

Macrocyclic Complexes: Part XII – Complexes of Ni(II) with Fluoro-boro Bridged Macrocyclic Ligands, Dimethyl, Diacetyl Cyclopean & Dimethyl, Dicarbethoxy Cyclopean

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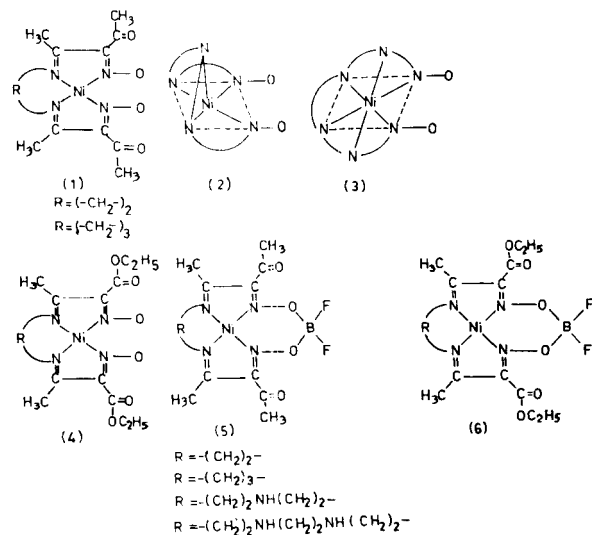
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A new series of tetraaza, pentaaza and hexaaza fluoro-boro-bridged macrocyclic nickel(II) complexes, containing methyl and $-\text{CH}_3\text{CO}$ or $-\text{COOC}_2\text{H}_5$ as pendants on the macro-ring, have been synthesized. The precursor nitroso complexes are remarkably different in spectral, magnetic and electrochemical behaviour from the respective macrocyclic complexes. The macrocyclic ligands provide a facile electron delocalization, resulting in a weaker ligand field corresponding to the spin crossover region. The precursors and macrocycles undergo two-step one-electron reduction and the redox behaviour depends on macrocyclic effect, ring size and substituents on the macro-ring apart from the electrostatic interaction of the donor nitrogen atoms.

Syntheses, structures and electrochemical redox properties of macrocyclic metal complexes of tetraaza, pentaaza and hexaaza Me_4 cyclopean and Ph_4 cyclopean ligands have been described earlier^{1,2}. Spectrochemical and electrochemical behaviour of these two cyclopean series of complexes show distinct effect of the substituents on the macro-ring and are remarkably different from the FBOX series of complexes³.

Though works on adducts appear to be wide-ranging with fluoroboro-bridged macrocyclic complexes⁴⁻¹⁰, the study of the effect of substituents on the macro-ring on the physicochemical properties of the cyclops has been limited. The substituents on the tetraaza macrocycles, with rings varying from 12 to 16, and even substituents on naturally occurring macrocycles such as chlorophylls and porphyrins have remarkable effect on their physicochemical properties. The behaviour of the Me_4 cyclopeans and Ph_4 cyclopeans systems reported earlier from this laboratory has prompted us to study the effect of new substituents in the ring on the physicochemical properties of cyclopean macrocycles. During the course of this study, we have succeeded in isolating two new series of cyclopean ligands and the results of these investigations are reported here.

Intermolecular condensation of nitrite ions with 2,4-pentanedione in the presence of nickel(II) and ammonium acetate was found to give a diamagnetic bright red compound, $\text{Ni}(\text{C}_5\text{H}_7\text{O}_2\text{N}_2)_2$ ¹¹. The investigations were extended later using diamines and several other metal ions^{12,13}. When the reaction was carried out with ethylenediamine, nickel(II) ion, acetylacetone, sodium nitrite, acetic acid and sodium acetate, compound (1) was isolated.



Use of propylenediamine in place of ethylenediamine gave a similar quadratically bonded complex. A capped pentacoordinated (structure 2) and an octahedral hexa-coordinated complex (structure 3) have been prepared by us using diethylenetriamine and triethylenetetramine respectively. A new series of nitroso complexes has been isolated following similar reactions involving the amines, ethylacetoacetate, sodium nitrite, acetic acid, sodium acetate and nickel(II) ions, where the carbethoxy groups are introduced as the pendant substituents (4). The nitroso ligands are versatile enough to react with the lewis acid BF_3 producing a new series of

cyclopean macrocyclic complexes. Reactions with silane derivatives are currently being investigated and the results will be communicated in due course to this journal.

