

## Synthesis and electrochemical studies of phenylazo substituted tetraaza macrocyclic complexes of Ni(II)

RANDHIR SINGH\*, SURESH KUMAR and  
AMARENDRA BHATTACHARYA

Department of Chemistry, Gurukula Kangri University, Harwar 249 404  
India

MS received 15 May 2000; revised 23 October 2000

**Abstract.** Synthesis and characterization of some phenylazo substituted tetraaza macrocyclic complexes of Ni(II) are reported. Electrochemical behaviour of these macrocyclic complexes has been examined using polarographic, voltammetric and spectroscopic techniques. These studies show that both the ligand and the metal are electrochemically active. The electrochemical behaviour of the azo function has been shown to occur through a single four-electron process. When a nitro group is also present, the nitro function of the azo moiety is reduced in a six-electron cathodic wave.

**Keywords.** Phenylazo macrocyclic complex; electrochemical studies.

### 1. Introduction

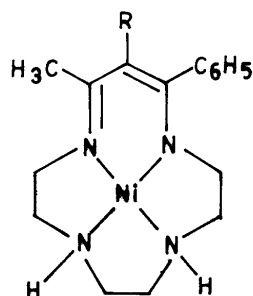
The multifarious roles played by the naturally occurring macrocycles in the functioning of biological systems are now well known<sup>1-13</sup>. Their role in the physiology and biochemistry of life forms is of paramount importance. The chemistry of macrocyclic complexes is also of significant general interest due to the use of such complexes as dyes and pigments, as well as MRI contrast agents and models for naturally occurring macrocyclic systems<sup>15</sup>.

In spite of the prodigious development of other physical methods, electrochemistry and electronic absorption spectroscopy remain the most widely used tools in the study of macrocycles. A proper understanding of their redox nature and spectra is of great importance in the investigation of the behaviour of the central metal atom and the molecular and electronic structure of the chromophores. In this paper, the Ni(II) complexes of a Schiff's base ligand and a substituted tetraaza macrocycle and their electrochemical behaviour are described (figure 1).

### 2. Experimental

Electronic absorption spectra of complexes were recorded on a Shimadzu 160A UV-Vis spectrophotometer. Electrochemical studies were performed at  $pH = 7.0$  (buffered) using a Swiss-made Metrohm Merisau System (Polarecord E506, VA Scanner E612). A saturated calomel electrode as reference electrode and Pt-foil as counter electrode were

\*For correspondence



- (A): R = H  
 (B): R = -N=N-PC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>  
 (C): R = -N=N-PC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NH<sub>2</sub>

**Figure 1.** Structure of the Ni(II) complexes discussed.

used for electrochemical studies using *tris* (hydroxymethyl) aminomethane and HCl as buffer or tetra *n*-butylammonium tetrafluoroborate as the supporting electrolyte.

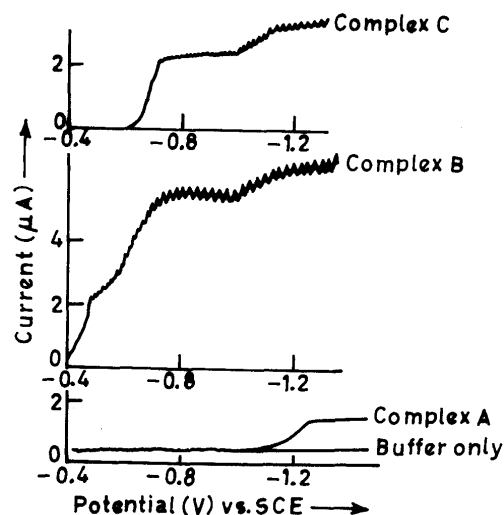
### 2.1 Preparation of complexes

**2.1a Complexes A and B:** Complex A (figure 1) was prepared according to the method reported earlier<sup>16</sup>. Complex B was prepared by adding 7.4 g (0.01 M) *p*-nitrobenzenediazonium tetrafluoroborate (0.01 M) to a stirred solution containing 3.6 g of complex A (0.01 M) in dry pyridine at 0°C. The mixture was stirred for further 5 h and thereafter it was added to a saturated aqueous solution of sodium tetrafluoroborate. The brownish-green precipitate obtained was filtered and recrystallized from CH<sub>3</sub>CN. The yield was 65%. Elemental analysis results were found to be in good agreement with calculated values.  $I_{\max}$  (nm) in DMF: 485 (*sh*), 510 (*sh*), 322 (*sh*).

**2.1b Complex C:** The macrocyclic complex was prepared first by diazotizing the sulphanilamide according to the method reported earlier<sup>17</sup>. Equimolar quantities of complex A in pyridine at 0°C and a solution of the diazonium salt were mixed and stirred for about 2 h. The resulting solution was poured into a saturated solution of sodium tetrafluoroborate and pH adjusted to 9 with NaOH. The reddish precipitate obtained was filtered off and recrystallized from CH<sub>3</sub>CN (yield 60%). Elemental analysis results were found to be in good agreement with the calculated values.  $I_{\max}$  (nm) in DMF: 365 (*sh*), 410 (*sh*), 390 (*sh*), 470 (*sh*).

