

About 1.2 g (0.02 mol) of 1,2-diaminoethane in 100 ml of methanol was treated with 0.02 mol of hydrogen chloride. The solution was cooled to 5°C and 3.36 g (0.02 mol) of 3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione in 25 ml of methanol was added slowly with constant stirring. The stirring was continued for 30 min at low temperature when a wine-red solution was formed. The solution was allowed to stand at room temperature for about 20 min and was then treated with 5 g (0.02 mol) of nickel(II) acetate tetrahydrate. The colour of the solution readily turned to dark-brown. It was stirred for about 4 hr and then concentrated to a small volume. Zinc chloride (2.8 g, 0.02 mol) was added to it when a dark brown precipitate was formed. The product, $[\text{Ni}_2(\text{Me}_8[20]\text{octaeneN}_8)](\text{ZnCl}_4)_2$, was filtered. It was found to be hygroscopic and was immediately dissolved in the minimum volume of water and an excess of potassium thiocyanate was added. A brown solid was readily formed. The compound was filtered, washed with water, ethanol followed by ether and dried *in vacuo*.

The perchlorate complex, $[\text{Ni}_2(\text{Me}_8[20]\text{octaeneN}_8)(\text{H}_2\text{O})_4](\text{ClO}_4)_4$ was obtained in a similar way by the metathetical reaction.

The $\text{Ni}_2(\text{Me}_8[22]\text{octaeneN}_8)\text{X}_4 \cdot 4\text{H}_2\text{O}$ complexes were prepared by following similar procedures using 1,3-diaminopropane. Cobalt(II) complexes were prepared by analogous procedures.

Colour and analytical data of the complexes are recorded in Table 1.

Results and Discussion

Binuclear macrocyclic complexes of $(\text{Me}_8[20]\text{octaeneN}_8)$ and $(\text{Me}_8[22]\text{octaeneN}_8)$ have

been synthesized by *in situ* condensation of 3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione with 1,2-diaminoethane and 1,3-diaminopropane, respectively in the presence of nickel(II) or cobalt(II) acetate. The hygroscopic macrocyclic zinc salts, $[\text{M}_2(\text{Me}_8[20]/[22]\text{octaeneN}_8)](\text{ZnCl}_4)_2$ were obtained as dark-brown precipitates by the action of ZnCl_4^{2-} ion. The thiocyanato, nitrito and perchlorate complexes were synthesized by metathetical reactions from the aqueous tetrachlorozincate solution. The compounds were obtained in low yields (30-35 per cent). All the complexes are stable at room temperature for indefinite periods except the perchlorate complexes which are explosive and hence cannot be stored over long periods. All the macrocyclic complexes contain water either in the coordinated form or as associated lattice water. It may be stated that the dinucleating macrocyclic ligand, $(\text{Me}_8[20]\text{octaeneN}_8)$ has the smallest macrocyclic-cavity reported so far accommodating two metal ions.

Infrared spectra

All the macrocyclic complexes show a strong and broad band near 3400 cm^{-1} which may be assigned to νOH mode of water; its width as well as position indicates the presence of either hydrogen bonding or coordinated water. The deformation mode of water appears as a shoulder of medium intensity near 1650 cm^{-1} for the thiocyanato and nitrito complexes and near 1625 cm^{-1} for the perchlorate salts. In the perchlorate salts a band, reminiscent of coordinated water³, appears near 640 cm^{-1} but is conspicuously absent in the thiocyanato and nitrito complexes.

