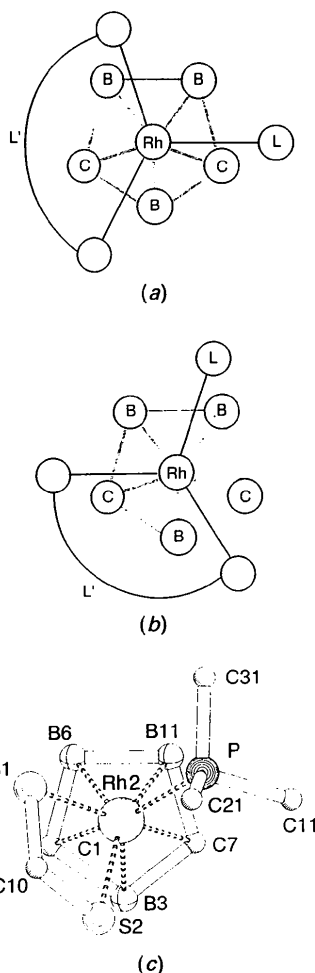


Fig. 2. Views of possible (a), (b) and actual (c) Rh coordination in one of the molecules of (II) from a viewpoint normal to the C_2B_3 plane showing the orientation of the η^2 - S_2CH and phosphine ligands on the Rh atom.

Experimental

Crystal data

$C_{22}H_{27}B_9PRhS_2$
 $M_r = 586.77$
 Monoclinic
 $P2_1/c$
 $a = 15.3522$ (21) Å
 $b = 18.8760$ (36) Å
 $c = 18.4228$ (41) Å
 $\beta = 103.71$ (1)°
 $V = 5187$ (3) Å³
 $Z = 8$
 $D_x = 1.503$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.70930$ Å
 Cell parameters from 25 reflections
 $\theta = 10.04$ – 19.59°
 $\mu = 0.875$ mm⁻¹
 $T = 293$ K
 Plate
 $0.48 \times 0.41 \times 0.25$ mm
 Orange-red

Data collection

Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical
 $T_{\min} = 0.7072$, $T_{\max} = 0.7795$
 12236 measured reflections
 11812 independent reflections

8400 observed reflections
 $[I_{\text{net}} > 3.0\sigma(I_{\text{net}})]$
 $R_{\text{int}} = 0.011$
 $\theta_{\max} = 26.92^\circ$
 $h = 0 \rightarrow 19$
 $k = 0 \rightarrow 24$
 $l = -23 \rightarrow 23$
 3 standard reflections
 frequency: 120 min
 intensity variation: <2%

Refinement

Refinement on F
 Final $R = 0.027$
 $wR = 0.038$
 $S = 1.44$
 8400 reflections
 614 parameters
 $w = 1/[\sigma^2(F) + 0.0008F^2]$
 $(\Delta/\sigma)_{\max} = 0.004$

$\Delta\rho_{\max} = 0.93$ e Å⁻³
 $\Delta\rho_{\min} = -0.29$ e Å⁻³
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: Enraf-Nonius CAD-4 software. Cell refinement: Enraf-Nonius CAD-4 software. Data reduction: *SDP-Plus* (Frenz, 1983). Program(s) used to solve structure: *Patterson heavy-atom method*. Program(s) used to refine structure: *SDP-Plus*. Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *SDP-Plus* and *WordPerfect 5.1*. Software used to prepare drawings: *PLUTON-92* (Spek, 1992).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Rh(2)	0.17242 (1)	-0.17836 (1)	-0.02017 (1)	0.03188 (5)
S(1)	0.05600 (5)	-0.13098 (4)	0.02829 (4)	0.0505 (3)
S(2)	0.21975 (6)	-0.18032 (4)	0.11550 (4)	0.0543 (3)
P(1)	0.22929 (4)	-0.06506 (3)	-0.02219 (4)	0.0320 (1)
C(10)	0.1197 (2)	-0.1470 (2)	0.1135 (2)	0.0599 (9)
C(11)	0.3409 (2)	-0.0706 (1)	-0.0400 (1)	0.0357 (6)
C(12)	0.4063 (2)	-0.1096 (2)	0.0095 (2)	0.0455 (8)
C(13)	0.4908 (2)	-0.1181 (2)	-0.0029 (2)	0.0546 (9)
C(14)	0.5113 (2)	-0.0886 (2)	-0.0646 (2)	0.0591 (9)
C(15)	0.4461 (2)	-0.0524 (2)	-0.1156 (2)	0.0594 (9)
C(16)	0.3616 (2)	-0.0432 (2)	-0.1035 (2)	0.0445 (8)
C(21)	0.2400 (2)	-0.0130 (1)	0.0636 (1)	0.0371 (6)
C(22)	0.1671 (2)	0.0269 (2)	0.0725 (2)	0.0484 (8)
C(23)	0.1690 (2)	0.0622 (2)	0.1381 (2)	0.0599 (9)
C(24)	0.2449 (3)	0.0578 (2)	0.1969 (2)	0.0647 (10)

