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AXIAL LIGATION OF ORGANIC AND INORGANIC GROUPS AND IMIDAZOLE OR ITS DERIVATIVES IN COBALOXIMES AND RELATED COMPOUNDS

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Bis-(dimethylglyoximato) cobalt(III) complexes (cobaloximes) containing the $Co(DH)_2^+$ moiety (DH^- is the monoanion of dimethylglyoxime, DH_2) reproduce many fundamental reactions of cobalamins and are of importance in the study of vitamin-B_{12} catalysed biochemical processes. Imidazole is of significant biological importance and is a component of enzymes and proteins. The macrocyclic ligand systems are also of importance in view of their presence in many biologically significant naturally occurring metal complexes, such as metallo-proteins, vitamin B_{12} and chlorophyll etc. For a closer understanding of the interaction between the cobaloxime and imidazole and between the macrocyclic complexes derived from cobaloxime and imidazole, a wide variety of such types of complexes have been synthesized where the axial octahedral positions are occupied by the CH_3 group or several halides, pseudohalides or anions like ClO_4, BF_4, NO_2, NO_3 etc. and by imidazole or derivatives of imidazole. A range of techniques including PMR, CMR, electrochemical, thermogravimetric as well as mass spectral investigations have been employed to throw light on their stability and stereochemistry. These complexes [$Co(DH)_2$ (Im) (*X*)] or [$Co(DBF_2)_2$ (Im) (*X*)] [DBF_2^- is the monoanion of the macrocyclic boronic ester ligand difluoroborondimethylglyoxime (1,8-diboro-1,1,8,8-tetrafluoro-2,7,9,14-tetraoxa-3,6,10,13-tetraaza-4,5,11,12-tetramethyl cyclotetradeca-3,5,10,12-tetraene] are shown to have rigid six-coordinate stereochemistry with a *trans*-configuration in contrast to the facile *cis* ⇌ *trans* isomerism observed for [$Co(en)_2$ (*X*) (Im)] and [Co(*acac*) (*X*) (Im)] complexes.

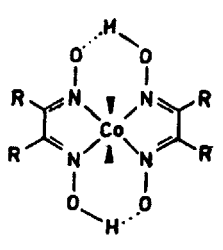
Key Words : Cobaloximes; Vitamin B_{12}; Macrocyclic Complexes; CMR; Cyclic Voltammetry; Mass Spectrometry

INTRODUCTION

THE chemistry of chelate compounds of cobalt containing stable σ-cobalt-carbon bonds are of importance in view of their very striking analogies with vitamin-B_{12} group of complexes, where organic groups are directly bonded to the metal atom.[1] These are nature's only organometallic compounds and also vitamin-B_{12} is the only vitamin known to contain a metal. So far, the only important biochemical role of cobalt that is recognised is in vitamin-B_{12} which is a co-factor for a number of enzymes.[2] This vitamin is essential for all higher animals but seems to

be synthesised exclusively by bacteria. Several compounds containing conjugated systems which act as *bis*-bidentate or tetradentate chelating ligands lying in the equatorial plane of square-pyramidal or square-bipyramidal (octahedral) structures were thus proposed as 'models' for the naturally occurring complexes of the corrin ring.[1,3,4] The corrin (tetrapyrrole) macrocyclic ring system occupies the four equatorial coordination positions while the pseudo-octahedral cobalt(III) coordination sphere is completed by the N(3) of a 5,6-dimethylbenzimidazole ring in the lower axial site and the 5'-C of 5'-deoxyadenosine in the upper coordination site. This unique Co-C linkage has generated unusual interest in the inorganic chemist. The complexes of dimethyl and other glyoximes (the so-called 'cobaloximes') and related macrocyclic ligand complexes have been invariably used as 'model' compounds as they reproduce the fundamental reactions of cobalamins and closely simulate the reactions of vitamin-B_{12}.[1,5–9] Since the dimethylglyoxime moiety imposes less steric restrictions than the corrin ligand, the stability of cobaloximes is frequently greater than that of the corresponding cobalamines. Cobaloximes are useful reagents in synthetic organic chemistry and are employed as protecting groups in the synthesis of certain amino acids.[10] Methylcobaloxime, the simplest organocobaloxime, is formed by reaction of CH_3I with the Co(I) form of cobaloxime and undergoes photolysis under nitrogen in presence of cob(II) alamin to yield some methylcobalamin and the methyl radical thus formed combines with cob(II)alamin to form a new cobalt-carbon bond.[11] The redox chemistry of cobaloximes is very similar to that of vitamin-B_{12}, producing blue or green cobalt(I) species that are very powerful reducing agents and nucleophiles.

The study of macrocyclic ligand systems is of importance in view of their presence in many biologically significant naturally occurring metal complexes, where both the metal ion and the size of the ring play an important role.[12] Investigations of macrocyclic complexes of cobalt(III) throws light on different aspects of stereochemistry,[13,14] molecular rearrangement and electrochemistry.[15,16] Imidazole behaves both as a good σ-donor as well as a π-acceptor and is a fundamental component of nucleic acids (*via* purines) and enzymes or proteins (*via* the amino acid histidine), providing a potential binding site for metal ions.[17,18]



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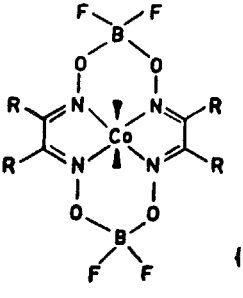

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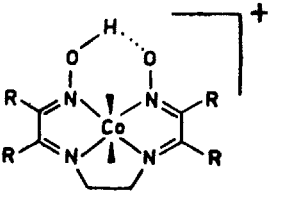


(R = CH_3 C_6H_5)

