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SPECTRAL AND ELECTROCHEMICAL STUDIES OF NI (II) MACROCYCLIC COMPLEXES OF ME_2 PH_2 R BZO_2 [14] TETRAENE-N_4

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ABSTRACT

Synthesis of Ni (II) macrocyclic complexes and their spectral and redox behavior have been carried out. Different substituent on phenyl ring of macrocyclic complexes were attached and the effects of these groups R=OCH_3 , Cl and NO_2 were observed . the cyclic voltammetric studies showed two irreversible oxidation peals Ep (A) in the range from 0.40 to 0.80 V and from 1.00 to 1.40 Vs SCE respectively. During these studies a reversible reduction was also observed in the range 1.50 to -1.80V. Electrochemical studies showed that the oxidation process seems to be ligand based. The UV visible spectrum showed a charge transfer characteristics that may be assigned as ligand to metal. The substituted effect was also examined by means of Hammett plots of Ep (A), Ep (B) and $E_{½}$ V_s 2σp which were linear and slopes of 0.21 and 0.24 respectively.[1-3] The evidence for ligand oxidation can be made by comparing potentials for oxidation of the copper (II) complexes to its nickel (II) analogue. The peal potentials occur in the same potential region but are shifted Σ0.1 V more negative. Since copper (III) is unusual oxidation sate, the shift is due to the electronic changes due to different metal centers. The larger shift (Σ0.3 V) in the positive direction for reduction of the copper complex has also been observed may due to the reduction of copper (II) to copper (I). It is also noteworthy that the redox behavior of the tetraazaannulenes complexes can be tuned by the appropriate choice of substituents attached to the macrocyclic ligand and the effect can be controlled by the precise location of the substituents.[4-6]

KEYWORDS: Macrocyclic complexes, Electrochemical studies, and cyclic voltammetry studies.

INTRODUCTION

The importance of the design and synthesis of macrocyclic complexes been recognized now-a-days. In particular, the efforts towards superoxide dismutase (SOD) have been made because several low molecular weights copper (II) macrocyclic and nickel (II). Macrocyclic complexes have shown superoxide dismutase activity. An approach towards SOD active model would involve a metal complex whose redox potentials are tuned to that required to oxidize O^-_2 in the lower oxidation state.[7] The present work here represents the efforts to design and synthesis of the complexes with appropriate redox potentials, for which a study of a series of Ni (II) macrocyclic complexes has taken into account. Literature also reveals that the electrochemical studies of the products formed upon oxidation of the nickel (II) complex have also been carried out.[8] This type of ligand systems were first reported by Jager and later studied by other worker in this field. An attempted has also been made for such type of the series by making various derivative of ligand and the effects of varying the substituent R group on the redox and spectral properties of the nickel (II) macrocyclic complexes have been observed.[9-10]

EXPERIMENTAL

All the chemicals used were reagent grade and Tetraetheylammonium perchorate (TEAP) and Tetrabutylammonium hexafluorophosphate (TBAH) were used as base electrolyte purchased from Sigma-Aldrich (USA) and Fluka (USA). TEAP was dried overnight under vacuum. Acetonitrile and propylene carbonate were dried 48 hrs over 4-Å molecular sieves before use. Methylene chloride and N, N-dimethylformamide (DMF) were reagent grade and were dried over molecular sieves.[11] Nitrogen was bubbled into the solution for inert medium during electrochemical studies. Elemental analyses were recorded on a Perkin Elmer CHN analysis and proton NMR spectra were recorded on a model spectrophotometer NMR AC- 300 in DMSO-d_6 with TMS as an internal standard. Electronic spectra were recorded in acetonitrile solution with Shimadzu spectrophotometer 7000.[12-13]

Electrochemical studies were carried out in acetonitrile, propylene carbonate, methylene chloride, and in DMF solutions containing 0.10M TEAP as supporting electrolyte. The concentrations of the metal complexes were prepared in the ranger 2×10^{-4}M. Cyclic voltammograms were obtained with the EG and G Parc model 362 potentiostate and recorded with GraphtecW-4000 X-Y recorder made in Japan. The measurement were made at on a Pt or glassy-carbon (GC) working electrode vs a saturated calomel electrode (SCE). The electrodes were polished sequentially with the 0.25-µm diamond polishing compound followed by cleaning in distilled water and acetonitrile before use.[14-15]

