

Macrocyclic Metal Complexes : Part I—Cobalt(II), Nickel(II) & Copper(II) Complexes Containing Fluoro-boro-bridged 14- & 16-Membered Macrocyclic Ligands

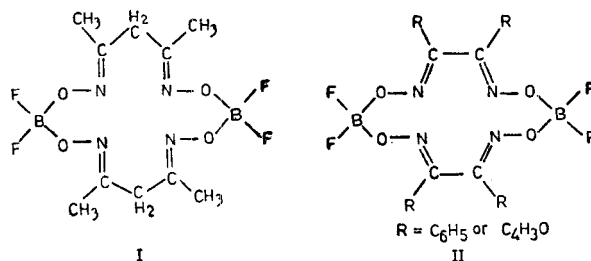
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A number of 14- and 16-membered macrocyclic complexes of nickel(II) and cobalt(II) of the type, $\text{NiL}_2(\text{BF}_2)_2$ and $\text{CoL}_2(\text{BF}_2)_2 \cdot 2\text{H}_2\text{O}$ (LH_2 = pentane-2,4-dione dioxime, 1,2-diphenylethane-1,2-dione dioxime or 1,2-difuryl-ethane-1,2-dione dioxime) have been synthesized along with a copper(II) macrocyclic complex $\text{CuL}_2(\text{BF}_2)_2$, where L represents the dianion of 1,2-diphenylethane-1,2-dione dioxime. The preparative procedure involves a non-template cyclization of the neutral complexes of cobalt(II), nickel(II) and copper(II) of the corresponding oximes (LH_2) by reaction with boron trifluoride. The nickel(II) and cobalt(II) compounds are respectively diamagnetic and of low-spin type having one unpaired electron with a nominal d^7 -configuration, while the copper(II) complex is square-planar. Spectral data support a square-planar environment about the metal ion, coordination occurring through the nitrogen atoms of the ligands. The complexes are resistant to moderately concentrated acids, dilute alkalis and a variety of organic liquids at ambient temperatures. They exhibit thermal stabilities to varying degrees.

METAL complexes of macrocyclic ligands containing porphyrin, corrin and phthalocyanine ring systems and a number of synthetic mono- and poly-macrocycles of varying ring sizes with nitrogen, sulphur and oxygen as donor atoms have been investigated¹⁻⁹. Boron halides have strong affinity for oxime protons and these have been found to link the adjacent coordinated oximes in bis(dioximate)metallates to give halo-borobridged macrocycles¹⁰⁻¹⁶. Rose and coworkers¹⁷ have isolated *in situ* five low-spin Fe(II) clathrochelates from alcoholic and aqueous solutions using Fe(II) salts, dimethylglyoxime and boric acid. Recently we have reported two series of low-spin alkoxy boron bridged encapsulation compounds of iron(II) with pentane-2,4-dione dioxime and 1,2-diphenylethane-1,2-dione dioxime by following a metal ion directed template syntheses and have proposed structures for the complexes intermediate between octahedral and trigonal-prismatic¹⁸. In the present paper we report the syntheses of nickel(II) and cobalt(II) complexes with the macrocyclic ligands 1,9-diboro-1,1,9,9-tetrafluoro-2,8,10,16-tetraoxa-3,7,11,15-tetraaza-4,6,12,14-tetramethylcyclohexadeca-3,6,11,14-tetraene [abbr. bofaphcycladeca(16)](I), 1,8-diboro-1,1,8,8-tetrafluoro-2,7,9,14-tetraoxa-3,6,10,13-tetraaza-4,5,11,12-tetraphenylcyclotetradeca-3,5,10,12-tetraene [abbr. bofaphcycladeca(14)](II), and 1,8-diboro-1,1,8,8-tetrafluoro-2,7,9,14-tetraoxa-3,6,10,13-tetraaza-4,5,11,12-tetra-furylcyclotetradeca-3,5,10,12-tetraene [abbr. bofafurylcycladeca(14)](II). A novel macrocyclic complex of Cu(II) with the ligand, bofaphcycladeca(14) has also been synthesized during the present work. One of these complexes Ni[bofaphcycladeca(14)] has been



reported earlier by Schrauzer¹⁰ but its properties do not appear to have been studied in detail.

