CHAPTER I

INTRODUCTION

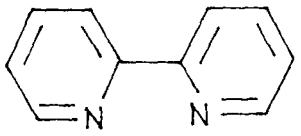
CHAPTER I

INTRODUCTION

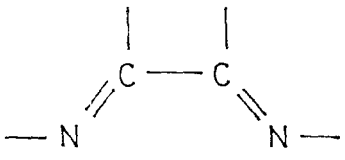
ABSTRACT : In this chapter the scope, aim and purpose of the present work namely exploration of mixed - ligand complexes of ruthenium and osmium containing 2-(arylazo)pyridines (L, **1**) are delineated.

I.1 PURPOSE OF THE PRESENT INVESTIGATION

The chemistry of ruthenium[1-9] and osmium[10-14] with polypyridine ligands particularl 2.2′-bipyridine (bipy, **1**) with diimine (**2**) chromophore has been the cynosure for last thre



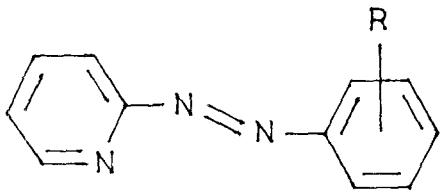
bipy; 1



2

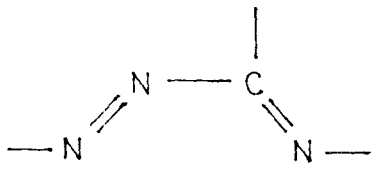
decades. The interest arises due to novel synthetic methods, different isomer populations and their stabilisation in varied oxidation levels, ability to serve as building units in supramolecular arrays, veracity in reactivities like catalytic, photochemical, photophysical, ground and excited state redox behaviours with fascinating chemical implications. The number of heteroatoms, ring size, and substituents in the rings significantly modify the π-acidity and regulate the properties of the coordination molecules.

2-(Arylazo)pyridines (L, **3**) have the azoimine (**4**) function which is isoelectronic with α-diimine function in bipy. **3** has substatial[15-35] chemistry with different transition metal ions. The



R = H, *m*-Me, *p*-Me

L; 3



4

azo group is one of the potential functional units which may be photochromatic, pH-responsive, redox active and mediate electronic communications between photoredox active groups[28,36]. Ru-L complexes are of particular chemical interest because of the rich synthetic methods,

isomeric structural pattern, stereoretentive/stereodynamic reaction pathways, chemical stability, reversible redox behaviour and excited state phenomena. The literature shows that although ruthenium chemistry of L is explored to a great[20-30] extent, the corresponding chemistry with its congener, osmium, has been attracted[31-35] very little. This encourages us to investigate the Os-L chemistry that remains unexplored. The present work focuses attention on :

(i) The synthesis and characterisation of new mixed-ligand complexes of ruthenium and osmium, particularly the latter,

(ii) Thorough investigation of spectroscopic and magnetic properties,

(iii) Elucidation of stereochemistry and bonding, structure and electronic structure,

(iv) Investigation of electrochemical electron transfer properties pertaining to metal and/or ligands, and

(v) Comment on the tractable chemistry emphasizing the present work over the reported ones.

REFERENCES

All references in this thesis are given in the following format : Name(s) of the authors, *journ* year, **volume**, page.