Synthesis of Macrocycles

[Ni ($Me_2ph_2BzO_2$[14]tetraene N_4)], [Ni (Me_2ph_2 CH_3BzO_2[14] tetraene N_4)], [Ni (Me_2ph_2 $ClBzO_2$[14]tetraene N_4)], [Ni (Me_2ph_2 CO_2 CH_3BzO_2[14]tetraene N_4)] and [Ni (Me_2ph_2 CO_2 CH_2 CH_2 CH_3BzO_2[14]tetraene N_4)] were synthesized by literature.[16]

[Ni (Me_2ph_2 NO_2BzO_2[14]tetraene N_4)] The nitro-substituted macrocyclic complex was prepared by a modified procedure of Jager. 114 Under a N_2 atmosphere, 0.2 mol of 1, 2 diamino-4-nitrobenzene and 0.1 mol of nickel (II) acetate tetrahydrate were dissolved in Σ100ml of DMF and refluxed for 3hrs and then, 0.10mol of 1, phenyl, 1-3 butanedione in Σ25 ml of DMF was added dropwise for further refluxing the entire solution upto 8hrs.

The resulting solution was reflux for two days finally and a dark precipitate was obtained. The precipitate was separated by filtration. The desired compound was isolated as a dark blue microcrystalline product by addition of water to the resulting filtrate. The solid was collected on Rota-evaporator, and washed with hot water and methanol, and dried under vacuum yield 25% , 1H NMR (DMSOd6) values δ 2.01 (d, 12), 4.95 (s, 2), 6.85 (m,2), 7.46 (m,4).[17-19]

[Cu (Me_2ph_2 $ClBzO_2$[14]tetraene N_4)] The preparation of this component was also carried out with a modified procedure from the one described for preparation of the analogous Nickel (II) compound. Under an inert atmosphere, 0.50 mol of Cupper (II) acetate hydrate and 0.10 mol of 4-chloro o-phenylenediamine were dissolved in Σ200 ml of dried ethanol and refluxed with stirring for Σ 4 hrs. After drop wise addition of 0.10 mol of 1, phenyl,1-3butanedione in Σ 25 mL of methanol, the resulting solution was refluxed for three days. The suspension was cooled in ice water , and the blue solid was removed by filtration and washed with hot water and methanol, recrystallized from methylene chloride, and dried under vacuum yield 30%.[20-24]

Preparation of Compounds. Divalent complexes of the type [M (Me_2ph_2 -$RBzO_2$[14]tetraene N_4)] were synthesized. The initial step in the by template by the condensation of 1, phenyl, 1-3butanedione to produce the desired macrocycle. Elemental analyses of macrocycles compounds give in table 1.

The free macrocyclic ligand was also obtained following the method of Jager. 114 Nickel (II) can be removed from the macrocycle by bubbling HCl through a solution of the appropriate nickel (II) complex, and the ligand was isolated as the hydrochloride salt. Neutralization of the solution with base yielded the free ligand.[25]

RESULTS AND DISCUSSION

Electrochemistry A typical cyclic voltammograms are shown in figure 2. The voltammogram consists of two irreversible oxidations, a broad irreversible reduction peaking at Σ -0.50 V, and a reversible reduction at a more negative potential. The cyclic voltammograms for all complexes were recorded. The first oxidation, $E_{p(1)}$ and the irreversible reduction are redox coupled pairs and a decrease in current was also observed.[26]

Cyclic voltammograms of [Ni (Me_2 ph_2 $CO_2CH_2CH_2CH_3$ $RBzO_2$[14] tetraene N_4)] in a 0.10 M TEAP-acetonitrile solution (sweep rate 200 mV/s) (A) + 1.4 to -1.8 V vs.SCE, (B) +1.0 V vs.SCE, (C) + 1.0 to – 1.8V vs. SCE Figure 2 reveals that the overall scan shows the second oxidation peak $Ep_{(2)}$. A slight distortion in the reduction region for this voltammogram compared to the one obtained in the +1.0 to -2.0 V was also observed and a reversible reduction was observed.[27]

