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THE REACTION OF NITROUS OXIDE
WITH THE
AQUOPENTA-AMMINERUTHENIUM(II) ION

*Characterisation of penta-ammine(dinitrogen oxide)-
ruthenium(II) complexes*

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Tables (which are not included in the text), figures and references are at the end of the respective chapter.

SUMMARY

In the presence of an external reducing agent, nitrous oxide reacts with $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$ to form the dinitrogen complexes, $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$ and $[(\text{NH}_3)_5\text{RuN}_2\text{Ru}(\text{NH}_3)_5]^{4+}$, which were isolated as the tetrafluoroborate salts. The reaction conditions can be controlled so that very little of the di-nuclear complex is formed. The dinitrogen complexes are also formed in the absence of an external reducing agent when concentrated solutions of $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$ (10^{-2} M) are used. In this case $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$ acts as the reducing agent. A preliminary kinetic investigation of the reaction indicated that a nitrous oxide complex is formed as an intermediate but spectral evidence for it could not be obtained. However, when dilute solutions of $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$ (3×10^{-4} M) were exposed to nitrous oxide, Armor and Taube did observe a nitrous oxide complex, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2\text{O})]^{2+}$, but they could not isolate it.

From an understanding of the reaction between nitrous oxide and $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$, and the results of Armor and Taube, it was possible to design reaction conditions which have enabled the nitrous oxide complex to be isolated. The bromide, iodide, tetrafluoroborate and hexafluorophosphate salts have been characterised as $[\text{Ru}(\text{NH}_3)_5(\text{N}_2\text{O})]\text{Br}_2$, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2\text{O})]\text{I}_2$, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2\text{O})](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ and $[\text{Ru}(\text{NH}_3)_5(\text{N}_2\text{O})](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ respectively. Complexes containing $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ and $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ have also been prepared.

A powder photograph of $[\text{Ru}(\text{NH}_3)_5(\text{N}_2\text{O})]\text{Br}_2$ indicated that it has a

SUMMARY (cont'd)

structure similar to that of the dinitrogen complex, $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$, in which the nitrous oxide is linearly co-ordinated. A normal co-ordinate analysis of the infrared spectra of the co-ordinated nitrous oxide was made, and it indicated that the nitrous oxide is co-ordinated to the ruthenium atom through its oxygen atom.

The aquopenta-ammineruthenium(II) ion has also been isolated. Its bromide, iodide and hexafluorophosphate salts have been characterised as $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]\text{Br}_2$, $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]\text{I}_2$ and $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ respectively. A tetrafluoroborate salt was also isolated, but it could not be characterised.

Also, two reactions were found which yielded the penta-amminecarbonylruthenium(II) complex. In one reaction carbon dioxide was the source of the carbonyl group, and in the other it was abstracted from formamide.

STATEMENT

This thesis contains no material which has been accepted for any other degree in any University. To the best of my knowledge, the work described here is original and no part of it has been reported elsewhere by any other person, except where due reference is made in the text.

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ABBREVIATIONS

The following list of abbreviations will be used in this thesis.

monomer	$[\text{RuA}_5\text{N}_2]^{2+}$
dimer	$[\text{A}_5\text{RuN}_2\text{RuA}_5]^{4+}$
i	initially
f	finally
A	ammonia, NH_3
en	ethylenediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
trien	triethylenetetra-amine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
py	pyridine
dipy	2,2'-dipyridyl
diphos	1,2-bis(diphenylphosphino)ethane
DMGH ₂	dimethylglyoxime
THF	tetrahydrofuran
Me	methyl, CH_3
Et	ethyl, C_2H_5
Ph	phenyl, C_6H_5

for the reducing agents:-

Zn/Hg	amalgamated zinc
Pt(H ₂)	dihydrogen on platinum black

in reference to infrared spectra:-

s	strong	sh	shoulder
m	medium	br	broad
w	weak	a	region covered by the anion