Materials and Methods

All the chemicals used were BDH, E. Merck or S. Merck reagents. Pentane-2,4-dione dioxime, 1,2-diphenylethane-1,2-dione dioxime and 1,2-difuryl-ethane-1,2-dione dioxime were prepared following literature methods and their melting points agreed well with the reported values^{19,20}. Boron trifluoride etherate was distilled before use.

Bis(dioximate)metallates(II) — Pentane-2,4-dione dioximate, 1,2-diphenylethane-1,2-dione dioximate and 1,2-difuryl-ethane-1,2-dione dioximate metal chelates formulated as $\text{M}(\text{C}_5\text{H}_9\text{N}_2\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ [$\text{M} = \text{Co(II)}$ and Ni(II)], $\text{M}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2)_2 \cdot n\text{H}_2\text{O}$ and $\text{M}(\text{C}_{10}\text{H}_7\text{N}_2\text{O}_2)_2 \cdot n\text{H}_2\text{O}$ [$n = 0$ when $\text{M} = \text{Ni(II)}$ and $n = 2$ when $\text{M} = \text{Co(II)}$] respectively were prepared along with $\text{Cu}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2)_2$ by the reaction of aqueous ethanolic solution of the corresponding metal(II) acetate and the corresponding oxime. Analytical data satisfactorily agreed with the formulae given above.

1,9-Diboro-1,1,9,9-tetrafluoro-2,8,10,16-tetraoxa-3,7,11,15-tetraaza-4,6,12,14-tetramethylcyclohexadeca-3,6,11,14-tetraenecobalt(II), $[\text{Ni}(\text{C}_{10}\text{H}_{16}\text{N}_4\text{O}_4\text{B}_2\text{F}_4)] - \text{Ni}(\text{C}_5\text{H}_9\text{N}_2\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ (3.5g) was dissolved in 30 ml of dichloromethane and 15 ml of boron trifluoride etherate was slowly added to a mechanically stirred solution of the complex over a period of 10-15 min. There was rapid change of colour from green to bright-yellow and a crystalline product was formed. It was filtered, washed with acetone and finally with ether and the product was dried *in vacuo* at room temperature.

1,9-Diboro-1,1,9,9-tetrafluoro-2,8,10,16-tetraoxa-3,7,11,15-tetraaza-4,6,12,14-tetramethylcyclohexadeca-3,6,11,14-tetraenecobalt(II) dihydrate, $[\text{Co}(\text{C}_{10}\text{H}_{16}\text{N}_4\text{O}_4\text{B}_2\text{F}_4)] \cdot 2\text{H}_2\text{O}$ —This compound was prepared in a similar way as the corresponding Ni(II) compound except that boron trifluoride etherate was added to an ethereal suspension of $\text{Co}(\text{C}_5\text{H}_9\text{N}_2\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ and the reaction was carried out in nitrogen atmosphere. After recrystallisation from acetonitrile the product was obtained in the form of deep-brown crystals.

1,8-Diboro-1,1,8,8-tetrafluoro-2,7,9,14-tetraoxa-3,6,10,13-tetraaza-4,5,11,12-tetrafurylcyclotetradeca-3,5,10,12-tetraenecobalt(II), $[\text{Ni}(\text{C}_{20}\text{H}_{12}\text{N}_4\text{O}_8\text{B}_2\text{F}_4)] - \text{Ni}(\text{C}_{10}\text{H}_7\text{N}_2\text{O}_4)_2$ (~1g) was suspended in ether (15 ml) and the suspension was treated dropwise with boron trifluoride etherate (5 ml) when the colour of suspension underwent rapid change from red to bright orange-red. It was stirred for about an hour and allowed to stand overnight. The product was filtered, washed with ether and dried *in vacuo*.