A band appearing near 1600 cm^{-1} in all the complexes is assigned to the $\text{C}\cdots\text{N}$ stretching

Table 1—Colour and Analytical Data of the Macrocyclic Complexes of Cobalt(II) and Nickel(II) with $(\text{Me}_8[20]\text{octaeneN}_8) = (\text{C}_{20}\text{H}_{32}\text{N}_6)$ and $(\text{Me}_8[22]\text{octaeneN}_8) = (\text{C}_{22}\text{H}_{36}\text{N}_8)$

Complexes	Colour	Found (Calculated), %				
		C	H	N	Metal	S
$[\text{Ni}_2(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{SCN})_4]4\text{H}_2\text{O}$	Dark-brown	35.51 (35.73)	4.72 (4.96)	20.72 (20.84)	14.61 (14.64)	15.70 (15.88)
$[\text{Ni}_2(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{H}_2\text{O})_4](\text{ClO}_4)_4$	Light-brown	24.42 (24.69)	3.91 (4.11)	11.50 (11.52)	12.07 (12.14)	—
$[\text{Co}_2(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{SCN})_4]4\text{H}_2\text{O}$	Bright-green	35.61 (35.72)	4.80 (4.95)	20.60 (20.83)	14.61 (14.63)	15.64 (15.87)
$[\text{Co}_2(\text{C}_{20}\text{H}_{32}\text{N}_8)(\text{NO}_2)_4]4\text{H}_2\text{O}$	Brown	31.43 (31.66)	4.91 (5.27)	21.83 (22.16)	15.52 (15.30)	—
$[\text{Ni}_2(\text{C}_{22}\text{H}_{36}\text{N}_8)(\text{SCN})_4]4\text{H}_2\text{O}$	Yellowish-green	37.23 (37.41)	4.82 (5.27)	19.96 (20.14)	14.01 (14.14)	15.25 (15.34)
$[\text{Ni}_2(\text{C}_{22}\text{H}_{36}\text{N}_8)(\text{H}_2\text{O})_4](\text{ClO}_4)_4$	Olive-green	26.12 (26.40)	4.21 (4.40)	11.10 (11.20)	11.50 (11.80)	—
$[\text{Co}_2(\text{C}_{22}\text{H}_{36}\text{N}_8)(\text{SCN})_4]4\text{H}_2\text{O}$	Dull-green	37.22 (34.40)	5.10 (5.26)	20.00 (20.13)	14.32 (14.13)	15.22 (15.33)

vibrations. Its non-multiplicity implies equivalence of all the azomethine C $\cdots$ N groups. Earlier workers have reported bands at similar positions for the coordinated C $\cdots$ N groups of the macrocyclic complexes⁴⁻⁸. Hence, the IR data suggest that the metal atoms are coordinated, in the present macrocycles, through the azomethine nitrogen atoms. This is further substantiated by the fact that all the macrocyclic complexes show bands near 540 cm⁻¹ which may be assigned to the metal-nitrogen vibrations.

A number of bands are observed in the region 1400-800 cm⁻¹ due to deformation modes of CH₃ or CH₂ groups. Apart from these vibrations, a strong and sharp band appears at about 2080 cm⁻¹ along with another sharp band at 485 cm⁻¹ in all the thiocyanato complexes confirming the coordination of the thiocyanato ions through their nitrogen atoms as terminal groups⁹.

The nitrito complex shows a strong band at 830 cm⁻¹. Besides, a relatively sharp band observed for thiocyanato and perchlorate complexes near 1440 cm⁻¹, on account of CH₂ and CH₃ deformation vibrations, is broadened in the nitrito complex (1440-1420 cm⁻¹) due to overlap with O-NO stretching vibrations. The third band of coordinated nitrito groups could not be ascertained because of multiplicity of bands near 1050 cm⁻¹; however all the other features clearly suggest coordination of the NO₂⁻ ion through one of its oxygen atoms.

The above spectral data combined with the non-existence of any band attributable to free C=O or -NH₂ groups provide unequivocal evidence for the condensation of 3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione with 1,2-diaminoethane or 1,3-diaminopropane in the mole ratio 1:1 to give the macrocycles (Me₈[20]octaeneN₈) and (Me₈[22]octaeneN₈) respectively. A pair of metal ions is accommodated in two separate compartments of the macrocyclic ligands involving coordination of four nitrogen atoms with each metal ion. The *trans*-axial positions are occupied

by SCN⁻, NO₂⁻ ions and H₂O molecules in the thiocyanato, nitrito and perchlorate complexes respectively.