## 3. Results and discussion

Nickel macrocyclic complexes (A), substituted with diazonium groups having *p*-nitro and sulphanilamide substituents, were obtained in good yields. The complexes have been characterized by elemental analysis and spectroscopic techniques. DC polarographic studies were made between +0.1 V and -1.6 V vs SCE. Typical polarograms for these complexes are shown in figure 2. Macrocyclic complex A shows an irreversible wave with  $E_{1/2} = -1.17$  V. The diffusion current increases linearly with concentration and comparison with the corresponding diffusion plateau for cadmium ion indicates that a two-electron reduction of the macrocyclic complex occurs with the value of diffusion



**Figure 2.** Polarograms of complexes A, B and C (0.5 mM) in pH 7.0 buffer containing 0.01% gelatin.

coefficient  $4.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  in aqueous medium at pH 7.0. The irreversible reduction wave occurs at a potential where two electron reductions have been reported for a number of Ni(II) compounds<sup>18,19</sup> and is ascribed to the reduction of the nickelous ion.

It is well-known that  $E_{1/2}$  is pH dependent when protons are involved in the electron transfer processes. The irreversible reduction wave was also examined as a function of pH between pH 3 and 9. A linear relation with a slope 58 mV per increasing pH unit was observed which is consistent with the deprotonation/protonation of macrocyclic complex A. From pH 6 to pH 9,  $E_{1/2}$  was independent of the  $\text{H}^+$  concentration indicating a  $pK_a$  value in the region of 6. These observations are consistent with reported values<sup>20</sup>.

The macrocyclic complex B showed three reduction waves corresponding to four-electron ( $E_{1/2} -0.41 \text{ V}$ ), six-electron ( $E_{1/2} -0.63 \text{ V}$ ) and two-electron ( $E_{1/2} -1.08 \text{ V}$ ) processes consistent with reduction of the azo group, the nitro group and Ni(II). But their authentic reduction behaviour is still unclear as the nitro group can be reduced through either a single six-electron wave or sequential four- and two-electron processes. Thus the initial reduction could represent the reduction of the azo group or nitro group. By adding varying amounts of DMF and running the polarograms, it has been observed that the addition of DMF removes the wave at  $-1.08 \text{ V}$  and separates the four- and six-electron processes. The controlled potential electrolysis was carried out at  $-0.63 \text{ V}$  for the nitro compound. After sometime, the samples of the cathodic solution were removed, diluted to a fixed volume with DMF and spectral examinations were made. It was found that there is a decrease in the peak at 518 nm due to the dye, with increasing coulombs and a peak due to a product was also noted at 371 nm, which corresponded to the peak observed for *p*-nitroaniline in DMF. Furthermore, the evidence of nitroaniline formation during electrolysis was obtained by isolating *p*-nitroaniline from the cathodic solution. The reddish solution was removed from the electrochemical cell and *p*-nitroaniline was separated and its formation confirmed by qualitative tests.

**Table 1.** Polarographic data of compounds A, B and C in pH 7 buffer.

|           | $E_{1/2}$ , V vs SCE | $E_{1/2}$ , V vs SCE | $E_{1/2}$ , V vs SCE |
|-----------|----------------------|----------------------|----------------------|
| Complex A |                      |                      | -1.17 V (2e)         |
| Complex B | -0.46 V (4e)         | -0.63 V (6e)         | -1.08 V (2e)         |
| Complex C |                      | -0.66 V (4e)         | -1.10 V (2e)         |

pH 7 buffer was made using *tris* (hydroxymethyl) aminomethane and HCl. No. of electrons in parentheses

**Table 2.** Cyclic voltammetric data of complexes A, B and C in DMF. Sweep rate = 0.1 V s<sup>-1</sup>.

|           | $E_p$ , V vs SCE | $E_{p/2}$ , V vs SCE |
|-----------|------------------|----------------------|
| Complex A | 0.72             | 0.62                 |
| Complex B | 0.91             | 0.84                 |
| Complex C | 0.84             | 0.7                  |

For macrocyclic complex C, two cathodic irreversible waves were observed at pH 7 (table 1, figure 2). Furthermore, cathode waves for both molecules (B and C) corresponded to two-electron processes and were found in such a region where Ni(II) reduction would be expected. Initially, four-electron processes resulted from the reduction of the azo group. This is in support of the earlier studies made for azo-compounds<sup>21-22</sup>. It is also observed that the  $E_{1/2}$  values change with pH and over the range of 4 to 8 linearly.

