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The Uptake of Carbon Dioxide by some Ruthenium(II) Complexes

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It is now widely recognised that carbon dioxide could become a feedstock for the synthesis of some organic compounds. References [1] to [5], drawn from a much greater number of literature reports, indicate this recognition. Usually but not invariably [6, 7] transition metal species play some part in the chemical conversions of CO_2 into other species.

It is difficult to investigate the behaviour of carbon dioxide as a ligand since the bonds formed between it and metal ions are usually weak. When complex formation does occur it is often incomplete or readily reversible [8], while hydrolysis or inter-ligand reactions frequently accompany the uptake of carbon dioxide [7, 9]. Data from physical techniques, such as infra-red spectroscopy, are usually difficult to use for ligand characterisation. In a limited number of cases the formation of complexes containing the CO_2 unit as a ligand has been firmly demonstrated. The acquisition of X-ray crystallographic data is the best source of such proof. To date, three different modes of attachment of carbon dioxide to a single metal centre are known. There are also instances of CO_2 bridging between three metal ions. For convenience the three modes are shown diagrammatically in Figs. 1a–1c. A bent CO_2 unit can be attached to the metal through the central carbon atom [10], or through both that atom and one of the oxygen atoms [8]. The third alternative is for the ligand to retain its linearity and attach end-on to the metal. Cases a) and b) have been proven crystallographically, while c) depends on infra-red observations made during adsorption studies [11].

Free carbon dioxide shows two infra-red active bands, ν_3 at 2349 cm^{-1} and ν_2 at 667 cm^{-1}. Coordination without the loss of the linearity of the OCO should result in the retention of these bands, probably with some slight shifting. That has been observed by other workers [11] and is also found here. ν_1 at 1388 cm^{-1} in Fermi resonance with $2\nu_2$ at 1275 cm^{-1} may become infra-red active as well. The observation of the uptake of carbon dioxide gas and the appearance of some of these bands may be taken as strong evidence for the formation of a linear carbondioxido species. Recently [12] the formation of lanthanide complexes containing linear CO_2 ligands has been claimed. Infra-red bands were found at 2180, 1520, and sometimes 1620 cm^{-1}.

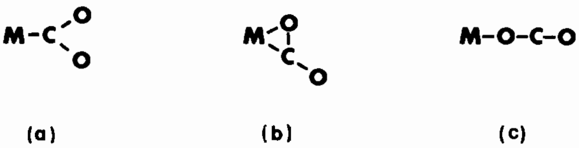

Fig. 1. Possible coordination modes of CO_2.

More usually the uptake of carbon dioxide results in its conversion into another compound. During interaction with metal centres, CO_2 often undergoes the making [13] or breaking [14] of C–O bonds, or even undergoes disproportionation [14, 15]. Thus there is ample precedent for our report of the formation of a carbonyl complex from carbon dioxide.

The results described below set out our findings in experiments in which we attempted to substitute CO_2 for other poor ligands, *e.g.* N_2, or to use CO_2 in place of the isoelectronic N_2O in published procedures. These results strengthen the evidence for the occurence of linear CO_2 ligands. While that geometry is commonly recognised in physical adsorption studies it has only rarely been found by coordination chemists [16].

Results and Discussion

The reduction of $[RuCl(NH_3)_5]Cl_2$ by zinc amalgam in dilute sulphuric acid under argon yields a yellow solution containing Ru(II). A solid product, $[Ru(NH_3)_5H_2O](PF_6)_2$ can be precipitated from the solution [17]. We have investigated the interaction of carbon dioxide with both this solid and its preceding aqueous solution. Also we have attempted to replace coordinated dinitrogen by carbon dioxide in the related complex $[Ru(NH_3)_5N_2]^{2+}$.

When solid $[Ru(NH_3)_5H_2O](PF_6)_2$ is left to stand at room temperature for a day under carbon dioxide at an elevated pressure some interaction between the two reagents occurs. After removing the solid from the autoclave, we obtain elemental analytical data that show the incorporation of a small amount (0.6%) of carbon, while the infra-red spectrum exhibits a weak new absorption band at 2340 cm^{-1}. Similar observations were made when the yellow solution containing $[Ru(NH_3)_5H_2O]^{2+}$ was decanted from the zinc amalgam and allowed to stand for a day under carbon dioxide before NH_4PF_6 was added to the precipitate. On exposure to air, this solid lost its carbon dioxide as shown by the disappearance of

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the band at 2340 cm^{-1}. That band reappears after reexposure to a carbon dioxide atmosphere, while its intensity increases with the period of exposure. These observations could be explained either by the physical adsorption of the gas by the solid, or the incomplete uptake of CO_2 as a ligand which retains the linear geometry of the gas. We prefer the latter interpretation.

