

Spectral and Electrochemical Studies on Some Co(II), Ni(II) and Cu(II) Macrocyclic Complexes

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An interesting group of 34- and 36-membered macrocyclic trinuclear copper(II) and binuclear nickel(II)/cobalt(II) complexes have been isolated by synergic template condensation of bis-(malonodihydrazide) metal(II) complexes with metal(II) complexes of 1,4-bis(2'-formylphenyl)-1,4-dioxabutane or 1,5-bis(2'-formylphenyl)-1,5-dioxapentane in molar ratio 1 : 2 in aqueous ethanolic medium in the presence of sodium acetate. The complexes were obtained in fine crystalline state. Spectral analysis corroborates the macrocyclic structure for the complexes.

Key Words: Spectral, Electrochemical, Co(II), Ni(II), Cu(II) Macrocyclic complexes.

INTRODUCTION

Though structurally diverse mononuclear and dinuclear macrocyclic complexes have taken a pivotal position in macrocyclic chemistry, trinuclear complexes have been rare so far¹⁻³. Thus, in continuation of our work in the field⁴, we report, here, a couple of trinuclear complexes of copper(II) and dinuclear complexes of nickel(II)/cobalt(II) with the macrocyclic ligands H₄mac and H₄mac' where mac⁴⁻ stands for 34-membered macrocyclic ligand.

5,6:16,17:22,23:33,34-(bzo)₄-10,12,27,29-(oxo)₄-5,7,14,16,22,24,31,33-octaenato₍₄₋₎-8,9,13,14,25,26,30,31-N₈-1,4,18,21-O₄

and mac⁴⁻ stands for

to₍₄₋₎-6,7:17,18:24,25:35,36-(bzo)₄-11,13,29,31-(oxo)₄-6,8,15,17,24,26,33,35-octaenato₍₄₋₎-9,10,14,15,27,28,32,33-N₈-1,5,19,23-O₄.

EXPERIMENTAL

Salicylaldehyde and 1,2-dibromoethane were E. Merck reagents. 1,3-Dibromopropane was of Fluka grade. Metal salts were of BDH quality. The dialdehydes 1,4-bis(2'-formylphenyl)-1,4-dioxabutane (dial) and 1,5-bis(2'-formylphenyl)-1,5-dioxapentane (dial') were prepared by a slight modification of the published work⁵. Hydrazine and malonic acid used were Aldrich reagents. Malonodihydrazide was prepared according to literature procedure⁶.

Preparation of a trinuclear copper(II) and a dinuclear Ni(II)/Co(II) complex is described here as representative examples.

Dihydroxo tetraaquo[6,7:17,18:24,25:35,36-(bzo)₄-11,13,29,31-(oxo)₄-[36]-6,8,15,17,24,26,33,35-octaenato(4-)-9,10,14,15,27,28,32,33-N₈-1,5,19,23-O₄]tri-copper(II):[Cu₃(C₄₀H₃₈N₈O₁₀)(H₂O)₄].

A warm solution (150 mL) of malonodihydrazide (1.32 g, 0.01 mol) was treated with copper(II) acetate monohydrate (1 g, 0.005 mol) dissolved in 50 mL of water followed by addition of 5 g of sodium acetate with stirring. An ethanolic solution (100 mL) of copper(II) chloride dihydrate (1.70 g, 0.01 mol) was taken separately and was added to a hot ethanolic solution (200 mL) of 1,5-bis-(2'-formylphenyl)-1,5-dioxapentane. The resulting solution was added to the former solution with constant stirring. A deep green product precipitated out immediately. The reaction mixture was kept for a week undisturbed. Then the product was filtered, washed with hot water and hot ethanol successively and finally dried *in vacuo* and analysed.

