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A methyl-coordinated Rh^{III} ion in methylpentaamminerhodium(III)–chloropentaamminerhodium(III)–dithionate (0.73/2.27/3)

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Key indicators

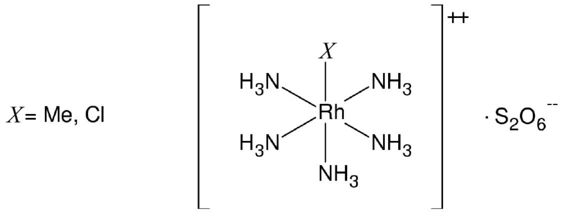
Single-crystal X-ray study
T = 122 K
Mean σ(S–O) = 0.004 Å
H-atom completeness 96%
Disorder in solvent or counterion
R factor = 0.036
wR factor = 0.102
Data-to-parameter ratio = 32.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Some disorder is seen in the crystal structure of $[Rh(CH_3)(NH_3)_5]_{0.73}[RhCl(NH_3)_5]_{2.27}(S_2O_6)_3$. It is, however, clear that the methyl group has a pronounced *trans* influence on the Rh—N distance, with an elongation of 0.11 Å. No *trans* influence is observed for the Rh—N distance due to the Cl^- ion. Both observations are in agreement with observations in equivalent cobalt complexes.

Comment

In continuation of our earlier investigations on methylcobalt(III) compounds (Kofod *et al.*, 1997), we have initiated studies on similar Rh^{III} coordination compounds.



(I)

The pentaamminerhodium(III) series, $[Rh(NH_3)_5(X)]^{2+}$, include, in addition to a range of inorganic anionic ligands, the hydrido ligand and alkyl ligands (X = H^-, RCH_2^-, RCF_2^-; Thomas *et al.*, 1968; Skapski & Throughton, 1969). These alkylrhodium(III) compounds have been prepared by addition of alkenes to $[Rh(NH_3)_5(H)]^{2+}$ and, therefore, the corresponding methyl and aryl derivatives cannot be prepared in this way.

In a search for ways to prepare $[Rh(NH_3)_5CH_3]^{2+}$, we tried methylation of pentaamminerhodium(III) compounds with methyllithium, which was unsuccessful. The reason is probably the acidic nature of the ammine ligands together with the poor solubility in ether solvents.

$[Rh(NH_3)_5(CH_3)]^{2+}$ was prepared by utilizing methyl transfer from tetramethyltin(IV) to $[Rh(NH_3)_5(CF_3SO_3)]^{2+}$. The trifluoromethanesulfonate ion, $CF_3SO_3^-$, is a weak ligand and thus constitutes a good leaving group in inorganic substitution reactions (Dixon *et al.*, 1984).

In the crystal structure, we found a mix of $[Rh(NH_3)_5(CH_3)]^{2+}$ and $[Rh(NH_3)_5Cl]^{2+}$ cations linked by hydrogen bonds to $S_2O_6^{2-}$ anions. The $[Rh(NH_3)_5Cl]^{2+}$ originates from incomplete conversion of $[Rh(NH_3)_5Cl]Cl_2$ to $[Rh(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$. The $[Rh(NH_3)_5Cl]^{2+}$ cation and one $S_2O_6^{2-}$ anion were found on general positions, while the reaction product $[Rh(NH_3)_5(CH_3)]^{2+}$ and another $S_2O_6^{2-}$ anion were found on the mirror plane. Furthermore, the crystal structure showed disorder of the position of the methyl

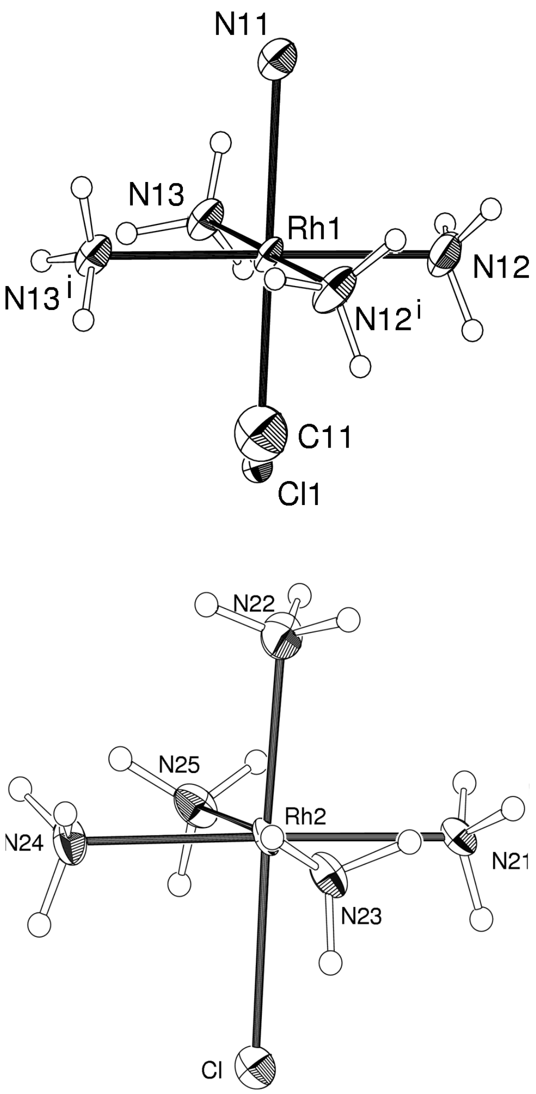


Figure 1
Views of the $[Rh(NH_3)_5(CH_3)]^{2+}$ and $[Rh(NH_3)_5Cl]^{2+}$ cations, including the labelling of the atoms. The displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres with an arbitrary radii.

