The Enhanced Reactivity of Methylamine Co-ordinated to Ruthenium(II)

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Summary The cation $[Ru^{II}(MeNH_2)_6]^{2+}$ has been isolated as the iodide, bromide, or tetrafluoroborate salt; the methylamine ligands are much more susceptible to oxidation than the free base and produce co-ordinated cyanide upon exposure to oxygen under ambient conditions.

Few Group VII transition-metal complexes containing aliphatic or side chain amines as ligands have been reported.[1,2] Morgan and Burstall[2] ascribed the formula $[RuCl_2(EtNH_2)_4]Cl$ to a stable pink product derived from ethylamine and ruthenium trichloride. We were unable to repeat this preparation, but have prepared the hexakismethylamine complex of ruthenium(II) by an adaptation of Lever and Powell's reaction,[3] using a solution of methylamine (25%) in water.† The solid yellow salts yield analytical results in agreement with the formula $C_6H_{30}N_6RuX_2$, (X = I, Br, or BF_4). The i.r. spectra of freshly prepared products show that methylamine is present and water absent.

On being kept in the presence of air or oxygen at room temperature the solids turned black. When a freshly prepared, anhydrous, sample of $Ru(MeNH_2)_6I_2$ is sealed under a slight excess of pure dry oxygen, the colour change occurs over a period of hours. The majority of the oxygen is consumed, and mass spectral analysis shows the remaining gas to be mainly oxygen, with some water and carbon dioxide present. The i.r. spectrum of the black solid formed shows the presence of water and methylammonium ions and also shows a strong asymmetric band centred at 2040 cm^{-1}. All the methylammonium iodide present may be removed by extraction with nitromethane, followed by washing with a warm dilute solution of potassium hydroxide.‡ The i.r. spectrum of the insoluble black solid only shows the peak at 2040 cm^{-1} and water bands.

Although the behaviour of complexes containing Ru^{II} and higher unidentate aliphatic or side chain aromatic amines is different in detail from that of the methylamine complex, one general reaction appears to occur. When Ru^{II} is co-ordinated entirely by amines of type RCH_2NH_2, some of the ligand molecules are oxidized at room temperature, in

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† A sample of the complex was precipitated as the perchlorate. This solid exploded violently while still damp.
‡ That the extracted material is methylammonium iodide is confirmed analytically and spectroscopically.

oxygen, to nitriles. The oxidized products of these complexes of higher amines show no new i.r. absorptions other than those ascribed to nitrile, and are clear around 2040 cm^{-1}. Thus we believe that the band at 2040 cm^{-1} is due to the oxidation of methylamine to cyanide. Full details of the observations on higher amines will be reported elsewhere. Further support for the postulate that co-ordinated methylamine has been oxidized to cyanide comes from the position of the new spectral band, and from C,H,N analytical data for the product. $K_4Ru(CN)_6$ shows[4,5] ν (CN) at 2060 cm^{-1}, while the analytical data are consistent with the formulation $Ru(CN)_3,3H_2O$. The data for higher amines suggest that the new i.r. band is due solely to co-ordinated cyanide. The i.r. bands assigned to water are removed by heating to 180°, the spectrum of the residual material then containing only bands assignable to cyanide ligands. The absence of hydride from the product cannot be proved by analysis or by direct examination of this intractable material. The following experiments provide partial confirmation of its absence. When the methylamine complex is prepared in a mixed H_2O–D_2O medium, $MeND_2$ can be detected in the yellow unoxidized complex, whereas there is no detectable change in the spectrum of the oxidation product. Thus if any hydride is present, it must have been derived solely from the methyl group. The product is presumably related to the dark green[6] $Ru(CN)_3,5H_2O$ and $Ru(CN)_3,H_2O$.

We believe that these experiments show that methylamine, a saturated molecule, becomes activated upon co-ordination to ruthenium(II) and may be easily oxidized to cyanide. The only similar processes known to us are the electrolytic oxidation of amines in basic solution at silver electrodes,[7] and a deprotonated ethylenediamine product.[8] The activation of the organic ligand probably accounts for the behaviour of the perchlorate salt.

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