Found	Cu, 18.08	C, 45.47	H, 4.32	N, 10.58
Calculated	Cu, 18.11	C, 45.60	H, 4.37	N, 10.64

Tetraaquo-5,6:16,17:22,23:33,34-(bzo)₄-10,12,27,29-(oxo)₄-[34]-5,7,14,16,22,24,31,33-octaenato-(4-)-8,14,25,31-N₄-1,4,18,21-O₄-(9,13,26,30-N₄)-dinickel (II):[Ni₂(C₃₈H₃₂N₈O₈)(H₂O)₄].

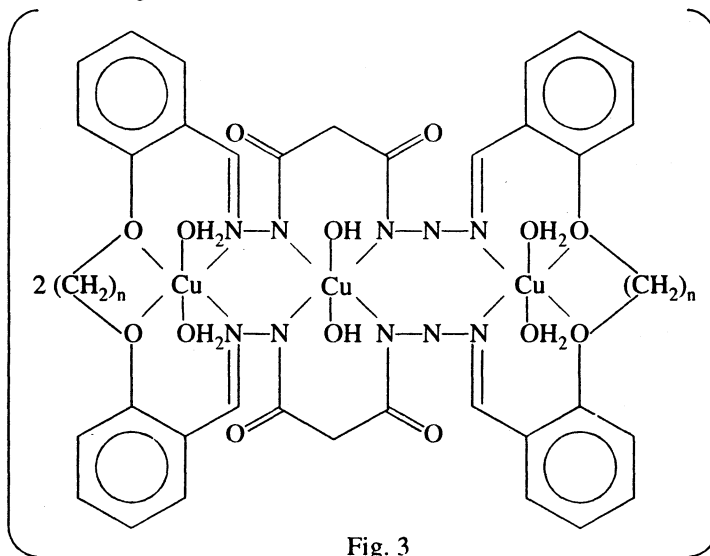
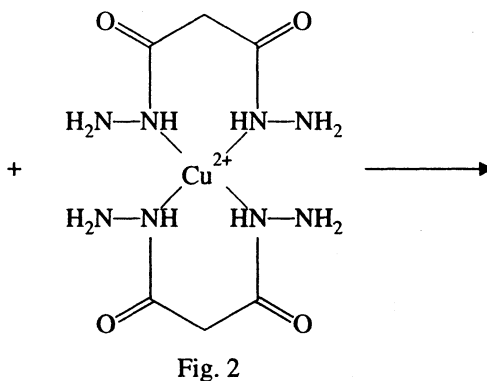
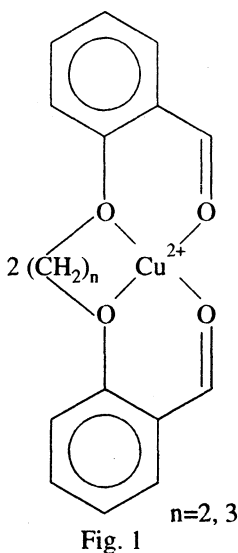
Malonodihydrazide (1.32 g, 0.01 mol) was dissolved in 150 mL of hot water and to this was added an aqueous solution (50 mL) of nickel chloride hexahydrate (1.19 g, 0.005 mol) followed by addition of 5 g of sodium acetate to make the medium basic. The resulting solution was refluxed. An ethanolic solution (100 mL) of nickel chloride hexahydrate (2.38 g, 0.01 mol) was added to a hot ethanolic solution (200 mL) of 1,5-bis-(2'-formylphenyl)-1,5-dioxapentane (2.8 g, 0.01 mol) and the resulting solution was added in small proportions to the refluxing solution. A yellowish green solid gradually separated out. The reflux was continued for 4 h. The reaction mixture was transferred to a 1 L beaker, covered with a clock glass, allowed to cool and kept overnight. Then the compound was filtered, washed with hot water followed by hot ethanol and dried *in vacuo* and analysed.

