Inorganica Chimica Acta, 204 (1993) 109–124

A detailed infrared and far-infrared spectral investigation of the alkyl- and (non-alkyl)cobalt(III) complexes of 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime and a study of ground state *trans*-effect in tetragonally distorted octahedral cobalt(III) complexes by far-infrared and electronic absorption spectroscopy

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(Received April 6, 1992; revised September 21, 1992)

Abstract

The tetraaza quadridentate chelate, 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime [$(DOH)_2$bzo], forms stable tetragonally distorted octahedral cobalt(III) complexes with monodentate ligands such as halogens, pseudohalogens and Lewis bases in the axial sites besides forming pseudooctahedral alkylcobalt(III) complexes. A detailed IR and far-IR spectral investigation has been made for nine alkyl- and nineteen (non-alkyl)cobalt(III) complexes, reported recently. These complexes exhibit IR absorptions such as ν(OH), ν(CH), ν(NO), ν(C=N), ν(C=C), ν(C–N), ν(C–C) and C–CH_3 symmetric and asymmetric deformation vibrations characteristic of the (DO)(DOH)bzo ligand framework and absorptions characteristic of the axial ligands. In the case of the complexes of aromatic Lewis bases vibrations such as ring deformation, ring breathing mode, ring stretchings and ring torsion characteristic of the aromatic rings are observed. Spectral evidence is obtained for the formation of an intramolecular hydrogen bond. The effect of hyperconjugative electron release and π-backbonding are manifested in the spectra of the complexes of 4-methylpyridine and triphenylphosphine, respectively. The far-IR spectra show vibrations such as ν(Co–N), ν(Co–Br), ν(Co–C) and ν(Co–base) (Lewis base in the axial site). The ground state *trans*-effect in a series of tetragonally distorted octahedral (non-alkyl)cobalt(III) complexes of the type $[LCo((DO)(DOH)bzo)Br]^+$ (where L = a Lewis base such as pyridine, imidazole, methylimidazole, 4-methylpyridine, benzimidazole, 5,6-dimethylbenzimidazole, ethylamine, diethylamine, triethylamine, 2-aminopyridine, triphenylphosphine) is studied by following the variation of the Co–Br stretching frequency on the field strength, Dq^z, of the Lewis base in the axial site, *trans* to Br^-. A plot of ν(Co–Br) frequency versus Dq^z is linear and as the Dq^z increases ν(Co–Br) frequency decreases. As the electron donating power of the axial Lewis base increases it transmits more electron density to Co^{3+} with a concomitant transmission of electron density to Br^-, *trans* to the Lewis base, thereby weakening the Co–Br bond. This is the first report of the ground state *trans*-effect being studied using a quantitative measure of the electron donating ability of a series of test ligands on the ground state property of a probe ligand involving a heavy atom in six-coordinate cobalt(III) complexes.

Introduction

One of the fascinating properties of coordination compounds is the effect of one ligand on the physical and chemical properties of another ligand caused by the internal electronic transmission through the central metal ion, called the *cis*- and *trans*-effect [1–35]. The existence of ground state [1–15], thermodynamic [3, 7, 13, 16–21] and kinetic [3, 19, 20, 22–35] *cis*- and *trans*-effects in pseudooctahedral cobalt(III) complexes has been extensively studied. The ground state *trans*-effect reflects the effect of one ligand on the ground state properties of another ligand in the *trans* position of a complex. The biochemical reactivity of alkylcobalamin coenzymes is largely influenced by axial ligation through the electronic effects. The influence of the electronic effects on the Co–N (axial base) bond lengths in non-organometallic Costa-type complexes studied very recently by Gerli and Marzilli [36] reveals lengthening of the Co–N distances with the σ-donor power of the *trans* axial ligand. A similar observation has been made by Marzilli and co-workers [37, 38] in their studies on the structural properties of cobaloximes and Costa-type models.

Vibrational spectroscopic techniques (i.e. IR and Raman) hold the promise of providing molecular information in both the solid state and solution. IR spectroscopy has been employed to study the ground

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state *trans*-effect in alkyl- and (non-alkyl)cobalt(III) complexes [2, 6–9]. The frequency of the CN stretching vibration of the axially bound CN^- in organocobalamins [7], organocobaloximes [8] and organopentacyanocobaltates [9] has served as a monitor of the ground state *trans*-effect. In these compounds the ground state *trans*-effect was studied by following the effect of alkyl groups on the CN stretching frequency. It has been observed that as the electron donating power of the alkyl group increases the cyanide coordinated in the *trans* position becomes more ionic and the CN stretching frequency decreases [7]. In these studies the ground state *trans*-effect of the axial ligands is not related to a quantitative measure of their electron donating ability and the dependence of the ν(CN) frequency on the *trans* ligand is studied qualitatively.

The near-IR-excited Fourier transform Raman spectroscopic investigations of the coenzyme B_{12} and organocobalt model compounds have been reported very recently by Marzilli and co-workers [39–41]. This new technique percludes electronic transitions and thus completely eliminates fluorescence interference and Co–C bond photolysis encountered previously in the resonance Raman studies [42–45] of related organocobalt compounds and is capable of providing rich vibrational information of the Co–C bond moiety, the axial ligand and the equatorial ligand system in both the solid state and in solution [39–41]. The non-resonant FT-Raman spectra of these compounds provide informations such as conclusive identification of the Co–C stretching frequency, the *trans*-effect and the environmental effect. The FT-Raman results clearly demonstrate that the nature of the *trans* ligand profoundly influences the Co–C bond stretching frequency [39]. The dependence of the corrin vibrational frequencies on the nature of the sixth axial ligand in coenzyme B_{12}, methylcobalamin and cyanocobalamin demonstrates the existence of the ground state *cis*-effect [40]. Thus the *trans* electronic effects, *cis* electronic effects, and *trans* steric influence on the Co–C bond cleavage in the biologically active cobalamins and in the coenzyme B_{12} model compounds have been studied. In all these IR and FT-Raman spectral studies the electronic transmission of the axial ligands is not related to a quantitative measure of their electron donating ability. Therefore a quantitative study of the influence of the electronic transmission of the axial ligands (test ligands) using a quantitative measure of their electron donating ability on the ground state properties of a probe ligand seems imperative. The quadridentate oxime-imine chelate, 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime [46] forms a wide variety of six-coordinate cobalt(III) complexes with halogens [46], pseudohalogens [46], Lewis bases [46, 47] and sulfur ligands [40] in the axial sites. It also forms organocobalt(III) complexes which serve as intriguing coenzyme B_{12} models [46]. These complexes enable the systematic study of the spectral properties of the axial ligands in an identical ligand framework. Therefore a detailed IR and far-IR spectral investigation of the alkyl- and (non-alkyl)cobalt(III) complexes of the $(DOH)_2$bzo chelate is undertaken and the ground state *trans*-effect of eleven Lewis bases is studied by following the variation of the ν(Co–Br) frequency on the field strength, Dq^z, of the Lewis bases in tetragonally distorted octahedral (Lewis base)cobalt(III) complexes. The results are presented herein.