Two oxidation irreversible waves were observed but their behavior seems to be Nernstian. The correlation coefficient was 0.99, and the slope 58mV, were observed which seems to be consistent with a one-electron-transfer process.[28] A consistence was observed with the 56-mV value of $E_{3/4}$ –$E_{1/4}$ 145. Further evidence for the one-electron assignment was obtained by coulometry. Aliquots (Σ0.10 mL) of a 1.15×10^{-3} M [Ni ($Me_2ph_2BzO_2$[14]tetraene N_4)] – propylene carbonate solution were added to 90 mL of a 0.10 M TEAP-propylene carbonate solution containing a electrode set at a potential of 0.55 V vs .SCE Table 2 . The number of coulombs required to oxidize each added sample was determined, and a plot of Q (total) vs. the volume of added reagent was plotted which was observed linear with a slope corresponding to an n value of 1.1. The value generally observed in nonaqueous systems for reversible on-electron processes.[29]

The reduction was observed with the metal center. (Figure 3) which shows two irreversible oxidations for [H_2($Me_2ph_2ClBzo_2$[14] tetraene N_4)] in 0.10 M TEAP – acetonitrile. The two oxidation waves, $E_{p(1)}$ and $E_{p(2)}$, were also observed in the same region as shown in Figure 2. On repetitive scanning from 0 to + 1.4 V resulted in the passiveness of the electrode due to solid formation on the electrode surface. The small wave between $E_{p(1)}$ and $E_{p(2)}$ may be a prewave associated with deposition of compound on the electrode surface.

Prewaves are often found in cases where materials are surface bound. The one-electron oxidation of the parent nickel (II) macrocycle (R=H) has been reported for the formation of very interesting dimmer as both complexes joined at the δ position of the diiminate framework. The dimmer could be deprotonated to give a second dimmer that was found in many respect to the starting complex too.[30-32]

The electrochemical studies data were carried out for the series (R=CH_2, H, CO_2 CH_3 CO_2 CH_2 CH_2 CH_3, Cl, NO_2) are given in Table 2. All the potentials are listed as peak values for the two oxidation steps and $E_{½}$ values for the reversible reduction. The series contains macrocycles with various electron donor and withdrawing groups that have different $σ_p$ values. The Hammett plot $E_{p(1)}$, $E_{p(2),}$ and $E_{½}$ vs. 2 $σ_p$ are linear Figure 4. With correlation coefficients of 0.98, 0.99, and 0.99 respectively.[33] The slopes fall in the 0.18 – 0.24 range, which is intermediate between slopes of 0.07 found for other macrocycle and metalloporphyrins containing substituents and 0.50 for similar systems containing substituents bound to a skeletal carbon atom of the macrocycle ring.[34]

The redox potentials for a given process listed in Table 3 are solvents and electrolytes dependent Table 3. In DMF, the potentials were shifted Σ 0.1 V more positive than in acetonitrile but are somewhat less positive than reported by Kadish and co-workers.[35] The potentials for the oxidation in CH_2Cl_2 solvent were consistent with those reported in literature.[36]

Spectral studies were made over the 210-810 nm range, shown in Table 4. The complexes showed one intense absorption bands in the visible and in the near-UV regions of the spectrum. The higher energy bands appeared in the region characteristic of the free base ligand. The band in the visible region is for metal complex and their energy maxima ranging form 577 to 605 nm, with extinction coefficients of 1620-8820 $M^{-1}cm^{-1}$. Which are indicative of charge-transfer absorptions.[37]