Found	Ni, 12.48	C, 49.32	H, 4.07	N, 12.12
Calculated	Ni, 12.79	C, 49.71	H, 4.39	N, 12.20

RESULTS AND DISCUSSION

Condensation of pre-formed metal complexes of the dialdehyde dial or dial' in aqueous ethanolic medium and bis-(malonodihydrazide) complexes of nickel(II), cobalt(II) or copper(II) in the mole ratio 2 : 1 was considered to be a convenient route to get the desired polynuclear macrocyclic complexes. It is spectacular that the copper(II) (dial/dial') complexes (Fig. 1) react with the bis-(malonodihydrazide)-copper(II) complexes (Fig. 2) to yield trinuclear copper(II) complexes with the macrocyclic anionic ligands mac and mac' (Fig. 3) having the stoichiometry Cu₃(mac/mac')(OH)₂(H₂O)₄. The reaction is facile in presence of sodium acetate and the products are obtained in microcrystalline state

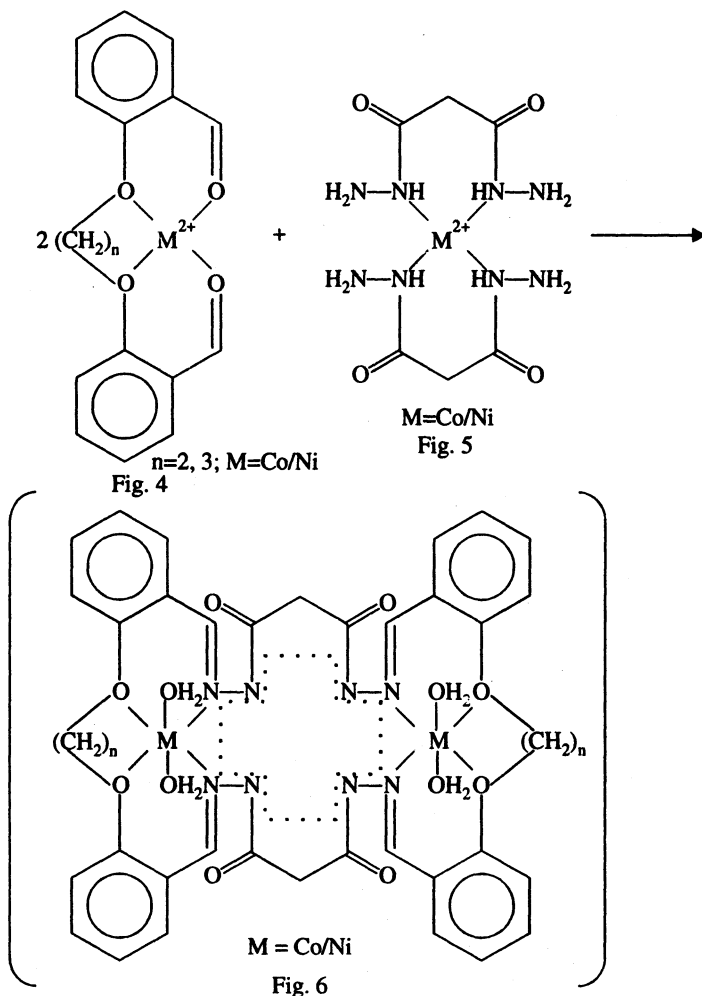
in satisfactory yield. Dilute conditions were adopted to avoid polymerisation reactions. The reaction is represented in **Scheme-1**.



Scheme 1

Marked differences are observed in the stoichiometry of the complexes of nickel(II) and cobalt(II) on one hand and copper(II) on the other. The coordination of the precursor metal(II) (dial/dial') complexes (Fig. 4) with the parent dihydrazide complexes (Fig. 5) under similar conditions gave only dinuclear complexes with the stoichiometry $[M_2(\text{mac}/\text{mac}' \cdot (\text{H}_2\text{O})_4)]$ (Fig. 6). Repeated preparations in different solvent media with different basic catalysts yielded the same result. The

apparent reasons for the displacement of a metal ion and subsequent formation of dinuclear complexes are difficult to explain. However, difference in the size of the cavity in the ligand frame work with the metal cations may presumably be one of the causes. Striking similarities in infrared spectra of the nickel(II) and cobalt(II) complexes and comparing them with those of the trinuclear complexes suggests the $\text{Ni}^{2+}/\text{Co}^{2+}$ metal centres to be symmetrically coordinated to N_2O_2 donor atoms of the macrocyclic ligands as shown in Scheme- 2.



