The Structural *trans*-Influence in Ethylpentamminerhodium(III) Bromide

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Summary The strong *trans*-influence of the alkyl group is demonstrated by bond-length differences in ethylpentamminerhodium(III) bromide.

THE cation $[RhEt(NH_3)_5]^{2+}$ has been isolated by Wilkinson and his co-workers[1] as pure crystalline salts with anions such as bromide, and is one of the first examples of a transition-metal alkyl in the presence of low-field ligands with no π-acceptor properties. Wilkinson *et al.* found that the alkyl group exerts a strong *trans*-labilising effect in solution. We have determined the structure of $[RhEt(NH_3)_5]Br_2$ to see if there is a corresponding strong *trans*-influence in the crystal, and find that the rhodium–nitrogen bond-length of the *trans*-ammine group is substantially longer than those of the other ammine groups.

Ethylpentamminerhodium(III) bromide crystallises from water as almost colourless octahedra which are orthorhombic. The unit-cell dimensions are $a = 11{\cdot}289$, $b = 9{\cdot}132$, $c = 11{\cdot}132$ Å; $U = 1147{\cdot}6$ Å^3, $D_m = 2{\cdot}17$, $Z = 4$, $D_c = 2{\cdot}18$ g.cm.$^{-3}$, space group *Cmcm*.

Three-dimensional X-ray data were collected on a Siemens four-circle automatic diffractometer. Using Cu-K_α radiation a total of 617 independent reflections were measured (to $\theta = 70°$) of which 26 were judged to be unobserved. The structure was solved by standard methods and least-squares refinement has now reached $R = 0{\cdot}031$.

The rhodium atom has the expected octahedral environment, with a σ-bonded ethyl group on one side and an ammine group on the other side of the almost perfect square-plane of four ammine groups (see Figure); the bromide ions play no role in the co-ordination. Although the complex cations lie on two mutually perpendicular crystallographic mirror planes, the ions in fact attain the apparent *mm* (C_{2v}) symmetry by statistical disorder of the ethyl group in one of the mirror planes. The hydrogens of the disordered methylene carbon were successfully located: all other hydrogens are disordered but have been allowed for in the refinement. The bond angles are given in the Table.

TABLE

		σ
N(1)–Rh–N(2)	89·0°	0·2
N(1)–Rh–N(3)	90	—
N(1)–Rh–C(1)	78·9	0·5
N(1)′–Rh–C(1)	103·1	0·5
N(2)–Rh–N(3)	90·1	0·2
N(3)–Rh–C(1)	90·0	0·2
Rh–C(1)–C(2)	121·2	1·1

In the square-plane the two independent Rh–N distances are identical (2·072 Å): the sum of covalent radii is 2·06 Å. The relative lengthening of the *trans* Rh–N distance of 0·184 Å (23 σ) is one of the largest *trans*-influences yet observed in structures of octahedral d^6 transition-metal complexes.

The rhodium–carbon (alkyl) bond-lengths, 2·048 ($\pm 0{\cdot}016$) Å, can be compared with 2·083 ($\pm 0{\cdot}007$) Å in $RhI_2Me(PPh_3)_2,C_6H_6$[2] and 2·08 Å in $Rh_2I_2(SMe_2)_3(CH_3)_4$,[3] while 2·09 Å would be expected from the sum of covalent radii. The N(1)–Rh–C(1) and Rh–C(1)–C(2) angles are distorted from their ideal 90° and 109° respectively: this appears to occur so that the hydrogen contacts of both the methylene and the methyl groups with the hydrogens of the ammine groups are equalised at the rather short distance of *ca.* 2·2 Å in the most favourable case. However, an angle of 120·9° has been observed for the Mo–C(1)–C(2) angle in π-$C_5H_5Mo(CO)_3Et$[4] where no such interference seems to occur; angles varying from 116°—121°[5–7] have been observed in metal–perfluoroalkyl linkages, and have been cited as evidence for some double-bond character in the metal–carbon(perfluoroalkyl) bond.

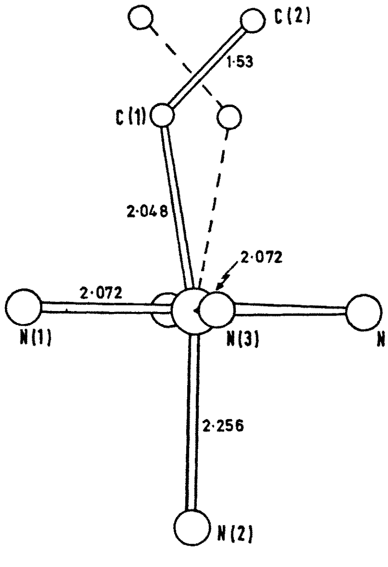

FIGURE. *The* $[Rh(NH_3)_5ethyl]^{2+}$ *ion. Standard deviations*: Rh–N(1), 0·007; Rh–N(2), 0·008; Rh–N(3), 0·006; Rh–C(1), 0·016; C(1)–C(2), 0·023 Å.

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