III

Indeed it is one of the choicest ligands in nature. The biological significance of cobaloximes, the macrocyclic ring systems and the imidazole prompted us to synthesise a wide variety of non-homoleptic complexes of cobaloximes with imidazoles and study their stereochemical, electrochemical and biochemical characteristics. The main types of complexes synthesised are shown below (structures I, II and III) where the effects of axial substitution of Co-C or Co-N bonds in cobaloximes are shown to depend on the increased electron-donor ability of axial ligands.[19] Earlier work from this laboratory[20–23] and by others[24,25] were centred mostly around homoleptic complexes of imidazoles with divalent first-row transition metals. Attempts to synthesise such homoleptic complexes of cobalt(III) with imidazole met with no success, eventhough it was possible to synthesise mixed-ligand systems[26,27] using imidazole alongwith the chelating ligands-ethylenediamine and acetylacetonate anion. We have been able to synthesise a number of complexes of cobaloximes by interaction with imidazole derivatives that have the general formula $[Co(DH)_2\ (L)\ (X)]$ (DH = the monoanion of dimethylglyoxime; X = Cl, CNS, CNSe, N_3, ClO_4, BF_4, NO_2, NO_3 etc.; L = imidazole, benzimidazole and their derivatives.[28–34] The report of Schrauzer[35] on the reactivity of $BF_3.Et_2O$ with bis (dimethylglyoximato) nickel(II), $[Ni(DH)_2]$ to form yellow planar macrocyclic complex-*bis* (difluoroboron dimethylglyoximato) nickel(II), $[Ni(DBF_2)_2]$ also prompted us to synthesise and elucidate the stereochemistry and stability of six-coordinated cobalt(III) complexes – $[Co(DBF_2)_2\ (L)\ (X)]$* (X = Cl, CNS; L = Im or its derivative) containing a 14-membered macrocyclic ligand system resembling the corrin system,[36] and prepared by the reaction of $BF_3.Et_2O$ with the parent cobaloximes containing an imidazole base.

Discussion

All the imidazole cobaloxime complexes were synthesised as per our reported synthetic procedure[28–34,36–38] and characterised adequately by magnetic susceptibility, electrical conductivity, electronic, IR, ^1H NMR, ^{13}C NMR and mass spectra as well as thermogravimetric measurements. The room temperature magnetic susceptibility measurements indicate the complexes to be diamagnetic as have been shown for the cyanocobalamin,[39–41] aquocobalamin,[40,42] nitritocobalamin,[43] dicyanocobalamin[42] and adenosylcobalamin.[42] Accordingly, they do not give any EPR signal in either the crystalline solid state or in frozen solutions,[44] and are cobalt(III) complexes with d^2sp^3 octahedral bonding as has been confirmed for cyanocobalamin on the basis of X-ray absorption edge measurements.[45] Most of

*Throughout this discussion DH_2 represents neutral dimethylglyoxime and DH^- its monoanion, DBF_2^- represents the monoanion of the macrocyclic boronic ester ligand difluoroborondimethylglyoxime (1,8-diboro-1,1,8, 8-tetrafluoro-2, 7,9,14-tetraoxa-3,6,10,13-tetraaza-4,15,11,12-tetramethyl cyclotetradeca-3,5,10,12-tetraene) and the archaic symbolisms CNS and CNSe indicate only the presence of the pseudohalides without specifying their mode of bonding. Further abbreviations are as follows: Im-imidazole, Me-methyl, Et-ethyl, Pr-propyl, iPr-isopropyl, Vi-vinyl, Al-allyl and DiMe-dimethyl.

these complexes are uncharged in solutions of $MeNO_2$, MeOH, Me_2CO giving only very low molar conductivity values [$\Lambda_M(\Omega^{-1}cm^2mol^{-1})$].[46]

The entire range of complexes synthesised as models for vitamin-B_{12} are beautifully coloured compounds with colours varying from yellow, red to brown. Consequently, they exhibit a very distinctive electronic spectrum (Fig. 1). The ligand field spectra of the complexes in MeOH show a peak of weak to moderate intensity[47] at around 18,000cm^{-1}. There are two other main bands centred at 40,000–42,500cm^{-1} region attributable to the intra-ligand $\pi \rightarrow \pi^*$ transition of the coordinated oxime group, whereas the band at 28,000–30,000cm^{-1} (sometimes appearing as an ill-defined shoulder) may be due to the intraligand $\pi \rightarrow \pi^*$ transition in the coordinated dimethylglyoximato anion and to the imidazole → cobalt transitions, respectively. The strong band at 47,000cm^{-1} may be due to the $d\pi(Co) \rightarrow \pi^*(DH^-)$ transition,[48,49] The general features in the spectrum of these complexes are very similar to those observed for the corrins and other alkylcobaloximes.[50]

The IR spectra of the free ligands and the complexes have been carefully analysed since this technique serves as a probe to distinguish between the *cis*- and *trans*-forms in organocobalt(III) compounds,[51,52] and they are all shown to have indeed the *trans*-configuration similar to the organocobaloximes,[53] which is further substantiated on the basis of NMR evidences, discussed below. Most of the important bands appeai in almost similar positions with identical intensity depicting the similarity in structure. In addition to the vibrational bands of the dimethylglyoximato ligand and its complexes, the vibrational spectra of the 14-membered macrocyclic ring complexes of the DBF_2^- ligand in the 1200–700cm^{-1} region demonstrates the presence of the BF_2 group. An intense band at 1005–