Experimental

Synthesis of the ligand and complexes

The ligand, 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime [$(DOH)_2$bzo], was synthesized by the reported procedure [46]. It coordinates with cobalt in the equatorial plane as a monoanion with the concomitant formation of an intramolecular hydrogen bond. Coordination of monodentate ligands in the axial sites yields six-coordinate cobalt(III) complexes. Dihalo cobalt(III) complexes are synthesized by treating the free ligand with cobalt(II) halide hexahydrate. By making use of the lability of the axial bromide ions in the dibromo complex, [Co((DO)(DOH)bzo)Br_2], Lewis base complexes of the type $[LCo((DO)(DOH)bzo)Br]^+$ are synthesized by treating the dibromo complex with the respective base in a 1:1 mole ratio. The following alkyl- and (non-alkyl)cobalt(III) complexes are used for the IR and far-IR spectral investigation: [Co((DO)(DOH)bzo)Br_2] (**1**), [Co((DO)(DOH)bzo)Cl_2] (**2**), [Co((DO)(DOH)bzo)I_2] (**3**), [(SCN)Co((DO)(DOH)bzo)Br] (**4**), [(CN)Co((DO)(DOH)bzo)Br] (**5**), [N_3Co((DO)(DOH)bzo)Br] (**6**), [pyCo((DO)(DOH)bzo)Br]$ClO_4 \cdot H_2O$ (**7**), [IzCo((DO)(DOH)bzo)Br]PF_6 (**8**), [pyCo($(DO)_2(BF_2)$bzo)Br]Br (**9**), [pyCo((DO)(DOH)bzo)CH_3]$ClO_4 \cdot H_2O$ (**10**), [IzCo((DO)(DOH)bzo)CH_3]$ClO_4 \cdot H_2O$ (**11**), [PPh_3Co((DO)(DOH)bzo)CH_3]$ClO_4 \cdot H_2O$ (**12**), [Me_2BIzCo((DO)(DOH)bzo)CH_3]$ClO_4 \cdot H_2O$ (**13**), [pyCo((DO)(DOH)bzo)C_2H_5]$ClO_4 \cdot H_2O$ (**14**), [IzCo((DO)(DOH)bzo)C_2H_5]$ClO_4 \cdot H_2O$ (**15**), [pyCo((DO)(DOH)bzo)-C_6H_{11}]$ClO_4 \cdot H_2O$ (**16**), [pyCo((DO)(DOH)bzo)i-Pr]$ClO_4 \cdot H_2O$ (**17**), [pyCo((DO)(DOH)bzo)$C_6H_5CH_2$]$ClO_4 \cdot H_2O$ (**18**), [MeIzCo((DO)(DOH)bzo)Br]Br$\cdot H_2O$ (**19**), [BIzCo((DO)(DOH)bzo)Br]$BF_4 \cdot H_2O$ (**20**), [Me_2BIzCo((DO)(DOH)bzo)Br]PF_6 (**21**), [PPh_3Co((DO)(DOH)bzo)Br]Br$\cdot 0.5H_2O$ (**22**), [$EtNH_2$Co((DO)(DOH)bzo)Br]$ClO_4 \cdot H_2O$ (**23**), [Et_2NHCo((DO)(DOH)bzo)Br]$ClO_4 \cdot 0.5H_2O$ (**24**), [Et_3NCo((DO)(DOH)bzo)Br]ClO_4 (**25**), [4-CH_3pyCo((DO)(DOH)bzo)Br]$PF_6 \cdot H_2O$ (**26**), [2-NH_2pyCo((DO)(DOH)bzo)Br]Br (**27**).

The complexes **1–18** are reported in ref. 46 and **19–27** are reported in ref. 47. All these complexes have been isolated in the solid state and characterized by C, H, N and Co analysis, conductivity and magnetic susceptibility measurements, IR, far-IR, UV–Vis and ^{1}H NMR spectroscopy and electrochemical studies.

Physical measurements

Electronic absorption spectra

The electronic absorption spectra were recorded on a Shimadzu UV 300 double-beam/difference/dual-wavelength recording spectrophotometer in the 225–800 nm region by using a matched pair of teflon-stoppered quartz cells having a path length of 1 cm at 25 °C. The spectra in the visible region were recorded using $\sim 10^{-3}$ M solution of the complex in electrochemically pure DMF [49] and the UV spectra were recorded in absolute methanol [50].

Infrared spectra

IR spectra were recorded in the solid state using potassium bromide plates on a Perkin-Elmer 598 infrared spectrophotometer in the 4000–200 cm^{-1} region. Spectroscopic grade KBr (Merck) was used to make the KBr plates.

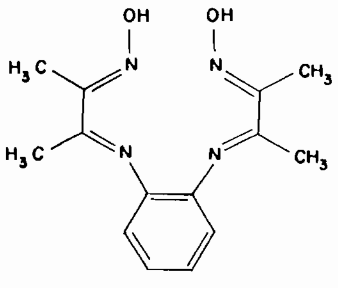
Far-infrared spectra

The far-IR spectra were recorded in the 500–50 cm^{-1} region on a Polytec IR 30 Fourier spectrometer using polyethylene disc and on a Hitachi model FIS-3 far-IR spectrophotometer in the 400–30 cm^{-1} region in nujol mull plastered on a polyethylene plate.

Results and discussion

Infrared spectrum of the ligand

The IR spectrum of the ligand (structure I) shows no characteristic absorption bands assignable to either a C=O or NH$_2$ function. The sharp bands of medium intensity occurring at 1575 and 1630 cm^{-1} are attributed to ν(C=N) [51–53] and ν(C=C) [54], respectively. The strong as well as sharp band at 1220 cm^{-1} is due to the N–O stretching vibration [53, 55]. The broad bands of medium intensity appearing at 3060 and 3200 cm^{-1} and the weak band at 3280 cm^{-1} are due to the CH stretching vibrations [56]. The broad band at around 2900 cm^{-1} is assignable to ν(OH) [57]. The C–CH$_3$ asymmetric stretching vibration is expected to occur at around 2900 cm^{-1}. Therefore the broadness of the band at 2900 cm^{-1} is due to the overlapping of the ν(OH) with ν_a(C–CH$_3$). Upon complexation with cobalt this band is shifted to a lower energy region due to hydrogen bonding. The very strong band of medium broadness at 1480 cm^{-1} and the weak band at 1430 cm^{-1} are assigned to the ring modes of *o*-disubstituted benzene moiety of the ligand framework [52]. The *o*-disubstituted phenyl ring also exhibits several additional bands in the lower energy region. Thus the sharp bands at 1260, 1130 and 990 cm^{-1} are due to the *o*-disubstituted benzene [54]. For the substituted benzene compounds the weak bands occurring in the 2000–1670 cm^{-1} region are characteristic of the substitution type. Therefore, the weak bands at 1940, 1825 and 1710 cm^{-1} are assigned to *o*-disubstituted benzene moiety. The sharp bands of medium intensity at 1375 and 1445 cm^{-1} are due to the C–CH$_3$ symmetric and asymmetric deformation vibrations, respectively [53].