The substituent effect was also examined by means of a Hammett plot, Figure 5. The relationship between $ν^{-}_{max}$ and 2 $σ_p$ was found linear, with a slope of -0.37 (-0.72/ $σ_p$) and a correlation coefficient of 0.98. in interesting by earlier workers found a positive slope of value 1.5/ $σ_p$ for other nickel (II) tetraaza N_4 macrocycles where the correlation was made with d-d band maxima. It is clear that a different orbital must be involved here to account for the negative slope found for the optical transition dependence with substituents for these tatraazaannulenes. The low-energy charge-transfer transition can perhaps be taken into account for the dependence of $ν^{-}_{max}$ on the redox potentials.[38]

The lowest occupied orbital seems to be ligand centered and this is consistent with the dimmer formation through the diiminate framework of the macrocycle following oxidation. It is noteworthy that this is similar to the reported behaviour of tetraphenylporphyrin and its nickel (II) complex. The evidence for ligand oxidation can be made by comparing potentials for oxidation of the copper (II) complex to its nickel (II) analogue Table 2. The peak potentials occur in the same potential region but are shifted Σ 0.1 V more negative. Since copper (III) is unusual oxidation state, the shift is due to the electronic changes due to different metal centers. The larger shift (Σ 0.3 V) in the positive direction for reduction of the copper complex has been observed may be due to the reduction of the copper (II) to copper (I).[39-40]

Table 1: Elemental Analysis of the Ni and Cu Macrocycles complexes.

Macrocyclic Complex	%C		%H		%N	
	Calcd	Found	Calcd	Found	Calcd	Found
[Ni ($Me_2ph_2BzO_2$[14]tetraene N_4)]	73.77	73.20	5.42	5.40	10.12	10.00
[Ni (Me_2ph_2 $ClBzO_2$[14]tetraene N_4)]	64.64	64.30	4.04	4.00	09.42	09.20
[Ni (Me_2ph_2 CO_2 CH_3BzO_2[14]tetraene N_4)]	67.39	67.10	4.68	4.20	08.73	08.40
[Ni (Me_2ph_2 CO_2 CH_2 CH_2 CH_3BzO_2[14]tetraene N_4)]	68.86	68.70	5.45	5.30	08.03	07.96
[Cu (Me_2ph_2 $ClBzO_2$[14] tetraene N_4)]	64.16	64.02	4.01	3.82	09.35	09.26

Table 2: Redox Values of [M (Me_2ph_2 NO_2BzO_2[14] tetraene N_4)].

M	R	$E_{p(1)}$ b	$E_{p(2)}$ b	$E_{p½}$ b	$2σ_p$c
Ni	CH_3	0.38	0.95	-1.80	-0.34
	H	0.46	1.00	-1.70	0
	Cl	0.55	1.12	-1.62	0.48
	$CO_2CH_2CH_2CH_3$	0.58	1.20	-1.50	0.90
	CO_2CH_3	0.58	1.20	-1.51	0.90
	NO_2	0.84	1.35	-------	1.56
Cu	Cl	0.48	0.99	-1.30	0.54
H_2	Cl	0.75	1.20	--------	0.46

0.1 M TEAP- acetonitrile solution ; ^{b} Volts vs SEC, ± 0.01 V; sweep rate 100 mV/s ^cσ_p values from literature. J. Am. Chem. Soc. 1986, 90, 4328.

Table 3: Redox Values of [Ni (Me_2ph_2 BzO_2[14] tetraene N_4)].

Solvent	**TEAP** $E_{p(1)}$	$E_{p(2)}$	$E_{p½}$	**TBAH** $E_{p(1)}$	$E_{p(2)}$	$E_{p½}$
CH_3CN	0.46	1.10	-1.72	0.50	1.04	-1.78
DMS	0.58	1.12	-1.72	0.56	1.30	-1.74
Propylene Carbonate	0.46	1.12	-1.80	0.52	1.10	-1.76
CH_2Cl_2				0.50	1.20	

Table 4: Electronic Absorption band for [Ni (Me_2ph_2 $RBzO_2$[14] tetraene N_4)].