The structures of cyclopean nickel(II) complexes prepared now are presented in (5) and (6). The tetraaza Cy^1 , Cy^2 , Cy^5 and Cy^6 systems are: $Cy^1 = 1,1$ -difluoro-5,10-dimethyl-4,11-diacetyl-1-bora-3,6,9,12-tetraaza-2,13-dioxocyclotrideca-3,5,9,11-tetraene, abbr. $\{Me_2Ac_2[13]N_4O_2BF_2\}^-$, $Cy^2 = 1,1$ -difluoro-5,11-dimethyl-4,12-diacetyl-1-bora-3,6,10,13-tetraaza-2,14-dioxocyclotetradeca-3,5,10,13-tetraene, abbr. $\{Me_2Ac_2[14]N_4O_2BF_2\}^-$, $Cy^5 = 1,1$ -difluoro-5,10-dimethyl-4,11-dicarbethoxy-1-bora-3,6,9,12-tetraaza-2,13-dioxocyclotrideca-3,5,9,11-tetraene, abbr. $\{Me_2(carbethoxy)_2[13]N_4O_2BF_2\}^-$, $Cy^6 = 1,1$ -difluoro-5,11-dimethyl-4,12-dicarbethoxy-1-bora-3,6,10,13-tetraaza-2,14-dioxocyclotetradeca-3,5,10,13-tetraene, abbr. $\{Me_2(carbethoxy)_2[14]N_4O_2BF_2\}^-$. The pentaaza systems are Cy^3 and Cy^7 : $Cy^3 = 1,1$ -difluoro-5,13-dimethyl-4,14-diacetyl-1-bora-3,6,9,12,15-pentaaza-2,16-dioxocyclohexadeca-3,5,12,14-tetraene, abbr. $\{Me_2Ac_2[16]N_5O_2BF_2\}^-$, $Cy^7 = 1,1$ -difluoro-5,13-dimethyl-4,14-carbethoxy-1-bora-3,6,9,12,15-pentaaza-2,16-dioxocyclohexadeca-3,5,12,14-tetraene, abbr. $\{Me_2(carbethoxy)_2[16]N_5O_2BF_2\}^-$. The hexaaza systems are Cy^4 and Cy^8 : $Cy^4 = 1,1$ -difluoro-5,16-dimethyl-4,17-diacetyl-1-bora-3,6,9,12,15,18-hexaaza-2,19-dioxocyclononadeca-3,5,15,17-tetraene, abbr. $\{Me_2Ac_2[19]N_6O_2BF_2\}^-$, $Cy^8 = 1,1$ -difluoro-5,16-dimethyl-4,17-dicarbethoxy-1-bora-3,6,9,12,15,18-hexaaza-2,19-dioxocyclononadeca-3,5,15,17-tetraene, abbr. $\{Me_2(carbethoxy)_2[19]N_6O_2BF_2\}^-$. They can act as donors through nitrogen lone pairs with metal ions. They have varying degree of unsaturation and electrophilic character on account of substituents like $-C(=O)-CH_3$ and $-C(=O)-OC_2H_5$ apart from a couple of α -diimine groups, a common feature in the backbone of the cyclopean ligands.

Materials and Methods

Ethylenediamine, propylenediamine, acetylacetone, ethyl acetoacetate, diethylenetriamine, sodium nitrite and boron trifluoride were BDH reagents while triethylenetetramine was a Riedel reagent.

The complexes NiL^{1-8} , where $L^1 = N,N'$ -ethylene-bis-(isonitrosoacetylacetoneimino)nickel(II), $L^2 = N,N'$ -propylene-bis-(isonitrosoacetylacetoneimino)nickel(II), $L^3 = N,N'$ -diethylenetriamine-bis-(isonitrosoacetylacetoneimino)nickel(II), $L^4 =$ triethylenetetramine-bis-(isonitrosoacetylacetoneimino)nickel(II), $L^5 = N,N'$ -ethylene-bis-(isonitrosoethylacetoacetateimino)nickel(II), $L^6 = N,N'$ -propylene-bis-(iso-

nitrosoethylacetoacetateimino)nickel(II), $L^7 = N,N'$ -diethylenetriamine-bis-(isonitrosoethylacetoacetateimino)nickel(II) and $L^8 = N,N'$ -triethylenetetramine-bis-(isonitrosoethylacetoacetateimino)nickel(II) were prepared following similar procedures. The method adopted for NiL^1 is given below.