1. M. Schroder and T. A. Stephenson, *Comprehensive Coordination Chemistry (The synthesi reactions, properties & applications of coordination compounds)*, Ed. G. Wilkinso Pergamon Press, New York, 1987, **Vol 4**, 277-518; (b) E. A. Seddon and K. R. Seddon, *Th Chemistry of Ruthenium*, Elsevier, New York, 1984.
2. (a) K. R. Seddon, *Coord. Chem. Rev.*, 1982, **41**, 79; (b) K. R. Seddon, *Coord. Chem. Rev* 1985, **67**, 171; (c) M. D. Ward, *Coord. Chem. Rev.*, 1993, **127**, 1; (d) S. –M. Lee and W. –T Wong, *Coord. Chem. Rev.*, 1997, **164**, 415; (e) J. W. –S. Hui and W. -T. Wong, *Coord. Chem Rev.*, 1998, **172**, 389.
3. (a) K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrine Complexes* Academic Press, New York, 1992; (b) J. –M. Lehn, *Supramolecular Chemistry*, VCH Weinheim, 1995.
4. (a) V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759 (b) V. Balzani, A. Credi and M. Venturi, *Coord. Chem. Rev.*, 1998, **171**, 3.
5. (a) S. I.Gorelsky, E. S. Dodsworth, A. B. P. Lever and A. A. Vlček, *Coord. Chem. Rev.*, 1998 **174**, 469; (b) A. A. Vlček, *Coord. Chem. Rev.*, 1982, **43**, 39.
6. (a) B. J. Coe, T. J. Meyer and P. S. White, *Inorg. Chem.*, 1995, **34**, 593 and refs therein; (b M. R. Rhodes and T. J. Meyer, *Inorg. Chem.*, 1988, **27**, 4772; (c) M. S. Thompson and T. J Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 4106.
7. (a) H. D. Abruna, A. Y. Deng, G. J. Samuels and T. J. Meyer, *J. Am. Chem. Soc.*, 1979, **101**, 6745; (b) T. Geiger, U. Kolle and M. Gratzel, *J. Chem. Soc., Chem. Commun.*, 1982, 681.
8. (a) B. P. Sullivan, D. J. Salmon and T. J. Meyer, *Inorg. Chem.*, 1978, **17**, 3334; (b) E. V. Dose and L. J. Wilson, *Inorg. Chem.*, 1978, **17**, 2660; (c) G. M. Brown, T. R. Weaver, F. R. Keene and T. J. Meyer, *Inorg. Chem.*, 1976, **15**, 190; (d) N. E. Tokel-Takvoryan , R. E. Hemingway and A. J. Bard, *J. Am. Chem. Soc.*, 1973, **95**, 6582.
9. (a) H. Nagao, H. Nishimura, H. Funato, Y. Ichikawa, F. S. Howell, M. Mukaida and H. Kakihana, *Inorg. Chem.*, 1989, **28**, 3955; (b) W. R. Murphy, Jr., K. J. Takeuchi, M. H. Barley and T. J. Meyer, *Inorg. Chem.*, 1986, **25**, 1041; (c) S. Sinha, P. K. Das and B. K. Ghosh, *Polyhedron*, 1994, **13**, 2665.

10. (a) W. P. Griffith, *Comprehensive Coordination Chemistry (The synthesis, reaction properties and applications of coordination compounds)*, Ed., G. Wilkinson, Pergamon Pres New York, 1987, **Vol 4**, 519-633.

11. (a) K. R. Seddon, *Coord. Chem. Rev.*, 1982, **41**, 159; (b) P. A. Lay and W. D. Harman, *Ad Inorg. Chem.*, 1991, **37**, 219.

12. (a) P. J. Bailey, *Coord. Chem. Rev.*, 1995, **138**, 87; (b) M. D. Ward, *Coord. Chem. Rev* 1997, **164**, 483; (c) J. P. H. Charmant, *Coord. Chem. Rev.*, 1998, **172**, 437.

13. (a) F. P. Dwyer, H. A. Goodwin and E. C. Gyarfas, *Aust. J. Chem.*, 1963, **16**, 42, 544; (b) R H. Fabin, D. M. Klassen and R. W. Sonntag, *Inorg. Chem.*, 1980, **19**, 1977; (c) B. P. Sulliva and T. J. Meyer, *Inorg. Chem.*, 1982, **21**, 1037; (d) D. S. Williams, T. J. Meyer and P. S White, *J. Am. Chem. Soc.*, 1995, **117**, 823.

14. (a) S. Decurtins, F. Felix, J. Ferguson, H. U. Güdel and A. Ludi, *J. Am. Chem. Soc.*, 1980 **102**, 4102; (b) B. J. Pankuch, D. E. Lacky and G. A. Crosby, *J. Phys. Chem.*, 1980, **84**, 2061 2068; (c) E. M. Kober and T. J. Meyer, *Inorg. Chem.*, 1982, **21**, 3967; (d) Ibid., 1983, **22** 1614.

15. P. V. Rolling, D. D. Kirt, J. L. Dill, S. Hall and C. Hallstorm, *J. Organomet. Chem.*, 1976, **116**, 39.

16. (a) S. Gupta and A. Chakravorty, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 109; (b) B. S. Raghavendra and A. Chakravorty, *Indian J. Chem., Sect. A*, 1976, **14A**, 166.

17. P. Bandyopadhyay, D. Bandyopadhyay, A. Chakravorty, F. A. Cotton, L. R. Falvello and S. Han, *J. Am. Chem. Soc.*, 1983, **105**, 6327.

