J. inorg. nucl. Chem. Vol. 41, pp. 1229–1232
Pergamon Press Ltd., 1979. Printed in Great Britain

SYNTHESIS AND POLAROGRAPHIC STUDIES OF SOME PHENYLAZO SUBSTITUTED TETRA-AZA MACROCYCLE COMPLEXES

J. D. GODDARD and T. A. JOSLIN[†]
Research Division, Kodak Limited, Headstone Drive, Harrow, Middlesex, HA1 4TY, England

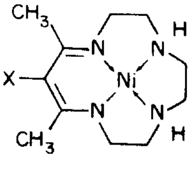
(*Received* 23 *October* 1978; *received for publication* 23 *January* 1979)

Abstract—The preparation of some phenylazo substituted tetra-aza macrocycle complexes is reported. The electrochemical properties of these compounds have been examined using polarographic and voltammetric techniques. These studies revealed that both the ligand and metal are electrochemically active. The reduction of the azo function has been shown to occur through a single four-electron process. When a nitro group was also present the nitro function was reduced in a six-electron wave, cathodic of the azo moiety.

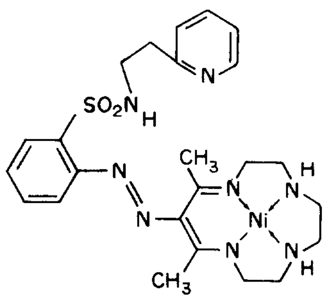
INTRODUCTION

The chemistry of the metal complexes of tetra-aza macrocyclic ligands is of general interest because such compounds have been used as dyes and pigments[1] as well as being advanced as models for more complex biological systems[2].

In a previous communication, the reaction of diazonium ions with coordinated ligands was described[3]. The Schiff's base ligand of the tetra-aza macrocycle complex (I) was also found to undergo rapid electrophilic substitution with diazonium ions to give highly coloured phenylazo derivatives (II), (III) and (IV). This report describes the synthesis and some electrochemical properties of these novel compounds.



(I) X = H
(II) X = —N=N—p-$C_6H_4NO_2$
(III) X = —N=N—p-$C_6H_4SO_2NH_2$



(IV)

EXPERIMENTAL

Equipment

A Jeol FX-100 NMR spectrometer was used to obtain 100 MHz ^1H spectra of the prepared compounds in $CDCl_3$ containing sufficient DMSO-d_6 to ensure solubility. The solvent-dependent shifts are reported in ppm relative to TMS.

The visible spectra of the azo dyes were recorded on a Unicam SP8000 UV Recording Spectrophotometer. Mass spectrometry was performed using a VG Micromass ZAB-2F reverse geometry mass spectrometer.

Polarography was performed using a Radiometer PO4 polariter. A known concentration of each sample was dissolved in "AnalaR" grade dimethylformamide and a quantity, sufficient to give a 0.3 mM solution, injected into the electrochemical cell containing aqueous buffer under nitrogen. Cyclic voltammetry was performed using the apparatus previously described[4]. Controlled potential electrolyses were performed in a two compartment cell similar to that previously described[5]. The anode and cathode were separated by a glass sinter.

Preparation of compounds

2-*Amino*-N-(2-*pyrid*-2′-*ylethyl*)*benzene sulphonamide* was prepared by heating *o*-aminobenzenesulphonyl fluoride (5.0 g, 0.029 mole) and 2-(2-aminoethyl)pyridine (8.71 g, 0.071 mole) in DMSO (100 ml) overnight on a steam bath. The mixture was cooled, poured into ice/water (2 l) and concentrated hydrochloric acid (2 ml) added to coagulate the precipitate. The crude product was filtered off, dissolved in ethyl acetate (200 ml) and filtered through a bed of silica. Slow evaporation of the solvent under vacuum afforded colourless needles which were filtered, washed with petrol and dried (60% yield). Calc. for $C_{13}H_{15}N_3O_2S$: C, 56.3; H, 5.5; N, 15.2; S, 11.6. Found: C, 56.2; H, 5.6; N, 15.0; S, 11.8%. M.p. 120–121°C.