N,N'-Ethylene-bis-(isonitrosoacetylacetoneimino)-nickel(II) $Ni(C_{12}H_{16}N_4O_4)$

$Ni(CH_3COO)_2 \cdot 4H_2O$ (2.5 g, 0.01 mol) dissolved in ethanol was treated with acetylacetone (2.0 g, 0.02 mol), ethylenediamine (0.6 g, 0.01 mol), sodium nitrite (5.0 g) and acetic acid (4 ml) and the mixture was continuously stirred for one hour when fine red crystals were separated. They were filtered, washed with ethanol and ether and dried.

The $(CH_3)_2(CH_3CO)_2$ cyclopean complexes were isolated by action of freshly distilled boron trifluoride on the above precursor complexes in the acetonitrile medium. The preparation of $(NiCy^1)BF_4$ is given below.

1,1-Difluoro-5,10-dimethyl-4,11-diacetyl-1-bora-3,6,9,12-tetraaza-2,13-dioxocyclotrideca-3,5,9,11-tetraenenickel(II) $Ni\{Me_2Ac_2[13]N_4O_2BF_2\}BF_4$:

NiL^1 (3.40 g, 0.01 mol) was suspended in acetonitrile; one drop of dilute fluoroboric acid was added to catalyze and enhance the reaction rate. Then boron trifluoride (freshly distilled, 3 ml) was added dropwise while stirring till the red colour transformed to orange. On allowing the solution to stand for three hours, an orange crystalline product was obtained. It was filtered, washed with acetonitrile and dried *in vacuo*.

$Me_2(carbethoxy)_2$ cyclopean complexes were prepared by following similar procedures; a typical preparation for one such compound is given here.

1,1-Difluoro-5,10-dimethyl-4,11-dicarbethoxy-1-bora-3,6,9,12-tetraaza-2,13-dioxocyclotrideca-3,5,9,11-tetraenenickel(II) $Ni\{Me_2(carbethoxy)_2[13]N_4O_2BF_2\}BF_4$:

NiL^5 (4.0 g, 0.01 mol) was suspended in 30 ml of acetonitrile and about 4 ml of boron trifluoride etherate was slowly added while stirring. The stirring was continued for about six hours when the colour of the compound changed from red to yellow. It was left overnight and finally filtered, washed with acetonitrile and dried *in vacuo*.

The analytical data are given in Tables 1 and 2.

Results and Discussion

The nitroso complexes have been obtained by the traditional method using 2,4-pentanedione, a diamine/triamine/tetramine, nickel(II) ion, sodium

Table 1—Analytical Data and Colour of Complexes NiL^{1-8}

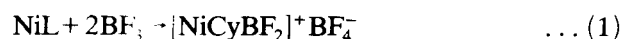
Sl. No.	Complexes	Colour	Found (Calc.) %			
			Metal	N	C	H
1	NiL^1	Red	17.32	16.35	42.32	4.54
	$\text{Ni}(\text{C}_{12}\text{H}_{16}\text{N}_4\text{O}_4)$		(17.40)	(16.51)	(42.47)	(4.71)
2	NiL^2	Red	16.62	15.71	44.05	4.98
	$\text{Ni}(\text{C}_{13}\text{H}_{18}\text{N}_4\text{O}_4)$		(16.71)	(15.86)	(44.19)	(5.09)
3	NiL^3	Red	15.36	18.22	43.80	5.34
	$\text{Ni}(\text{C}_{14}\text{H}_{21}\text{N}_5\text{O}_4)$		(15.44)	(18.32)	(43.97)	(5.49)
4	NiL^4	Reddish	13.82	19.62	44.98	5.96
	$\text{Ni}(\text{C}_{16}\text{H}_{26}\text{N}_6\text{O}_4)$	brown	(13.88)	(19.76)	(45.17)	(6.11)
5	NiL^5	Red	14.70	13.85	41.98	4.91
	$\text{Ni}(\text{C}_{14}\text{H}_{20}\text{N}_4\text{O}_6)$		(14.78)	(14.03)	(42.10)	(5.01)
6	NiL^6	Red	14.20	13.48	43.36	5.18
	$\text{Ni}(\text{C}_{15}\text{H}_{22}\text{N}_4\text{O}_6)$		(14.28)	(13.55)	(43.58)	(5.32)
7	NiL^7	Orange red	13.26	15.65	43.24	5.48
	$\text{Ni}(\text{C}_{16}\text{H}_{25}\text{N}_5\text{O}_6)$		(13.36)	(15.83)	(43.42)	(5.65)
8	NiL^8	Red	12.02	17.21	44.25	6.05
	$\text{Ni}(\text{C}_{18}\text{H}_{30}\text{N}_6\text{O}_6)$		(12.16)	(17.31)	(44.53)	(6.18)