Scheme 2

The successful synthesis of the present group of dinuclear and trinuclear macrocyclic complexes can be attributed to the cooperative template effect of two

kinds of precursor complexes, the bis-(malonodihydrazide) metal(II) and metal(II) (dial/dial'). Since the condensing species involve two kinds of metal complexes, we are inclined to call the synthetic procedure as synergetic template condensation. During the condensation process, the dialdehyde complexes play a major role in orienting the aldehyde function for reaction with the adjacent terminal NH_2 groups. The metal ion directed template condensation becomes facile due to polarisation of the aldehyde functions.

Salicylaldehyde itself exhibits a strong and broad band at about 3250 cm^{-1} which has been attributed to either inter- or intra-molecular hydrogen bonded OH stretching vibrations. This band disappears in the vibrational spectra of the intermediate dialdehydes, dial/dial' and demonstrates that the phenolic OH group of salicylaldehyde enters into condensation with 1,2-dibromoethane or 1,3-dibromopropane with elimination of hydrogen bromide.

Two other bands of medium intensities in the region $3000\text{--}2900\text{ cm}^{-1}$ are observed for salicylaldehyde as well as dial/dial' which originate due to $\nu(\text{C—H})$ vibrations. The aldehydic $\nu(\text{C—O})$ band appears with its intensity and characteristic structures at *ca.* 1680 cm^{-1} ; the position of this band approaches the usual carbonyl vibrations of arylaldehydes. Apart from these, there are a few additional features, which deserve consideration.

The phenolic $\nu(\text{C—O})$ band in salicylaldehyde which is recorded at *ca.* 1325 cm^{-1} disappears from this position in the dialdehydes and two new bands appear at 1270 and 1070 cm^{-1} which are attributed to ethereal asymmetric and symmetric (C—O—C) stretching vibrations respectively. Spectra of aryl and alkyl ethers display asymmetrical C—O—C stretching band at $1275\text{--}1200\text{ cm}^{-1}$ and symmetrical stretching vibrations near $1075\text{--}1020\text{ cm}^{-1}$.

A group of bands are observed in the dialdehydes in the region $1600\text{--}1400\text{ cm}^{-1}$ which can be attributed to the characteristic breathing mode of phenyl ring vibrations. Besides low intensity bands appear in the region $2000\text{--}1700\text{ cm}^{-1}$ which are overtones or combinations bands characteristic of the benzenoid structures. Wagging vibration are observed in the lower frequency region.

Infrared spectra of the dinuclear Co(II)/Ni(II) and trinuclear Cu(II) complexes have been recorded in KBr phase. Important vibrational bands of the macrocyclic complexes are recorded in Table-1. Majority of the vibrational bands are clearly distinguishable and characterize the structural features of the macrocyclic ligand and its mode of bonding with the metal ions. From structural considerations, the infrared spectra of the macrocycles are in many ways distinctly different from the spectra of malonodihydrazide and those of dialdehydes dial/dial'. At the same time some of the important features of the constituent moieties which are unaffected during the condensation reactions are retained in the spectra of the macrocyclic complexes.

At the outset it may be stated that copper(II) complexes contain hydroxyl groups and all the complexes of copper(II) and cobalt(II) are associated with water molecules. The asymmetric and symmetric vibrational bands for H_2O in the complexes appear as a broad band in the region $3500\text{--}3000\text{ cm}^{-1}$ and in a few cases this band is resolved into two components. The $\nu(\text{O—H})$ for the hydroxo group for the trinuclear copper(II) complexes appears as a strong band, but of moderate width

whose centre of gravity lies near 3405 cm^{-1} . The most spectacular feature of the spectra is the absence of any band in the vicinity of 3200 cm^{-1} as was observed in the case of parent dihydrazide, which unambiguously establishes the absence of any NH or NH_2 groups on the backbone of the macrocyclic ring. It indicates that the NH_2 groups of the malonodihydrazide moieties have undergone condensation with the $>\text{C}=\text{O}$ groups of the dialdehyde metal complexes. Moreover, absence of the acidic N—H stretching vibrations signifies the dissociation of the acidic protons during complexation reaction that was carried out in a basic medium yielding a tetra negative anionic form of the macrocycle.

