

## Structure of Tris(benzothiazole-*N*)trichlororhodium(III) Nitromethane Solvate

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**Abstract.** *mer*-[RhCl<sub>3</sub>(C<sub>7</sub>H<sub>5</sub>NS)<sub>3</sub>].CH<sub>3</sub>NO<sub>2</sub>,  $M_r = 675.87$ , monoclinic,  $P2_1/n$ ,  $a = 10.915(2)$ ,  $b = 19.869(4)$ ,  $c = 12.328(3)$  Å,  $\beta = 103.13(7)^\circ$ ,  $V = 2604(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.724$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71037$  Å,  $\mu = 12.15$  cm<sup>-1</sup>,  $F(000) = 1352$ ,  $T = 298$  K, final  $R = 0.0297$  for 4459 unique observed reflections. The complex was prepared as part of a series of complexes of Rh<sup>III</sup> with heterocyclic ligands of the type  $\text{RhL}_3\text{X}_3$ . On the basis of spectral data alone, the assignment of the geometry as *mer* or *fac* and the mode of coordination through N or S were ambiguous, so the X-ray structure of the title complex was determined. The Rh is coordinated to three Cl and three N atoms to give an approximately octahedral, meridional complex. The potentially ambidentate benzothiazole coordinates to the metal through the N atom of the thiazole ring. The average Rh—N and Rh—Cl distances are 2.064(5) and 2.34(2) Å, respectively.

**Experimental.** In 50 mL of a 30% water–ethanol solution, 0.3000 g (1.14 mmol) of RhCl<sub>3</sub>·3H<sub>2</sub>O were dissolved. After one minute of reflux, benzothiazole was added dropwise to the solution until a yellow precipitate formed. The precipitate was filtered and recrystallized using nitromethane. Yield: 0.4202 g (60.0%). Analysis: Calculated for C<sub>22</sub>H<sub>18</sub>N<sub>4</sub>S<sub>3</sub>Cl<sub>3</sub>O<sub>2</sub>Rh: C 39.08%, H 2.67%, Cl 15.77%. Found: C 39.30%, H 2.60%, Cl 15.77%, melting point > 573 K.

Orange rectangular solid,  $D_m$  not determined,  $0.2 \times 0.4 \times 0.4$  mm, Enraf–Nonius CAD-4 diffractometer, monochromated Mo  $K\alpha$ ,  $\omega$ - $2\theta$  scan, scan width  $(0.9 + 0.34 \tan \theta)^\circ$ ,  $2\theta_{\text{max}} = 53^\circ$ , lattice parameters from least-squares fit of 25 reflections in the range  $6 < \theta < 10^\circ$ . Systematic absences  $h0l$  ( $h + l = 2n + 1$ ),  $0k0$  ( $k = 2n + 1$ );  $\pm h$ ,  $+k$ ,  $+l$ ,  $|h| \leq 13$ ,  $k \leq 24$ ,  $l \leq 15$ ; three standard reflections, intensities constant within experimental error, total unique reflections measured 5398, 4459 with  $F^2 > 3\sigma^2(F_o)$ ,  $\sigma(F_o) = [\sigma^2(I_{\text{raw}}) + (0.04F_o^2)^2]^{1/2}/2F_o$ . Structure was solved with the Enraf–Nonius *Structure Determination Package* (Frenz, 1986), heavy-atom and difference-Fourier methods; isotropic, then anisotropic refinement of  $F$  of all non-H atoms, H atoms on the complex at calculated positions, riding model [C—H 0.95 Å,

$U(\text{H}) = 1.3U(\text{C})$ ]; 316 parameters refined,  $R = 0.0297$ ,  $wR = 0.0498$ ,  $w = 1/[\sigma^2(F_o)]$ ,  $S = 2.02$ ; difference syntheses showed no densities above  $0.70$  e Å<sup>-3</sup> (min.  $-0.51$  e Å<sup>-3</sup>); max.  $\Delta/\sigma = 0.01$ . Neutral-atom scattering factors were used (*International Tables for X-ray Crystallography*, 1974), and were corrected for anomalous dispersion (Cromer & Liberman, 1970). No correction for absorption or secondary extinction.