Table 2—Analytical Data and Colours of the Complexes $[\text{NiCy}^{1-8}]\text{BF}_4$

Sl No.	Complexes	Colour	Found (Calc.) %			
			Metal	N	C	H
1	$[\text{NiCy}^1]\text{BF}_4$	Orange	12.30	11.62	30.12	3.22
	$\text{Ni}(\text{C}_{12}\text{H}_{16}\text{N}_4\text{O}_4\text{B}_2\text{F}_6)$		(12.42)	(11.78)	(30.31)	(3.36)
2	$[\text{NiCy}^2]\text{BF}_4$	Yellow	11.98	11.34	31.74	3.52
	$\text{Ni}(\text{C}_{13}\text{H}_{18}\text{N}_4\text{O}_4\text{B}_2\text{F}_6)$		(12.06)	(11.45)	(31.90)	(3.68)
3	$[\text{NiCy}^3]\text{BF}_4$	Orange	11.30	13.36	32.28	3.92
	$\text{Ni}(\text{C}_{14}\text{H}_{21}\text{N}_5\text{O}_4\text{B}_2\text{F}_6)$	yellow	(11.38)	(13.51)	(32.43)	(4.05)
4	$[\text{NiCy}^4]\text{BF}_4$	Orange	10.42	14.78	34.08	4.48
	$\text{Ni}(\text{C}_{16}\text{H}_{26}\text{N}_6\text{O}_4\text{B}_2\text{F}_6)$	yellow	(10.51)	(14.97)	(34.22)	(4.63)
5	$[\text{NiCy}^5]\text{BF}_4$	Yellow	10.86	10.30	31.20	3.52
	$\text{Ni}(\text{C}_{14}\text{H}_{20}\text{N}_4\text{O}_6\text{B}_2\text{F}_6)$		(11.02)	(10.46)	(31.40)	(3.73)
6	$[\text{NiCy}^6]\text{BF}_4$	Yellow	10.64	10.02	32.52	3.86
	$\text{Ni}(\text{C}_{15}\text{H}_{22}\text{N}_4\text{O}_6\text{B}_2\text{F}_6)$		(10.74)	(10.20)	(32.78)	(4.00)
7	$[\text{NiCy}^7]\text{BF}_4$	Yellow	10.12	11.96	33.10	4.28
	$\text{Ni}(\text{C}_{16}\text{H}_{25}\text{N}_5\text{O}_6\text{B}_2\text{F}_6)$		(10.20)	(12.11)	(33.21)	(4.32)
8	$[\text{NiCy}^8]\text{BF}_4$	Orange	9.48	13.44	34.56	4.78
	$\text{Ni}(\text{C}_{18}\text{H}_{30}\text{N}_6\text{O}_6\text{B}_2\text{F}_6)$	yellow	(9.50)	(13.52)	(34.78)	(4.83)

nitrite and acetic acid. As the reaction proceeds, the green colour of the solution gradually changes and a bright red precipitate progressively appears. The reaction is almost complete in about an hour in the case of diamines; however, in the case of tri- and tetramines it takes about 10-12 hr. The complexes are obtained in about 60-80% yield and are diamagnetic.

The diamagnetic red complexes react with boron trifluoride in methyl cyanide medium. Gradual change in colour occurs and finally an yellow or orange yellow product is obtained. From analytical and physical data it is seen that the reaction is consistent with equation 1.



The complexes possess anomalous magnetic properties, but the ligand field spectra correspond to those expected for such behaviour.

IR Spectra

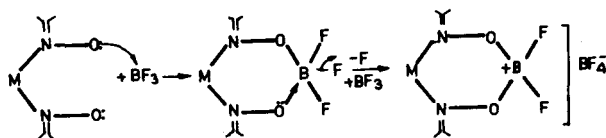
We have recorded the spectral and magnetic data for the complexes $\text{N,N}'$ -ethylene-bis-(isonitrosoacetylacetoneimino)nickel(II) [1] and our results closely resemble the results reported by earlier workers^{12,14}. The structurally important IR bands pertain to $\nu\text{C}=\text{O}$, $\nu\text{C}=\text{N}$, and $\nu\text{N}-\text{O}$ vibrations. The dimethyl, diacetyl cyclopean complexes show a strong band at $\sim 1700\text{ cm}^{-1}$ and the dimethyl, dicarbethoxy cyclopeans at $\sim 1750\text{ cm}^{-1}$ which has been assigned to the free carbonyl groups. The $\nu\text{C}=\text{N}$ band in $\text{N,N}'$ -ethylene-bis-(isonitroso-

acetylacetonimine)nickel(II) and N,N'-propylene-bis-(isonitrosoacetylacetonimine)nickel(II) is observed below 1600 cm^{-1} (ref. 15).