Substituent R	v^{-} **Cm^{-1}× 10^{-3} €**	**Transition (v, cm^{-1} ×10^{-3} €)**
H	17.14 (6250)	26.50 (36 250), 26.80 (20 000) 29.92 (7500), 37.76 (27 100) 43.72 (27 500)
CH_3	17.40 (1600)	25.52 (8600), 42.78 (17 700)
Cl	17.12 (6700)	23.32 (14 600), 25.30 (41 000) 37.30 (31 800)
$CO_2CH_2CH_2CH_3$	16.90 (8700)	23.50 (24 500), 37.80 (40 000)
NO_2	16.70 (8800)	21.22 (19 000), 24.10 (22 500) 27.04 (16 500)
H_2L		28.92 (29 100), 36.40 (10 400) 39.30 (10 900)

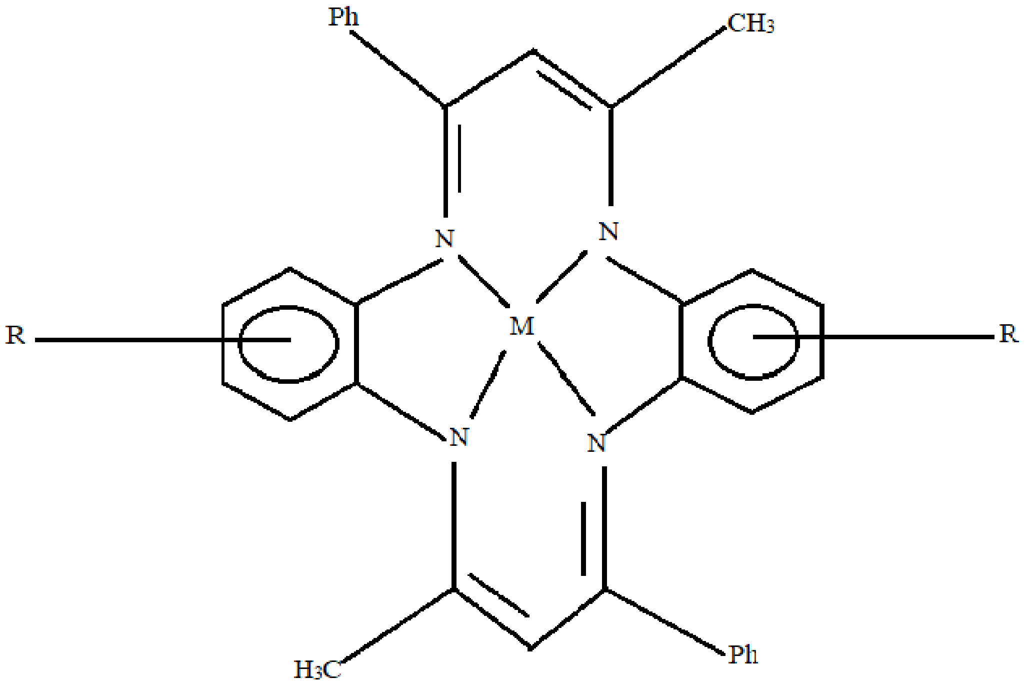

Fig.1 Where M = Ni (II), Cu (II)