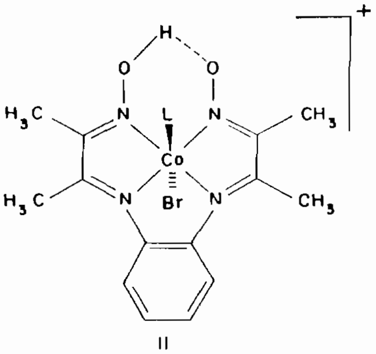
I

(DOH)$_2$bzo

The strong and sharp bands appearing at 1260, 1180 and 1130 cm^{-1} are assignable to ν(C–C), ν(C–N) or the coupled vibrations of these modes. The metal sensitive strong as well as sharp band at 765 cm^{-1} may be attributed to C=N–O deformation vibration. Upon complex formation with cobalt this band is shifted to 740 cm^{-1} (*vide infra*). The strong and sharp band at 705 cm^{-1} is due to the C–H deformation vibration of the benzene ring. Metal dependent IR absorption bands appearing in the 990–900 cm^{-1} region can be ascribed to the deformation vibrational modes of the ligand. A similar observation has been made in the IR spectral studies of metalloporphyrins by Boucher and Katz [58] and by Ogoshi *et al.* [56]. The ligand exhibits three strong and sharp bands at 990, 920 and 910 cm^{-1}. The intensity of the band at 990 cm^{-1} is reduced considerably while the bands at 920 and 910 cm^{-1} disappear in the complexes. This indicates that the higher intensity of the 990 cm^{-1} band of the ligand should be due to strong coupling of the *o*-disubstituted phenyl ring vibration with the deformation mode of the macrocycle. The bands which occur in the 670–290 cm^{-1} region are difficult to assign empirically.

Infrared spectra of the dihalo complexes

The characteristic IR absorption bands of the ligand are shifted to lower energy with reduction in intensity on complex formation and new absorption bands characteristic of the complexes appear. The broad band of medium intensity occurring at 2290 cm^{-1} in the free ligand is shifted to 2400 cm^{-1} in [Co((DO)(DOH)-bzo)Br_2] (structure II). This is attributed to the



II

$[LCo((DO)(DOH)bzo)Br]^+$

L = Lewis base

ν(OH) of the hydrogen bond. Blinc and Hadzi [57] in their IR spectral studies of bis(dimethylglyoximato)-nickel(II) complexes also report the occurrence of ν(OH) of the hydrogen bond in the 2300–2900 cm^{-1} region. The sharp band of medium intensity occurring at 2920 cm^{-1} is assigned to the asymmetric C–CH_3 stretching vibration. Disappearance of the δ(OH) band which appears at 1405 cm^{-1} in the free ligand is further evidence for O–H - - O bond formation on complexation. The ν(C=N) band appearing at 1575 cm^{-1} in the free ligand is shifted to 1490 cm^{-1} as a broad band. This suggests that the ligand is coordinated to the metal ion through the nitrogen donors. The dibromo complex exhibits ν(NO) at 1220 cm^{-1} as in the free ligand. The C–CH_3 symmetric and asymmetric deformation vibrations occur at 1370 and 1435 cm^{-1}, respectively. The unique feature of the IR spectra of the complexes is the occurrence of a new strong and sharp band in the 1070–1090 cm^{-1} region and another sharp band at around 520 cm^{-1} which are not found in the spectrum of the free ligand. In agreement with the detailed IR spectral studies on cobaloximes by Yamazaki and Hohokabe [53], the latter band is assigned to ν(Co–N) (N donors of (DO)(DOH)bzo). In organic nitroso compounds ν(N=O) vibration occurs in a wider energy region depending upon the double bond character [59]. For simple oximes [60] it appears between 930 and 960 cm^{-1} and for quinone oxime [61] it is found at a higher frequency probably due to increase in double bond character due to resonance. Therefore the sharp band occurring in the 1090–1070 cm^{-1} region in all the complexes is assigned to ν(NO)*. The appearance of only one band at 1220 cm^{-1} in the free ligand shows that the two –NOH groups are identical while the appearance of two bands at 1220 and 1075 cm^{-1}, both assignable to ν(NO), in [Co((DO)(DOH)bzo)Br_2] confirms the presence of two unequal N–O linkages, C=N–O - - H and C=N–O–H. Studies on cobaloximes by Schrauzer and Windgassen [55], Yamazaki and Hohokabe [53] and Blinc and Hadzi [57] also confirm the presence of two unequal N–O linkages. The characteristic IR absorption bands of the dihalo complexes are presented in Table 1.

Infrared spectra of the pseudohalogeno complexes

The CN stretching frequency of the free cyanide ion occurs at 2080 cm^{-1} (aqueous solution) [62]. Upon coordination to a metal ν(CN) shifts to higher frequency, a property unique to CN^-. In [(CN)Co((DO)-(DOH)bzo)Br] ν(CN) occurs at 2160 cm^{-1}. This enhancement in ν(CN) frequency of the cyanide ion upon coordination is attributed to its better σ-donor and poor π-acceptor property. The weak band at 440 cm^{-1} is ascribed to ν(Co–C)(CN). This vibration occurs within the region (600–300 cm^{-1}) of the M–C stretching vibration found in various hexacyano complexes [63]. The CN stretching frequency of the free thiocyanate ion occurs at 2068 cm^{-1} in aqueous solution [64]. Upon coordination ν(CN) changes in frequency depending on the mode of coordination. The CN stretching frequencies are generally higher for thiocyanato complexes than for isothiocyanato complexes [65]. The ν(CN) occurs in the former near and below 2050 cm^{-1} whereas in the latter it occurs above 2100 cm^{-1}. [(SCN)Co((DO)(DOH)bzo)Br] exhibits a very strong and sharp band at 2150 cm^{-1} assignable to ν(CN). The higher energy of ν(CN) may probably be due to the formation of thiocyanato complex. Another criteria employed in structural diagnosis is the frequency of the ν(CS) vibration. The N-bonded isomer exhibits ν(CS) vibration in the 860–760 cm^{-1} range and the S-bonded isomer in the 720–690 cm^{-1} range [65]. Therefore the strong absorption band of medium broadness occurring at 740 cm^{-1} in [(SCN)Co((DO)(DOH)bzo)-Br] may be attributed to the ν(CS) vibration of the thiocyanato complex**. The weak band appearing at 485 cm^{-1} is attributed to the Co–SCN vibration. The sulfur atom is a weaker σ-donor than the nitrogen atom in SCN^-. The M–S bond is stabilized by π-backbonding from metal to sulfur. When the ligand is a strong π-acceptor, the M–S π-bond is so reduced in strength that the N-bonded isomer becomes the stable one. Since the $(DOH)_2$bzo ligand with four imine nitrogen donors is a poor π-acceptor the Co–S π-bond character is not

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*The two NO stretching vibrations occurring at 1220 cm^{-1} and in the 1075 cm^{-1} region are labelled as ν(NO) and ν'(NO), respectively.