C(25)	0.3178 (2)	0.0204 (2)	0.1879 (2)	0.0627 (10)	B(4)—B(5)	1.761 (5)	B(4')—B(5')	1.747 (8)
C(26)	0.3153 (2)	-0.0154 (2)	0.1221 (2)	0.0505 (9)	B(4)—B(8)	1.765 (6)	B(4')—B(8')	1.760 (6)
C(31)	0.1657 (2)	-0.0045 (1)	-0.0919 (1)	0.0361 (6)	B(4)—B(9)	1.796 (6)	B(4')—B(9')	1.759 (6)
C(32)	0.1994 (2)	0.0626 (2)	-0.0997 (2)	0.0470 (8)	B(5)—B(6)	1.793 (5)	B(5')—B(6')	1.785 (5)
C(33)	0.1513 (2)	0.1102 (2)	-0.1509 (2)	0.0555 (9)	B(5)—B(9)	1.762 (6)	B(5')—B(9')	1.752 (6)
C(34)	0.0686 (2)	0.0920 (2)	-0.1934 (2)	0.0609 (9)	B(5)—B(10)	1.779 (6)	B(5')—B(10')	1.790 (6)
C(35)	0.0326 (2)	0.0257 (2)	-0.1859 (2)	0.0574 (9)	B(6)—B(11)	1.836 (5)	B(6')—B(11')	1.793 (5)
C(36)	0.0819 (2)	-0.0232 (2)	-0.1352 (2)	0.0429 (8)	B(6)—B(10)	1.791 (5)	B(6')—B(11')	1.817 (5)
C(1)	0.1105 (2)	-0.2838 (1)	-0.0442 (2)	0.0455 (8)	C(7)—B(8)	1.688 (5)	C(7')—B(8')	1.690 (5)
B(3)	0.2258 (3)	-0.2859 (2)	-0.0174 (2)	0.0504 (10)	C(7)—B(11)	1.694 (4)	C(7')—B(11')	1.700 (5)
B(4)	0.1631 (3)	-0.3556 (2)	-0.0691 (2)	0.0565 (10)	C(7)—B(12)	1.694 (4)	C(7')—B(12')	1.695 (4)
B(5)	0.0702 (3)	-0.3165 (2)	-0.1307 (2)	0.0526 (10)	B(8)—B(9)	1.773 (5)	B(8')—B(9')	1.761 (7)
B(6)	0.0738 (2)	-0.2228 (2)	-0.1142 (2)	0.0410 (8)	B(8)—B(12)	1.755 (5)	B(8')—B(12')	1.755 (6)
C(7)	0.2621 (2)	-0.2352 (2)	-0.0807 (2)	0.0439 (8)	B(9)—B(10)	1.768 (5)	B(9')—B(10')	1.801 (6)
B(8)	0.2603 (3)	-0.3237 (2)	-0.0938 (2)	0.0564 (10)	B(9)—B(12)	1.761 (5)	B(9')—B(12')	1.756 (6)
B(9)	0.1632 (3)	-0.3414 (2)	-0.1655 (2)	0.0543 (10)	B(10)—B(11)	1.795 (5)	B(10')—B(12')	1.767 (6)
B(10)	0.1105 (3)	-0.2589 (2)	-0.1918 (2)	0.0489 (9)	B(10)—B(12)	1.761 (5)	B(11')—B(10')	1.785 (5)
B(11)	0.1768 (2)	-0.1906 (2)	-0.1375 (2)	0.0407 (8)	B(11)—B(12)	1.784 (5)	B(11')—B(12')	1.788 (5)
B(12)	0.2282 (2)	-0.2653 (2)	-0.1695 (2)	0.0514 (9)	S(1)—Rh(2)—S(2)	71.64 (3)	S(1')—Rh(2')—S(2')	71.67 (3)
Rh(2')	0.30611 (1)	0.29888 (1)	0.11731 (1)	0.03423 (5)	S(1)—Rh(2)—P(1)	88.75 (3)	S(1')—Rh(2')—P(1')	87.90 (3)
S(1')	0.28631 (5)	0.22934 (4)	0.00899 (4)	0.0507 (3)	S(1)—Rh(2)—C(1)	95.10 (9)	S(1')—Rh(2')—C(1')	94.24 (8)
S(2')	0.15142 (5)	0.25979 (4)	0.08283 (5)	0.0543 (3)	S(1)—Rh(2)—B(3)	131.1 (1)	S(1')—Rh(2')—B(3')	128.6 (1)
P(1')	0.26734 (4)	0.39683 (4)	0.04034 (4)	0.0344 (1)	S(1)—Rh(2)—B(6)	90.07 (9)	S(1')—Rh(2')—B(6')	90.6 (1)
C(10')	0.1797 (2)	0.2181 (2)	0.0133 (2)	0.0583 (9)	S(1)—Rh(2)—C(7)	169.03 (7)	S(1')—Rh(2')—C(7')	168.47 (8)
C(11')	0.2552 (2)	0.4738 (1)	0.0973 (1)	0.0358 (6)	S(1)—Rh(2)—B(11)	128.13 (8)	S(1')—Rh(2')—B(11')	129.2 (1)
C(12')	0.2002 (2)	0.4691 (2)	0.1479 (2)	0.0450 (8)	S(2)—Rh(2)—P(1)	90.49 (3)	S(2')—Rh(2')—P(1')	89.37 (3)
C(13')	0.1970 (2)	0.5241 (2)	0.1963 (2)	0.0538 (9)	S(2)—Rh(2)—C(1)	101.65 (8)	S(2')—Rh(2')—C(1')	104.7 (1)
C(14')	0.2492 (2)	0.5841 (2)	0.1960 (2)	0.0579 (9)	S(2)—Rh(2)—B(3)	86.71 (9)	S(2')—Rh(2')—B(3')	87.3 (1)