group, *viz*. 27% of the atom in this position was modelled by a chloride ion. The model gives a sensible hydrogen-bonding pattern, with no hydrogen-bond possibilities to the methyl group.

In $[Rh(NH_3)_5(CH_3)]^{2+}$, the average Rh—N distance of the ammine groups equatorial to the methyl group is 2.067 (1) Å, and the Rh—N distance of the ammine group *trans* to the methyl group is significantly longer by 0.11 Å with a value of 2.177 (6) Å. The Rh—C distance is 1.99 (2) Å. In $[Rh(NH_3)_5Cl]^{2+}$, the Rh—N distance *trans* to Cl$^-$ is 2.057 (4) Å and the average Rh—N distance for the ammine groups *cis* to Cl$^-$ is 2.071 (15) Å; these values are in agreement with earlier results from the literature (West, 1935; Weishaupt *et al.*, 1978).

The methyl is seen to have a strong structural *trans* influence, in agreement with it being a strong σ-donor ligand. We observed a *trans* influence of 0.13 Å compared with the analogous Co complex (Kofod *et al.*, 1997), where the average Co—N distance for the ammine group *cis* to the methyl group was 1.974 (3) Å and the Co—N distance for the ammine group *trans* to the methyl group was 2.105 (1) Å. The *trans*-influence in $[Rh(NH_3)_5(C_2H_5)]^{2+}$ (Skapski & Throughton, 1969) was found to be 0.18 Å, with the distances changing from 2.07 Å (with the ammine groups *cis* to the ethyl group) to 2.25 Å (with the ammine *trans* to the ethyl group).

The Cl$^-$ ion shows no *trans* influence on the ammine group. This is also in agreement with the structure of the equivalent cobalt complex (Messmer & Amma, 1968), where the Co—N distance *trans* to the Cl$^-$ group was 1.964 (6) Å and the average Co—N distance *cis* to the Cl$^-$ group was 1.975 (17) Å.

Experimental

$[Rh(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ in tetramethylene sulfone (sulfolane) (Dixon *et al.*, 1984) was mixed with excess tetramethyltin(IV) and heated in an argon atmosphere at 383 K in a closed Teflon container for 16 h (to be published elsewhere). Elemental analysis showed that the crude product contained significant amounts of $[Rh(NH_3)_5Cl]^{2+}$ and $[Rh(NH_3)_5(CH_3)]^{2+}$. Crystals of $[Rh(NH_3)_5(CH_3)]_{0.73}[Rh(NH_3)_5Cl]_{2.27}(S_2O_6)_3$ were grown by slow diffusion of a solution of crude $[Rh(NH_3)_5(CH_3)](CF_3SO_3)_2$ in saturated aqueous ammonia into a saturated solution of $Na_2S_2O_6$.

Crystal data

$[Rh(CH_3)(NH_3)_5]_{0.73}$-
$[RhCl(NH_3)_5]_{2.27}(S_2O_6)_3$
$M_r = 1135.58$
Monoclinic, *Im*
$a = 6.271$ (2) Å
$b = 27.205$ (3) Å
$c = 9.871$ (2) Å
$\beta = 97.29$ (1)°
$V = 1670.4$ Å^3
$Z = 2$

$D_x = 2.258$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 474 reflections
$\theta = 4.4$–31.0°
$\mu = 2.11$ mm^{-1}
$T = 122$ (1) K
Rod, colourless
0.37 × 0.17 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
θ and φ scans
Absorption correction: by Gaussian integration (Coppens, 1970)
$T_{\min} = 0.542$, $T_{\max} = 0.898$
34422 measured reflections
7322 independent reflections

7148 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.057$
$\theta_{\max} = 35.0°$
$h = -10 \rightarrow 10$
$k = -43 \rightarrow 43$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.102$
$S = 1.07$
7322 reflections
225 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0598P)^2 + 6.9449P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.023$
$\Delta\rho_{\max} = 3.30$ e Å^{-3}
$\Delta\rho_{\min} = -1.68$ e Å^{-3}
Absolute structure: Flack (1983), 3578 Friedel pairs
Flack parameter = 0.43 (3)

Table 1
Selected geometric parameters (Å, °).