Magnetic susceptibilities and electronic spectra

The magnetic moments of nickel(II) macrocyclic complexes are ~ 2.84 B M per ion of nickel, which are somewhat below the normal values observed for magnetically dilute octahedral nickel(II) complexes.

The electronic spectral data are recorded in Table 2. The spectral data of these complexes show multiplet band structures and are reminiscent of tetragonal ligand field about the metal ions. In the low frequency region two weak bands at 10,400 cm⁻¹ and 12,100-12,500 cm⁻¹ are attributed to ${}^3B_{1g} \rightarrow {}^3E_g$ and ${}^3B_{1g} \rightarrow {}^3B_{2g}$ transitions respectively. The latter transition is related directly to Dq^{xy} which provides a measure of the in-plane ligand field strength of the macrocycle. In the high frequency region of the spectra bands observed at 16350-16600 and 23530-25000 cm⁻¹ are assigned to the transitions ${}^3B_{1g} \rightarrow {}^3A_{2g}$ and $\rightarrow {}^3E_g(F)$ respectively. Besides, all the macrocyclic complexes show an intense band at $\sim 32,000$ cm⁻¹ attributable to ${}^3B_{1g} \rightarrow {}^3T_{1g}(P)$ or 3E_g transition which seems to possess substantial charge-transfer character.

The spectroscopic parameters Dq^{xy} , Dt and Dq^z were calculated by the equations described earlier¹³. The value of Dq^{xy} decreases with increase in ring size with the same axial ligands though the change is not remarkable. In a series of mononuclear N₄[14]-[16]-membered macrocyclic complexes containing saturated and unsaturated rings, the values of Dq^{xy} , Dq^z , Dt and Ds has been reported¹⁴. The Dq^{xy} values range from 1100 to 1800 cm⁻¹ and the present data compare well with these spectroscopic parameters.

The macrocyclic complexes of cobalt(II) show magnetic moments in the range 4.2-4.4 B.M. per g ion of the metal, which are slightly below the expected values for octahedral cobalt(II) complexes. The spectra of the present series of complexes (Table 3) resemble one

Table 2—Electronic Spectral and Magnetic Moment Data of Nickel(II) Complexes with the Macrocyclic Ligands (Me₈[20]octaeneN₈) and (Me₈[22]octaeneN₈) (cm⁻¹)

Complexes	μ_{eff} (B.M.)	λ_{max}	Dq^{xy}	Dq^z	Dt	Ds
[Ni ₂ (Me ₈ [20]octaeneN ₈)(SCN) ₄].4H ₂ O	2.88	10, 500; 12, 800; 16, 600; 23, 530; 32, 260	1280	820	263	1210
[Ni ₂ (Me ₈ [20]octaeneN ₈)(H ₂ O) ₄](ClO ₄) ₄	2.86	10, 400; 12, 500; 16, 350; 23, 530	1250	830	240	1247
[Ni ₂ (Me ₈ [22]octaeneN ₈)(SCN) ₄].4H ₂ O	2.86	10, 400; 12, 400; 16, 360; 25, 000	1240	840	230	1490
[Ni ₂ (Me ₈ [22]octaeneN ₈)(H ₂ O) ₄](ClO ₄) ₄	2.85	10, 300; 12, 100; 16, 350; 24, 400;	1210	850	206	1385

Table 3—Electronic Spectral and Magnetic Moment Data of Cobalt(II) Complexes of the Macrocyclic Ligands (Me₈[20]octaeneN₈) and (Me₈[22]octaeneN₈)

Complexes	$\mu_{eff.}$ (B.M.)	λ_{max}
[Co ₂ (Me ₈ [20]octaeneN ₈)(SCN) ₄]4H ₂ O	4.45	16,000; 17,350(sh); 22,200
[Co ₂ (Me ₈ [20]octaeneN ₈)(NO ₂) ₄]4H ₂ O	4.25	16,350; 17,850(sh); 21,000
[Co ₂ (Me ₈ [22]octaeneN ₈)(SCN) ₄]4H ₂ O	4.39	16,000; 17,550(sh); 21,050

