Asian Journal of Chemistry Vol. 12, No. 3 (2000), 771–774

Spectral and Electrochemical Studies on Some Trinuclear Copper(II) and Dinuclear Cobalt(II) and Nickel(II) Macrocyclic Complexes

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Condensation of copper(II) complexes of the dialdehydes with bis-(oxalodihydrazide) copper(II) complexes in aqueous ethanolic solution in the mole ratio 2 : 1 in presence of sodium acetate yielded the trinuclear complexes. Attempts to prepare analogous trinuclear complexes of cobalt(II) and nickel(II) resulted in only dinuclear complexes. The complexes were obtained in fine crystalline state. Analysis of the IR spectra of the precursor dialdehydes and the macrocycles corroborate the macrocyclic structure.

INTRODUCTION

Dinuclear macrocyclic complexes have attracted for the last two decades since Robson *et al.*[1] introduced the term *binucleating ligands* for such complexes. These molecules are well known to manifest cooperative phenomena in their magneto-chemical and electrochemical behaviour. Though structurally diverse dinuclear macrocyclic complexes have taken a pivotal position in macrocyclic chemistry, trinuclear complexes have been rare so far.[2,3]

The major constraint for the synthesis of trinuclear macrocyclic complexes has been due to the rarity of structurally appropriate macrocyclic systems with rigid frameworks and adequate number of coordinating sites requiring high degree of molecular organisation.

The bis-(dihydrazide) metal complexes with *trans*-disposition of the terminal NH_2 groups were considered suitable to yield trinuclear macrocyclic complexes. It was contemplated that pre-formed metal complexes with dialdehydes (Fig. 1) have the potential ability for the metal ion directed template condensation with bis-(dihydrazide) metal(II) complexes (Fig. 2) to yield trinuclear metal complexes (Fig. 3). In the present communication trinuclear complexes of copper(II) and dinuclear complexes of nickel(II) and cobalt(II) have been reported.

EXPERIMENTAL

AnalaR grade reagents from Aldrich were used in these experiments. Dialdehyde ligands as well as dihydrazone metal(II) complexes were prepared as reported earlier[4–6]. Standard procedures were adopted for analyses. Analytical data agree well with the proposed formulations. Magnetic moments were measured by the Gouy method using $Hg[Co(CNS)_4]$ as a calibrant. IR spectra were recorded on a Beckmann IR-20 spectrophotometer. The absorption spec-

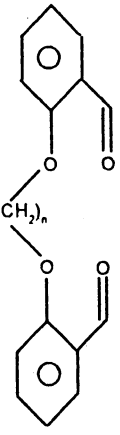
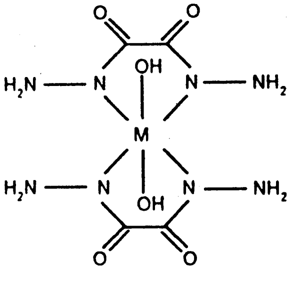
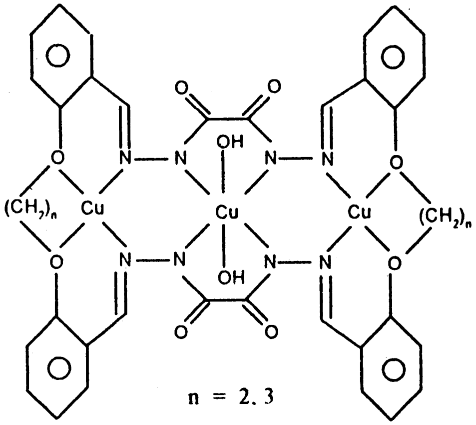


Fig.-1



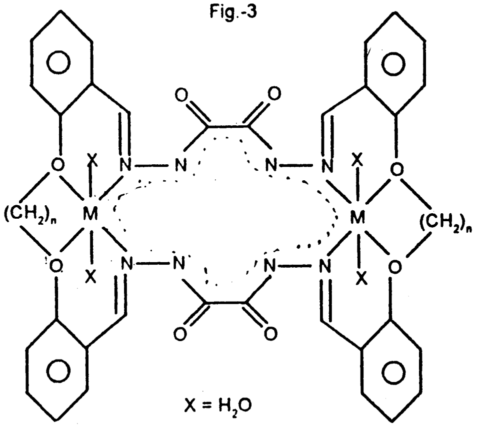
M = Co(II). Ni(II). Cu(II)

Fig.-2



n = 2. 3

Fig.-3



X = H_2O
M = Co(II). Ni(II) n = 2. 3

Fig.-4

tra of DMSO solutions of complexes were recorded on a Cary-2390 spectrophotometer.