1,8-Diboro-1,1,8,8-tetrafluoro-2,7,9,14-tetraoxa-3,6,10,13-tetraaza-4,5,11,12-tetrafurylcyclotetradeca-3,5,10,12-tetraenecobalt(II) dihydrate, $[\text{Co}(\text{C}_{20}\text{H}_{12}\text{N}_4\text{O}_8\text{B}_2\text{F}_4)] \cdot 2\text{H}_2\text{O}$ —This compound was obtained in a similar way as the corresponding Ni(II) compound and the product was recrystallized from methyl cyanide.

1,8-Diboro-1,1,8,8-tetrafluoro-2,7,9,14-tetraoxa-3,6,10,13-tetraaza-4,5,11,12-tetrafurylcyclotetradeca-

3,5,10,12-tetraenecobalt(II), $[\text{Ni}(\text{C}_{20}\text{H}_{12}\text{N}_4\text{O}_8\text{B}_2\text{F}_4)]$ —This compound was prepared according to the procedure given in literature¹⁰. The compound was orange-yellow in colour and was recrystallized from acetone.

1,8-Diboro-1,1,8,8-tetrafluoro-2,7,9,14-tetraoxa-3,6,10,13-tetraaza-4,5,11,12-tetrafurylcyclotetradeca-3,5,10,12-tetraenecobalt(II) dihydrate, $[\text{Co}(\text{C}_{20}\text{H}_{12}\text{N}_4\text{O}_8\text{B}_2\text{F}_4)] \cdot 2\text{H}_2\text{O}$ —It was prepared in a similar way from an ethereal medium under nitrogen. On addition of boron trifluoride etherate to a suspension of $\text{Co}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ (0.5 g) the complex went into solution and the colour of the solution rapidly darkened. The solution was stirred for 2 hr and then it was tightly stoppered and allowed to stand overnight. Finally the volume of the solution was reduced to 5 ml and water was added. The reddish-brown solid that appeared was removed by filtration, washed with a small quantity of ethanol-ether (1:1) mixture, recrystallized from acetonitrile and dried *in vacuo*.

1,8-Diboro-1,1,8,8-tetrafluoro-2,7,9,14-tetraoxa-3,6,10,13-tetraaza-4,5,11,12-tetrafurylcyclotetradeca-3,5,10,12-tetraenecopper(II), $[\text{Cu}(\text{C}_{20}\text{H}_{12}\text{N}_4\text{O}_8\text{B}_2\text{F}_4)]$ —The compound was prepared almost in a similar way except that the reaction was carried out in open atmosphere. The colour of the suspended solid, $\text{Cu}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2)_2$ changed from reddish-brown to violet. The stirring was continued for 6 hr and the product was filtered, washed with ether and dried *in vacuo*.

Analytical data of the complexes are given in Table 1.

The estimations of cobalt, nickel and copper were done by standard methods²¹. The IR and electronic spectra and magnetic susceptibility determinations were carried out as described earlier²². The thermogravimetric measurements (TG and DTA) were done using MOM Derivatograph (Paulik-Paulik Eradey system) with a heating rate of 5° per min. The instrument records simultaneously the temperature

TABLE 1 — ANALYTICAL DATA AND COLOUR OF THE MACROCYCLIC COMPLEXES OF NICKEL(II), COBALT(II) AND COPPER(II)

