Properties of Co-ordinated N_2 in the $[Os^{II}(NH_3)_5N_2]^{2+}$ Ion

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SEVERAL complexes containing co-ordinated N_2 are known[1] and interest in this field is shifting to the chemistry of the co-ordinated nitrogen. We have been studying the properties of co-ordinated N_2 in the complex $[Os^{II}(NH_3)_5N_2]^{2+}$, prepared according to Allen and Stevens,[2] and report here our observations on two aspects relevant to the biological fixation, *viz.*, ease of reduction and the possibility of further co-ordination to other metal ions.

The reduction of *ca.* 10^{-3}M-solutions of $Os(NH_3)_5N_2Cl_2$ in 0·1M-KCl was studied by polarography over the range of pH 2—9 (HCl and NaOH). No reduction waves were observed in addition to those due to hydrogen discharge. This places a threshold for the reduction of the osmium–nitrogen complex of −1·3 v at pH 2 and −2·0 v at pH 9 (*versus* S.C.E.). Since diazonium cations are readily reduced at the dropping electrode and the overvoltage for the reduction of O_2, H_2O_2, NO_3^-, *etc.*, is considerably reduced by complexing with metal ions,[3] this negative result strongly suggests that the reduction of co-ordinated N_2 by reagents of the potential normally available in biological cells (approx. that of the H_2/H^+ couple) may be thermodynamically very unfavourable, as distinct from merely slow kinetically. This is readily understood in the light of the very endothermic heat of formation of di-imine, HN=NH, ($\Delta H_f = 48{\cdot}7 \pm 5$ kcal./mole at 25°c)[4] which, either

NN *and* CN *stretching frequencies* (*in cm.*$^{-1}$)

Complex		Other ions		
	Cl^-	ClO_4^-	Ag^+,ClO_4^-	Cu^{2+},Cl^-
$[Os^{II}(NH_3)_5N_2]^{2+}$	2010	2050	2235	2225
$[Co^{III}(NH_3)_5CN]^{2+}$ *	2135	2145	2200	—

* Data from ref. 7.

free or complexed, is expected to be an intermediate in reductive fixation.[5,6]

The possibility of further complexing of the co-ordinated N_2 has been studied by infrared spectroscopy (Nujol mulls). Solids were prepared by evaporating under reduced pressure mixed aqueous solutions of the osmium–nitrogen complex with various metal salts, such as Na_2SO_4, $BaCl_2$, $Pb(NO_3)_2$, TlCl, $ZnCl_2$, $CdCl_2$, $Hg(NO_3)_2$, $Hg_2(NO_3)_2$ CH_3HgNO_3, $CuCl_2$, $AgClO_4$, $NiCl_2$, $CoCl_2$ and $FeSO_4$. Rapid reaction occurred with Ag^I, Hg^{II}, and Hg^{II}_2 leading to the liberation of N_2 and precipitation of metal, which could be avoided in the case of Ag^I by working at or below 0°. The N–N stretching frequency varies slightly with the nature of the anion,[2] but significant changes were observed only in the presence of Ag^I and Cu^{II} (see Table). The shift to higher frequency can be reversed (*e.g.* by treating the silver adduct with a solution of NaCl) and the ratio of the intensities of the two bands is related to the ratio of the concentrations of osmium and silver (or copper). The formation constants of the adducts are too low to permit studies in solution, and we have so far not found a reagent to precipitate the mixed complex. But from the marked change in frequency and the parallel with $[Co^{III}(NH_3)_5CN]^{2+}$, where Ag^I is known to co-ordinate to the nitrogen atom of cyanide,[7] we conclude that Ag^I and Cu^{II} can form unsymmetrically bridged complexes such as $[(NH_3)_5Os.N_2.Ag]^{3+}$. These results show that N_2 may, in certain circumstances, exhibit donor properties towards simple metal cations of the type that are stable in air and water. In addition, such unsymmetrically bridged complexes may be of importance in the biological fixation, since the enzymes contain both iron and molybdenum.[8]

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