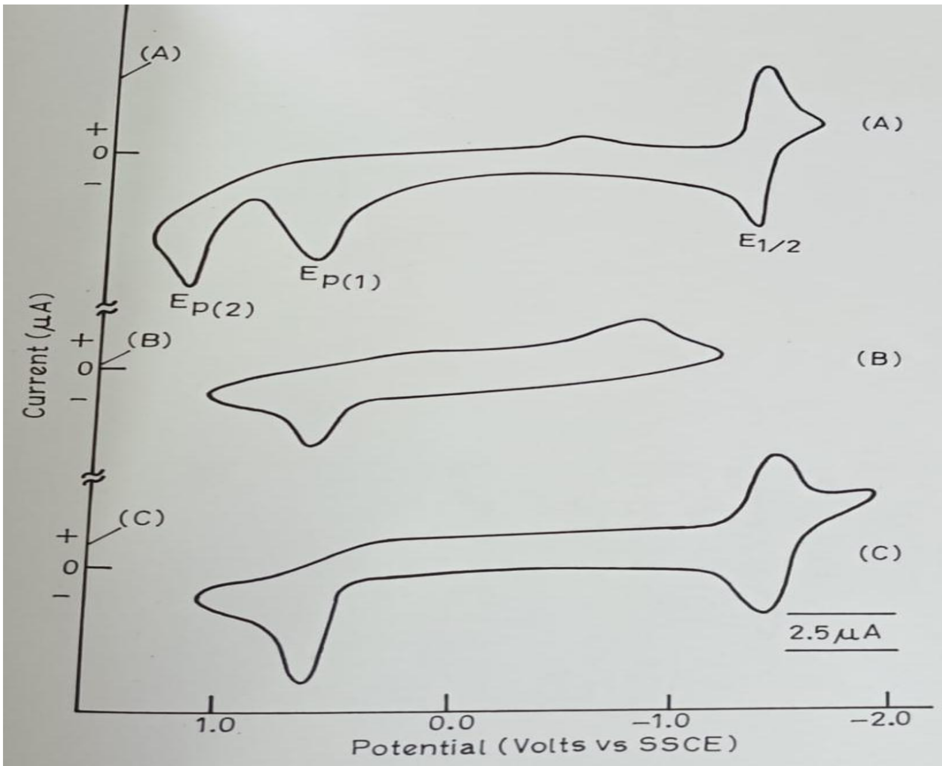

Fig.2. Cyclic Voltammograms of substituted with R Nickel macrocycle in Acetonitrile solution using 0.1M TEAP as base electrolyte (sweep rate 200 mv/s) R = $CH_3CH_2CH_2COO^-$

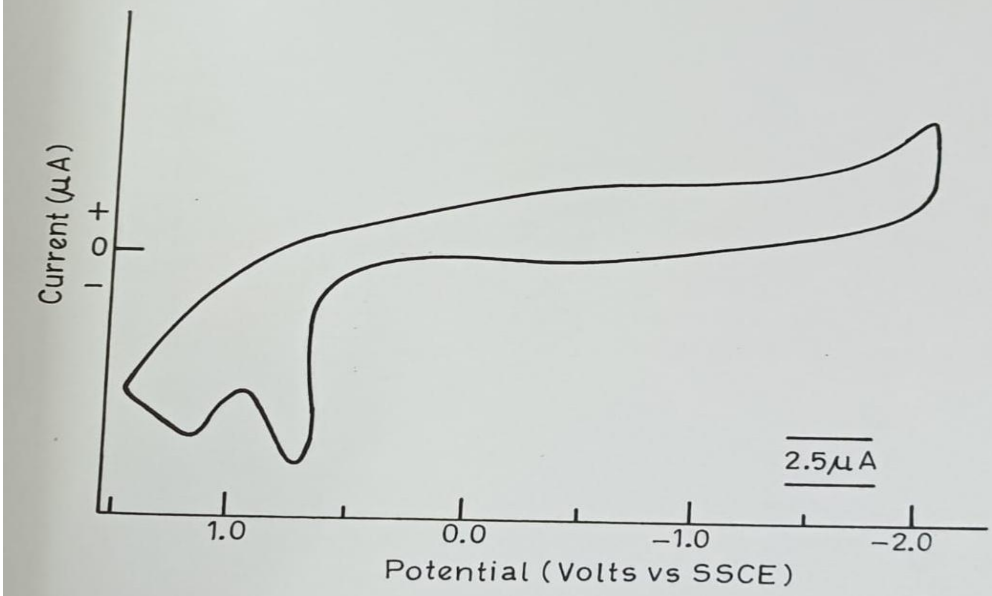

Fig.3. Cyclic Voltammograms of methyl substituted macrocyclic ligand in Acetonitrile solution using TEAP as base electrolyte (sweep rate 200 mv/s).