Complex	Empirical formula	Colour	Found (Calc.), %			
			Metal	C	H	N
Ni[bofamcycloaene(14)]	$\text{Ni}(\text{C}_{10}\text{H}_{16}\text{N}_4\text{O}_4\text{B}_2\text{F}_4)$	Yellow	14.05 (14.2)	28.90 (29.07)	3.80 (3.87)	13.2 (13.6)
Co[bofamcycloaene(16)]. 2H ₂ O	$\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_4\text{O}_6\text{B}_2\text{F}_4)$	Deep-brown	12.82 (13.1)	26.40 (26.73)	4.29 (4.45)	12.0 (12.5)
Ni[bofafucycloaene(14)]	$\text{Ni}(\text{C}_{20}\text{H}_{12}\text{N}_4\text{O}_8\text{B}_2\text{F}_4)$	Orange-red	9.7 (9.9)	39.80 (40.50)	1.90 (2.03)	9.14 (9.45)
Co[bofafucycloaene(14)]. 2H ₂ O	$\text{Co}(\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_{10}\text{B}_2\text{F}_4)$	Reddish-brown	9.2 (9.36)	37.46 (38.16)	2.40 (2.54)	8.7 (8.9)
Ni[bofaphcycloaene(14)]	$\text{Ni}(\text{C}_{28}\text{H}_{20}\text{N}_4\text{O}_4\text{B}_2\text{F}_4)$	Orange-yellow	9.04 (9.27)	52.80 (53.15)	3.0 (3.16)	8.6 (8.85)
Co[bofaphcycloaene(14)]. 2H ₂ O	$\text{Co}(\text{C}_{28}\text{H}_{24}\text{N}_4\text{O}_6\text{B}_2\text{F}_4)$	Reddish-brown	8.6 (8.8)	49.80 (50.23)	3.30 (3.58)	8.02 (8.37)
Cu[bofaphcycloaene(14)]	$\text{Cu}(\text{C}_{28}\text{H}_{20}\text{N}_4\text{O}_4\text{B}_2\text{F}_4)$	Violet	10.22 (9.97)	52.48 (52.70)	3.06 (3.14)	9.20 (8.78)

(t), thermogravimetric (TG) and differential thermal analysis (DTA) curves photographically.

Results and Discussion

A series of nickel(II) and cobalt(II) macrocyclic complexes having the stoichiometry, $NiL_2(BF_2)_2$ and $CoL_2(BF_2)_2 \cdot 2H_2O$ have been prepared employing a non-template cyclization procedure by the action of boron trifluoride on bis(pentane-2,4-dione dioximato/1,2-diphenylethane-1,2-dione dioximato/1,2-difuryl-ethane-1,2-dione dioximato) metal complexes, in ether or dichloromethane medium. Synthesis of the macrocyclic copper(II) complex of the type $CuL_2(BF_2)_2$ was successful with bis(1,2-diphenyl-ethane-1,2-dione dioximato)copper(II) chelate only. Attempts were made to prepare analogous copper(II) macrocycles with bis(pentane-2,4-dione dioximato) copper(II) chelate, but no satisfactory result could be achieved. The complexes are unaffected by strong mineral acids and dilute alkalis at room temperature but decompose in boiling mineral acids and strong alkalis. They are generally soluble in common organic solvents such as dimethyl sulphoxide, acetone and methyl cyanide. The yellow or orange-yellow nickel(II) complexes react with several nitrogen donors like ammonia, pyridine, substituted pyridines and methyl amine to yield either rosy-red or carnelian adducts. These adducts, when reacted with mineral acids, regenerate the respective parent macrocyclic complexes. The macrocyclic ligands are found to be strong field complexing agents and consistently promote spin-pairing within the metal ions. For example, bis(pentane-2,4-dione dioximato) nickel(II) is a paramagnetic complex; but on cyclization by reaction with BF_3 it gives the diamagnetic macrocyclic complex of Ni(II). In the case of Co(II) complexes, the final products are of low-spin type containing one unpaired electron per cobalt(II).

