Dinitrogen Complex Formation with the Breakage of the C–N Bond on a Co-ordinated Ethylenediamine

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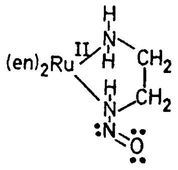
Summary Treatment of $Ru(en)_3^{3+}$ with NO in alkaline solution results in the ready production of a dinitrogen complex with concomitant breakage of the C–N bond of the ethylenediamine chelate ring.

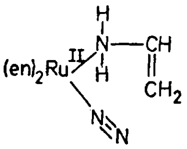
In recent reports of dinitrogen complex formation unusual coupling reactions of two remote nitrogen atoms have occured,[1,2] and we have discussed[3,4] the reaction: $Ru(NH_3)_6^{3+} + OH^- + NO \rightarrow Ru(NH_3)_5N_2^{2+} + 2H_2O$. We now report a similar reaction for $Ru(en)_3^{3+}$, in which the ethylenediamine C-N bond is broken, and which may be driven, in part, by the inherent stability of the metal–dinitrogen bond.[5]

Injection of a deoxygenated solution of $Ru(en)_3^{3+}$ (0·04 mmol) into 0·4M-NaOH (2 mmol) (NO-saturated, 0·02 mmol) resulted in an immediate discoloration. The mixture was purged with NO (g) 0—120 min before degassing with Ar (25 min) and then acidifying with HBr to pH < 2. Solid products could not be obtained directly from fresh solutions using Br^-, I^-, BF_4^-, and PF_6^-, but cold, saturated $Na[BPh_4]$ solution gave a solid with an i.r.

band at 2120 cm^{-1}. Microanalysis and its u.v. and i.r. spectra were consistent[1] with the formula: $[Ru(en)_2(N_2)OH_2][BPh_4]_2$.



(I)



(II)

The distribution of products of this reaction can be obtained upon roto-evaporation of the product solution (containing only Br^- anions) to dryness. If the reaction is performed at 2 °C, only one i.r. band is observed above 1800 cm^{-1}, at 2113 cm^{-1}. At room temperature, two new bands of similar intensity are observed at 2113 and 1905 cm^{-1}. At lower pH values or longer times of contact of $Ru(en)_3{}^{3+}$ with the alkaline solution, the 2113 cm^{-1} band decreases in intensity, while the 1905 cm^{-1} band increases. A band at 1638 cm^{-1} was always associated with the 2113 cm^{-1} band in fresh preparations. N–H bands in Ru–ethylenediamine complexes are well removed from this position,[6–8] and deuteriation studies confirmed that this band was not due to OH or NH. In the absence of NO, the bands at 2113 and 1905 cm^{-1} are not observed.

$Ru(en)_3{}^{3+}$ reacts with NO in acidic media (pH $\leqslant$ 2) to yield a nitrosyl complex[9] with ν(NO) at 1905 cm^{-1}. Since the 2100 cm^{-1} region is characteristic of metal–dinitrogen complexes, it appears that the reaction proceeds under conditions analogous to those in the competition between substitution and diazotization by NO upon $Ru(NH_3)_6{}^{3+}$.[3,4] A diazonium salt structure with a free diazo-linkage might also produce a band in the 2100 cm^{-1} region,[10] but such a structure would be reactive. The following facts also indicate that we have prepared a dinitrogen complex. i, Use of ^{15}NO gives a band at 2067 cm^{-1}, as expected for a N_2 complex derived from attack of NO upon the amine;[10] ii, cerium (IV) sulphate and the tetraphenylborate salt produces 1 (±10%) mol of N_2, per mol Ru; iii, ion exchange gives a species of charge +2, stable in aqueous solution, with λ_{max} 221 nm, characteristic of $Ru^{II}–N_2$ complexes.

The 1638 cm^{-1} band may be assigned[10] to ν(C=C), and compounds (I) and (II) may be intermediates in the reactions. Vinylamine is unstable, and neither it nor acetaldehyde, the expected decomposition product, were detected. The expected product of such a reaction would be the observed $[Ru(en)_2(N_2)(H_2O)]^{2+}$.

From the 221 nm u.v. band,[12] we estimated the yield of the N_2 complex to be *ca.* 40%. A >60% yield of $[Ru(en)_2(N_2)OH_2][BPh_4]_2$ can be achieved by the controlled addition of aliquot portions of $Ru(en)_3{}^{3+}$ (at pH 3) into a large excess of alkaline, NO-saturated solutions (at pH 13).

This remarkable reaction of $Ru(en)_3{}^{3+}$ finds some parallel with the air oxidation of $Ru(en)_3{}^{3+}$ in alkaline solution to yield an α-di-imine chelate ring.[13,14] The NO similarly oxidises the ethylenediamine ligand, ultimately resulting in a reduction of the metal centre.

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[1] L. Kane-Maguire, G. Sheridan, F. Basolo, and A. G. Pearson, *J. Amer. Chem. Soc.*, 1968, **90**, 5295.
[2] H. Scheidegger, J. N. Armor, and H. Taube, *J. Amer. Chem. Soc.*, 1968, 2363.
[3] S. Pell and J. Armor, *J. Amer. Chem. Soc.*, 1972, **94**, 686.
[4] S. Pell and J. Armor, *J. Amer. Chem. Soc.*, 1973, 7625.
[5] J. Armor and H. Taube, *J. Amer. Chem. Soc.*, 1970, **92**, 6170.
[6] J. Broomhead and L. Kane-Maguire, *Inorg. Chem.*, 1969, **8**, 2124.
[7] A. D. Allen and C. V. Senoff, *Canad. J. Chem.*, 1965, **43**, 888.
[8] J. Broomhead and L. Kane-Maguire, *J. Chem. Soc.* (*A*), 1967, 546.
[9] S. Pell and J. Armor, to be published.
[10] L. J. Bellamy, 'The Infra-Red Spectra of Complex Molecules,' Wiley, New York, 1962, pp. 34—36, 273.
[11] S. Pell, A. Mann, H. Taube, and J. Armor, *Inorg. Chem.*, 1974, 479.
[12] L. Kane-Maguire, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3964.
[13] B. C. Lane, J. Lester, and F. Basolo, *Chem. Comm.*, 1971, 1618.
[14] Sr. H. Elsbernd and J. K. Beattie, *J. Chem. Soc.*, (*A*), 1970, 2598.