**The dibromo complex also exhibits a sharp band at 740 cm^{-1}. The increase in intensity and broadening of this band in [SCNCo((DO)(DOH)bzo)Br] may probably be due to the coupling of the ν(CS) vibration with a vibration characteristic of the dibromo complex.

TABLE 1. Characteristic IR absorption bands (cm^{-1}) of the dihalo and pseudol

Complex	Assignments[b]							Absorption of the axial ligands	
	ν(CH)	ν(OH)	ν(C=C)	ν(C=N)	ν(NO)	ν'(NO)	ν(Co–N)	Band (cm^{-1})	Assignments[b]
[Co((DO)(DOH)bzo)Br$_2$]	3040w,b 3200w,b	2400b,s	1605sp,w	1490s	1220vs,sp	1075vs,sp	520vs,sp		
[Co((DO)$_2$(BF$_2$)bzo)Br$_2$]	3450s,b		1620vs,sp	1515vs,sp	1210vs,sp		510w,sp		
[Co((DO)(DOH)bzo)Cl$_2$]	3040b,w 3200b,w	2420b	1650w	1500w	1225vs,sp	1080s,sp	515vs,sp		
[Co((DO)(DOH)bzo)I$_2$]	3400b	2380b	1605s,sp	1500s,sp	1225vs,sp	1090vs,sp	525vs,sp		
[CNCo((DO)(DOH)bzo)Br][c]	~3200vb	2400b,w		1560s,mb	1240s,sp	1095s,sp	520s,sp	2160s,sp 440s,sp	ν(CN) ν(Co–C)(CN)
[SCNCo((DO)(DOH)bzo)Br][c]	3200vb	2370b,s		1545s,mb	1230s,sp	1090s,sp	520s,sp	2150s,sp 740s,sp 485w	ν(CN)(SCN) ν(CS) ν(Co–SCN)
[N$_3$Co((DO)(DOH)bzo)Br][c,d]	~3000vb	2400b,s		1565s,mb	1230s,mb	1085s,sp	520s,sp	2030s,sp 760w,mb 295w,mb	v_a(NNN) δ^a(NNN) ν(Co–N)(N$_3$)

[a] Medium: KBr disk. Abbreviations: s = strong, sp = sharp, vs = very strong, w = weak, b = broad, sh = shoulder, ms = medium strong, mb = medium broad. [b] For references see text. [c] The intensity of the ν(C=C) vibration of the ligand framework is very low. [d] The ν_s(NNN) vibration of the free azide ion occurring at 1344 cm^{-1} disappears upon complexation.

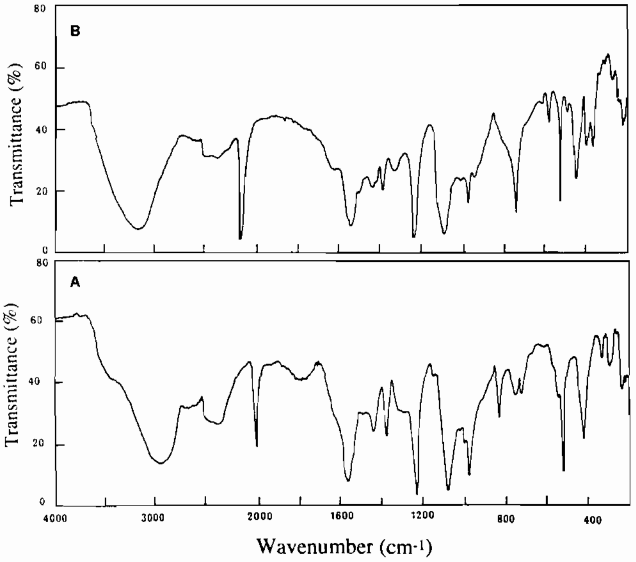

Fig. 1. IR spectra of [(SCN)Co((DO)(DOH)bzo)Br] (A) and [N$_3$Co((DO)(DOH)bzo)Br] (B) on KBr disk.

reduced in strength and hence the formation of the thiocyanato complex is more favoured*. The IR spectrum of [(SCN)Co((DO)(DOH)bzo)Br] is depicted in Fig. 1(A). The azide ion provides two equivalent coordination sites to the metal and hence it is termed an isoalterdentate ligand by von Zelewsky [70]. The azide ion in KN$_3$ exhibits ν_a(NNN) and ν_s(NNN) at 2041 and 1344 cm^{-1}, respectively [71]. The azido complex, [N$_3$Co((DO)(DOH)bzo)Br], exhibits only one band at 2030 cm^{-1} assignable to ν_a(NNN). Upon complexation the symmetric stretching vibration found in the free azide ion disappears. It exhibits two weak bands of medium broadness at 760 and 295 cm^{-1} assignable to the in-plane bending or deformation vibration of the coordinated azide** and to the ν(Co–N)(N$_3$) vibration, respectively. The IR spectrum of [N$_3$Co((DO)(DOH)bzo)Br] is shown in Fig. 1(B). The IR spectral data for these complexes are presented in Table 1.

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*The formation of the thiocyanato isomer is substantiated by electronic absorption spectroscopy and by cyclic voltammetry. The electronic absorption spectrum of [(SCN)Co((DO)(DOH)bzo)Br] consists of an intense absorption band at 34.48 kK diagnostic of the Co(III)-S bond and has been assigned to ligand to metal charge transfer (LTMCT) transition [66–69]. The cyclic voltammetric $E_{1/2}$ value for the Co(III)/Co(II) redox couple of the thiocyanato complex lies at a less negative potential than that of the dibromo and Lewis base complexes indicating that the Co–S bond renders cobalt more susceptible for reduction [48, 49].

**In the azido complex ν(NNN) vibration occurs at a higher energy than that of free azide and that of the azido complexes of various metal ions (see ref. 62, p. 278).

Infrared spectra of Lewis base complexes

These complexes exhibit absorption bands characteristic of the axially bound Lewis base and the (DO)(DOH)bzo chelate. The out-of-plane and the in-plane deformation vibrations of the pyridine ring occurring at 405 and 604 cm^{-1}, respectively, suffer significant shift towards higher frequencies [72] on complexation. [pyCo((DO)(DOH)bzo)Br]ClO_4 exhibits ν(CH) of the pyridine ring and that of the ligand framework at 3040 and 3120 cm^{-1}, respectively. The C=C and C=N stretching vibrations and the CH deformation vibration of the pyridine ring occur at 1610, 1560 and 770 cm^{-1}, respectively [53]. The in-plane and the out-of-plane deformation vibrations of the coordinated pyridine occur at 700 and 425 cm^{-1}, respectively. The IR spectrum of [pyCo((DO)(DOH)bzo)Br]ClO_4 is depicted in Fig. 2(A). The 4-methylpyridine complex, [4-CH_3pyCo((DO)(DOH)bzo)Br]PF_6, exhibits ν(CH) vibrations at 3040 and 3110 cm^{-1}. The ν(C=C) appears as a strong and sharp band at 1620 cm^{-1} probably due to the coupling with the HOH bending mode of lattice water. The unsymmetric and the totally symmetric ring breathing modes occur at 1040 and 1005 cm^{-1}, respectively [73]. The IR spectrum of [4-CH_3pyCo((DO)(DOH)bzo)Br]PF_6 is given in Fig. 2(B).