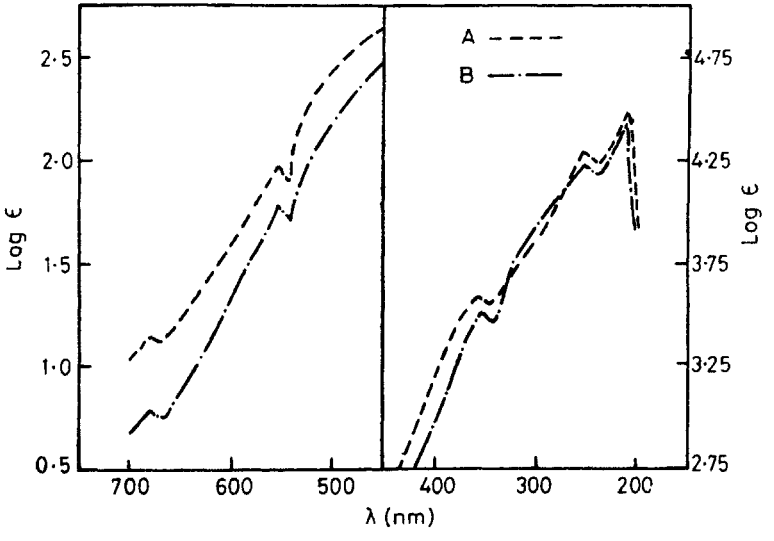


FIG 1 Electronic spectra of (A) [Co(DH)$_2$ (SCN) (2-iPrIm)] (– – –) and (B) [Co(DH)$_2$ (SCN) (2-MeIm)] (— · — · —) in MeOH

1030cm^{-1} is assignable to the ν(B-F) and two other bands of reduced intensity at 1190–1200 and 830–850cm^{-1} are attributable to ν(B–O) vibrations.[35,54] A band of moderate intensity observed around 750cm^{-1} either as a singlet or as an ill-defined doublet is assigned to the vibrations of the BF_2 group.[55] All these observations indicate the presence of the $[Co(DBF_2)_2]^+$ group in a square-plane making room for orthogonal coordination of imidazole base and an anion to the Co(III) centre to complete the octahedron. The ν(Co—N) frequencies observed at 515 and 430cm^{-1} indicate the coordination of the oximato group and the imidazole base, respectively, to the cobalt(III) centre.[28–34] The IR bands of all the polyatomic anions determine their mode of attachment to the metal centre. Particular mention is made here about the coordination of the ambidentate thiocyanate or selenocyanate ions to the cobalt(III) centre, which is a typical hard acid[56] and therefore, should be attached through the hard N-end of both the pseudohalides. However, the intensity and sharpness of the ν(CN) band for both the pseudohalo complexes clearly show Co-S (or Se) bonding[57] (Fig 2). This change in behaviour from hard to soft character of cobalt(III) is facilitated by ligands like dimethylglyoxime (DH_2) that are soft or have π-acceptor capacity and imidazole which is also a good π-acceptor, inspite of its being a good σ-donor.

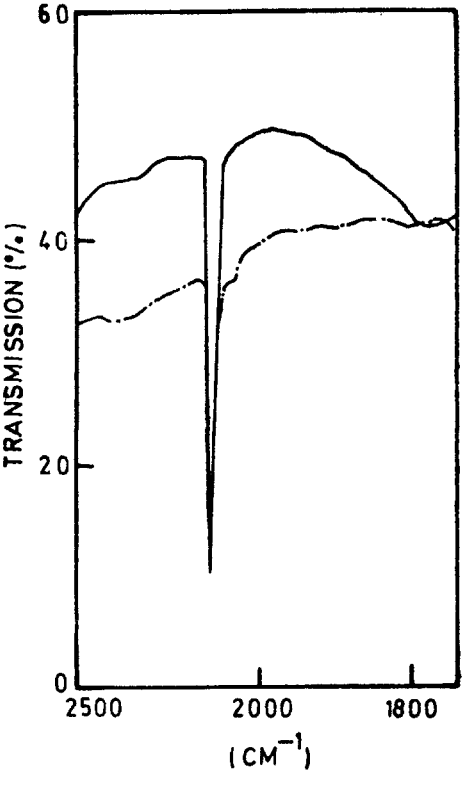


FIG 2 Partial i.r. spectra, ν (CN), of (a) [Co(DH)$_2$ (SeCN) (1-AlIm)] (———) and (b) [Co(DH)$_2$ (SeCN) (1-Vi, 2-MeIm)] (— · —)

^{1}H NMR (PMR) spectroscopy has found extensive use in the study of organocobalt(III) complexes including the cobaloximes for the examination of *cis-* and *trans-* influences, axial ligand equilibria and conformational equilibria.[58] The chemical shift of the organic group depends on several factors, including electronic and steric effects of the axial and equatorial ligands. We had earlier observed using variable temperature NMR technique[27,59] that with certain cobalt(III) complexes containing bis-bidentate ligands, e.g. ethylenediamine or acetylacetonate ion, facile *cis-trans* interconversion took place. However, the PMR shifts of the (imidazole) cobaloximes are discussed in terms of their *trans-* structure based on measurements at room temperature and at–40 °C. Some typical PMR shifts for the thiocyanato (imidazole) cobaloximes are shown in Table I.