Bands near 1160 cm^{-1} have been attributed to N–O stretching vibrations. Coordination of isonitroso groups through nitrogen is considered to increase the N–O frequency and in many nitrogen coordinated multidentate isonitroso complexes, the N–O frequency occurs around $1250\text{--}1150\text{ cm}^{-1}$ (refs. 16–18).

The IR spectra of N,N'-diethylenetriamine-bis-(isonitrosoacetylacetonimine)nickel(II) and N,N'-triethylenetetramine-bis-(isonitrosoacetylacetonimine)nickel(II) complexes and the corresponding bis-(isonitrosoethylacetoacetateimine)nickel(II) complexes possess a few additional bands which are observed near 3315 and 1320 cm^{-1} , the former band is attributed to the stretching vibrations of secondary NH groups and the latter band has been assigned to $\nu\text{C}=\text{N}$ vibrations.

The dimethyl, diacetyl cyclopean complexes and the dimethyl, dicarboethoxy cyclopean complexes, the products of interaction of boron trifluoride with the parent metal complexes of the nitroso ligands, NiL^{1-8} in methyl cyanide medium, show several new bands apart from the $\nu\text{C}=\text{O}$, $\nu\text{C}=\text{N}$ and $\nu\text{N}=\text{O}$ frequencies in their respective regions. The bands occurring at 1020 and 795 cm^{-1} have been identified from their characteristic features to be $\nu(\text{B}-\text{F})$ and $\nu(\text{B}-\text{O})$ vibrations, respectively. These spectral features unambiguously manifest that the oximato oxygen atoms act as nucleophilic groups and react with boron trifluoride according to the Scheme 1, finally yielding the macrocyclic structures presented in [5 and 6]. In the reaction process the oximato group is first bonded on account of donor-acceptor bond formation with the lewis acid BF_3 , forming an intermediate product which is subsequently subjected to another nucleophilic attack from the adjacent oximato group displacing a halogen atom as the halide ion and completing the cyclization. The displaced halide ion reacts with boron trifluoride to form fluoroborate ion and is accommodated in the outer sphere.



Scheme 1

These observations lead us to suggest the structure and mode of bonding in these complexes as presented in [5 and 6] which show that the

$\text{O}=\text{C}-\text{CH}_3$) and carboethoxy ($-\text{COOC}_2\text{H}_5$) groups are pendants on the macrocyclic rings.

Electronic spectra

The diamagnetic isonitroso complexes show a ligand field band around $22,000\text{ cm}^{-1}$ which would normally suggest that the coordination environment around the metal ion is square-planar. However, the polarographic data which are discussed below exhibit two-step one-electron reduction processes. The mode of reduction from tetraaza to hexaaza series of ligands follows a parallel pattern as has been observed for Me_4 cyclopeans and Ph_4 cyclopeans, i.e., going from tetraaza to pentaaza and hexaaza the reduction wave becomes more cathodic in character. This picture is consistent with the capped five-coordinated structure for N,N'-diethylene-triamine-bis-(isonitrosoacetylacetonimine)nickel(II) complex and N,N'-diethylenetriamine-bis-(isonitrosoethylacetoacetateimine)nickel(II) complex and octahedral hexacoordinated structure for N,N'-triethylenetetramine-bis-(isonitrosoethylacetoacetateimine)nickel(II) complexes. However, the axial nitrogen coordination is not strong enough for spin cross-over to occur for the penta- and hexa-coordinated complexes from spin singlet to lower energy triplet states.

In contrast to parent nitroso complexes, the dimethyl, diacetyl cyclopean and dimethyl, dicarboethoxy cyclopean ligands of nickel(II) are magnetically subnormal and the magnetic moments at the ambient temperatures have been observed in the range 1.8 to 2.4 B.M. The electronic spectra of these complexes show distinct features which can be satisfactorily explained on the basis of structures where nickel(II) ions occur in spin-singlet and spin-triplet equilibrium¹⁹.