Complex (*I*): was prepared according to the method of Cummings and Sievers[6].

Complex (*II*): *p*-Nitrobenzenediazonium tetrafluoroborate (2.4 g, 0.01 mole) was added slowly as a solid to a stirred solution of (I) (3.6 g, 0.01 mole) in dry pyridine (75 ml) at 0°C. The mixture was stirred for a further hour, then added to a saturated aqueous solution of sodium tetrafluoroborate (1800 ml). The precipitate was filtered and recrystallised from acetonitrile to yield lustrous brown/green crystals (70% yield). Calc. for $C_{17}H_{24}N_7O_2BF_4Ni$: C, 40.5; H, 4.8; N, 19.5; Ni, 11.7. Found: C, 40.4; H, 4.8; N, 19.4; Ni, 11.8%. M.p. 241–242°C (decomp.); λ_{max}^{DMF}: 490 (sh), 516 (ϵ = 32,000) nm.

Complex (*III*): Sulphanilamide was diazotized according to the method of Zollinger[7]. The solution of the diazonium salt was added to an equimolar quantity of (I) in pyridine at 0°C and stirred for 1 hr at 4°C. The resulting solution was poured into an excess of saturated sodium tetrafluoroborate solution and the pH adjusted to 9 with 3 N sodium hydroxide. The bright red precipitate was filtered off and recrystallised from acetonitrile (60% yield). Calc. for $C_{17}H_{26}N_7O_2SBF_4Ni$: C, 37.9; H, 4.9; N, 18.2; S, 6.0; Ni, 10.9. Found: C, 37.9; H, 4.8; N, 18.5; S, 5.9; Ni, 11.0%. M.p. 233–235°C (decomp.); λ_{max}^{DMF}: 360 (sh), 412 (ϵ = 23,800), 470 (sh) nm.

Complex (*IV*): This was prepared by the same method as complex (III) with 2 - amino - N - (2 - pyrid - 2′ - ylethyl)benzene sulphonamide instead of sulphanilamide. Calc. for $C_{24}H_{33}N_8O_2SBF_4Ni$: C, 44.8; H, 5.2; N, 17.4; S, 5.0; Ni, 9.1. Found: C, 44.6; H, 5.0; N, 17.4; S, 5.1; Ni, 8.9%. M.p. 219–220°C (decomp.); λ_{max}^{DMF}: 360 (sh), 412 (ϵ = 24,000), 470 (sh) nm.

[†] Present address: Diamond Shamrock Electrosearch S.A., 3 rte de Troinex, 1227 Carouge-Geneva, Switzerland.

Table 1. ^1H NMR spectra of the complexes (II)–(IV) in $COCl_3/DMSO\text{-}d_6$

(II)	(III)	(IV)	Multiplicity	Assignment
2.47† (6)	2.42 (6)	2.38 (6)	Singlet	$\underline{CH_3}$-
2.86‡ (8)	2.86 (8)	2.84 (8)	Overlapping multiplets	-$\underline{CH_2}$-N
3.50‡(4)	3.50(4)	3.50(8)	Overlapping multiplets	-$\underline{CH_2}$-N= $SO_2N\underline{CH_2CH_2}$
5.40 (1) 5.80 (1)	5.15 (1) 5.55 (1)	5.48 (1) 5.88 (1)	Broad Humps	NH
		6.25 (1)	Triplet	-SO_2NH-
	7.13 (2)		Broad singlet	-SO_2NH_2
7.55 (2) 8.17 (12)§	7.55 (2) 7.84 (2)§	6.9–8.5(8)	Complex overlapping resonance	Aromatic

†Integration in parentheses.
‡Centre of complex pattern.
§AB pattern.

RESULTS AND DISCUSSION

The reaction of diazonium ions with the nickel complex (I) of a tetra-aza macrocyclic ligand has provided a new series of mono-substituted phenylazo-derivatives. The coupling reaction is rapid, even at −5°C and proceeds in good yield in pyridine.

