A Ruthenium(II) Dinitrogen Complex

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WE present evidence for the existence of a tetrammine dinitrogen complex of ruthenium(II) *viz.* $[Ru(NH_3)_4(N_2)_2]Br_2$ similar to that found for osmium[1] and more stable than the ruthenium(II) complex $[Ru\,en_2(N_2)_2]\,(Ph_4B)_2$ recently reported.[2]

It has been shown[3] that the formation of $[Ru(NH_3)_5N_2]^{2+}$ from ruthenium(III) and hydrazine hydrate gives a product contaminated with up to 50% of a ruthenium–ammine–hydrazine complex. In an attempt to isolate a pure hydrazine complex, we carried out reactions at low temperatures and obtained small amounts of a dinitrogen complex, probably $[Ru(NH_3)_4(N_2)_2]Br_2$, together with $[Ru(NH_3)_5N_2]Br_2$ and a ruthenium(II)–hydrazine product.

Treatment of $[Ru(NH_3)_5Cl]Cl_2$ or *cis*-$[Ru(NH_3)_4Cl_2]Cl$ with hydrazine hydrate at $-23°$ for 1 hr. or 10 min., respectively, gave an oily product on the addition of sodium bromide. From its i.r. spectrum, the oily compound appears to be a ruthenium(III)–ammine–hydrazine complex. The i.r.-active mode $\delta(NH_3)$ sym is at 1310 cm.$^{-1}$ and $\rho r(NH_3)$ is at 810 cm.$^{-1}$, typical of a ruthenium(III) ammine complex;[4] in addition, strong bands at 1115 and 955 cm.$^{-1}$ are due to co-ordinated hydrazine.[5,6] The product also contains a little of the complex $[Ru(NH_3)_5N_2]Br_2$ as indicated by the sharp band in the i.r. spectrum at 2110 cm.$^{-1}$.[7]

The oily compound decomposes at room temperature and gives rise to two additional sharp bands in the i.r. region at 2220 and 2185 cm.$^{-1}$, similar in position to the bands assigned to $\nu(N{\equiv}N)$ in $[Ru\,en_2(N_2)_2]^{2+}$.[2] If water is added to the original reaction mixture at $-23°$, followed by sodium bromide, a solid material is obtained which has the same three sharp bands in the i.r. spectrum. In addition, the i.r. spectrum contains bands typical of ammonia co-ordinated to ruthenium(II)[4] [δ (NH_3)sym at 1240 cm.$^{-1}$, $\rho r(NH_3)$ at 760 cm.$^{-1}$] and bands due to co-ordinated hydrazine. The two weak bands at 2220 and 2185 cm.$^{-1}$ decrease slightly in intensity over a period of three days.

The results suggest that the reaction at $-23°$ gives a ruthenium(III)–ammine–hydrazine complex which decomposes at higher temperatures, or on the addition of water at room temperature, to give a mixture of at least three products $[Ru(NH_3)_4(N_2)_2]^{2+}$, $[Ru(NH_3)_5N_2]^{2+}$, and a ruthenium(II)–ammine–hydrazine complex.

A similar reaction carried out on $[Ru\,en_2Cl_2]Cl$ did not give a dinitrogen complex, suggesting that the tetrammine dinitrogen complex is the more thermally stable of the two. The much slower rate of disappearance of the two bands (2220 and 2185 cm.$^{-1}$) in the i.r. spectrum of $[Ru(NH_3)_4(N_2)_2]^{2+}$ compared with their loss for $[Ru\,en_2(N_2)_2]^{2+}$ [1] supports this contention.

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[1] H. A. Scheidegger, J. N. Armor, and H. Taube, *J. Amer. Chem. Soc.*, 1968, **90**, 3263.
[2] L. A. P. Kane-Maguire, P. S. Sheridan, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1968, **90**, 5295.
[3] J. Chatt, R. L. Richards, J. E. Fergusson, and J. L. Love, *Chem. Comm.*, 1968, 1522.
[4] A. D. Allen and C. V. Senoff, *Canad. J. Chem.*, 1967, **45**, 1337.
[5] K. Brodersen, *Z. anorg. Chem.*, 1957, **290**, 24.
[6] A. Braibanti, F. Dallavalle, M. A. Pellinghelli, and E. Leporate, *Inorg. Chem.*, 1968, **7**, 1430.
[7] A. D. Allen, F. Bottomley, R. D. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, 1967, **89**, 5595.