The atomic coordinates and equivalent isotropic temperature factors are listed in Table 1, and selected bond lengths and angles in Table 2.\* An ORTEP plot (Johnson, 1976) of the title complex with the atom numbering is shown in Fig. 1, and the packing of the molecules (Motherwell & Clegg, 1976) in Fig. 2. The solvent nitromethane molecule, N(4), O(1), O(2) and C(22), showed evidence of disorder, consistent with the abnormally large temperature factors, but the occupancy of the second set of sites was too low (ca 10%) to permit refinement of both sets of sites to give chemically reasonable distances and angles.

**Related literature.** Although Rh—S coordination might be expected according to the hard and soft acid and base principle (Pearson, 1963), it is evident from this study that benzothiazole is coordinated through the N atom. This behavior has also been observed in a Pd<sup>II</sup> benzothiazole complex (Churchill, Wasserman & Young, 1980), and in a Pt<sup>II</sup> styryl-benzothiazole complex (Muir, Gomez, Muir, Cox & Cadiz, 1987). The average C—N and C—S distances for the C between N and S [1.306(3) and 1.702(2) Å] are shorter than the average C—N and C—S distances to the C atoms in the phenyl ring [1.411(8) and 1.736(2) Å]. These distances and the average N—C—S, C—S—C, C—N—C, N—C—C and S—C—C angles [116.4(4), 89.5(4), 111.0(6), 112.8(2) and 110.4(5)°] within the thiazole ring for the coordinated benzothiazoles are similar to those

\* Lists of structure factors, anisotropic thermal factors, H-atom parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51999 (66 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and equivalent isotropic temperature factors ( $\text{\AA}^2$ )