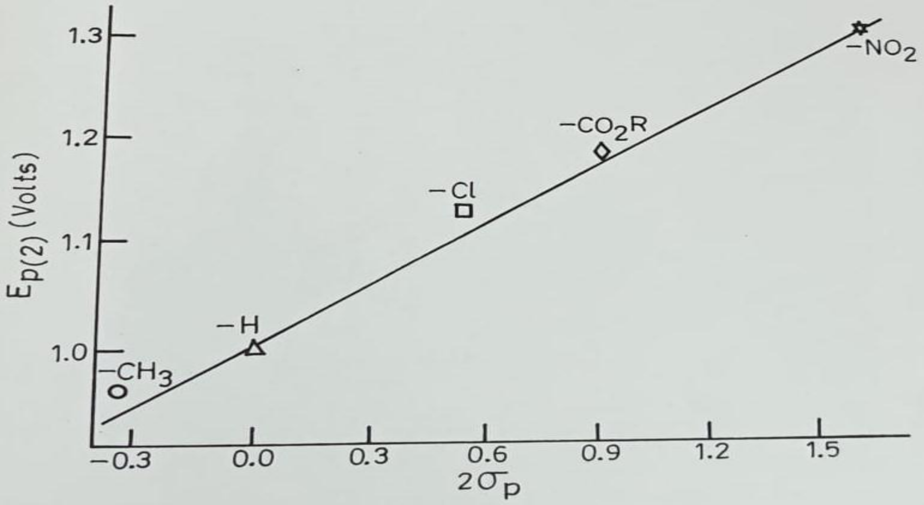

Fig. 4. Hammett plot showing the dependence of Redox potential σp parameter.

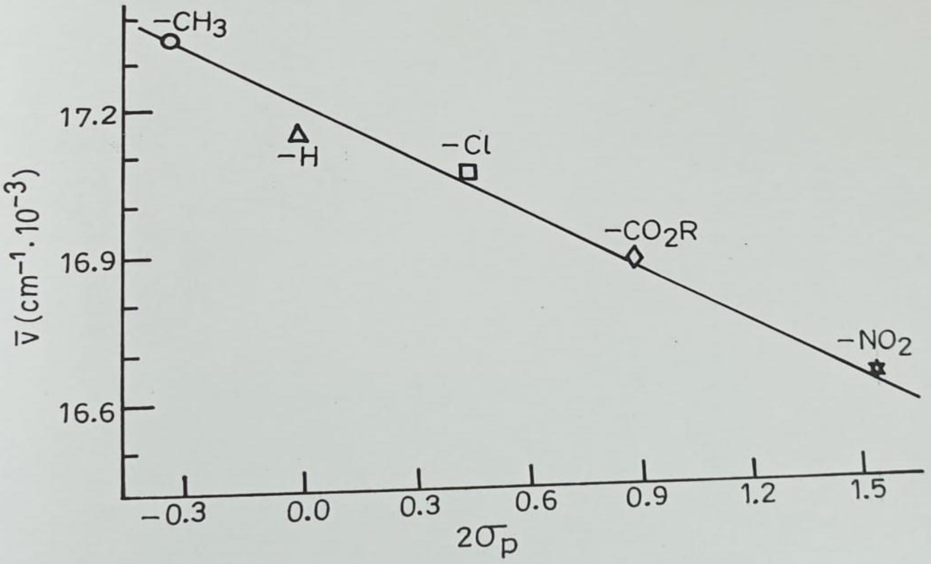

Fig.5. Correlation between the energy maximum of Visible transition and Hammett σp parameter.

CONCLUSION

Based on various studies, such as elemental analysis, Redox behavior, Electronic Absorption, Cyclic Voltammograms, and Electronic Spectral studies, octahedral, square planar and tetragonal geometry for the Ni (II) of Me_2 Ph_2 R BZO_2[14] Tetraene-N_4 Macrocyclic complexes, respectively. It has been suggested that chelation/coordination reduces the polarity of the metal ion mainly because of the partial sharing of its positive charge with the donor group within the whole chelate ring system. Many other factors, such as solubility, dipole moment, conductivity influenced by the metal ion, may possibly explain these complexes. The redox behaviour of the tetraazaannulenes complexes can be tuned by the appropriate choice of substituents attached to the macrocyclic ligand and the effect can be controlled by the precise location of the substituents.

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