C(15')	0.3031 (2)	0.5890 (2)	0.1476 (2)	0.0528 (9)	S(2)—Rh(2)—B(6)	142.5 (1)	S(2')—Rh(2')—B(6')	145.4 (1)
C(16')	0.3058 (2)	0.5339 (2)	0.0980 (2)	0.0434 (8)	S(2)—Rh(2)—C(7)	115.77 (7)	S(2')—Rh(2')—C(7')	114.92 (8)
C(21')	0.1625 (2)	0.3909 (2)	-0.0325 (2)	0.0429 (8)	S(2)—Rh(2)—B(11)	160.19 (9)	S(2')—Rh(2')—B(11')	158.9 (1)
C(22')	0.1649 (2)	0.3582 (2)	-0.0999 (2)	0.0562 (9)	P(1)—Rh(2)—C(1)	167.86 (8)	P(1')—Rh(2')—C(1')	165.7 (1)
C(23')	0.0863 (3)	0.3488 (2)	-0.1538 (2)	0.0760 (11)	P(1)—Rh(2)—B(3)	135.9 (1)	P(1')—Rh(2')—B(3')	139.6 (1)
C(24')	0.0060 (3)	0.3721 (2)	-0.1411 (2)	0.0836 (13)	P(1)—Rh(2)—B(6)	122.43 (9)	P(1')—Rh(2')—B(6')	120.2 (1)
C(25')	0.0037 (2)	0.4044 (2)	-0.0756 (2)	0.0700 (11)	P(1)—Rh(2)—C(7)	98.97 (8)	P(1')—Rh(2')—C(7')	101.32 (7)
C(26')	0.0813 (2)	0.4143 (2)	-0.0211 (2)	0.0540 (9)	P(1)—Rh(2)—B(11)	88.95 (9)	P(1')—Rh(2')—B(11')	89.05 (9)
C(31')	0.3467 (2)	0.4219 (1)	-0.0146 (1)	0.0375 (6)	C(1)—Rh(2)—B(3)	46.2 (1)	C(1')—Rh(2')—B(3')	45.7 (2)
C(32')	0.3245 (2)	0.4775 (2)	-0.0657 (2)	0.0464 (8)	C(1)—Rh(2)—B(6)	46.2 (1)	C(1')—Rh(2')—B(6')	45.8 (1)
C(33')	0.3832 (2)	0.4964 (2)	-0.1091 (2)	0.0522 (9)	C(1)—Rh(2)—C(7)	75.8 (1)	C(1')—Rh(2')—C(7')	75.1 (1)
C(34')	0.4612 (2)	0.4599 (2)	-0.1036 (2)	0.0537 (9)	C(1)—Rh(2)—B(11)	79.6 (1)	C(1')—Rh(2')—B(11')	78.7 (1)
C(35')	0.4825 (2)	0.4044 (2)	-0.0540 (2)	0.0512 (9)	B(3)—Rh(2)—B(6)	81.2 (1)	B(3')—Rh(2')—B(6')	81.0 (2)
C(36')	0.4259 (2)	0.3853 (2)	-0.0095 (2)	0.0419 (8)	B(3)—Rh(2)—C(7)	45.2 (1)	B(3')—Rh(2')—C(7')	45.7 (1)
C(1')	0.3771 (3)	0.2151 (2)	0.1919 (2)	0.0579 (10)	B(3)—Rh(2)—B(11)	80.0 (1)	B(3')—Rh(2')—B(11')	80.4 (1)
B(3')	0.3080 (3)	0.2652 (2)	0.2315 (2)	0.0561 (10)	B(6)—Rh(2)—C(7)	79.2 (1)	B(6')—Rh(2')—C(7')	78.8 (1)
B(4')	0.3993 (4)	0.2169 (2)	0.2857 (2)	0.0735 (13)	B(6)—Rh(2)—B(11)	49.7 (1)	B(6')—Rh(2')—B(11')	49.1 (1)
B(5')	0.4846 (3)	0.2180 (2)	0.2376 (3)	0.0722 (13)	C(7)—Rh(2)—B(11)	45.0 (1)	C(7')—Rh(2')—B(11')	45.1 (1)
B(6')	0.4457 (2)	0.2655 (2)	0.1523 (2)	0.0500 (9)	Rh(2)—S(1)—C(10)	87.7 (1)	Rh(2')—S(1')—C(10')	87.8 (1)
C(7')	0.3477 (2)	0.3501 (2)	0.2296 (2)	0.0448 (8)	Rh(2)—S(2)—C(10)	85.5 (1)	Rh(2')—S(2')—C(10')	85.8 (1)
B(8')	0.3808 (3)	0.3047 (2)	0.3105 (2)	0.0646 (13)	Rh(2)—P(1)—C(11)	108.92 (9)	Rh(2')—P(1')—C(11')	109.18 (8)
B(9')	0.4904 (3)	0.2753 (2)	0.3134 (2)	0.0684 (13)	Rh(2)—P(1)—C(21)	115.99 (9)	Rh(2')—P(1')—C(21')	116.77 (9)
B(10')	0.5198 (3)	0.3075 (2)	0.2303 (2)	0.0594 (11)	Rh(2)—P(1)—C(31)	116.74 (8)	Rh(2')—P(1')—C(31')	115.98 (8)
B(11')	0.4258 (2)	0.3559 (2)	0.1781 (2)	0.0433 (9)	C(11)—P(1)—C(21)	106.9 (1)	C(11')—P(1')—C(21')	106.1 (1)
B(12')	0.4556 (3)	0.3597 (2)	0.2780 (2)	0.0534 (10)	C(11)—P(1)—C(31)	106.2 (1)	C(11')—P(1')—C(31')	106.6 (1)
					C(21)—P(1)—C(31)	101.2 (1)	C(21')—P(1')—C(31')	101.3 (1)
					S(1)—C(10)—S(2)	115.1 (2)	S(1')—C(10')—S(2')	114.7 (2)