TABLE I

Proton chemical shifts for some [*Co*(*DH*)$_2$ (*SCN*) (*Im*)] *complexes in* CD_3NO_2[a]

Compound	DH_2 protons	Imidazole protons			
	$-CH_3$ group	H-2	H-4	H-5	R
Imidazole[b]	—	7.82	7.14	7.14	—
Dimethylglyoxime[b]	1.98	—	—	—	—
[*Co*(*DH*)$_2$ (*SCN*) (1-*EtIm*)]					
(A) Room Temp.	2.39 2.33 2.31	7.35 7.28	7.15 6.68	6.65 6.50	3.91q (1-Et) 1.28t
B —40 °C	2.41 2.39 2.32	7.37 7.21	7.00 6.92	6.66 6.50	3.92q (1-Et) 1.31t
[*Co*(*DH*)$_2$ (*SCN*) (1-*AllIm*)]					
(A) Room Temp.	2.40 2.39 2.31	7.37 7.14	6.87 6.78	6.63 6.48	5.70m 5.04m (1-Al) 4.52m
(B) —40 °C	2.44 2.41 2.32	7.38 7.20	6.93 6.83	6.65 6.50	5.80m 5.10m (1-Al) 4.71m
[*Co*(*DH*)$_2$ (*SCN*) (2-*MeIm*]					
(A) Room Temp.	2.41 2.38	—	7.29	6.80	2.31 (2-Me)
(B) —40 °C	2.50 2.43 2.41	—	7.34	6.80	2.30 (2-Me)
[*Co*(*DH*)$_2$ (*SCN*) (2-*iPrIm*)]					
(A) Room Temp.	2.42 2.39	—	6.81	6.78	1.05d (2-iPr)
(B) —40 °C	2.44 2.41	—	6.84	6.73	1.06d (2-iPr)
[*Co*(*DH*)$_2$ (*SCN*) (1, 2-*DiMeIm*)]					
(A) Room Temp.	2.38	—	7.30	6.90	3.46 (1-Me) 2.25 (2-Me)

[a]—all values in ppm downfield to TMS as internal standard.

[b]—in DMF-d7.

These show that on coordination, the CH_3 groups of DH_2 at 1.98ppm undergoes a clear downfield shift by about 0.4 to 2.36–2.40ppm. The imidazole protons also undergo a considerable downfield shift and further the H-4 and H-5 protons of imidazole give rise to separate signals on complexation. The *trans*-structure is clearly observed for the chloro-and azido-complexes with imidazoles[30,32] and other N-donor ligands,[60] as only one clear signal is observed for the four equivalent methyl groups of $Co(DH)_2^+$. The *cis*-compound would have given more number of signals due to a lower symmetry. However, with the thiocyanato complexes, instead of a single peak for the four CH_3 groups as expected for the trans-configuration, either two-or three-signals are obtained indicating the presence of more than one distinct chemical species in solution. Eventhough, the available evidences in solid state favour the formulation as *trans*-$[Co(DH)_2\,(Im)\,(SCN)]$, the complexes seem on the basis of NMR evidences, to be mixtures of the neutral species

$$[Co(DH)_2\,(Im)\,(SCN)]$$

and the salt

$$[Co(DH)_2\,(Im)_2]^+\,[Co(DH)_2\,(SCN)_2]^-.$$

This tendency of salt formation was not observed in the chloro-, azido-or other cobaloximes complexes with imidazoles[28–32] and also in the difluoro-boro bridged 14-membered macrocyclic complexes[36] (Table II). The PMR signals shown in Table I indicate that in some cases the CH_3 protons of $Co(DH)_2^+$ are superimposed giving less number of peaks than expected. The imidazole protons are assigned following our earlier work[27] and signals of imidazole protons in the neutral and cationic species are also noted. The ion-pair formation shown above is believed to have been catalysed by traces of cobalt(II) (present as an impurity before the oxidation is complete).

TABLE II

Proton chemical shifts of trans-$[Co(DBF_2)_2\,(X)\,(L)]$ *complexes*[a]

Compound	DBF_2^- protons —CH_3 group	Imidazole protons				
		H-2	H-4	H-5	R	
$[Co(DBF_2)_2\,(Cl)\,(Im)]$[b]	2.30	7.50	7.02	6.75	—	
$[Co(DBF_2)_2\,(Cl)\,(1\text{-MeIm})]$[b]	2.48	7.52	7.05	6.60	3.75	(1-Me)
$[Co(DBF_2)_2\,(Cl)\,(2\text{-MeIm})]$[b]	2.36	—	7.78	6.95	2.31	(2-Me)
$[Co(DBF_2)_2\,(Cl)\,(4\text{-MeIm})]$[b]	2.28	7.35	—	6.75	2.75	(4-Me)
$[Co(DBF_2)_2\,(SCN)\,(Im)]$[c]	2.32	7.55	7.15	6.68	—	
$[Co(DBF_2)_2\,(SCN)\,(1\text{-MeIm})]$[c]	2.30	7.50	7.22	6.56	3.65	(1-Me)
$[Co(DBF_2)_2\,(SCN)\,(2\text{-MeIm})]$[c]	2.34	—	7.65	6.87	2.38	(2-Me)

a-all values in ppm downfield to TMS

b-measurements in DMSO-d_6

c-measurements in CD_3NO_2

^{13}C NMR spectroscopy (CMR) has been recognised as one of the most promising tools for the study of vitamin-B_{12} and its model compounds.[61,62] Proton decoupled natural abundance carbon-13 Fourier Transform NMR spectra are much more informative than the PMR because nearly all the lines in the ^{13}C spectrum are well resolved single carbon resonances.[62–64] The CMR spectra of the acido-cobaloxime complexes with imidazoles (Table III) indicate a downfield

TABLE III

^{13}C Chemical shifts of some [Co(DH)$_2$ (X) (Im)] complexes[a]