The ν(NH) vibration appearing in solid imidazole as a very broad band due to the intermolecular hydrogen bonding appears in [IzCo((DO)(DOH)bzo)Br]PF_6 as a sharp band at 3140 cm^{-1}. The NH in-plane deformation vibration occurring at 1540 cm^{-1} for the free imidazole [74] is not observed as a separate band. This may probably couple with the ν(C=N) of the ligand framework. The ring stretching modes appear as shoulders at 1490 and 1500 cm^{-1} as observed by Cordes and Walters [75]. The very weak band appearing at 920 cm^{-1} may be attributed to the ring mode of coordinated imidazole. The ν(NH) vibration occurring at 3140 cm^{-1} in the imidazole complex is absent in the 1-methylimidazole complex indicating the absence of the imino hydrogen in the latter. The sharp band appearing at 3120 cm^{-1} may be assigned to the C–CH_3 vibration of the coordinated 1-methylimidazole. The IR spectrum of [MeIzCo((DO)(DOH)bzo)Br]Br is shown in Fig. 3(A).

In the complex of benzimidazole, [BIzCo((DO)(DOH)bzo)Br]BF_4, the weak bands above 3250 cm^{-1} are apparently due to the imidazole CH vibration and those at 2980 and 3040 cm^{-1} are assignable to the combined CH vibrations of the benzene portion of benzimidazole and the equatorial ligand. The strong band appearing at 3120 cm^{-1} may be due to ν(NH) of benzimidazole. The sharp bands at 1500 and 1310 cm^{-1} are assigned to the aromatic ring stretching modes [76]. The sharp bands at 1625, 1560, 1440 and 1370 cm^{-1} are attributed to the ν(C=C), ν(C=N), and C–CH_3 asymmetric and symmetric deformation vibrations, respectively. Based on the IR studies of Cordes and Walters [76] on the bis(benzimidazole) metal complexes the sharp band at 1280 cm^{-1} is assigned to the CH bending vibration. In analogy with the above work, the weak band at 635 cm^{-1} is assigned to ring torsion because of its appearance in the complexes of both imidazole and benzimidazole. The IR spectrum of [Me_2BIzCo((DO)(DOH)bzo)Br]PF_6 resembles that of the benzimidazole complex except for the appearance of a sharp band at 1470 cm^{-1} which may be attributed to the C–CH_3 vibration of the coordinated 5,6-dimethylbenzimidazole. One common feature observed

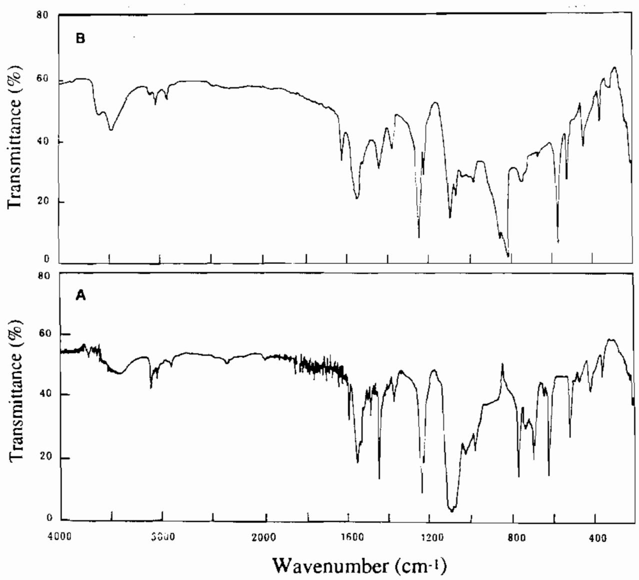

Fig. 2. IR spectra of [pyCo((DO)(DOH)bzo)Br]ClO_4 (A) and [4-CH_3pyCo((DO)(DOH)bzo)Br]PF_6 (B) on KBr disk.

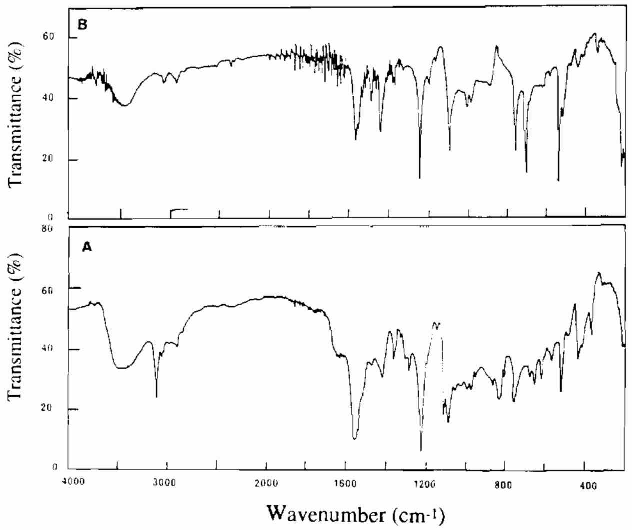

Fig. 3. IR spectra of [MeIzCo((DO)(DOH)bzo)Br]Br (A) and [PPh_3Co((DO)(DOH)bzo)Br]Br (B) on KBr disk.

in the imidazole family of complexes is the appearance of a sharp band in the 1310–1330 cm^{-1} region. Since this band is not found in the complex of 1-methylimidazole it is assigned to the NH bending vibration. (The authors [75] reported that the band at 1328 cm^{-1} is assignable to the CH or NH bending mode in their studies on imidazole complexes. If this were due to the CH bending mode, [MeIzCo((DO)(DOH)bzo)Br]Br would also give a band around 1328 cm^{-1}.) This spectral behaviour illustrates that imidazole, benzimidazole and 5,6-dimethylbenzimidazole coordinate to the metal ion through the tertiary nitrogen.

The characteristic feature of the IR spectrum of the triphenylphosphine complex is the appearance of a number of sharp bands around 1620 cm^{-1} due to the phenyl ring vibrations* and a sharp as well as a strong band at 700 cm^{-1}. Since the latter band is absent in the dibromo complex and in the other Lewis bases complexes it can be attributed to the vibrations characteristic of coordinated triphenylphosphine. The IR spectrum of [PPh_3Co((DO)(DOH)bzo)Br]Br is presented in Fig. 3(B).