Table 4—Electrochemical Data of Macrocyclic Complexes of Cobalt(II) and Nickel(II) with the Ligands (Me₈[20]octaeneN₈) and (Me₈[22]octaeneN₈) in Aqueous DMF

Complexes	First wave			Second wave		
	$-E_{1/2}$ in V (vs SCE)	Slope ⁻¹ (mV)	I_d	$-E_{1/2}$ in V (vs SCE)	Slope ⁻¹ (mV)	I_d
[Co ₂ (Me ₈ [20]octaeneN ₈)(NO ₂) ₄]4H ₂ O	1.14	65	2.2	1.57	68	2.68
[Co ₂ (Me ₈ [20]octaeneN ₈)(SCN) ₄]4H ₂ O	1.06	62	2.84	1.53	66	2.86
[Co ₂ (Me ₈ [22]octaeneN ₈)(SCN) ₄]4H ₂ O	0.91	63	2.54	1.36	67	2.71
[Ni ₂ (Me ₈ [20]octaeneN ₈)(SCN) ₄]4H ₂ O	1.26	61	2.65	1.58	69	2.62
[Ni ₂ (Me ₈ [20]octaeneN ₈)(H ₂ O) ₄](ClO ₄) ₄	0.96	74	2.45	1.55	70	2.66
[Ni ₂ (Me ₈ [22]octaeneN ₈)(SCN) ₄]4H ₂ O	0.91	61	2.75	1.51	67	2.59
[Ni ₂ (Me ₈ [22]octaeneN ₈)(H ₂ O) ₄](ClO ₄) ₄	0.89	62	2.62	1.45	68	2.92

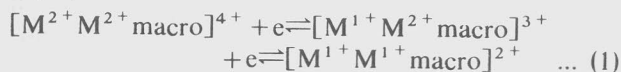
another and are consistent with the electronic spectral features of spin-free octahedral cobalt(II) complexes. All the macrocyclic complexes show an intense band at $\sim 16,300\text{ cm}^{-1}$ with a shoulder on the high frequency side near $17,500\text{ cm}^{-1}$. The former band can be attributed to ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition. Though electronic spectra of several high-spin cobalt(II) macrocyclic complexes have been reported^{15,16}, their assignments have not been always unambiguous. Apart from these bands, cobalt(II) complexes show bands in the region $22,000\text{--}24,000\text{ cm}^{-1}$ which seem to arise from intra-ligand transitions.

Electrochemical studies

The macrocyclic complexes, $M_2(\text{Me}_8[20]\text{octaeneN}_8)\text{X}_4\text{nH}_2\text{O}$ and $M_2(\text{Me}_8[22]\text{octaeneN}_8)\text{X}_4\text{nH}_2\text{O}$ ($\text{X} = \text{ClO}_4^-$, SCN^- , NO_2^-) have been subjected to polarographic studies in aqueous DMF medium with tetraethylammonium perchlorate as the supporting electrolyte at an ionic strength of 0.1 M (Table 4).

The polarogram for each binuclear macrocyclic complex, irrespective of the metal ion or the ring size, shows two well-defined one electron reversible or

quasireversible redox waves. In the first step of reduction the complex is stabilized with metal ions in a mixed oxidation state, and in the final step both the metal ions are reduced to formal oxidation state of + 1. The redox processes can be represented as shown in Eq. 1,



Apart from these usual characteristic patterns associated with the redox behaviour of macrocyclic complexes enclosing two metal centres, the present series of complexes show some outstanding features. The most conspicuous observation relates to the magnitude of the thermodynamic parameter ($E_{1/2}$) with respect to those of the earlier reported complexes. The $E_{1/2}$ values for the first redox waves are most cathodic for the present series of complexes, even when comparisons are made with identical axial ligands, and this clearly implies that the ligand field due to the macrocycle vitally influences the $E_{1/2}$ values. The $E_{1/2}$ values for the second redox waves are also observed to be most cathodic and again show the persistent influence of the macrocyclic ligands.