The present series of complexes show ligand field transitions at 9000 , 17000 , 22000 and 27000 cm^{-1} respectively. The new features in lower frequency and high frequency regions, in sharp contrast to a single ligand field band at $22,000\text{ cm}^{-1}$ for isonitroso complexes, are attributes of nickel(II) ions in spin-singlet and spin-triplet ground terms coexisting together. The first two bands at $9,000$ and $17,000\text{ cm}^{-1}$ are attributed to transitions $^3A_{2g} \rightarrow ^3T_{1g}(F)$ and $^3A_{2g} \rightarrow ^3T_{2g}(F)$ under octahedral ligand field of the nickel ion. The highest frequency band at $27,000\text{ cm}^{-1}$ is attributed to the transition $^3A_{2g} \rightarrow ^3T_{1g}(P)$ while the band at $22,000\text{ cm}^{-1}$ originates from the spin-singlet to singlet transition $^1A_{1g} \rightarrow ^1A_{2g}$ under

square planar field. The results manifest that cyclization with BF_3 of the oxygen atoms of nitroso groups leads to creation of ligand fields around the metal ion that are in the spin cross-over region and the singlet-triplet equilibrium occurs.

Electrochemical studies

Majority of the tetraaza nickel(II) macrocyclic complexes undergo one electron reduction; however, the products obtained occur in different states. An examination of the results shows two extreme cases. Ligands with α -diimine groups, on electrochemical reduction, give nickel(II)-ligand radical anion species as shown by EPR studies. On the other hand, with nonconjugated ligands, the reduced products contain Ni(I) complexes. In a recent report²⁰, a fluoro-boro cyclopean complex has been reported to give one electron reduction product; EPR spectrum has two signals, one attributable to Ni(I) at $g=2.133$ and second at $g=2.048$ assignable to a nickel(II)-ligand radical anion species.

There are examples of nickel(II) macrocyclic complexes²¹ which show two reversible one-electron reduction waves near $E_1^1 = -1.0$ V and $E_2^2 = -1.55$ V. From ESR studies the reduced species have been found to correspond to the formation of $[\text{Ni}^{\text{II}}(\text{L}^-)]^+$ and $[\text{Ni}^{\text{I}}(\text{L}^-)]^0$, respectively. Such macrocycles possess structures with diimino groups, behaving as good π -acceptors and possess energetically favourable low-lying π -orbitals.

The electrochemical data for the present series of cyclopean ligands together with those for the open chain precursor molecules are reported in Table 3. The macrocyclic complexes undergo two reversible or quasireversible reductions in DMF:water medium (80:20) at $\mu = 0.1$ M (sodium perchlorate), and, as in the earlier cases, the redox processes are diffusion-controlled and each of the redox step corresponds to transfer of one electron. It has been reported earlier that the Me_4 - and Ph_4 -cyclopeans and their precursors are characterised by a one electron redox wave^{1,2}.

The effect of ligand structure on the thermodynamic parameters E_1 for the redox processes of the macrocycles and their open chain analogues is shown in Figs 1 and 2 and for the Me_4 - and Ph_4 -cyclops in Fig. 3. The E_1 values are plotted against ligand atomicity (i.e., the number of C,N,O and B atoms present in the chain of the precursors and in the macrocycles) and coordination number (given in parentheses). The plots clearly indicate the effect of cyclisation, role of electron donating and withdrawing ability of the substituents on the ligands as well as on the macro-rings,

Table 3—Polarographic Data of the Complexes NiL^{1-8} in Aqueous DMF

Complexes	$-E_1^1(\text{V})$	Slope ⁻¹ (mV)	$-E_2^2(\text{V})$	Slope ⁻¹ (mV)
NiL^1	0.820	80	1.350	88
NiL^2	0.88	86	1.50	76
NiL^3	0.905	78	1.55	88
NiL^4	0.935	85	1.62	76
NiL^5	0.850	86	1.420	70
NiL^6	0.895	88	1.525	86
NiL^7	0.920	75	1.60	84
NiL^8	0.955	70	1.63	86
$[\text{NiCy}^1]\text{BF}_4$	0.785	75	1.10	88
$[\text{NiCy}^2]\text{BF}_4$	0.840	80	1.150	86
$[\text{NiCy}^3]\text{BF}_4$	0.875	90	1.300	90
$[\text{NiCy}^4]\text{BF}_4$	0.880	84	1.366	90
$[\text{NiCy}^5]\text{BF}_4$	0.795	96	1.320	94
$[\text{NiCy}^6]\text{BF}_4$	0.855	92	1.350	98
$[\text{NiCy}^7]\text{BF}_4$	0.892	95	1.56	96
$[\text{NiCy}^8]\text{BF}_4$	0.90	98	1.60	96