The complexes have been characterised by elemental analysis, melting point and NMR. The ^1H NMR spectra for each complex were consistent with the above structures, as shown in Table 1. Direct current polarographic studies were made between +0.1V and −1.6V vs SCE. Typical polarograms for all complexes (0.3 mM in pH 7 buffer containing 0.01% gelatin) are shown in Fig. 1.

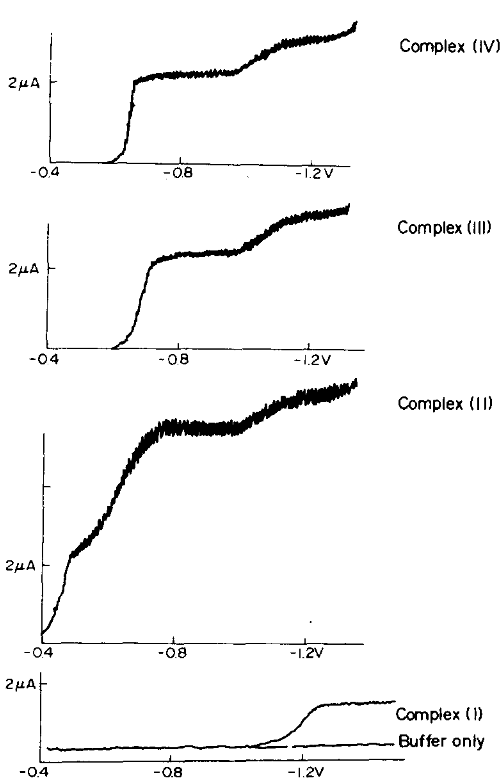


Fig. 1. Polarograms of complexes (I) to (IV), (0.3 mM) in pH 7.0 buffer containing 0.01% gelatin. Reference Electrode: SCE.

Compound (I) showed one irreversible wave $E_{1/2} = -1.17$ V. The diffusion current increased linearly with concentration and comparison with the corresponding diffusion plateau for cadmium ion indicated that a two-electron reduction of (I) was occurring. This comparison also allowed calculation of the diffusion coefficient of (I) to be $4.9 \times 10^{-10}\,m^2\,s^{-1}$ in aqueous solution. The irreversible reduction wave occurs at a potential where aqueous two-electron reductions have been reported for a number of nickel(II) compounds[8, 9] and is ascribed to the reduction of nickelous ion.

Since it is known that when protons are involved in electron transfer processes the half-wave potential is pH dependent and that compound (I) can be protonated[10], the irreversible reduction wave at −1.17 V was also examined as a function of pH between pH 3 and 9. A linear relation of slope-58 mV per increasing pH unit, which is consistent with the deprotonation/protonation of the Schiff's base (I), was observed between pH 9 and 6. From pH 6 to 3 the half-wave potential was independent of the hydrogen ion concentration, indicating a pK_a value in the region of 6. These observations are consistent with the equilibrium and pK_a value previously reported for this nickel macromolecule[10].

Compound (II) gave a more complex response (Fig. 1). Three reduction waves corresponding to a four-electron, a six-electron and a two-electron process are consistent with the reductions of the azo group, the nitro group and nickel(II), although the polarographic results alone are insufficient to assign each wave because the nitro-group can be reduced through either a single six-electron wave, or a four-electron and a two electron-process. The initial reduction could therefore represent the reduction of the azo-group or nitro-group.