TABLE-1
STRUCTURALLY IMPORTANT INFRARED BANDS (cm^{-1}) OF DINUCLEAR
NICKEL(II) and COBALT(II) AND TRINUCLEAR COPPER(II)
MACROCYCLIC COMPLEXES

$[\text{Ni}_2\text{mac}(\text{H}_2\text{O})_4]$	$[\text{Ni}_2\text{mac}'(\text{H}_2\text{O})_4]$	$[\text{Co}_2\text{mac}(\text{H}_2\text{O})_4]$	$[\text{Co}_2\text{mac}'(\text{H}_2\text{O})_4]$	$[\text{Cu}_3\text{mac}(\text{OH})_2(\text{H}_2\text{O})_4]$	$[\text{Cu}_3\text{mac}'(\text{OH})_2(\text{H}_2\text{O})_4]$	Band assignments
3400	3350	3350 3292	3450 3260	3400	3440	$\nu(\text{OH})$, $\nu_{\text{asym}}(\text{OH}_2)$, $\nu_{\text{sym}}(\text{OH}_2)$
1680	1665	1690	1680	1685	1680	Amide I
1590	1585	1600	1600	1605	1600	$\nu(\text{C—N})$
1560	—	—	1550	1560	1563	Amide II
1500	1500	1530	1520	1510	—	Phenyl ring Vibrations
1490	1460	1490	1490	1490	1480	
1450	1420	1430	1455	1455	1455	
1360	1400	1390	1390	1355	1394	$\delta(\text{CH}_2)$
1300	1300	1287	1290	1300	1296	Amide III
1210	1230	1230	1245	1245	1243	$\nu_{\text{asym}}(\text{C—O—C})$
1155 1150 1105	1160	1180	1160	1160 1105	1162 1110	$\delta(\text{CH}_2)$
1050	1040	1045	1050	1050	1048	$\nu_{\text{asym}}(\text{C—O—C})$
	940	940	—	955	961	
820	840	840	810	935	847	
755	750	750	750	755	757	Skeletal
655	650	655	650	670	653 599	Vibrations

In the fingerprint region, $1700\text{--}600\text{ cm}^{-1}$, the spectra are rich in bands, several of which show the characteristic feature of functional groups and are self-consistent with the macrocyclic structures.

The first high-energy band in the region $1700\text{--}1660\text{ cm}^{-1}$ is quite intense and possesses the characteristic features of C—O stretching vibrations. This is the only strong band of its kind in the region and accounts for the fact that all the $>\text{C}=\text{O}$ groups present in the organic ligand are equienergetic and we attribute this band to arise due to amide stretching vibrations, or in other words to the amide I band.

The next band which is sharp as well as strong appears in the range $1610\text{--}1585\text{ cm}^{-1}$. Taking into account its features and its intensity which is lower than $>\text{C}=\text{O}$ stretching vibrations (amide band), it is assigned to the stretching vibrations of $>\text{C}=\text{O}$ groups coordinated to the metal atoms. The imine groups originate from the condensation of the aldehyde groups with the terminal —NH_2 functions of the parent dihydrazide. The phenyl ring vibrations and the amide II band are observed in the range $1565\text{--}1420\text{ cm}^{-1}$.