Compound	DH_2 carbons		Imidazole carbons			
	Oxime CH_3	imine C = N	C-2	C-4	C-5	R
(1)	(2)	(3)	(4)	(5)	(6)	(7)
Imidazole[b]			136.0	122.3	122.3	
Dimethylglyoxime[b]	9.23	154.12				
[Co(DH)$_2$ (Cl) (1-EtIm)][b]	12.42	151.97		127.6	121.8	15.89
						43.86
[Co(DH]$_2$ (Cl) (1-AlIm)][b]	12.45	151.97	138.6	127.6	122.4	50.05
						118.93
						133.63
[Co(DH)$_2$ (Cl) (2-iPrIm)][b]	12.45	152.45	158.01	127.03	117.21	21.75
						25.37
[Co(DH)$_2$ (N_3) (1-MeIm)][c]	13.02	153.68	140.39	129.11	123.99	35.67
[Co(DH)$_2$ (N_3) (1-ViIm)][c]	13.04	154.05	139.20	129.93	119.13	130.49
						105.61
[Co(DH)$_2$ (N_3) (1, 2-DiMeIm)][c]	13.05	162.28	135.15	128.41	121.84	45.33
						10.91
[Co(DH)$_2$ (N_3) (1-Vi, 2-MeIm)][c]	13.12	154.46	—	129.52	120.51	129.76
						106.67
						34.85
[Co(DH)$_2$ (N_3) (2-PrIm)][c]	13.08	154.21	—	125.9	—	95.69
						23.30
Co(DH)$_2$ (SCN) (1-EtIm)][c]	13.01	154.59	138.97	128.73	122.23	44.84
			138.73	128.49	122.06	15.88
[Co(DH)$_2$ (SCN) (1-AlIm)][c]	13.13	155.99	139.55	128.85	122.88	133.53
	13.01	154.65	139.32	128.61	122.70	120.81
						51.92
[Co(DH)$_2$ (SCN) (2-MeIm)][c]	13.36	155.00	—	129.26	116.97	13.07
		154.82				
[Co(DH)$_2$ (SCN) (2-iPrIm)][c]	13.42	155.17	—	128.15	117.56	26.30
	13.13	155.00	—	—	—	22.08
[Co(DH)$_2$ (SCN) (1, 2-DiMeIm)][c]	13.18	155.32	—	127.74	—	34.53
		154.14	—	—	—	14.00

a-all values in ppm relative to internal CD_3NO_2 or DMF-d_7 at ambient temperatures downfield to TMS

b-in DMF

c-in CD_3NO_2

shift of ^{13}C signals of ligands on complexation and the CMR measurements support the conclusions drawn on the basis of PMR measurements. The CMR spectra of some cobaloximes was reported by Trogler *et al.*[65] who suggested that the changes of CMR shifts as a function of the axially coordinated anions in cobaloximes are caused by the electronically induced (e.g., through bond) changes in the electronic environment about the carbon centre. On going from $X = Cl$ to N_3 to NCS in $[Co(DH)_2(Im)(X)]$ complexes (Im = imidazole derivative) the ^{13}C chemical shifts of the CH_3 groups of $(DH)_2$ change progressively from 12.4 to 13.0 to 13.2ppm and the imine carbon chemical shifts vary from 152.0 to 154.2 to 155.1ppm. The CMR shifts are presented in Table III. A single peak was observed as expected for the ^{13}C of the CH_3 groups of $Co(DH)_2^+$ for the chloro- and azido-imidazole cobaloxime, but for the thiocyanato-analogues, in practice invariably two (or more) signals were obtained indicating the presence of more than one distinct chemical species, i.e. the neutral compound and the ion-pair in variable proportions in solution. The CMR signals of the imidazole ligands also undergo a downfield shift to complexation and C-4 and C-5 now resonate at different fields. The C-2, C-4 and C-5 signals of the imidazole ring resonating at 136.0, 122.38 and 122.38ppm in the free ligand are shifted to 139–140, 127–129 and 116–122ppm, respectively, on complexation. The CMR signals of the substituents at 1-and 2-positions of the imidazole ring have also been appropriately assigned. Even though the CMR signals of imidazoles are obtained as single peaks for all the chloro-, azido- and most of the thiocyanato- complexes, at least in some thiocyanato complexes, more than one peak is obtained for each