In one informative experiment, a freshly prepared solution containing $[Ru(NH_3)_5H_2O]^{2+}$ was added to zinc amalgam and then exposed to carbon dioxide for two days in an autoclave. The aqueous solution was subsequently decanted from the amalgam and treated with a saturated solution of NH_4BF_4, under carbon dioxide. A yellow precipitate of the known [18] compound $[Ru(NH_3)_5CO](BF_4)_2$ was obtained, which showed ν(CO) at 1980 cm^{-1}. This process is accompanied by a change in the ultra-violet spectrum of the aqueous solution. While $[Ru(NH_3)_5H_2O]^{2+}$ shows one absorption maximum at 310 nm ($\epsilon = 2.3 \times 10^4$), a solution which has stood under CO_2 for 20 hours shows two maxima at 255 nm (4.5×10^4) and 325 nm (3.6×10^4).

We found stronger evidence for carbon dioxide incorporation in the infra-red spectra of products obtained from a different reaction sequence. When pentaamminohydratoruthenate(II) reacts with nitrous oxide it can yield complexes containing N_2O as a ligand [19]; or in the presence of a reducing agent it can give the bi- nuclear dinitrogeno complex [20]. We have used the latter route as a starting point for experiments with carbon dioxide. Thus we also found that when an aqueous solution containing $[Ru(NH_3)_5H_2O]^{2+}$, in contact with zinc amalgam, is let stand under nitrous oxide for three hours before a saturated solution of ammonium hexafluorophosphate is added, a precipitate is formed. Infra-red and elemental analytical data indicate it to be predominantly $[(Ru(NH_3)_5)_2N_2](PF_6)_4$, but with some mononuclear dinitrogeno-contaminant.

If that procedure is altered at the point where precipitation is induced, a different product can be obtained. Thus after exposure to N_2O, the aqueous solution was decanted off the amalgam and placed in an autoclave at room temperature under carbon dioxide for 30 hours. Only then was a precipitating counterion added, BF_4^- in this instance. A yellow solid was obtained which exhibits strong new infra-red bands at 2340 and 660 cm^{-1}. There is no detectable change in the region from 1200 to 1400 cm^{-1} and usually, but not always, the solid shows residual traces of a band assignable to coordinated N_2. Data from elemental analysis are close to those expected for $[(Ru(NH_3)_5)_2CO_2](BF_4)_4$. (Found 1.3% C, 3.8% H, 20.4% N: expected 1.6% C, 3.9% H, 18.3% N).

We obtained similar results when the impure solid $[(Ru(NH_3)_5)_2N_2](PF_6)_4$ was treated with CO_2 in the autoclave. In that case the band at 2165 cm^{-1} is reduced in intensity, but not completely lost, while a stronger band grows in at 2340 cm^{-1}. The product is sufficiently stable for the bands attributable to CO_2 to remain, at reduced intensities, after the solid has been warmed to 80 °C for 4 hours in the air.

As a further check on this type of reaction procedure we have prepared $[Ru(NH_3)_5N_2]^{2+}$ by a different route, starting from commercial ruthenium trichloride and hydrazine hydrate [21], and then treated it with carbon dioxide. When aqueous solutions containing this species are treated with CO_2 before a precipitating anion is added, solids can again be obtained which show infra-red absorptions at 2330 and 660 cm^{-1}. The use of solid $[Ru(NH_3)_5N_2]X_2$, where X = ClO_4 or PF_6, gives stronger infra-red bands. In the case of the hexafluorophosphate, the elemental analytical data were very close to those expected for $[(Ru(NH_3)_5)_2CO_2](PF_6)_4$. Thus we found 1.3% C, 3.5% H and 15.3% N; while the expected data are 1.2, 3.0 and 14.1% respectively.

In conclusion, there are two reports in the literature [12, 16] of the chemical uptake of carbon dioxide in what is probably an end-on fashion, attached to Cu, Pr or Nd. We believe that our observations demonstrate this same phenomenon with the $(NH_3)_5$-Ru(II) moiety. The products described here possess poor stability and are not fully purified and characterised; a common feature in the chemistry both of ruthenium(II) complexes with weak ligands, and of carbondioxido systems generally. Nonetheless, we have been able to obtain sufficient evidence to demonstrate their occurrence.

Experimental

Published procedures were followed in the preparations of known compounds, using commercially available reagents, as referenced in text. The Results section also contains most of the necessary details for our own preparations. Note that 2% zinc amalgam was always freshly prepared [22] before use. Reactions involving carbon dioxide at elevated pressures were carried out in a 100 cm^3 autoclave, at room temperature, by placing a piece of solid CO_2 of suitable weight inside the autoclave followed by a small beaker containing all other reagents. The autoclave was then sealed and left to equilibrate for one or more days. No attempt was made to carry out any reactions under rigorously anhydrous conditions.

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