Asian Journal of Chemistry Vol. 12, No. 3 (2000), 922–924

NOTE

Fluoroboro Bridged Cyclopean-Type Macrocyclic Co(II), Ni(II) and Cu(II) Complexes

H.C. RAI*, SUSHMA SINHA† AND B.K. RAI‡
Department of Chemistry
L.S. College, Muzaffarpur-842 001, India

Diacetylmonohydrazonemonoxime (Fig. 1) reacts with formaldehyde, glyoxal and diacetyl to yield a group of ligands (Figs. 2–3) which in turn react with metal salt to give complexes as shown in Figs. 4–5. These complexes react with boron trifluoride in butanol medium to give fluoroboro-bridged macrocyclic complexes as shown in Figs. 6–8 respectively. Characterization has been done on the basis of elemental analyses, IR and electronic spectral studies as well as electrochemical study.

An interesting group of fluoroboro-bridged macrocyclic complexes derived from dioximato metal complexes have been developed since the era of synthetic macrocyclic complexes began. Complexes familiarly known as cyclops are a group of fascinating molecules and have been extensively investigated[1, 2]. Parallel to these investigations a more interesting class of clathrochelates derived from tris-(dioximato) metal complexes have been reported[3]. Electrochemical properties of these complexes have emerged in recent years[4]. More recently dinuclear clathrochelates deduced from diacetylmonohydrazonemonoxime[5] and diacetylazinedioxime have been reported. Investigations in this area offer wide scope to isolate novel complexes with diverse structural features and the present communication deals with some mononuclear fluoroboro-bridged macrocycles and some clathrochelates.

The metal salts used were of BDH make. Diacetylmonohydrazonemonoxime were prepared as reported in the literature[1, 2.] Complexes were prepared by *in situ* metal ion catalysed method. Analytical data were obtained as reported earlier[6].

Structure and bonding of the fluoroboro-bridged macrocyclic complexes have been established on the basis of infrared spectral data of well-founded molecules[1, 2] (Fig. 8). Structurally important vibrational bands corresponding to $\nu_{C=N}$, ν_{N-O}, ν_{B-O}, $\nu_{BF_4^-}$ and δ_{BF_2} are given in Table-1 for nickel(II) complexes. Infrared spectra of cobalt(II) and copper(II) macrocyclic complexes are similar. The results of infrared spectra unequivocally point to macrocyclic structure as depicted in Figs. 6–7.

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†Department of Chemistry, M.S.K.B. College, B.R.A. Bihar University, Muzzaffarpur-842 001, India.

‡Department of Chemistry, L.N.T. College, B.R.A. Bihar University, Muzzaffarpur-842 001, India.