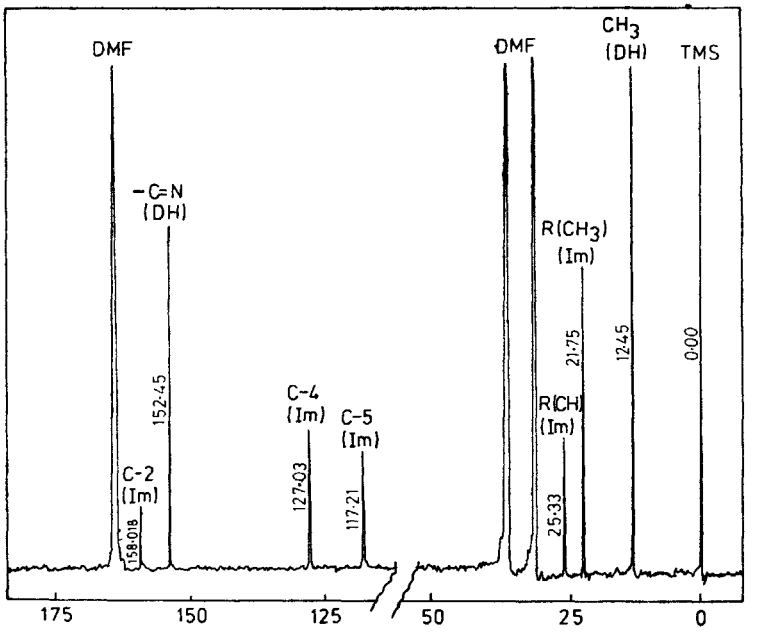


FIG 3 ^{13}C NMR spectrum of $(Co(DH)_2(Cl)(2\text{-iPrIm})]$ in DMF

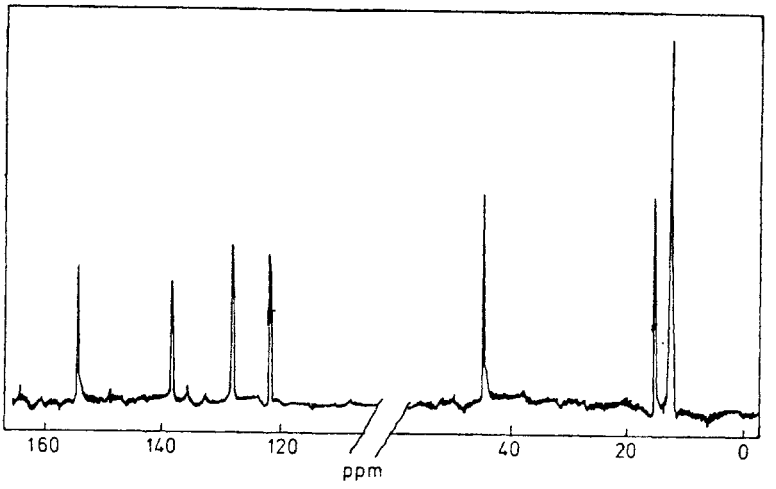
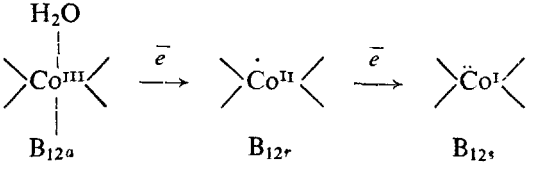


FIG 4 ^{13}C NMR spectrum of $[Co(DH)_2(SCN)(1\text{-EtIm})]$ in CD_3NO_2

of the carbons again favouring the formulation of the compounds as a mixture of the neutral species and the ion-pair, in solution, as discussed (Figs. 3 and 4).

Cyanocobalamin or any of the alkylcobalamins contain cobalt formally in the 3 + oxidation state and like all cobalt(III) complexes are diamagnetic. These cobalt(III) species, usually as cyano- or aquocobalamin, can be reduced in one-electron steps to a cobalt(II) species, B_{12r}, and then to the cobalt(I) species, B_{12s} (Eq. 1), by several reducing agents, or by electrochemical means.[66]



...(1)

Most electrochemical work on B_{12} has been centred on polarography. Hogenkamp[67] and others[68–71] investigated the polarographic behaviour of a series of cobalamins and cobinamides and observed, in general, two waves corresponding to one-electron reductions, though in some cases where the upper axial ligand is a strong nucleophile, one two-electron wave has been observed. The polarographic behaviour of cobaloximes[6] and other related complexes[72–74] indicate that a major factor in the first reduction step Co(III) → Co(II) is the nature of the axial ligand while the reduction to Co(I) depends primarily on other properties of the complex, probably the ability of the equatorial ligands to stabilise the Co(I) oxidation state. The alkylcobalt(III) complexes may be electrochemically oxidised to alkylcobalt(IV) complexes.[75–81] The $E_{1/2}$(ox) values respond to changes in the axial and equatorial ligands in manner similar to $E_{1/2}$ (red) values.[74,79] The electrochemistry of nonalkyl model compounds are similar to to alkyl cases.[74,82]

Cyclic voltammetric measurements of the *trans*- azido (imidazole) cobaloxime complexes in MeCN were carried out and the results shown in Table IV and Figs. 5 and 6. Five reductive steps were obtained negative of the saturated calomel electrode, some not well defined. The first two ill-defined reductive responses which almost mask each other may be attributed to a gradual reduction of cobalt(III) to cobalt(II) resulting in total transfer of one-electron at the end of the second step. The third distinctive step at *ca.* −1.6V, is due to the reduction of cobalt(II)

TABLE IV

Cyclic voltammetric peak potential (V vs SCE) data[a] of azidocobaloximes in MeCN at 25 °C, glassy carbon working electrode

Compound	+ve side of SCE E°_{298} V(E_p mV)	−ve side of SCE E_{pc}, *V vs* SCE
$[Co(DH)_2(N_3)$ (1-ViIm)]	1.06 (60 mV)	−0.80, −1.10, −1.60, −2.16, −2.31
$[Co(DH)_2(N_3)$ (1-AlIm)]	1.04 (70 mV)	−0.91, −1.15, −1.60, −2.18, −2.37
$[Co(DH)_2(N_3)$ (1-Vi 2-MeIm)]	1.04 (80 mV)	−0.66, −1.08, −1.64, −2.12, −2.28
$[Co(DH)_2(N_3)$ (BzIm)]	1.08 (70 mV)[b]	−0.90, −1.15, −1 62, −2.12, −2.28[c]

a-conditions are as follows : Scan rate 50mv s^{-1}, solute concentration 2.0—2.6 × 10^{-3} M, supporting electrolyte TEAP. The reported E_{pc} values are uncorrected for junction potentials.

b-Pt electrode

c-HMDE electrode.