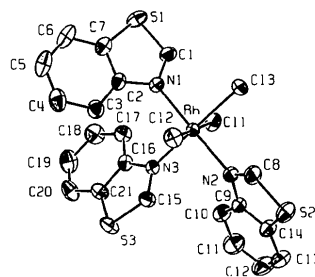
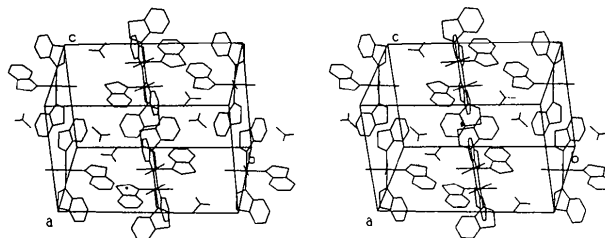
|       | x           | y            | z            | B*        |
|-------|-------------|--------------|--------------|-----------|
| Rh    | 0.75080 (2) | 0.03762 (1)  | 0.24329 (2)  | 1.826 (4) |
| Cl(1) | 0.54498 (7) | 0.00359 (5)  | 0.16750 (6)  | 2.95 (2)  |
| Cl(2) | 0.96062 (7) | 0.06860 (5)  | 0.32409 (7)  | 3.07 (2)  |
| Cl(3) | 0.80611 (9) | -0.07459 (4) | 0.28076 (7)  | 3.32 (2)  |
| S(1)  | 0.79841 (9) | -0.02909 (5) | -0.09632 (7) | 3.31 (2)  |
| S(2)  | 0.7510 (1)  | 0.02129 (6)  | 0.60889 (7)  | 4.25 (2)  |
| S(3)  | 0.72487 (9) | 0.26449 (5)  | 0.25234 (8)  | 3.26 (2)  |
| N(1)  | 0.7932 (3)  | 0.0277 (1)   | 0.0889 (2)   | 2.37 (5)  |
| N(2)  | 0.7125 (3)  | 0.0444 (1)   | 0.3994 (2)   | 2.38 (5)  |
| N(3)  | 0.7046 (2)  | 0.1374 (1)   | 0.2123 (2)   | 2.05 (5)  |
| C(1)  | 0.7555 (3)  | -0.0251 (2)  | 0.0276 (3)   | 2.73 (7)  |
| C(2)  | 0.8624 (3)  | 0.0714 (2)   | 0.0363 (3)   | 2.39 (6)  |
| C(3)  | 0.9138 (3)  | 0.1337 (2)   | 0.0740 (3)   | 2.99 (7)  |
| C(4)  | 0.9774 (4)  | 0.1689 (2)   | 0.0069 (3)   | 3.93 (8)  |
| C(5)  | 0.9942 (4)  | 0.1425 (2)   | -0.0931 (3)  | 4.62 (9)  |
| C(6)  | 0.9439 (3)  | 0.0819 (2)   | -0.1313 (3)  | 4.00 (9)  |
| C(7)  | 0.8759 (3)  | 0.0472 (2)   | -0.0673 (3)  | 2.77 (7)  |
| C(8)  | 0.7909 (4)  | 0.0164 (2)   | 0.4834 (3)   | 3.17 (7)  |
| C(9)  | 0.6092 (3)  | 0.0736 (2)   | 0.4330 (3)   | 2.59 (6)  |
| C(10) | 0.5085 (3)  | 0.1081 (2)   | 0.3675 (3)   | 3.41 (8)  |
| C(11) | 0.4170 (4)  | 0.1337 (3)   | 0.4181 (4)   | 4.9 (1)   |
| C(12) | 0.4256 (4)  | 0.1235 (3)   | 0.5326 (3)   | 5.5 (1)   |
| C(13) | 0.5237 (4)  | 0.0894 (2)   | 0.5976 (3)   | 4.72 (9)  |
| C(14) | 0.6155 (4)  | 0.0651 (2)   | 0.5465 (3)   | 3.56 (8)  |
| C(15) | 0.7475 (3)  | 0.1820 (2)   | 0.2893 (3)   | 2.57 (6)  |
| C(16) | 0.6442 (3)  | 0.1696 (2)   | 0.1117 (2)   | 2.23 (6)  |
| C(17) | 0.5854 (3)  | 0.1382 (2)   | 0.0117 (3)   | 2.83 (7)  |
| C(18) | 0.5380 (4)  | 0.1787 (2)   | -0.0782 (3)  | 3.78 (9)  |
| C(19) | 0.5485 (4)  | 0.2488 (2)   | -0.0709 (3)  | 4.22 (9)  |
| C(20) | 0.6017 (4)  | 0.2805 (2)   | 0.0263 (3)   | 3.62 (8)  |
| C(21) | 0.6495 (3)  | 0.2391 (2)   | 0.1190 (3)   | 2.77 (7)  |
| N(4)  | 0.7913 (5)  | 0.2635 (3)   | 0.6047 (4)   | 8.6 (1)   |
| O(1)  | 0.7565 (7)  | 0.2442 (5)   | 0.5162 (5)   | 18.6 (2)  |
| O(2)  | 0.8237 (6)  | 0.3190 (4)   | 0.6290 (6)   | 14.2 (2)  |
| C(22) | 0.798 (2)   | 0.2198 (6)   | 0.686 (1)    | 27.3 (7)  |

\* Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$$\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