Table 2. Geometric parameters (Å, °)

Rh(2)—S(1)	2.355 (1)	Rh(2')—S(1')	2.347 (1)
Rh(2)—S(2)	2.432 (1)	Rh(2')—S(2')	2.423 (1)
Rh(2)—P(1)	2.314 (1)	Rh(2')—P(1')	2.320 (1)
Rh(2)—C(1)	2.204 (3)	Rh(2')—C(1')	2.206 (3)
Rh(2)—B(3)	2.186 (3)	Rh(2')—B(3')	2.190 (4)
Rh(2)—B(6)	2.181 (3)	Rh(2')—B(6')	2.179 (4)
Rh(2)—C(7)	2.240 (3)	Rh(2')—C(7')	2.235 (3)
Rh(2)—B(11)	2.190 (3)	Rh(2')—B(11')	2.195 (3)
S(1)—C(10)	1.669 (3)	S(1')—C(10')	1.670 (4)
S(2)—C(10)	1.652 (4)	S(2')—C(10')	1.648 (4)
P(1)—C(11)	1.823 (3)	P(1')—C(11')	1.827 (3)
P(1)—C(21)	1.835 (3)	P(1')—C(21')	1.839 (3)
P(1)—C(31)	1.821 (2)	P(1')—C(31')	1.821 (3)
C(1)—B(3)	1.722 (5)	C(1')—B(3')	1.708 (6)
C(1)—B(4)	1.696 (5)	C(1')—B(4')	1.681 (5)
C(1)—B(5)	1.684 (5)	C(1')—B(5')	1.667 (5)
C(1)—B(6)	1.722 (4)	C(1')—B(6')	1.705 (5)
B(3)—B(4)	1.769 (5)	B(3')—B(4')	1.769 (6)
B(3)—C(7)	1.701 (5)	B(3')—C(7')	1.717 (5)
B(3)—B(8)	1.768 (6)	B(3')—B(8')	1.776 (5)