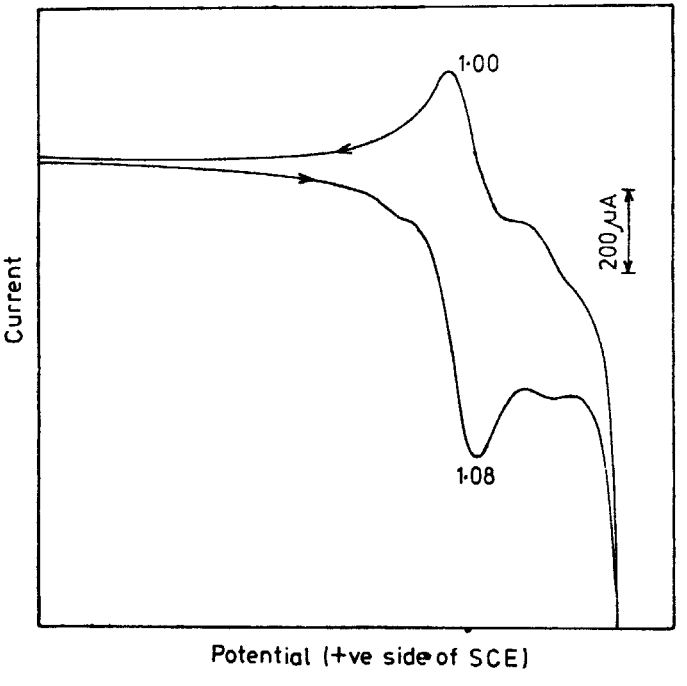


FIG 5 Cyclic voltammogram of $[Co(DH)_2(N_3)$ (1-Vi 2-MeIm)] (+ve side of SCE, oxidation)

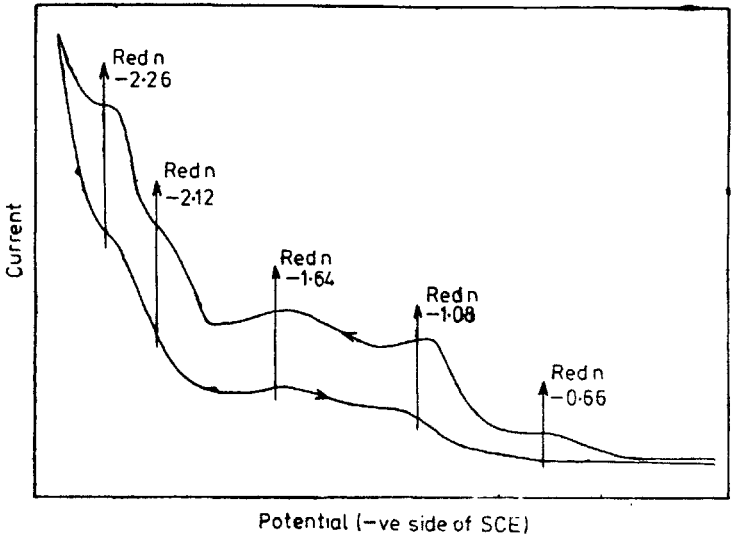


FIG 6 Cyclic voltammogram of $[Co(DH)_2(N_3)(1\text{-Vi }2\text{-MeIm})]$ (—ve side of SCE, reduction)

to cobalt(I). The fourth and the fifth waves seem to correspond to the reduction of cobalt(I) to cobalt(0). Under comparable conditions, these azidocobaloximes exhibit cathodic waves at *ca.* −0.66 to −0.90, −1.10, −1.60, −2.12 and −2.31V. Schrauzer *et al.*,[6] in the polarographic reduction of $[Co(DH)_2(Py)(Cl)]$, have reported four cathodic waves of which the first three are associated with the reduction of cobalt and the last one, with reduction of the pyridine ligand, indicating the presence of cobalt in the 3 + state. Our cyclic voltammetric studies point to an almost similar behaviour for $[Co(DH)_2(N_3)(Im)]$ and $[Co(DH)_2(Py)(Cl)]$, except for the existence of the fifth reduction wave, which is somewhat ill-defined and which may be due to the reduction either of the cobalt or of the ligand. However, the proximity of the not so well-defined fourth and fifth waves at −2.1 and −2.2V does not permit an unambiguous conclusion to be drawn. Nevertheless, all these observations clearly suggest the existence of cobalt in the 3 + state, in contrast to the alkylcobaloximes where the metal seems to be in a formal 2 + state.[6] An interesting observation in the cyclic voltammetric measurements of these complexes is the presence of a reversible oxidative peak at *ca.* + 1.0V (Pt electrode).[33] This is a very well-defined one-electron oxidation process, indicating the formation of cobalt(IV). A similar observation has been reported and formation of cobalt(IV) has been confirmed by spectral titrations and cyclic voltammetry.[83,84] For the macrocyclic boronic ester complexes, $[Co(DBF_2)_2(X)(Im)]$ (X = Cl, CNS), invariably three or four reductive responses on the negative side of SCE are obtained[36] under identical conditions (Table V) in contrast to the observation of five reductive waves for $[Co(DH)_2(N_3)(Im)]$ complexes.[33] The first three reductions are again due to the reduction of cobalt(III) → cobalt(II), cobalt(II) → cobalt(I) to cobalt(O), whereas the fourth one corresponds to the reduction of the ligand.[6] The reductions of these complexes which take place at a lower potential may be

TABLE V

Cyclic voltammetric peak potential (V vs SCE)·data[a] of macrocyclic boronic ester complexes in MeCN at 25 °C, platinum working electrode

Compound	+ve side of SCE (oxdn.)			—ve side of SCE (redn.)		
	E_{pa}	E_{pc}	E°_{298}	E_{pc}	E_{pa}	E°_{298}
$[Co(DBF_2)_2 (SCN) (Im)]$	1.32	1.23	1.275	—0.62	—0.53	—0.58
				—0.92	—0.80	—0.86
				—1.20	—1.09	—1.15
$[Co(DBF_2)_2 (SCN) (1\text{-MeIm})]$	1.30	1.20	1.25	—0.59	—0.46	—0.53
				—0.92	—0.76	—0.84
				—1.20	—1.08	—1.14
$[Co(DBF_2)_2 (SCN) (2\text{-MeIm})$	1.20	1.07	1.135	—0.56	—0.30	—0.43
				—0.86	—0.73	—0.81
				—1.18	—1.02	—1.10
				—1.97	—1.86	—1.92
$[Co(DBF_2)_2 (SCN) (4\text{-MeIm})]$	1.02	0.94	0.98	—	—	—
				—0.84	—0.74	—0.79
				—1.19	—1.12	—1.15
				—1.82	—1.26	—1.54

a—conditions are as follows : Scan rate 50mv s^{-1}, solute concentration 3.0×10^{-3} M, supporting electrolyte TEAP. The reported E_{pc} values are uncorrected for junction potentials

due to the $-BF_2$ group in close proximity to the cobalt centre. All these again indicate the existence of the cobalt(III) centre in contrast to the alkylcobaloxime complexes.[6] These macrocyclic complexes[63] also record a reversible oxidative peak at about + 1.0V(Pt electrode) similar to the azido-cobaloximes[33] due to the one-electron oxidation of cobalt(III) to cobalt(IV)[84] (Fig. 7).