Complexes of ethylamine and 2-aminopyridine exhibit symmetric and asymmetric NH stretching vibrations whereas the complexes of diethylamine and triethylamine exhibit ν(NH) as strong bands in the 3000–3280 cm^{-1} region. In the case of [2-NH_2pyCo((DO)-(DOH)bzo)Br]Br it is not possible to describe unequivocally the mode of bonding of 2-aminopyridine since it is a potential ambidentate ligand. The absence of a sharp band, characteristic of a free amino group, in the 3300–3500 cm^{-1} region [77] indicates that 2-aminopyridine coordinates through its exocyclic nitrogen. However, the presence of exocyclic and endocyclic bonded isomers in equilibrium is not ruled out [78].

All the complexes except [PPh_3Co((DO)(DOH)-bzo)Br]Br exhibit the ν(Co–N) (nitrogen donors of the equatorial ligand) vibration in the 515–530 cm^{-1} region. The triphenylphosphine complex exhibits the ν(Co–N) vibration at 540 cm^{-1}. The greater strength of the Co–N bond in this complex is due to the better π-accepting tendency of this soft ligand. Triphenylphosphine, being a better π-acceptor, removes electron density from the metal ion through π-backbonding which enables the metal ion to accept electrons from the nitrogen donors of the equatorial ligand through σ-bonding. This leads to an increase in the Co–N bond strength and the stretching frequency. The ν(C=C) vibration appears in the complexes of pyridine, 4-methylpyridine, benzimidazole, 5,6-dimethylbenzimidazole and 2-aminopyridine as the coupled ν(C=C) vibrations of the equatorial ligand and the Lewis base in the 1605–1625 cm^{-1} region. In the complexes of imidazole, 1-methylimidazole, ethylamine and triphenylphosphine it overlaps with the ν(C=N) vibration and appears as a broad band. In the complexes of diethylamine and triethylamine it appears as a shoulder.

The complexes containing lattice water exhibit a strong as well as sharp band in the 3420–3540 cm^{-1} region due to the antisymmetric and symmetric O–H stretching vibrations [79]. The H–O–H bending vibration expected to occur in the 1630–1600 cm^{-1} region overlaps with ν(C=C) in some complexes while in others it is obscured by the very strong band due to ν(C=N). All the complexes which crystallize with lattice water exhibit another band [80] at 440 cm^{-1}. Complexes containing perchlorate anion exhibit strong unsplit absorptions at ~1100 and 620 cm^{-1}. The absence of splitting of the ν_3 band at ~1100 cm^{-1} and the ν_4 band at 620 cm^{-1} indicates that the perchlorate anion is not coordinated [81, 82]. Complexes containing the fluoborate anion exhibit absorptions at 1075 and 535 cm^{-1} characteristic of ionic fluoborate [83] and complexes containing the hexafluorophosphate anion exhibit strong as well as sharp bands at ~835 and 565 cm^{-1} characteristic of ionic hexafluorophosphate [84, 85].

The characteristic IR absorption bands of the Lewis base complexes are given in Table 2.

Intramolecular hydrogen bond

The OH stretching vibration occurring in the IR spectrum of the free ligand at 2900 cm^{-1} is shifted to around 2400 cm^{-1} in the complexes [46, 47]. This indicates the formation of a hydrogen bond during the complexation of the ligand since the hydrogen bond reduces the strength of the O–H bond. The formation of an intramolecular hydrogen bond by the loss of one of the oxime protons during the complexation of the ligand accounts for the two non-identical =N–O– linkages, C=N–O–H and C=N–O - - H, in the complexes [46, 47]. Studies on the complexes of other oxime ligands also confirm the presence of two unequal =N–O– linkages due to hydrogen bonding. The hydrogen bonded proton can be chemically innocent and often escapes experimental detection by ^{1}H NMR spectroscopy, but it can be replaced by the BF_2 group. Thus indirect evidence for the presence of a hydrogen bond in the complexes is obtained by replacing the hydrogen bonded proton in [Co((DO)(DOH)bzo)Br_2] and [pyCo((DO)-(DOH)bzo)Br]ClO_4 by the BF_2 group by treating the respective hydrogen bonded complex with boron trifluoride etherate. The IR spectra of [Co($(DO)_2$bzo-(BF_2))Br_2] and [pyCo($(DO)_2$bzo(BF_2))Br]ClO_4 resemble that of the hydrogen bonded analogs except for the occurrence of new bands characteristic of BO and BF vibrations and the absence of the ν(OH) and ν'(NO)

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*The aromatic portion of the ligand framework also gives several sharp bands in the 1650–1800 cm^{-1} region. In the PPh_3 complex the sharp bands are further resolved.

TABLE 2. Characteristic IR absorption bands (cm^{-1}) of the Lewis base complexes[a]

Complex	Assignments[b]							Absorption of the axial base		Absorption of counter ion	Absorption due to lattice water	
	ν(CH)	ν(OH)	ν(C=C)	ν(C=N)	ν(NO)	ν'(NO)[c]	ν(Co–N)	Band (cm^{-1})	Assignments[b]		Band (cm^{-1})	Assignments[b]
$[PyCo((DO)(DOH)bzo)Br]ClO_4 \cdot H_2O$[d]	3040sp,w 3120sp,w		1605sp,w	1560s,sp	1245vs,sp	1085s,sp	520s,sp	700s,sp 425w,sp	CH in-plane def. CH out-of-plane def.	1100s,b 625s,b	3500s,b 425w,mb	$\nu_a(OH) + \nu_s(OH)$
$[IzCo((DO)(DOH)bzo)Br]PF_6$[e,f,g]	3300s,b	2380w,b		1550s,mb	1230vs,sp	1090s,sp	520s,sp	3140s,sp 1490sh 1500sh 920w,sp	ν(NH) ring str. mode ring mode of Iz	840s,b 565s,sp		
$[MeIzCo((DO)(DOH)bzo)Br]Br \cdot H_2O$[g]	3300b	2400w,b		1565s,mb	1240vs,sp	1100s,sp	525s,sp				3500s,b 425w,mb	$\nu_a(OH) + \nu_s(OH)$
$[BIzCo((DO)(DOH)bzo)Br]BF_4 \cdot H_2O$[d]	3280w,b 3000w,sp	2450w	1625sp,w	1560s,sp	1235vs,sp	1095sh,sp	520s,sp	3120sp 1500sp 1310sp 685w 1280sp	ν(NH) ring stretching ring torsion CH bending	1075s,b 535s,sp	3500s,b 430w,mb	$\nu_a(OH) + \nu_s(OH)$
$[Me_2BIzCo((DO)(DOH)bzo)Br]PF_6$[d,f]	3000w,b 3120w,b	2430w	1620mb,w	1560s,sp	1230vs,sp	1095sh	530s,sp	3135sp,w 1320sp 1470sp	ν(NH) NH bending CH_3 vibration	840s,b 565s,b		
$[PPh_3Co((DO)(DOH)bzo)Br]Br \cdot 0.5H_2O$[g]	3060w,mb			1560s,mb	1235vs,sp	1080s,sp	540vs,sp	1620sp 1850sp 700s,sp	Ph ring vib PPh_3 vib		3450s,b	$\nu_a(OH) + \nu_s(OH)$
$[4\text{-}CH_3PyCo((DO)(DOH)bzo)Br]PF_6 \cdot H_2O$[d,h]	3040sp,w 3110sp,w		1620s,sp	1560s,mb	1235s,sp	1090s,sp	520s,sp	1040w 1005w	unsym. ring breathing mode tot. sym. ring breathing mode	845s,b 565s,b	3450s,b 430s,mb	$\nu_a(OH) + \nu_s(OH)$
$[2\text{-}NH_2PyCo((DO)(DOH)bzo)Br]Br$[d]	3300b,w	2450b	1620s,sp	1565s,b	1230vs,mb	1100s,mb	520s,sp	3160b,w 3080b,w	ν(NH)			
$[EtNH_2Co((DO)(DOH)bzo)Br]ClO_4 \cdot H_2O$[g]	3420b,w 3180s,sp	2300b		1560vs,mb	1230vs,sp	1085s,mb	520vs,sp	3100vs,sp 3200vs,sp	ν(NH)	1100s,b 620s,b	3470 425	$\nu_a(OH) + \nu_s(OH)$
$[Et_2NHCo((DO)(DOH)bzo)Br]ClO_4 \cdot 0.5H_2O$	3450b,s	2380b	1630sh	1565s,mb	1230vs,sp	1075sh	520vs,sp	2950vb,s	ν(NH)	1100s,b 625s,b	3450 430	$\nu_a(OH) + \nu_s(OH)$
$Et_3NCo((DO)(DOH)bzo)Br]ClO_4$	2940vb	2400b	1630sh	1565s,mb	1230vs,sp		515s,sp			1100s,b 625s,b		