 Table 2. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

|                  |            |                  |            |
|------------------|------------|------------------|------------|
| Rh—Cl(1)         | 2.3288 (8) | S(3)—C(21)       | 1.738 (3)  |
| Rh—Cl(2)         | 2.3620 (8) | N(1)—C(1)        | 1.303 (4)  |
| Rh—Cl(3)         | 2.3285 (9) | N(1)—C(2)        | 1.403 (4)  |
| Rh—N(1)          | 2.069 (3)  | N(2)—C(8)        | 1.309 (4)  |
| Rh—N(2)          | 2.065 (3)  | N(2)—C(9)        | 1.411 (5)  |
| Rh—N(3)          | 2.059 (3)  | N(3)—C(15)       | 1.306 (4)  |
| S(1)—C(1)        | 1.699 (4)  | N(3)—C(16)       | 1.419 (4)  |
| S(1)—C(7)        | 1.734 (4)  | N(4)—O(1)        | 1.137 (8)  |
| S(2)—C(8)        | 1.702 (4)  | N(4)—O(2)        | 1.18 (1)   |
| S(2)—C(14)       | 1.737 (4)  | N(4)—C(22)       | 1.31 (1)   |
| S(3)—C(15)       | 1.704 (4)  | C—C (av.)        | 1.39 (1)   |
| Cl(1)—Rh—Cl(2)   | 177.95 (3) | N(1)—Rh—N(2)     | 177.9 (1)  |
| Cl(1)—Rh—Cl(3)   | 89.12 (3)  | N(1)—Rh—N(3)     | 91.0 (1)   |
| Cl(2)—Rh—Cl(3)   | 89.03 (3)  | N(2)—Rh—N(3)     | 91.0 (1)   |
| Cl(1)—Rh—N(1)    | 90.02 (7)  | Cl(3)—Rh—N(3)    | 178.98 (7) |
| Cl(1)—Rh—N(2)    | 90.66 (8)  | Rh—N(1)—C(1)     | 120.2 (2)  |
| Cl(1)—Rh—N(3)    | 91.82 (7)  | Rh—N(1)—C(2)     | 128.5 (2)  |
| Cl(2)—Rh—N(1)    | 90.84 (7)  | Rh—N(2)—C(8)     | 118.4 (2)  |
| Cl(2)—Rh—N(2)    | 88.42 (8)  | Rh—N(2)—C(9)     | 130.2 (2)  |
| Cl(2)—Rh—N(3)    | 90.02 (7)  | Rh—N(3)—C(15)    | 119.1 (2)  |
| Cl(3)—Rh—N(1)    | 89.40 (8)  | Rh—N(3)—C(16)    | 130.0 (2)  |
| Cl(3)—Rh—N(2)    | 88.62 (8)  | S(1)—C(7)—C(2)   | 109.9 (3)  |
| S(1)—C(1)—N(1)   | 116.3 (3)  | S(1)—C(7)—C(6)   | 128.1 (3)  |
| S(2)—C(8)—N(2)   | 116.0 (3)  | S(2)—C(14)—C(9)  | 110.4 (3)  |
| S(3)—C(15)—N(3)  | 116.9 (2)  | S(2)—C(14)—C(13) | 127.2 (3)  |
| C(1)—S(1)—C(7)   | 89.7 (2)   | S(3)—C(21)—C(16) | 110.8 (2)  |
| C(8)—S(2)—C(14)  | 89.7 (2)   | S(3)—C(21)—C(20) | 127.3 (3)  |
| C(15)—S(3)—C(21) | 89.0 (2)   | N(1)—C(2)—C(3)   | 127.9 (3)  |
| C(1)—N(1)—C(2)   | 111.3 (3)  | N(1)—C(2)—C(7)   | 112.8 (3)  |
| C(8)—N(2)—C(9)   | 111.4 (3)  | N(3)—C(16)—C(17) | 126.6 (3)  |
| C(15)—N(3)—C(16) | 110.3 (3)  | N(3)—C(16)—C(21) | 112.9 (3)  |
| N(2)—C(9)—C(10)  | 127.7 (3)  | C—C—C (av.)      | 120 (2)    |
| N(2)—C(9)—C(14)  | 112.6 (3)  | O(2)—N(4)—C(22)  | 117.6 (7)  |
| O(1)—N(4)—O(2)   | 125.2 (7)  |                  |            |
| O(1)—N(4)—C(22)  | 117.1 (8)  |                  |            |


 Fig. 1. Labeling of atoms in *mer*-[RhCl<sub>3</sub>(C<sub>7</sub>H<sub>5</sub>NS)<sub>3</sub>] (50% probability ellipsoids).

 Fig. 2. Packing diagram of *mer*-[RhCl<sub>3</sub>(C<sub>7</sub>H<sub>5</sub>NS)<sub>3</sub>].CH<sub>3</sub>NO<sub>2</sub>.

found in Pt<sup>II</sup>, Pd<sup>II</sup> and Rh<sup>III</sup> complexes of *N*-coordinated heterocyclic ligands (Muir, Gomez, Muir & Sanchez, 1987; Muir, Gomez, Muir, Cox & Cadiz, 1987; Churchill *et al.*, 1980; Acharya, Tavale & Row, 1984).

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