Cyclic voltammograms of all macrocyclic complexes were also recorded in DMF containing tetra *n*-butylammonium tetrafluoroborate (0.1 M)<sup>23</sup> using a microcell. The spectroelectronic studies showed that the number of electrons being transferred per molecule for these compounds ranged from 0.91 V to 1.10 V and that is in agreement with theoretical value for an electron transfer. Oxidation sweeps between 0.0 and 1.8 V vs SCE showed, for sweep rate up to 3.0 V s<sup>-1</sup>, one reversible oxidation wave for each macrocyclic complex ( $5 \times 10^{-3}$  M dm<sup>-3</sup>) (table 2). Earlier studies have showed that for the macrocyclic in non-aqueous media, the oxidation wave is due to the formation of Ni(II)<sup>24-25</sup>. The generated Ni(III) complex undergoes fast chemical reaction subsequent to electron transfer and probably result in the complex breaking down. The voltage differences between the peak ( $E_p$ ) and half peak potentials ( $E_{p/2}$ ) are consistent with the theoretical value (48/bn/mv), for a one-electron transfer<sup>26</sup>. The voltammograms were also recorded as functions of the charge passed during controlled potential oxidations and the number of coulombs required to oxidise the dye molecules at 0.95 V determined, i.e. electrolysis of the solution was carried out and the electrolysed solution was taken for cyclic voltammogram recording. Thus it was indicated the number of electrons being transferred per molecule for all these macrocyclic complexes range from 0.95 to 1.10 in agreement with the above measurements.

The electrochemical reduction of the azo linkage is usually observed as two equal electron waves except in the presence of electron donating group<sup>27</sup>. Similarly the reduction of aromatic nitro compounds usually exhibits two waves unless amines or

hydroxyl group are present in the aromatic rings<sup>27</sup>. The reason for this may be due to a catalytic effect by the central nickel atom in reducing the expected hydrazo and hydroxylamine intermediates.

### Acknowledgements

The authors are thankful to the Council of Scientific and Industrial Research, for financial assistance and to the Department of Chemistry, University of Roorkee, Roorkee for providing the electrochemical facility.

### References

1. Volbeda A, Charon M H, Piras C, Hatchikian E C, Frey M and Fontecilla-Cuellar P 1995 *Nature (London)* **373** 580
2. Marganisan C A, Vazir H, Baidya N, Olmstead M M and Mascharak P K 1995 *J. Am. Chem. Soc.* **117** 1584
3. Brooker S and Croucher P D 1995 *J. Chem. Soc., Chem. Commun.* **193** 2075
4. Brooker S and Davidson T C 1997 *Chem. Commun.* 2007
5. Brooker S, Croucher P D and Roxborgh F M 1996 *J. Chem. Soc., Dalton Trans.* 3031
6. Sirish M and Maiya B G 1994 *J. Photochem. Photobiol. A* **77** 189
7. Rao T A and Maiya B G 1995 *J. Chem. Soc., Chem. Commun.* 939
8. Basolo F, Hoffman B M and Ibers J A 1975 *Acc. Chem. Res.* **8** 344
9. Gutsche C D and Andreetti G D 1991 In *Inclusion compounds* (ed.) J L Atwood, J E D Davies and D D MacNicol (Oxford: University Press) vol. 4
10. Izatt R M, Lamb J D, Hawkins R T, Brown P, Izatt S R and Christensen J J 1983 *J. Am. Chem. Soc.* **105** 1782
11. Martel A E and Taqui Khan M M 1977 *Inorg. Biochem.* **2** 654
12. Geyes R P 1974 *Bull. Parenter. Drug Assoc.* **28** 10; Baldwin J E 1975 *Newsweek* 91
13. Price R 1970 In *Chemistry of synthetic dyes* (ed.) K Venkataraman (New York: Academic Press) vol. 3
14. Busch D H 1964 *Rec. Chem. Prog.* **2** 107
15. Cummings S C and Meyers R F 1970 *J. Am. Chem. Soc.* **92** 215
16. Zollinger H 1961 *Aliphatic and aromatic compounds* (New York: Interscience)
17. Kolthoff I M and Lingane J J 1952 In *Polarography* (New York: Interscience) vol. 2
18. Meites L 1967 In *Polarographic techniques* (New York: Interscience)
19. Martin J G, Wain R M and Cummings S C 1972 *Inorg. Chem.* **11** 475
20. Florence T M 1974 *J. Electroanal. Chem. Interfacial Electrochem.* **52** 115
21. Goddard J and Goslin T A 1979 *J. Inorg. Nucl. Chem.* **41** 1229
22. Mann K 1969 In *Electroanalytical chemistry* (ed.) A J Bard (New York: Marcel Dekker) vol. 3
23. Curtis N J and Cook D F 1967 *Chem. Commun.* 962
24. Olson D and Vasilevskis J 1969 *Inorg. Chem.* **8** 164
25. Barefield E K and Busch D H 1970 *Chem. Commun.* 522
26. Truex T J and Holm R H 1972 *J. Am. Chem. Soc.* **94** 4529
27. Thomas F G and Bato K G 1975 In *Chemistry of the hydrazo, azo and azoxy groups* (ed.) S Patai (London: Wiley)