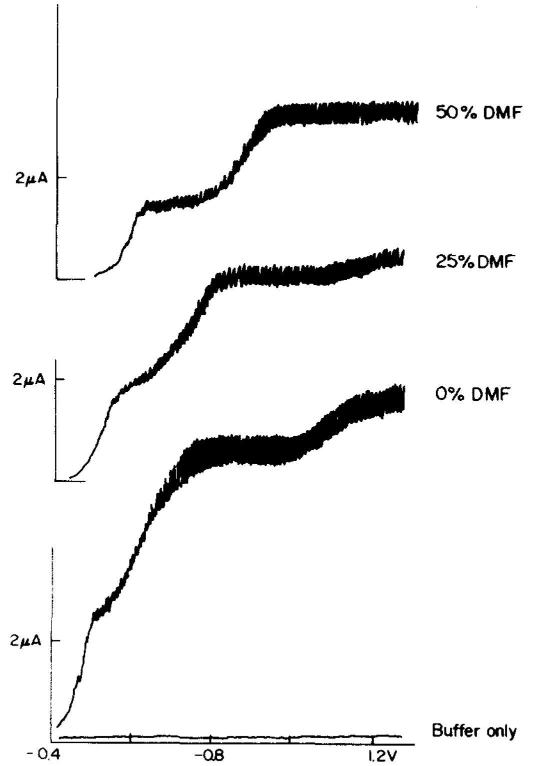


Fig. 2. Polarograms of complex (II) 0.3 mM in pH 7.0 buffer containing 0.01% gelatin and varying amounts of DMF.

Controlled potential electrolyses were thus attempted to resolve this problem. To obtain sufficient material in solution to make electrolyses practicable, polarograms were run on compound (II) using pH 7 buffer (0.01% gelatin) and varying quantities of "AnalaR" grade dimethylformamide. The results are shown in Fig. 2, where it can be seen that the addition of DMF removes the wave at -1.08 V and separates the four and six electron processes. Taking advantage of this increased separation between the two waves, electrolyses were performed at -0.68 V in 100 ml of 50:50 DMF/pH 7 buffer containing the nitro-compound (5 mM). As the charge was passed, samples of the cathodic solution were removed, diluted to a known volume with excess DMF, and examined spectroscopically between 700 and 335 nm. The peak at 518 nm due to the dye was observed to decrease with increasing coulombs whilst a peak due to a product was noted at 371 nm. This product peak corresponded to the peak observed for *p*-nitroaniline in DMF. Further evidence of the formation of nitroaniline as an electrolysis product was obtained by isolating *p*-nitroaniline from the cathodic solution.

The red solution was removed from the cell, the DMF/water removed and the organic material separated by preparative layer chromatography. With an eluant of chloroform:ethyl acetate (30:70) *p*-nitroaniline (30 mg) was obtained (current efficiency 92% for 80% conversion). The formation of *p*-nitroaniline was confirmed by accurate mass measurement ($C_6H_6N_2O_2$, requires: M^+, 138.042924; Found: M^+, 138.043048).

Compounds (III) and (IV) both showed two irreversible waves at pH 7 (Table 2 and Fig. 1). The more cathodic waves for both molecules corresponded to two-electron processes and were in a region where nickel(II) reduction would be expected to occur. The initial four-electron processes result from the reduction of the azo-group. In support of this suggestion, and in common with previous studies made upon azo-compounds[11], is the change in $E_{1/2}$ with pH. Over the range pH 4 to 8, experiments indicated the $E_{1/2}$ values changed linearly by accurate mass measurement ($C_6H_6N_2O_2$, requires: M^+, 138.042924; Found: M^+ 138.043048).

Table 2. Polarographic measurements of compounds (I) to (IV) in pH 7 buffer†

	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$
Compound (I)			-1.17 V (2*e*)‡
Compound (II)	-0.465 V (4*e*)	-0.630 V (6*e*)	-1.08 V (2*e*)
Compound (III)		-0.655 V (4*e*)	-1.10 V (2*e*)
Compound (IV)		-0.685 V (4*e*)	-1.07 V (2*e*)

†pH 7 buffer made up using tris (hydroxymethyl)aminomethane and hydrochloric acid.

‡Number of electrons in parenthesis.

