The Reversible Conversion of Co-ordinated Nitrosyl into Co-ordinated Nitrite in 2,2′-Bipyridyl Complexes of Ruthenium(II)

By THOMAS J. MEYER,* JOHN B. GODWIN, and NEIL WINTERTON

(*Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina* 27514)

Summary Nitric oxide bonded to ruthenium in 2,2′-bipyridyl complexes of ruthenium(II) exists as co-ordinated nitrosyl in acidic solution, but as co-ordinated nitrite in basic solution, and the interconversion between the two forms is reversible.

WE have prepared and isolated the complexes $[Ru(bipy)_2(NO)X]^{2+}$[X = Cl(Ia), Br(Ib), NO_2(Ic)] and $[Ru(bipy)_2(NO)(py)]^{3+}$ (II) [(bipy) = 2,2′-bipyridyl, (py) = pyridine] as their hexafluorophosphate salts. The co-ordinated nitrosyl behaves chemically as NO^+ in that the complexes react with hydroxide ion in aqueous solution to give the corresponding nitrite complexes (Equation 1). The nitrite

$$Ru(bipy)_2(NO)X^{2+} + 2\,OH^- \rightarrow Ru(bipy)_2(NO_2)X + H_2O \qquad (1)$$

complexes in turn react in aqueous acidic solution to regenerate the initial nitrosyl complexes (Equation 2).

$$2H^+ + Ru(bipy)_2(NO_2)X \rightarrow Ru(bipy)_2(NO)X^{2+} + H_2O \qquad (2)$$

Spectrophotometric experiments indicate that the conversion from one form into the other is quantitative and reversible.

The almost colourless nitrosyl complexes were prepared [except for (Ic)] by adding a stoicheiometric amount of sodium nitrite to aqueous acidic solutions of the corresponding aquo-complexes $[Ru(bipy)_2(OH_2)X]^+$ which were generated *in situ* and not isolated.[1] After 5—10 min an excess of ammonium hexafluorophosphate was added to the solutions to precipitate the complexes. At room temperature aqueous sodium nitrite itself does not react noticeably with the aquo-complexes, implying that co-ordination of nitrite preceding nitrosyl formation does not occur. The nitrite complex (Ic) can be made directly by suspending $[Ru(bipy)_2(NO_2)_2]$ (III) in methanol and adding concentrated perchloric acid dropwise. The perchlorate salt is converted into the hexafluorophosphate by dissolving it in acetonitrile and adding aqueous NH_4PF_6. The complexes were obtained in 60—100% yields.

By suspending (Ia) and (Ic) in 1M-aqueous sodium hydroxide with stirring for 10—15 min, good yields of $[Ru(bipy)_2(NO_2)Cl]$(IVa) and $[Ru(bipy)_2(NO_2)_2],H_2O$(IVb) have been obtained. The i.r. spectra of the complexes in KBr pellets indicate that nitrite is co-ordinated through nitrogen.[2] The geometry of all the complexes reported here is presumably *cis*.[1] Satisfactory analytical data have been obtained for complexes (Ia), (Ib), (Ic), (II), (III), (IVa), and (IVb).

The reversibility of the reactions of the nitrosyl complexes appear to be without precedent in ruthenium nitrosyl chemistry. The interconversion between nitrosyl and nitrite in nitroprusside ion has been studied in detail recently.[3] The NO stretching frequencies for the complexes in acetone where the ligand X is Cl, Br, NO_2, and (py) are at 1930, 1931, 1942, and 1950 cm^{-1} respectively. The relatively high NO frequencies further indicate that a high degree of positive charge resides on the co-ordinated nitrosyl.[3]

Acknowledgement is made to the U.N.C. Materials Research Centre through a contract with the Advanced Research Projects Agency and the University Research Council of the University of North Carolina.

(*Received, May 4th,* 1970; *Com.* 672.)

---

[1] F. P. Dwyer, H. A. Goodwin, and E. C. Gyarfas, *Austral. J. Chem.*, 1963, **16**, 544; B. Bosnich and F. P. Dwyer, *ibid.*, 1966, **19**, 2229.

[2] K. Nakamoto, J. Fujita, and H. Murato, *J. Amer. Chem. Soc.*, 1958, **80**, 4817.

[3] J. Mašek and H. Wendt, *Inorg. Chim. Acta*, 1968, **2**, 455.

[4] J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.