The structure was solved by the Patterson heavy-atom method. All H atoms were visible in difference maps calculated at an intermediate stage of the refinement; they were allowed for as riding atoms (C—H 0.95, B—H 1.08 Å) in subsequent structure-factor calculations but were not refined.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry, together with drawings of (IIb), have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55840 (100 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1043]

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Structure of (1,4,7,10,13-Pentaazacyclopentadecane- $N^1, N^4, N^7, N^{10}, N^{13}$)(perchlorato- O)nickel(II) Perchlorate

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Abstract

The structure consists of Ni^{II} with distorted octahedral N_5O coordination. The five $Ni-N$ distances span a very narrow range: 2.051 (7)–2.083 (8) Å. All five five-membered chelate rings are in stable *gauche* form; the chelate angles $N-Ni-N$ of these rings are in the range 82.6 (4)–84.7 (4)°. This structure is expected to be the most stable isomer of $[Ni(C_{10}H_{25}N_5)(ClO_4)]^+$. Four hydrogen bonds between amine groups and perchlorate ions help stabilize the crystal structure.

Comment

There is a great deal of interest in the crystal structures of the complexes of transition metals coordinated with macrocyclic ligands. The macrocyclic ligands form much more stable complexes with 3d transition metals than complexes formed with the corresponding open-chain ligands (Cabbiness & Margerum, 1969). A large volume of work has been

published on tetraaza macrocyclic ligands and their complexes, but little information is available on the pentaaza macrocyclic systems. In order to expand the knowledge in the field of coordination chemistry of pentaaza macrocyclic complexes, we have investigated the X-ray crystal structure of the title compound.

1,4,7,10,13-Pentaazacyclopentadecane was prepared by a published procedure (Bencini, Fabbrizzi & Poggi, 1981). The title complex was obtained by mixing the ligand with a hot equimolar aqueous solution of $Ni(ClO_4)_2 \cdot 6H_2O$. After refluxing for 2 h, the blue-violet crystals were obtained by slow evaporation of the solution. These crystals were recrystallized twice from methanol.

The structure consists of discrete $[Ni([15]aneN_5)(ClO_4)]^+$ cations. Five N atoms from the macrocyclic ligand and one O atom from the perchlorate ion constitute the distorted octahedral coordination polyhedron of the Ni atom. N(1), N(2), N(4) and N(5) of the macrocyclic ligand form a plane; the displacements of the atoms from this plane are shown in Fig. 1. The macrocyclic pentaamine is in a folded structure; the N(3) atom is *cis* to the other N atoms. An O atom of a perchlorate ion is *trans* to N(3); the other perchlorate ion is located far from the bonding range and has a disordered structure. The five $Ni-N$ distances span a very narrow range [2.051 (7)–2.083 (8) Å] and are slightly shorter than the average $Ni-N$ distance for six-coordinate Ni^{II} tetraamine complexes (Lu, Chung & Ashida, 1991). The five-membered chelate rings, except the one that contains disordered C(1) and C(2) atoms, are in stable *gauche* form; the chelate angles $N-Ni-N$ of these rings are in the range 82.6 (4)–84.7 (4)°. This

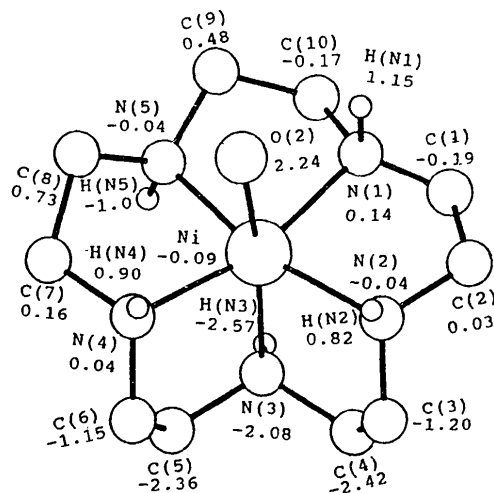


Fig. 1. A perspective view of the molecule excluding two perchlorate ions and the H atoms attached to the C atoms. The atom-numbering scheme is shown as well as the displacements of the atoms from the best plane formed by the atoms N(1), N(2), N(4) and N(5).