The structural factors that concertedly affect the $E_{1/2}$ values can be attributed to (i) ring size effect of the macrocycle (ii) number, size and sequence of the inner chelate rings and (iii) degree of unsaturation and π -acceptor properties of the macrocyclic ligands.

Amongst the reported compounds, the present macrocyclic ligand, (Me₈[20]octaeneN₈), possesses the smallest ring size incorporating two metal centres. Both the first and the second redox waves for the complexes of (Me₈[20]octaeneN₈) show the most cathodic $E_{1/2}$ values of all the reported binuclear complexes including (Me₈[22]octaeneN₈) studied here. The $E_{1/2}$ values for the [20]-membered macrocyclic complexes for the first and second waves are, glaringly, 50 to 200 mV more cathodic than those for [22]-membered macrocyclic complexes. The [20]-membered macrocycle, having the smallest ring size, experiences the greatest difficulty in accommodating the larger reduced cations and therefore the complexes get reduced at the highest cathodic potential.

In terms of structural considerations, both the macrocycles contain four α -di-imine chelate units. Besides these chelate rings, additional pairs of five- and six-membered chelate rings have been incorporated symmetrically into the [20]- and [22]-membered macrocyclic complexes, respectively, linking the α -di-imine groups. It is well known that complexes containing 5-membered chelate rings have higher thermodynamic stability^{1,18}. The combined effect of ring size and the sequence of inner chelate units namely 5,5,5 and 5,6,5 for (Me₈[20]octaeneN₈) and (Me₈[22]octaeneN₈) respectively is manifested in the relative $E_{1/2}$ values of these complexes.

The π -acceptor properties of the macrocyclic ligands are also of considerable significance for the $E_{1/2}$ values of the macrocyclic complexes. While the present series of complexes contain four α -di-imine π -acceptor units, the earlier reported complexes² (Me₁₂[24]dodecaeneN₁₂) contain six α -di-imine units. The $E_{1/2}$ values for these [24]-membered macrocycles have been already reported². The first and second $E_{1/2}$ values are observed at a substantial anodic potential in the range -0.28 to -0.36 V and -0.7 to -1.06 V (vs SCE) respectively for cobalt(II) complexes. Inclusion of a large number of α -di-imine units has significantly changed the potential π -acceptor properties of the macrocyclic ligands apart from enlarging the macrocyclic ring size with 5,7,5 chelate ring sequence about each metal ion. Thus the $E_{1/2}$ values of these [24]-membered macrocyclic complexes² are self-

consistent and can be explained in terms of the structural variations.

The formaldehyde condensation series of macrocycles¹ (Me₈[22]octaeneN₁₂) too have [22]-membered ring size and 5,6,5 chelate ring sequence. The six-membered chelate rings of (Me₈[22]octaeneN₁₂) are composed of units $-N-N-C-N-N-$ in contrast to the present series of complexes with chelate rings, $-N-C-C-C-N$. The chelate ring systems exhibit some unique features. While the former ring contains uncoordinated nitrogen atoms adjacent to coordinated nitrogen atoms, in the latter ring the uncoordinated nitrogen atoms are substituted by carbon atoms. The effects of ring atoms are well reflected in the polarographic data. The higher electronegativity of nitrogen atoms in the former ring pushes the $E_{1/2}$ values for (Me₈[22]octaeneN₁₂) series of complexes towards anodic direction in comparison with the present (Me₈[22]octaeneN₈) series of the macrocyclic complexes. A survey of the reported polarographic studies shows no similar example relating the $E_{1/2}$ values with the nature of atoms in the chelate rings. The complexes studied here are first of their kind. It is expected that further investigations on the effects of the nature of ring atoms on redox behaviour will be useful.

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