RESULTS AND DISCUSSION

Infrared spectra

The dialdehyde ligands (Fig. 1) exhibit the aldehydic ν(C═O) band with its characteristic intensity and structure near 1680 cm^{-1}. Two other bands of structural significance are the asymmetric and symmetric stretching vibrations of C—O—C groups and are located near 1275 and 1075 cm^{-1} respectively.

The vibrational spectra of the trinuclear/binuclear macrocyclic metal(II) complexes (Figs. 3–4) are remarkably different from the spectra of the dialdehydes (Fig. 1) and the dihydrazide metal(II) complexes (Fig. 2).

The first feature of the spectra that attracts attention is the absence of NH_2 stretching vibrations of the dihydrazide complexes in the vicinity of 3200 cm^{-1} implying their involvement in Schiff base condensation with the dialdehydes.

In the region 1700–1600 cm^{-1} the spectra of the macrocycles exhibit a lone ν(C═O) band which is strong and can be attributed to the amide I band. The next band which is sharp but relatively weaker than the amide I band appears near 1600 cm^{-1}. Its characteristic features demonstrate that it arises from C═N stretching vibrations. The imine C═N groups of the macrocycles have been generated from the condensation of the aldehyde and NH_2 groups during macrocyclization.

The ethereal C—O—C vibrations are clearly distinguishable and are located near 1230 and 1045 cm^{-1} in the macrocycles.

Apart from these frequencies, the vibrations arising from phenyl groups and deformation modes of CH_2 groups are also observed in their respective energy regions.

The spectral data show that the copper(II) ions are enclosed within the macrocyclic cavity as shown in Fig. 3. The structurally important vibrational bands of the dinuclear cobalt(II) and nickel(II) complexes are energetically comparable which lead me to postulate that the cobalt(II) and nickel(II) ions are encased in the macrocyclic cavity symmetrically with chromophores MO_4N_2 (Fig. 4).

Electronic Spectra

The dinuclear nickel(II) macrocyclic complexes are paramagnetic and possess magnetic moments about 3.0 B.M. per metal ion at 300 K. They are characterized by three ligand field bands near 10,000, 16,000 and 27,000 cm^{-1} respectively which indicate octahedral coordination about the metal ions. Besides these, there appear one or two charge transfer bands near 37,000 cm^{-1}.

The cobalt(II) complexes are also of high-spin type and show magnetic moments about 5.0 B.M. per metal ion. The electronic spectrum is dominated by a transition in the range 20,000–18,000 cm^{-1}. It undoubtedly originates due to the transitions $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$.

It is remarkable that from spectral and magnetic considerations the dinuclear cobalt(II) and nickel(II) complexes are different from the behaviour of the mononulear maxcrocyclic complexes and manifest that the potential features of bonding about the metal ions are different for the groups of macrocycles.

The copper(II) trinuclear macrocyclic complexes possess magnetic moments that are subnormal and the values are found to be about 1.2 B.M. per metal ion at ambient temperatures. The values indicate spin-spin coupling between metal centres. However, I refrain from making further comments since cryomagnetic studies are in progress.

Each trinuclear copper(II) complex shows a broad asymmetric band spreading over 14,000–16,000 cm^{-1} and the absorption is attributed to $^2E_g \longrightarrow {}^2T_{2g}$ electronic transitions.

Electrochemical Studies

The trinuclear copper(II) macrocyclic complexes show two well-defined reversible redox waves and each redox step is accompanied by one electron transfer. The $E_{1/2}$ values for the waves are observed at –0.17 and –1.39 V respectively. The first redox wave is attributed to the Cu(II) ⇔ Cu(I) couple and the metal ions occur at this step in ambivalent oxidation states.

The second step of reduction shows the thermodynamic parameter $E_{1/2}$ at a highly negative potential which is comparable to the redox values found for the mononuclear complexes and reflects the influence of the macrocyclic ring and this step of reduction is considered to be considerably influenced by the ligand structure and most probably the electron acceptor orbitals are dominated by the amidic moieties.

The dinuclear cobalt(II) and nickel(II) macrocycles undergo one-electron reduction and the $E_{1/2}$ values are observed in the range –1.3 to –1.4 V. In my opinion the redox process is accompanied by ligand-anion radical formation.

ACKNOWLEDGEMENT

The author is thankful to Dr. S.C. Prasad, Principal, for his kind cooperation and availability of laboratory and library facilities. He is also thankful to his colleagues of the Chemistry Department for support and encouragement.

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(*Received*: 14 January 2000; *Accepted*: 28 February 2000) AJC-1995