18. D. Datta and A. Chakravorty, *Inorg. Chem.*, 1983, **22**, 1085.

19. A. K. Deb and S. Goswami, *J. Chem. Soc., Dalton Trans.*, 1989, 1635.

20. (a) R. A. Krause and K. Krause, *Inorg. Chem.*, 1980, **19**, 2600; (b) R. A. Krause and K. Krause, *Inorg. Chem.*, 1982, **21**, 1714.

21. (a) R. A. Krause and K. Krause, *Inorg. Chem.*, 1984, **23**, 2195; (b) S. Wolfang, T.C. Strekas, H. D. Gafney, R. A. Krause and K. Krause, *Inorg. Chem.*, 1984, **23**, 2650.

22. S. Goswami, *Ph. D. Thesis*, The Jadavpur University, 1983.

23. (a) S. Goswami, A. R. Chakravarty and A. Chakravorty, *Inorg. Chem.*, 1981, **20**, 2246; (b) S. Goswami, A. R. Chakravarty and A. Chakravorty, *Inorg. Chem.*, 1982, **21**, 2737.

24. A. Seal and S. Ray, *Acta Cryst.*, 1984, **C40**, 929.

25. (a) S. Goswami, A. R. Chakravarty and A. Chakravorty, *J. Chem. Soc., Chem. Commun.* 1982, 1286; (b) S. Goswami, A. R. Chakravarty and A. Chakravorty, *Inorg. Chem.*, 1983, **22** 602.

26. (a) S. Goswami, R. N. Mukherjee and A. Chakravorty, *Inorg. Chem.*, 1983, **22**, 2825; (b) P Ghosh and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1985, 361.

27. (a) G. K. Lahiri, S. Bhattacharya, S. Goswami and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1990, 561; (b) N. Bag, A. Pramanik, G. K. Lahiri and A. Chakravorty, *Inorg. Chem.*, 1992, **31**, 40.

28. B. K. Ghosh and A. Chakravorty, *Coord. Chem. Rev.*, 1989, **95**, 239.

29. (a) A. K. Deb, P. C. Paul and S. Goswami, *J. Chem. Soc., Dalton Trans.*, 1988, 2051; (b) M. Kakoti, A. K. Deb and S. Goswami, *Inorg. Chem.*, 1992, **31**, 1302; (c) S. Choudhury, A. K. Deb and S. Goswami, *Polyhedron*, 1994, **13**, 1063.

30. P. Majumdar, S. M. Peng and S. Goswami, *J. Chem. Soc., Dalton Trans.*, 1998, 1569 and refs. therein..

31. (a) B. K. Ghosh, S. Goswami and A. Chakravorty, *Inorg. Chem.*, 1983, **22**, 3358; (b) A. K. Mahapatra, B. K. Ghosh, S. Goswami and A. Chakravorty, *J. Indian Chem. Soc.*, 1986, **63**, 101; (c) B. K. Ghosh, A. Mukhopadhyay, S. Goswami, S. Ray and A. Chakravorty, *Inorg. Chem.*, 1984, **23**, 4633.

32. A. Mukhopadhyay and S. Ray, *Acta Cryst.*, 1987, **C43**, 14.

33. (a) B. K. Roy, T. K. Mallick and B. K. Ghosh, *Polyhedron*, 1992, **11**, 1829; (b) T. K. Mallick, P. K. Das, S. Sinha and B. K. Ghosh, *Polyhedron*, 1994, **13**, 1817; (c) B. K. Roy, S. Sinha and B. K. Ghosh, *Transition Met. Chem.*, 1994, **19**, 521.

34. (a) P. K. Das, S. Sinha and B. K. Ghosh, *Indian J. Chem.*, 1996, **35A,** 586; (b) N. K. Mondal, P. K. Das, B. K. Roy and B. K. Ghosh, *Transition Met. Chem.*, 1999, **24**, 678.

35. (a) S. Sinha, P. K. Das and B. K. Ghosh, *Transition Met. Chem.*, 1995, **20,** 59; (b) S. Sinha, A. K. Banerjee and B. K. Ghosh, *Transition Met. Chem.*, 1997, **22**, 483; (c) S. Sinha, A. K. Banerjee and B. K. Ghosh, *Indian J. Chem.*, 1998, **37A,** 264.