The next group of bands of structural significance are the $\nu_{\text{asym}}(\text{C—O—C})$ and $\nu_{\text{sym}}(\text{C—O—C})$ stretching vibrations. These bands have undergone red shift in all the metal complexes compared to their energy in the precursor dialdehydes and are located precisely in the region $1245\text{--}1230\text{ cm}^{-1}$ and $1050\text{--}1040\text{ cm}^{-1}$ implying coordination of the ethereal oxygen atoms to the metal centres. Other skeletal vibrations corresponding to C—H deformation, amide III band and out of plane deformation vibrations are observed in their expected energy ranges as shown in Table-1. On the whole, the spectral data point to the structures of the organic macrocyclic species and is consistent with our expectation of the synergic template condensation.

In order to ascertain the mode of bonding of the metal ion in case of dinuclear macrocyclic complexes, we have examined the energy of the structurally important bands with the corresponding bands of trinuclear copper(II) complexes. The copper ions are placed in three compartments with $\text{CuO}_4\text{N}_2\text{—CuO}_2\text{N}_4\text{—CuO}_4\text{N}_2$ chromophores. While the nitrogen atoms coordinated to CuO_2N_2 chromophores come from imine groups $>\text{C}=\text{N—}$, the nitrogen atoms coordinated to the central metal ion are amidic in nature. The energies of the $\nu(\text{C—N})$ and $\nu(\text{C—O—C})$ bands are of the same order of magnitude as observed for the dinuclear nickel(II) and cobalt(II) complexes and lead us to believe that both the metal atoms are placed symmetrically within the supermacrocyclic cavity having the chromophore MO_4N_2 (Scheme 2).

Electronic spectra and Magnetic Properties

The electronic spectra of the dinuclear macrocyclic complexes of nickel(II) have been measured in ultraviolet and visible regions. The complexes possess magnetic moment near 3.0 B.M. per metal ion at 300 K and manifest a spin triplet ground state for each nickel(II) ion in the macrocycles. Electronic spectra of the macrocyclic complexes exhibit three ligand field bands in the range $29,000\text{--}10,000\text{ cm}^{-1}$. One or two charge transfer bands also appear near $36,000\text{ cm}^{-1}$. The spectra on the whole resemble the spectral features of nickel(II) ion under

octahedral symmetry and the ligand field bands can be assigned to ${}^3A_{2g} \longrightarrow {}^3T_{2g}$, ${}^3A_{2g} \longrightarrow {}^3T_{1g}$ and ${}^3A_{2g} \longrightarrow {}^3T_{1g}(P)$. It is significant to note that each component transition does not exhibit any multiplicity or significant asymmetry. It implies that the pair of nickel(II) ions occur within the macrocyclic cavities under similar ligand field environment and is consistent with the structure as proposed in Fig. 6.

Both the dinuclear cobalt(II) macrocyclic complexes are high spin paramagnetic compounds and the magnetic moments per metal ion are 4.9 B.M. and 5.0 B.M. for the macrocyclic complexes $[Co_2mac \cdot (H_2O)_4]$ and $[Co_2mac' \cdot (H_2O)_4]$ respectively. The electronic spectra clearly reflect octahedral environment about the metal ion. Both the complexes are dominated by a band whose maxima are observed in the region 18,000 to 20,000 cm^{-1} . This transition undoubtedly arises due to the transition ${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$. However, in the case of the 34-membered macrocycle $[Co_2mac \cdot (H_2O)_4]$ another band is observed in the lower energy region, *ca.* 8000 cm^{-1} . This band seems to rise from the transition, ${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$. A strong and sharp band is observed near 28,000 cm^{-1} which originates due to metal \rightarrow ligand charge transfer spectra.

A striking aspect of the spectra is that there are no split components to each of these transitions and it gives us the impression that both the metal centres are in equivalent ligand field environments. In other words, it suggests that the cobalt(II) ions are in the chromophores $CoN_2O_2O_2$; two nitrogen and two oxygen donor atoms originate from the macrocyclic ligands *mac/mac'*; the other two donor oxygen atoms are offered by coordinated water which occupy apical transposition.

Trinuclear copper(II) complexes are paramagnetic and the magnetic moment per metal ion is found to be *ca.* 1.2 B.M. This value is much lower than the value expected for the magnetically dilute copper(II) complexes. The results indicate a strong antiferromagnetic interaction between copper(II) centres. Since we have not made any magnetochemical study over a range of temperature, we refrain from making any further observation on the magnetic data.