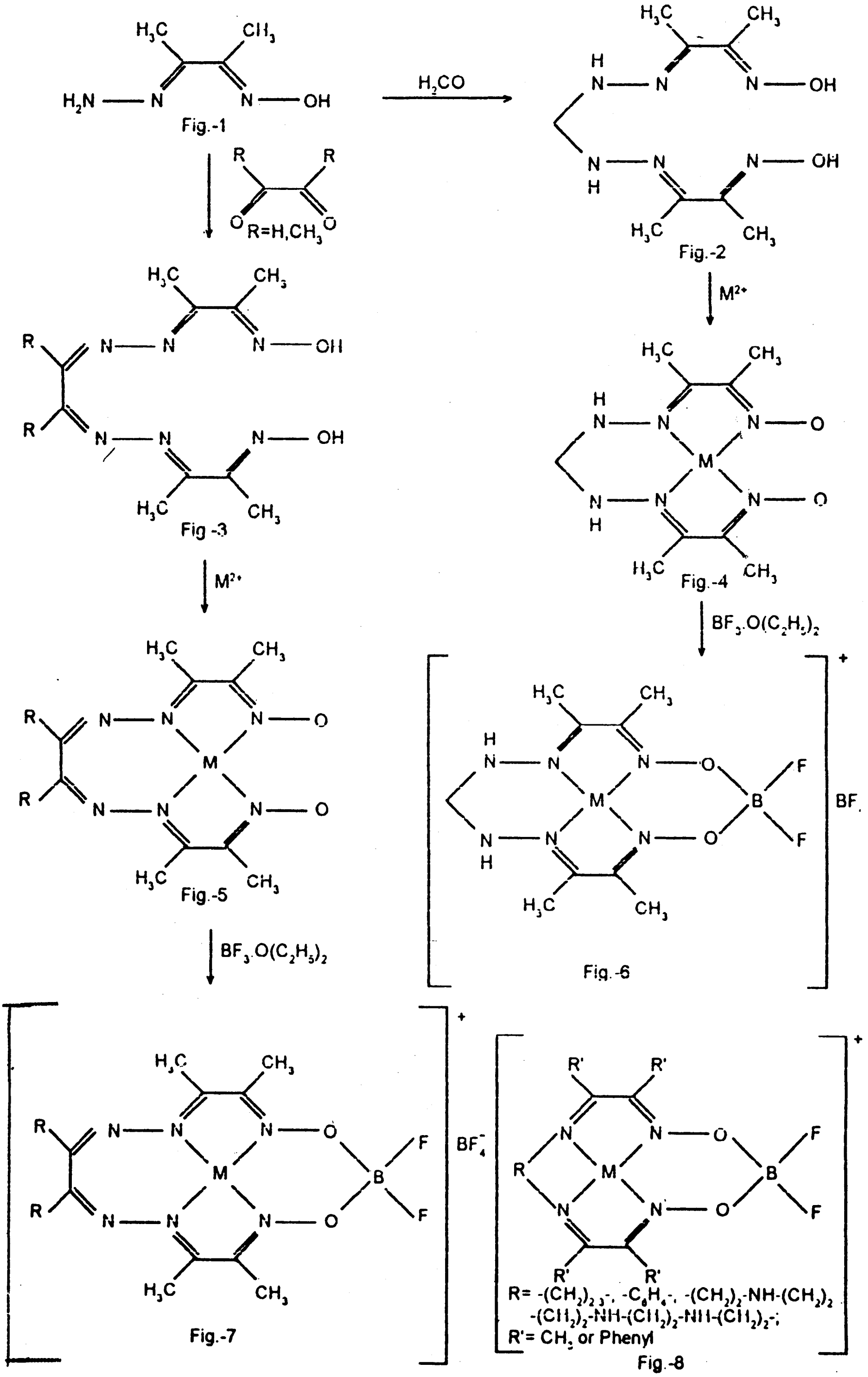
Fig.-1
H_2CO
Fig.-2
$R=H,CH_3$
Fig -3
M^{2+}
Fig.-4
$BF_3.O(C_2H_5)_2$
Fig.-5
$BF_3.O(C_2H_5)_2$
Fig.-6
BF_4^-
Fig.-7
$R= -(CH_2)_{2,3}-, -C_6H_4-, -(CH_2)_2-NH-(CH_2)_2$
$-(CH_2)_2-NH-(CH_2)_2-NH-(CH_2)_2-;$
$R'= CH_3$ or Phenyl
Fig.-8

TABLE-1

INFRA-RED SPECTRA (cm^{-1}) OF THE FLUOROBORO-BRIDGED MACROCYCLIC NICKEL(II) COMPLEXES Figs. (6–7) AND THE PRECURSORS Figs. (4–5)

Complex	ν(C=N)	ν(N—O)	$\nu(BF_4^-)$	$\delta(BF_2)$	ν(B—O)
Fig. 4	1573	1093, 1019	–	–	–
Fig. 5 (R=H)	1561, 1487	1096, 988	–	–	–
Fig. 5 (R=CH_3)	1595, 1563	1095, 1006	–	–	–
Fig. 6	1628	Buried under strong BF_4^-	1064	786	1190
Fig. 7 (R=H)	1621	-do-	1060	741	1180
Fig. 7 (R=CH_3)	1628, 1536	-do-	1057	737	1100

The cyclopean nickel(II) macrocyclic complexes are all diamagnetic which is consistent with similar complexes reported earlier. Their electronic spectrum is dominated by an intense band in the region 18,000 to 21,000 cm^{-1} and has been assigned to $^1A_{1g} \longrightarrow {}^1A_{2g}$ transitions. The results show that nickel(II) ion is placed under a square planar geometry.

The cobalt(II) macrocycles are also low-spin type. The ligand field bands for the complexes are located near 21,000 cm^{-1} originating from the $^2A_{2g} \longrightarrow {}^2E_g$ transitions.

The copper(II) mononuclear macrocyclic complexes are found to have subnormal magnetic moment (1.2–1.3 B.M.). They show a broad ligand field band near 15,000 cm^{-1} and another charge transfer band in the region 25,000 cm^{-1}.

Each cyclopean complex undergoes one electron reduction at the dropping mercury electrode and the redox process is reversible and diffusion controlled. The $E_{1/2}$ values for nickel(II), cobalt(II) and copper(II) complexes are found at about –0.73, –0.80 and –0.34 V respectively. The $E_{1/2}$ values for the precursors are observed at –0.78, –0.82 and –0.36 V respectively.

The redox process is attributed to the equilibrium for the metal(II)-metal(I) couple. The redox behaviour is primarly dependent on the ligand structure and also on the character of the metal ion.

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(*Received*: 19 February 2000; *Accepted*: 29 April 2000) AJC-2031