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Binuclear Macrocyclic Complexes of Ni(II), Co(II), Fe(II) and Cu(II) with 3,4,7,8,14,15,18,19 Octaphenyl 1,2,5,6,9, 10,12,13,16,17,20,21-dodecaaza-Cyclobicosa-3,4,7,8,14, 15,18,19-Octaene

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A series of binuclear macrocyclic complexes have been synthesised by the action of formaldehyde on tetra chloro, tetra bromo, tetra iodo and tetra thiocyanato bis-(1,2,5,6-tetra phenyl-1,6-dioxo-3,4-diazahexa-2,4-diene, 1,6-dihydrazone) dinickel(II), dicobalt(II), diiron(II) and dicopper(II). Structures of these complexes have been elucidated on the basis of IR and electronic spectra.

INTRODUCTION

A series of binuclear macrocyclic complexes have been synthesised using Schiff bases of polyketones[1–3] and crown ethers[4] recently. We have reported earlier[5] a series of binuclear bis-complexes of Ni(II), Co(II), Cu(II) and Fe(II) of the type $M_2L_2X_4$ where $X = Cl^-$, Br^-, I^-, SCN^-, NO_3^- with the ligand 1,2,5,6-tetraphenyl-1,6-dioxo-3,4-diazahexa-2,4-diene, 1,6-dihydrazone. The present paper deals with the isolation and structural elucidation of macrocyclic complexes of Ni(II), Co(II), Fe(II) and Cu(II) formed by the action of bis-dihydrazone complexes with formaldehyde.

EXPERIMENTAL

The macrocyclic complexes were prepared from bis-dihydrazone complexes[5] of Ni(II), Co(II), Fe(II) and Cu(II) according to the procedure given in the literature[3].

Tetra Thiocyanato (3,4,7,8,14,15,18,19 Octaphenyl-1,2,5,6,9,10,12,13,16,17, 20,21-Dodecaaza-cyclobicosa-3,4,7,8,14,15,18,19-octaene) Dinickel(II)

Bis-(benzil azine dihydrazone) dinickel(II) tetra thiocyanate complex compound (0.001 mol) was suspended in minimum quantity of acetonitrile. This mixture was heated to 45°C on a water bath. Now 37% formeldehyde solution was added to the above suspended solution dropwise, and one drop of perchloric acid was also added to catalyse the reaction. It was stirred vigorously and continuously. All the reacting mixtures formed a solution with gradual change in colour from brown to reddish brown. The solution was concentrated and kept overnight. Brown crystals were filtered, washed with ether and dried. Chloro, bromo, iodo

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and thiocyanato macrocyclic complexes of Ni(II), Co(II), Cu(II), Fe(II) have been synthesised by a similar procedure.

RESULTS AND DISCUSSION

The analytical and physical data of the compounds are presented in Table 1. In the IR spectra a pair of bands that appeared at 3290 and 3200 cm^{-1} which correspond to asymmetric and symmetric stretching vibrations of free NH_2 groups in the parent compounds are found absent in IR spectra of macrocyclic complexes which support the cyclisation of terminal $-NH_2$ groups. These bands have disappeared and a new band is seen in different macrocycles in the region 2940–2840 cm^{-1} and the band looks broad in every case. This band is assigned as ν(N—H) vibration. Besides this band, the spectra show one more band around 1200 cm^{-1}. This band is assigned to deformation mode of methylene group and a band *ca.* 900 cm^{-1} as wagging mode of secondary –NH groups[6]. The complexes show band around 1590 cm^{-1} implying C=N stretching vibration. This band moves towards a higher frequency region without any noticeable change in intensity which may be correlated with the high amount of interaction between the metal ion and the coordinated azomethine groups. The three phenyl ring vibrations are observed in all cases near about 1470 cm^{-1}.

TABLE 1

ANALYTICAL DATA OF THE MACROCYCLIC COMPLEXES AND MAGNETIC MOMENT

Macrocycle	Colour	Found (Calc.) %					Magnetic moment (BM)
		C	H	N	Metal	Anion	
1. $[(Ni_2(C_{58}H_{48}N_{12})(SCN)_4$	Brown	55.02 (55.19)	3.78 (3.81)	13.21 (13.32)	9.16 (9.28)	18.32 (18.40)	2.98
2. $[(Ni_2(C_{58}H_{48}N_{12})Cl_4$	Dark Yellowish.	59.38 (59.44)	3.98 (4.10)	14.32 (14.35)	9.92 (9.99)	12.00 (12.13)	2.95
3. $[(Co_2(C_{58}H_{48}N_{12})(SCN)_4$	Yellow	55.01 (55.18)	3.77 (3.82)	13.20 (13.31)	9.12 (9.30)	18.31 (18.41)	2.52
4. $[(Cu_2(C_{58}H_{48}N_{12})(NO_3)_4$	Green	53.95 (54.08)	3.52 (3.72)	17.32 (17.40)	9.75 (9.87)	—	1.68
5. $[(Fe_2(C_{58}H_{48}N_{12})I_4$	Yellow	10.87 (10.97)	3.10 (3.13)	45.33 (45.43)	7.28 (7.31)	33.08 (33.16)	2.64

Electronic Spectra

Ni(II) complexes with macrocyclic ligand are of high spin type as the magnetic moment values lie in the region 2.8 to 3.0 B.M. per metal ion. Their electronic spectral data are reminiscent of tetragonal field about the metal ion. The four bands observed at 9,500; 12,600; 16,800 and 28,500 cm^{-1} in their spectra originate due to the transitions $^3B_{1g} \rightarrow {}^3E_g$, $^3B_{1g} \rightarrow {}^3B_{2g}$, $^3B_{1g} \rightarrow {}^3T_{1g}(F)$ and $^3B_{1g} \rightarrow {}^3T_{1g}(P)$ respectively[7]. The magnetic moment value of Co(II) macrocyclic complexes is found to be 2.52 B.M. and is of low spin type. It shows a broad band in the region 22,800 cm^{-1} with multiple structure. The band is attributed to $^2A_{1g} \rightarrow {}^2A_{2g}$ transition under octahedral approximations[7,8]. Cu(II) macrocyclic complex with magnetic moment value 1.68 B.M. probably assumes square planar conformation giving one band in the region 25,000 cm^{-1} which may occur due to overlapping of the $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ bands of ligand field transitions[7]. Fe(II) macrocyclic complex with magnetic value 2.64 B.M. represents low spin case. The spectrum shows two bands around 15,200 and 28,000 cm^{-1}. The low energy band is assigned as $^1A_{1g} \rightarrow {}^1T_{1g}$ transition[9,10] and the other band is charge transfer in origin.

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