[a] Medium: KBr disk. Abbreviations: s = strong, sp = sharp, vs = very strong, w = weak, b = broad, sh = shoulder, ms = medium strong, mb = medium broad. [b] For references see text. [c] When ClO_4^- or BF_4^- is the counter ion, the ν'(NO) band is either appearing as a shoulder or overlapping with the band of ClO_4^- or BF_4^-. [d] The ν(C=C) vibration is the coupled ν(C=C) vibration of the ligand framework with that of the axial base. [e] The NH in-plane deformation vibration couples with the ν(C=N) vibration of the ligand framework. [f] A sharp band occurs in the region 1310–1330 cm^{-1}, assignable to the NH bending vibration. [g] The band due to ν(C=C) overlaps with that of ν(C=N) and appears as a broad band. [h] The ν(C=C) vibration couples with the HOH bending vibration.

bands. The weak band at 1175 cm^{-1} and the strong band at 826 cm^{-1} in $[Co((DO)_2bzo(BF_2))Br_2]$ are ascribed to the ν(BO) vibration and the weak bands occurring at 1026 and 1006 cm^{-1} are attributed to the ν(BF) vibration [86]. The BF_2 derivative of the pyridine complex exhibits the ν(BO) vibration as sharp bands at 1190 and 815 cm^{-1} while the ν(BF) vibration occurs as sharp and weak bands at 1025 and 1005 cm^{-1}. The appearance of only one band assignable to ν(NO) in the BF_2 derivatives indicates the presence of only one type of NO linkage, C=N–O–B.

Infrared spectra of alkylcobalt(III) complexes

The alkylcobalt(III) complexes exhibit absorptions such as ν(CH), ν(C=N), ν(NO) and C–CH_3 symmetric and asymmetric deformation vibrations characteristic of the ligand framework. The ν′(NO) band is obscured by the ν_3 band of ClO_4^- at ~1100 cm^{-1}. In a few cases this band appears as a shoulder. Bands characteristic of coordinated imidazole, *trans* to the alkyl group, are well resolved in these complexes. The weak bands appearing at 1500 and 1445 cm^{-1} are ascribed to the ring stretching modes of imidazole [75]. The latter band couples with the C–CH_3 antisymmetric deformation mode. The ring mode of coordinated imidazole appears at 945 and 940 cm^{-1} in $[IzCo((DO)(DOH)bzo)CH_3]ClO_4$ and $[IzCo((DO)(DOH)bzo)C_2H_5]ClO_4$, respectively. This observation is in conformity with the study of Davis and Smith [74] that the ring mode of imidazole is shifted to higher frequency upon complexation. (In the IR spectrum of $[IzCo((DO)(DOH)bzo)Br]PF_6$ this band occurs at 920 cm^{-1} contrary to the observation of Davis and Smith [74]). The IR spectra of $[IzCo((DO)(DOH)bzo)CH_3]ClO_4$ and $[IzCo((DO)(DOH)bzo)C_2H_5]ClO_4$ are depicted in Fig. 4(A) and (B), respectively.

The coordinated pyridine ring exhibits ν(CH) vibrations in the 3020–3080 cm^{-1} region and the coupled ν(C=C) and ν(C=N) vibrations at 1600 cm^{-1}. The CH deformation, in-plane deformation and out-of-plane deformation vibrations appear at 765, 700 and 425 cm^{-1}, respectively. The IR spectrum of $[pyCo((DO)(DOH)bzo)C_6H_5CH_2]ClO_4$ is depicted in Fig. 4(C). The $\nu_a(OH)+\nu_s(OH)$ of lattice water appears as a broad band around 3540 cm^{-1}. The HOH bending, expected in the 1640–1630 cm^{-1} region, is not observed. It may couple with the ν(C=C) and/or ν(C=N) vibration(s) of the pyridine ring occurring at ~1600 cm^{-1}. The ν(Co–N) vibration occurs in all these complexes at 520 cm^{-1} showing that the organic ligands do not have much effect on the Co–N bond with the equatorial ligand. The characteristic IR absorptions of the alkyl derivatives are given in Table 3.

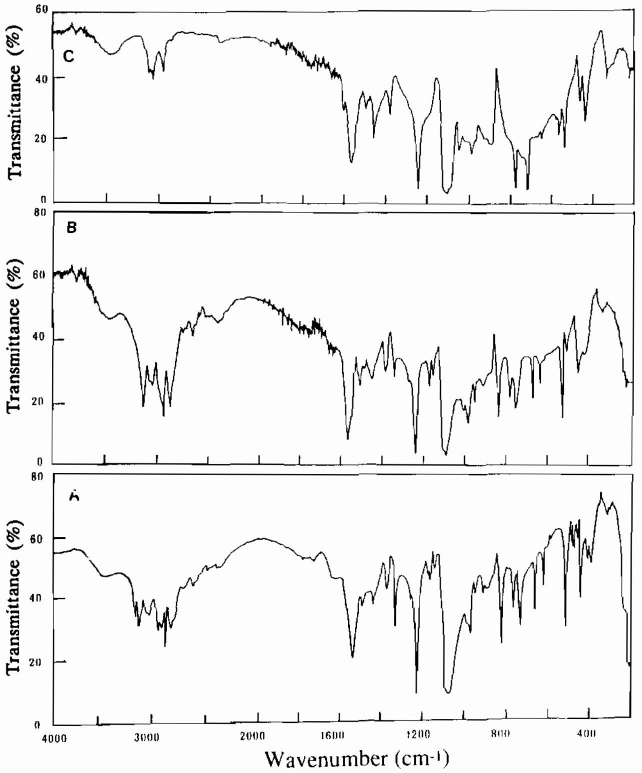

Fig. 4. IR spectra of $[IzCo((DO)(DOH)bzo)CH_3]ClO_4$ (A), $[IzCo((DO)(DOH)bzo)C_2H_5]ClO_4$ (B) and $[pyCo((DO)(DOH)bzo)C_6H_5CH_2]ClO_4$ (C) on KBr disk.