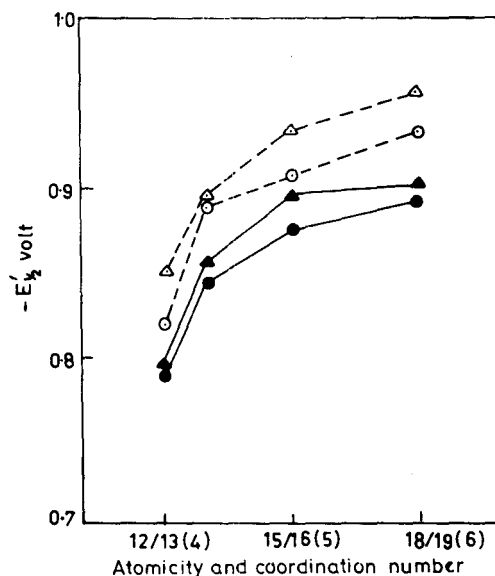


Fig. 1—Plot of E_1^1 for $[\text{NiMe}_2(\text{CH}_3\text{CO})_2\text{cyclopean}]$ and $[\text{NiMe}_2(\text{O}-\text{C}-\text{C}_2\text{H}_5)_2\text{cyclopean}]$ values for the open chain and macrocyclic complexes vs. ligand atomicity (number of carbon, nitrogen, oxygen and boron atoms in the chain or ring) [$\text{Me}_2(\text{CH}_3\text{CO})_2\text{cyclopean}$: open chain $\circ-\circ-\circ-\circ-$; macrocycle $\bullet-\bullet-\bullet-\bullet-$; $\text{Me}_2(\text{O}-\text{C}-\text{C}_2\text{H}_5)_2\text{cyclopean}$: open chain $\triangle-\triangle-\triangle-\triangle-$, macrocycle $\blacktriangle-\blacktriangle-\blacktriangle-\blacktriangle-$]

electrostatic interaction of the donor nitrogen atoms with the metal ion, coordination number and the electron delocalizing influence of the α -diimine groups coupled with the substituents.

An increase in coordination number of the metal ion though coordination with strong nucleophilic secondary amine groups shifts the E_1 values towards a higher cathodic region. The E_1 values manifest the propensity of the macrocyclic effect.

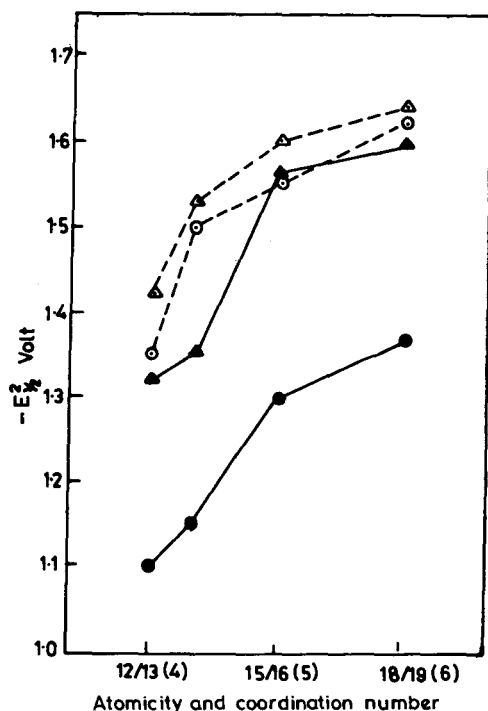


Fig. 2—Plot of $E_{1/2}[\text{NiMe}_2(\text{CH}_3\text{CO})_2\text{cyclopean}$ and NiMe_2

$(\text{O}-\text{C}-\text{C}_2\text{H}_5)_2\text{cyclopean}]$ values for the open chain and macrocyclic complexes vs. ligand atomicity (number of carbon, nitrogen, oxygen and boron atom in the chain or ring) [$\text{Me}_2(\text{CH}_3\text{CO})_2\text{cyclopean}$: open chain $-\circ-\circ-\circ-$, macrocycle $-\blacktriangle-\blacktriangle-\blacktriangle-$; $\text{Me}_2(\text{O}-\text{C}-\text{C}_2\text{H}_5)_2\text{cyclopean}$: open chain $-\circ-\circ-\circ-$, macrocycle $-\blacktriangle-\blacktriangle-\blacktriangle-$]

The reduction processes for the macrocyclic complexes with BF_2 bridgeheads are more facile and occur at more anodic potentials than those for the respective noncyclic parent complexes, with the exceptions of pentaaza and hexaaza Me_4 - and Ph_4 -cyclopeans. However, these distinctive features of the ligand field effect, are influenced by the substituents on the ligand systems to some degree, on account of their electrophilic character that directly affects the electron density on the metal atom.