Thermogravimetric and differential thermal analyses of the complexes have been done and the complexes are found to be thermally stable to varying degrees. The nickel(II) complexes undergo a single step decomposition at 453, 633, 583 K for bofamcycloaene(16), bofaphcycloaene(14) and bofafucycloaene(14) respectively giving nickel(II) oxide as the final residue. The previously reported decomposi-

tion temperature of 643 K for Ni[bofaphcycloaene(14)] agrees well with the present results. DTA data show intense exothermic peaks at the principal decomposition temperatures followed by one or two weak and broad exothermic peaks beyond the region for the respective macrocycles. The exothermicity shows rapid oxidation of the decomposition products. Each of the cobalt(II) complexes is associated with two molecules of water. The TGA curves for the complexes show two-step decomposition. The first step of the decomposition occurs in the region 373-420 K due to the loss of water molecules as indicated by an endothermic peak for each complex. The next step of the decomposition is an exothermic process and occurs at 550, 463, 543 K for Co[bofamcycloaene(16)], Co[bofaphcycloaene(14)] and Co[bofafucycloaene(14)] respectively. The copper(II) complex, Cu[bofaphcycloaene(14)] shows no significant weight change till 493 K when it starts decomposing rapidly as indicated by an exothermic peak in DTA curve at the same temperature; the final product of decomposition is CuO .

The IR bands of structural significance are recorded in Table 2. The oximes and the bis(dioximato)-nickel(II) and -copper(II) complexes exhibit a broad and smooth band at $\sim 3200\text{ cm}^{-1}$ which is assigned to $\nu O-H$ mode of the hydrogen bonded oximes. In the macrocyclic complexes, this band completely disappears clearly implying the break-down of O-H bonds during the reaction of the oximes with boron trifluoride. A sharp and intense band in the region $1640-1580\text{ cm}^{-1}$ is observed for all the complexes which has been assigned to $\nu C \cdots N$ in the coordinated macrocycles. It is observed that the $\nu C \cdots N$ mode in all the complexes appears at a higher frequency region as compared to that in free oximes²⁴⁻²⁷. All the metal complexes show two intense and sharp bands in regions $1290-1240$ and $1120-1050\text{ cm}^{-1}$ which have been attributed to $\nu N \cdots O$ vibrations in the coordinated macrocycles. These bands, like the $\nu C \cdots N$ vibration, also appear at higher frequencies in the complexes compared to their positions in the free oximes, and these results are consistent with earlier findings^{17,18}.

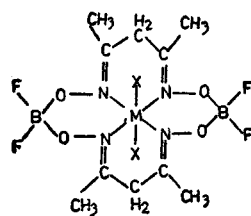
The most striking feature in the spectra of the macrocyclic complexes is the appearance of intense,

TABLE 2 — INFRARED SPECTRAL DATA (cm^{-1}) OF THE MACROCYCLIC COMPLEXES OF NICKEL(II), COBALT(II) AND COPPER(II)

Complex	$\nu C \cdots N$	$\nu N \cdots O$	$\nu B-O$	$\nu B-F$	$\nu O-H$
Ni[bofamcycloaene(16)]	1635 ms	1265 s 1075 s	1160 s 820 m	1010 vs	—
Co[bofamcycloaene(16)] $\cdot 2H_2O$	1615 ms	1290 s 1050 s	1165 s 810 m	1015 vs	3365 ms, b
Ni[bofaphcycloaene(14)]	1590 s	1240 s 1135 m	1200 s 790 m	1010 vs 1025 sh	—
Co[bofaphcycloaene(14)] $\cdot 2H_2O$	1570 m	1275 m 1120 m	1180 s 790 m	1010 vs	3400 ms, b
Cu[bofaphcycloaene(14)]	1595 s	1225 m 1125 s	1190 ms 780 m	975 vs 1000 sh	—
Ni[bofafucycloaene(14)]	1570 s	1280 m 1120 s	1180 s 835 m	1025 sh 1005 vs	—
Co[bofafucycloaene(14)] $\cdot 2H_2O$	1565s	1270 ms 1110 m	1200 ms 830 m	1005 s	3380 ms, b

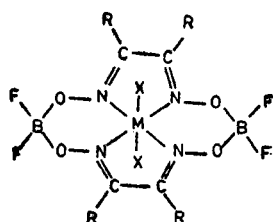
sharp and clearly identifiable bands in the region 1200-790 cm^{-1} which are absent in the spectra of the free oximes and bis(dioximato) metal complexes. These bands have been assigned to $\nu(\text{B-O})$ and $\nu(\text{B-F})$ vibrations on the basis of the findings of the earlier workers. Their presence provides evidence for the formation of new B-O bonds in the macrocycles. Since the band in the middle, i.e. near 1000 cm^{-1} is strongest, we have assigned this band to $\nu\text{-B-F}$ vibration.