Both the complexes exhibit a broad asymmetric band near 14,000 to 16,000 cm^{-1} attributable to the transition ${}^2E_g \longrightarrow {}^2T_{2g}$ under octahedral approximation. The width and asymmetry implies the existence of the metal centres in different ligand field environments which agree well with the structure shown in Fig. 3; at the same time, each is subjected to Jahn-Teller distortions.

Electrochemical studies

Polarographic studies of complexes have been made in deoxygenated DMF—water (90 : 10 v/v) medium using sodium perchlorate as the supporting electrolyte. Measurements have been taken with reference to saturated calomel electrode (S.C.E.). The data are recorded in Table-2.

The trinuclear copper(II) macrocyclic complexes exhibit two well defined reduction waves. The slope values for the first and the second step of reduction for the macrocyclic complexes are found to be acceptably close to reversible one-electron reduction waves. The one electron nature of each step was confirmed by wave-height comparison and from Ilkovic equation⁸. The redox processes are

diffusion controlled which have been indicated by the linear plots of i_d vs. $\sqrt{h_{\text{eff}}}$ (h = height of the mercury column) and i_d vs. concentration which pass through the origin. The $E_{1/2}$ value for the first step of reduction of the macrocyclic complexes is quite anodic and occurs near -0.17 V. The second step of reduction appears at $E_{1/2}$ values near -1.4 V. These data consistently signify that the redox processes occur in a stepwise manner and at the first redox process the macrocyclic complex ion is stabilized with the triad of metal ions encircled by the macrocyclic ligand in two different oxidation states.

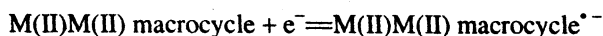
TABLE-2
POLAROGRAPHIC DATA FOR THE DINUCLEAR MACROCYCLIC COMPLEXES OF NICKEL(II) AND COBALT(II) AND TRINUCLEAR MACROCYCLIC COMPLEXES OF COPPER(II)

Sl. No.	Complexes	$E_{1/2}$ (V)	Slope (mv)	h
1.	[Cu ₃ (mac)(OH) ₂ (H ₂ O) ₄]	-0.17	67	0.88
		(1 st wave)	(1 st wave)	(1 st wave)
		-1.39	53	1.11
		(2 nd wave)	(2 nd wave)	(2 nd wave)
2.	[Cu ₃ (mac')(OH) ₂ (H ₂ O) ₄]	-0.17	66	0.89
		(1 st wave)	(1 st wave)	(1 st wave)
		-1.40	56	1.05
		(2 nd wave)	(2 nd wave)	(2 nd wave)
3.	[Ni ₂ (mac)(H ₂ O) ₄]	-1.42	60	0.98
4.	[Ni ₂ (mac')(H ₂ O) ₄]	-1.47	60	0.98
5.	[Co ₂ (mac)(H ₂ O) ₄]	-1.48	61	0.97
6.	[Co ₂ (mac')(H ₂ O) ₄]	-1.39	62	0.94

The second step of reduction is highly cathodic and the magnitude of the thermodynamic parameter $E_{1/2}$ is comparable to the $E_{1/2}$ values observed for the mononuclear complexes. It appears that the electron is transferred to the molecular orbital which is predominantly ligand based.

The dinuclear nickel(II) and cobalt(II) macrocyclic complexes show a well defined redox wave whose $E_{1/2}$ values are observed in the range -1.48 to -1.39 V. At higher potential, an ill defined wave is observed which has not been analyzed. The first wave on analysis shows that one electron transfer accompanies the redox process. The magnitude of the $E_{1/2}$ values is also observed in the same range as for the mononuclear macrocyclic complexes which are in tune with literature reports⁹.

In our opinion, the redox process follows a similar mechanistic pathway for this group of dinuclear complexes where the reduction is associated with the formation of a ligand anion radical.



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