Rh2—N22	2.057 (4)	Rh1—C11	1.99 (2)
Rh2—N21	2.057 (4)	Rh1—N12	2.066 (4)
Rh2—N23	2.061 (4)	Rh1—N13	2.068 (4)
Rh2—N24	2.076 (4)	Rh1—N11	2.177 (6)
Rh2—N25	2.091 (4)	Rh1—Cl1	2.368 (5)
Rh2—Cl	2.3492 (12)		
N22—Rh2—N21	88.21 (15)	N25—Rh2—Cl	88.33 (11)
N22—Rh2—N23	90.91 (15)	C11—Rh1—N12	89.0 (3)
N21—Rh2—N23	92.04 (14)	N12—Rh1—N12^{i}	89.7 (3)
N22—Rh2—N24	92.90 (16)	C11—Rh1—N13^{i}	90.8 (3)
N21—Rh2—N24	177.83 (15)	N12—Rh1—N13^{i}	179.34 (18)
N23—Rh2—N24	89.81 (15)	N12—Rh1—N13	89.67 (16)
N22—Rh2—N25	91.04 (15)	N13^{i}—Rh1—N13	91.0 (2)
N21—Rh2—N25	89.69 (14)	C11—Rh1—N11	180.0 (5)
N23—Rh2—N25	177.43 (15)	N12—Rh1—N11	91.04 (17)
N24—Rh2—N25	88.42 (16)	N13—Rh1—N11	89.17 (15)
N22—Rh2—Cl	177.54 (13)	N12—Rh1—Cl1	89.40 (15)
N21—Rh2—Cl	89.40 (10)	N13—Rh1—Cl1	90.40 (14)
N23—Rh2—Cl	89.79 (11)	N11—Rh1—Cl1	179.4 (2)
N24—Rh2—Cl	89.46 (11)		

Symmetry code: (i) $x, -y, z$.

The structure solution in the monoclinic space group *Im* showed pseudo-centrosymmetry. Therefore, structure solution and refinement was attempted in other space groups. The structure could also be solved in $P\overline{1}$, but the model suffered from disorder and very unrealistic displacement parameters and the conventional *R* factor could not be reduced below 0.14. The solution and refinement in *P*1 was identical to the solution in *Im*. $[Rh(NH_3)_5Cl]^{2+}$ was found in a general position, and $[Rh(NH_3)_5(CH_3)]^{2+}$ was found on the mirror plane. The position of the CH_3 group was found by examining the hydrogen-bond possibilities. An NH_3 group in the position of the CH_3 group would have no reasonable hydrogen-bond acceptors. Initially, the displacement parameter of the C atom was very elongated and the Rh—C distance very long. This was interpreted as disorder, so that 27% of the positions which were mainly occupied by $[Rh(NH_3)_5(CH_3)]^{2+}$ were found to be occupied by $[Rh(NH_3)_5Cl]^{2+}$, giving the stoichiometry in the asymmetric unit: $1.135[Rh(NH_3)_5Cl]^{2+}$ and $0.365[Rh(NH_3)_5(CH_3)]^{2+}$. The CH_3 position was allowed to refine freely, but the Rh1—Cl1 distance in $[Rh(NH_3)_5(CH_3)]^{2+}$ was restrained to be similar to the Rh2—Cl distance in $[Rh(NH_3)_5Cl]^{2+}$. The maximum and minimum difference densities were found to be 3.30 and −1.68 e Å^{-3}, respectively. These relatively high values were in the close vicinity of the rhodium ions. The H atoms of the ordered NH_3 groups were included at ideal positions and allowed to ride on the parent atom. The isotropic displacement parameters were constrained to $1.5U_{eq}$. The H atoms of the CH_3 group were on top of the Cl^- ion and therefore they were not included. Refinement of the Flack (1983) parameter showed that the crystal was a racemic twin, with a twin fraction of 0.43 (3).

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EvalCCD* (Duisenberg, 1998) and *DREAD* (Blessing, 1987); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976).

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References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Blessing, R. H. (1987). *Crystallogr. Rev.* **1**, 3–58.

Coppens, P. (1970). *The Evaluation of Absorption and Extinction in Single-Crystal Structure Analysis. Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall and C. P. Huber, pp. 255–270. Copenhagen: Munksgaard.

Dixon, N. E., Lawrence, G. A., Lay, P. A. & Sargeson, A. M. (1984). *Inorg. Chem.* **23**, 2940–2947.

Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.

Duisenberg, A. J. M. (1998). PhD thesis, University of Utrecht, The Netherlands.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kofod, P., Harris, P. & Larsen, S. (1997). *Inorg. Chem.* **36**, 2258–2266.

Messmer, G. G. & Amma, E. L. (1968). *Acta Cryst.* B**24**, 417–422.

Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Skapski, A. C. & Throughton, P. G. H. (1969). *J. Chem. Soc. Chem. Commun.* pp. 666–667.

Thomas, K., Osborn, J. A., Powell, R. & Wilkinson, G. (1968). *J. Chem. Soc. A*, pp. 1801–1809.

West, C. D. (1935). *Z. Kristallogr.* **91**, 181–186.

Weishaupt, M., Bezler, H. & Strähle, J. (1978). *Z. Anorg. Allg. Chem.* **440**, 52–64.