In view of the limited solubility of the macromolecules cyclic voltammograms on platinum anodes were made in "AnalaR" grade dimethylformamide[12] containing tetra-*n*-butylammonium tetrafluoroborate (10^{-1} mol dm^{-3}). Oxidation sweeps between 0.0 V and 1.8 V vs SCE showed, for sweep rates up to 30 V s^{-1}, one reversible oxidation wave for each compound (5×10^{-3} mol dm^{-3}) (Table 3). Previous studies on nickel complexes of cyclic tetramine ligands in non-aqueous media suggest the oxidation wave is due to the formation of nickel(III)[13–16]. The generated nickel(III) complex undergoes fast chemical reaction subsequent to electron transfer and probably results 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 ($48/\beta n$ mV) for a one-electron transfer[17]. Cyclic voltammograms were also obtained as a function of the charge passed during controlled potential oxidations and the coulombs required to oxidise the dye molecules at 0.95 V determined. These experiments indicated the number of electrons being transferred per molecule for compounds (II) to (IV) ranged from 0.95 to 1.10 in agreement with the above measurements. Electrochemical measurements on compound (IV) in both DMF and water showed no significant difference in the oxidation and reduction potentials of nickel(II) present in compounds (III) and (IV) (Tables 2 and 3). This result is in agreement with absorption measurements. Both compounds (III) and (IV) have similar spectra, having λ_{max} 412 nm. The electrochemical and spectroscopic measurements indicate that the Schiff's base in complex (IV) is not acting as a pentadentate ligand.

Also of interest are the single polarographic reduction waves for the azo (4*e*) and nitro (6*e*) groups. The reduction of the azo linkage is usually observed as two equal

Table 3. Cyclic voltammetry data of compounds (I) to (IV) in DMF

	E_p	$E_{p/2}$	Sweep rate
Compound (I)	0.72 V	0.62 V	0.1 V s^{-1}
Compound (II)	0.91 V	0.84 V	0.1 V s^{-1}
Compound (III)	0.84 V	0.75 V	0.1 V s^{-1}
Compound (IV)	0.87 V	0.78 V	0.1 V s^{-1}

two-electron waves, except in the presence of electron donating groups[18]. Similarly the reduction of aromatic nitro compounds usually exhibits two waves unless amine or hydroxyl groups are present in the aromatic ring[18]. The reason for the above observations is not known but may be due to a catalytic effect by the central nickel atom in reducing the expected hydrazo and hydroxylamine intermediates.

Acknowledgements—The authors are indebted to Dr. Eileen Hyde and Mr. Alan Payne for the nuclear magnetic resonance and mass spectrometric measurements.

REFERENCES

1. R. Price, In *The Chemistry of Synthetic Dyes* (Edited by K. Venkataraman), Vol. 3. Academic Press, New York (1970).
2. D. H. Bush, *Rec. Chem. Progr.* **25**, 107 (1964).
3. J. D. Goddard, *J. Inorg. Nucl. Chem. Lett.* **13**, 555 (1977).
4. H. H. Adam and T. A. Joslin, *J. Electroanal. Chem. Interfacial Electrochem.* **58**, 393 (1975).
5. C. Moinet and D. Peltier, *Bull. Soc. Chim. Fr.*, 2657 (1968).
6. S. C. Cummings and R. E. Sievers, *J. Am. Chem. Soc.* **92**, 215 (1970).
7. H. Zollinger, In *Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds.* Interscience, New York (1961).
8. I. M. Kolthoff and J. J. Lingane, In *Polarography*, Vol. 2. Interscience, New York (1952).
9. L. Meites, In *Polarographic Techniques.* Interscience, New York (1965).
10. J. G. Martin, R. M. C. Wei and S. C. Cummings, *Inorg. Chem.* **11**, 475 (1972).
11. T. M. Florence, *J. Electroanalyt. Chem. Interfacial Electrochem.* **52**, 115 (1974).
12. C. K. Mann, In *Electroanal. Chem.* (Edited by A. J. Bard), Vol. 3. Marcel Dekker, New York (1969).
13. N. F. Curtis and D. F. Cook, *Chem. Commun.* 962 (1967).
14. D. C. Olson and J. Vasilevskis, *Inorg. Chem.* **8**, 1611 (1969).
15. E. K. Barefield and D. H. Bush, *Chem. Commun.* 522 (1970).
16. T. J. Truex and R. H. Holm, *J. Am. Chem. Soc.* **94**, 4529 (1972).
17. R. N. Adams, In *Electrochemistry at Solid Electrodes*, p. 126. Marcel Dekker, New York (1969).
18. F. G. Thomas and K. G. Boto, In *The Chemistry of the Hydrazo, Azo and Azoxy Groups* (Edited by S. Patai). Wiley, London (1975).