For the complexes (either open chain or macrocycles) with constant atomicity and coordination number, the E_1 values for the first redox wave are

in the order: $-(\text{CH}_3)_4 > (\text{CH}_3)_2(\text{C}_2\text{H}_5-\text{O}-\text{C}-\text{O})_2 > (\text{CH}_3)_2(\text{CH}_3-\text{C}-\text{O})_2 > (-\text{C}_6\text{H}_5)_4$ cyclops. The positions of methyl, carboxy and acetyl substituents are consistent with their relative electrophilic

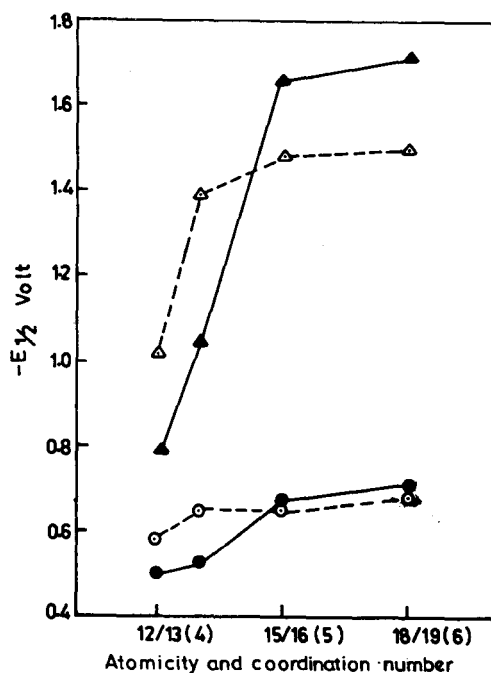


Fig. 3—Plot of E_1 ($\text{NiMe}_4\text{cyclopean}$ & $\text{NiPh}_4\text{cyclopean}$) values for the open chain and macrocyclic complexes vs. ligand atomicity (number of carbon, nitrogen, oxygen and boron atoms in the chain or ring) [$\text{Me}_4\text{cyclopean}$: open chain $-\circ-\circ-\circ-$, macrocycle $-\blacktriangle-\blacktriangle-\blacktriangle-$; $\text{Ph}_4\text{cyclopean}$: open chain $-\circ-\circ-\circ-$, macrocycle $-\blacktriangle-\blacktriangle-\blacktriangle-$]

character and are in the order of their respective Taft constants or Hammett substitution constants²²⁻²⁴, but the position of phenyl group is rather atypical. This atypical behaviour of $\text{Ph}_4\text{cyclops}$ seems to arise on account of the presence of a quartet of phenyl groups in conjugation with α -diimines that enhance the charge delocalization over a wider ligand frame.

The polarographic results can be interpreted in terms of two pathways. According to path 1 the first wave in the range -0.82 to -0.95 V and -0.78 to -0.90 V for the precursors and macrocyclic complexes, respectively, gives the metal-stabilized ligand radical species.

Path I: $[\text{Ni}^{\text{II}}\text{L}]^+ + e \rightleftharpoons [\text{Ni}^{\text{I}}(\text{L}^-)]^0$

A nickel(I) species is formed in the second step of the redox process,

$[\text{Ni}^{\text{II}}(\text{L}^-)]^0 + e \rightleftharpoons [\text{Ni}^{\text{I}}(\text{L}^-)]^0$

The latter step might be associated with the formation of a ligand dianion radical followed by intramolecular ligand to metal electron transfer. In the second pathway, we attribute the successive waves to be due to metal centred reduction processes,

Path II: $[\text{Ni}^{\text{II}}\text{L}]^+ + e \rightleftharpoons [\text{Ni}^{\text{I}}\text{L}]^+ + e \rightleftharpoons [\text{Ni}^{\text{0}}\text{L}]^+$

From a careful comparison of the electrochemical data of several macrocyclic complexes containing α -diimine and β -diimine groups, it appears that the redox mechanism may be depicted by path I rather than path II. In the first step of reduction the electron resides on the unsaturated part of the macrocyclic ligand. This conclusion is pronounced from the observations that $\Delta E_{\frac{1}{2}} (= E_{\frac{1}{2}}^1 - E_{\frac{1}{2}}^2)$ values for different complex species are variable and are ligand-dependent.

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