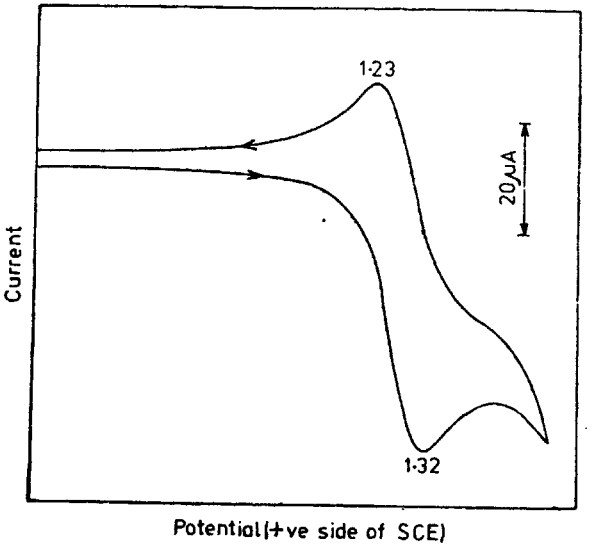


FIG 7 Cyclic voltammogram of $[Co(DBF_2)_2 (SCN) (Im)]$ (+ve side of SCE)

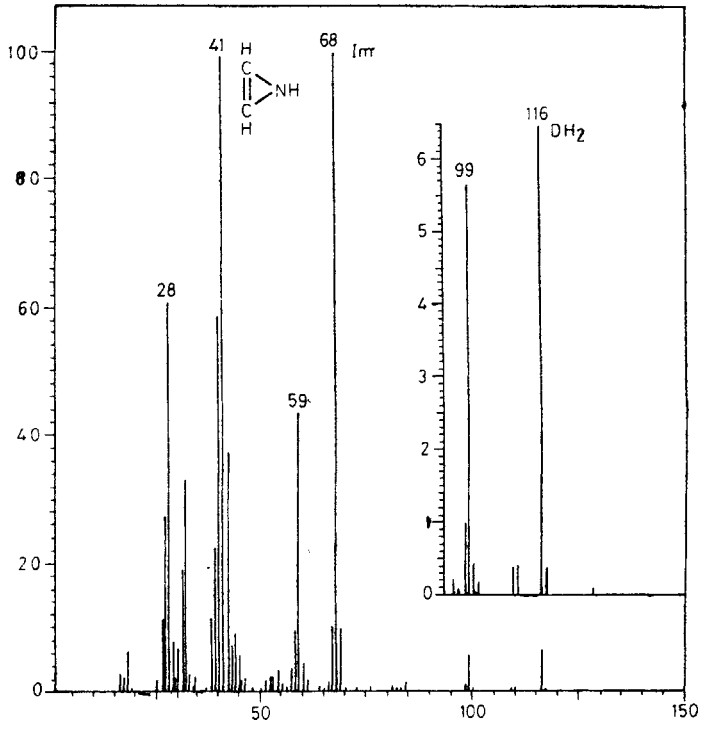


FIG 8 Mass spectra of [Co(DH)$_2$ (SCN) (Im)]

A comparative investigation of the mass spectral studies of free DH_2, $Ni(DH)_2$, [$Co(DH)_2$ (*X*) (Im)] and [$Co(DBF_2)_2$ (*X*) (Im)] complexes reveal the formation of molecular-ion peaks for both DH_2 and $Ni(DH)_2$ but not for the macrocyclic complexes[36] [$Co(DBF_2)_2$ (*X*) (Im) and the precursor cobaloxime complexes[28,34] [$Co(DH)_2$ (*X*) (Im)], indicating the comparable stability of the parent cobaloximes and the derived macrocyclic complexes (Fig. 8). The thermal-decomposition studies indicate that the thermal stability of all the cobaloximes is very high as compared to the macrocyclic derivatives. However, all the complexes decompose on heating, yielding polymeric intermediates and finally, Co_3O_4 as the ultimate end product.

CONCLUSION

Our extensive investigations show that eventhough imidazole and its derivatives form a wide variety of both homo- and hetero-leptic complexes with cobalt(II), only heteroleptic mixed-ligand complexes are formed by the interaction of imidazole with cobalt(III). With ethylenediamine, complexes of the type *cis*-[$Co(en)_2$ (*X*) (Im)] are formed whereas with acetylacetonate the *trans*-[$Co(acac)_2$ (*X*) (Im)] complexes are formed which undergo facile *cis* $\rightleftharpoons$ *trans* interconversion in solution. However, with dimethylglyoxime and related ligands only rigid *trans*-[$Co(DH)_2$ (*X*) (Im)] complexes are formed, which is further substantiated by

their interaction with $BF_3.Et_2O$ to form the 14-membered macrocyclic complexes $[Co(DBF_2)_2\ (X)\ (Im)]$ which have the necessary *trans*-configuration.

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