The infrared and the electronic spectral data (discussed below) support an exclusive use of nitrogen atoms as donor groups with a planar environment about the metal ion in the macrocycles which can be structurally represented by (III) and (IV).



M = Ni(II), X = nil
M = Co(II), X = H₂O

III



R = C₆H₅, M = Cu(II), Ni(II) and X = nil

M = Co(II), X = H₂O.

R = C₆H₃O, M = Ni(II) and X = nil.

M = Co(II), X = H₂O

IV

The nickel(II) macrocycles are diamagnetic with a spin singlet, $^1A_{1g}$, as the ground term, and their electronic spectra are dominated by intense bands in the visible and UV regions. The first band in each complex (Table 3) is observed near 22,000 cm^{-1} which is lowest in intensity. In the case of Ni[bofamacyclaene (16)], it is fairly broad and in other cases two distinct peaks are observed near 22,000 and 25,000 cm^{-1} . These bands have been assigned to the transitions $^1A_{1g} \rightarrow ^1A_{2g}$ and $^1A_{1g} \rightarrow ^1B_{1g}$ under a square-planar environment having NiN_4 chromophore²⁸. The more intense bands observed beyond 30,000 cm^{-1} are believed to arise due to $\text{M} \rightarrow \text{L}$ (π^*) charge-transfer transitions.

TABLE 3 — ELECTRONIC SPECTRAL AND MAGNETIC DATA OF THE COMPLEXES

Complex	λ_{max} (cm^{-1})	μ_{eff} (B.M.)
Ni[bofamacyclaene(16)]	22,500 (s,b)	Diamagnetic
Ni[bofaphcyclaene (14)]	22,200; 25,000; 30,700	Diamagnetic
Ni[bofacycliclaene(14)]	22,500; 24,000	Diamagnetic
Co[bofamacyclaene(16)]. 2H ₂ O	20,000; 28,000	2.30
Co[bofaphcyclaene(14)]. 2H ₂ O	18,100; 28,500	2.10
Co[bofacycliclaene(14)]. 2H ₂ O	19,600; 28,500; 31,000	2.23
Cu[bofaphcyclaene(14)]	18,000-21,000; 28,000 (sh), 32,800	1.69

The cobalt(II) macrocycles are of low-spin type having magnetic moments in the range 2.10-2.30 B. M. The electronic spectra of this series of macrocycles show a strong and moderately broad band near 20,000 cm^{-1} followed by a more intense band near 28,000 cm^{-1} . The band near 20,000 cm^{-1} may be attributed to spin-allowed $d-d$ transitions^{23,29}. However, the relatively higher intensity of the band, leads us to believe that charge-transfer transitions also contribute to this part of the spectra. The higher energy intense bands are assigned to $\text{M} \rightarrow \text{L}$ (π^*) charge-transfer transitions.

The macrocyclic complex of copper(II) with the ligand bofaphcyclaene (14) exhibits a magnetic moment of 1.69 B.M. per copper atom suggesting the ground term to be 2D . A broad band in the range 18,000-21,000 cm^{-1} , the centre of gravity of which lies around 20,000 cm^{-1} , has been attributed to the ligand field band due to the chromophore, CuN_4 . The width of the band manifests two or three superimposed absorptions. A shoulder around 28,000 cm^{-1} followed by a strong and intense band around 32,800 cm^{-1} may be attributed to $\text{M} \rightarrow \text{L}$ (π^*) charge-transfer transition.

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