Far-infrared spectra of dihalo complexes

The far-IR spectrum of $[Co((DO)(DOH)bzo)Br_2]$ is shown in Fig. 5 and the characteristic absorptions are presented in Table 4. The sharp bands of medium intensity at 355 and 410 cm^{-1} may be assigned to Co–N vibrations since these bands are absent in the spectrum of the free ligand. The absorption bands occurring at 370 and 435 cm^{-1} in the free ligand are shifted to 385 and 445 cm^{-1} with higher intensity in the complexes. This may be due to the coupling of the ligand vibrations with the Co–N vibrations. Thus certain of the low frequency vibrations (deformations) that involve motion of the C–N framework would also involve motion of the metal ion. The shift in the absorption bands of the free ligand towards higher frequency upon complexation indicates the stability and strength of the coordinate bond as observed by Saito *et al.* [87]. In their detailed IR studies of metalloporphyrins, Boucher and Katz [58] and Ogoshi *et al.* [56] have also observed such a shift in the higher energy region with an increase in intensity indicative of the metal sensitive M–N vibrations and the strength of the M–N bond. The Co–N vibration in $[Co((DO)(DOH)bzo)Br_2]$ occurs in a higher energy region compared to the energy of Co–N vibrations observed in the divalent metal complexes of pyridine, bipyridyl and quinone, and in metalloporphyrins. This

TABLE 3. Characteristic IR absorption bands (cm^{-1}) of the alkylcobalt(III) complexes[a,b,c]

Complex	Assignments[d,e,f]					Absorptions of the axial base	
	ν(CH)	ν(OH)	ν(C=N)	ν(NO)	ν(Co–N)[g]	Band (cm^{-1})	Assignments[d]
[PyCo((DO)(DOH)bzo)CH$_3$]ClO$_4$·H$_2$O[h]	2910s,sp 3050sp,w 3120sp,w	2350b	1555s,mb	1235vs,sp	520s,sp	765s,sp 700s,sp 425sp,w 1600sp	CH def. CH in-plane def. CH out-of-plane def. ν(C=C) + ν(C=N)
[PyCo((DO)(DOH)bzo)C$_2$H$_5$]ClO$_4$·H$_2$O[h]	2880sp,w 2940s,sp 3000w,b		1560s,mb	1235vs,sp	525vs,sp	765s,sp 700s,sp 425sp,w 1605sp	CH def. CH in-plane def. CH out-of-plane def. ν(C=C) + ν(C=N)
[PyCo((DO)(DOH)bzo)i-Pr]ClO$_4$·H$_2$O[h]	2865w,sp 2940w,sp 2980s,sp	2375b	1550s,mb	1230vs,sp	520s,sp	765s,sp 700s,sp 425sp,w 1600sp	CH def. CH in-plane def. CH out-of-plane def. ν(C=C) + ν(C=N)
[PyCo((DO)(DOH)bzo)C$_6$H$_5$CH$_2$]ClO$_4$·H$_2$O[h]	2950s,sp 3020s,sp 3080sh	2400b	1560s,mb	1240vs,sp	520s,sp	765s,sp 700s,sp 425sp,w 1600sp	CH def. CH in-plane def. CH out-of-plane def. ν(C=C) + ν(C=N)
[PyCo((DO)(DOH)bzo)C$_6$H$_4$]ClO$_4$·H$_2$O[h]	2850s,sp 2920vs,sp		1550s,mb	1230vs,sp	520s,sp	765s,sp 700s,sp 425sp,w 1600sp	CH def. CH in-plane def. CH out-of-plane def. ν(C=C) + ν(C=N)
[IzCo((DO)(DOH)bzo)CH$_3$]ClO$_4$·H$_2$O[i]	2860w,sp 2900s,sp 3040w,mb	2400b	1550s,mb	1230vs,sp	520vs,sp	3150sp 1500w 1445w 945w,sp	ν(NH) ring str. mode of Iz ring mode of Iz
[IzCo((DO)(DOH)bzo)C$_2$H$_5$]ClO$_4$·H$_2$O[i]	2860s,sp 2920s,sp 3040w,mb	2400b	1565vs,mb	1230vs,sp	530vs,sp	3120sp 1500w 1445w 945w,sp	ν(NH) ring str. mode of Iz ring mode of Iz
[Me$_2$BIzCo((DO)(DOH)bzo)CH$_3$]ClO$_4$·H$_2$O	2930s,sp 3235w,b 3300w,b	2450b	1550s,mb	1235vs,sp	525vs,sp	3130s,sp 1320sp,w 1465sp	ν(NH) NH bending CH$_3$ vib.
[PPh$_3$Co((DO)(DOH)bzo)CH$_3$]ClO$_4$·H$_2$O	2920s,sp 3000w,mb 3070w,sp	2350vb	1555s,mb	1240vs,sp	525vs,sp	700vs,sp	PPh$_3$ vib.

[a]Medium: KBr disk. Abbreviations: s = strong, w = weak, sp = sharp, b = broad, vs = very strong, mb = medium broad, sh = shoulder. [b]All these complexes exhibit the ν_3 band of ClO$_4^-$ at ~1100 cm^{-1} and the ν_4 band at 620 cm^{-1} indicating the presence of ionic perchlorate. [c]The coupled ν_a(OH) and ν_s(OH) vibration of the lattice water appears in all these complexes as a broad band ~3500 cm^{-1}. A weak band occurring at 430 cm^{-1} is also characteristic of lattice water. [d]For references see text. [e]The ν'(NO) band is obscured by the ν_3 band of ClO$_4^-$ at ~1100 cm^{-1}. [f]The ν(C=C) vibration of the equatorial chelate is not resolved. [g]N refers to the nitrogen donors of the (DO)(DOH)bzo chelate. [h]The coupled ν(C=C) and ν(C=N) vibration of the pyridine ring occurs at 1600 cm^{-1}. [i]The ring stretching mode of Iz occurring at 1445 cm^{-1} couples with the antisymmetric deformation mode of Iz.

is due to the fact that cobalt(III) accepts electrons more readily than cobalt(II) from the (DO)(DOH)bzo chelate with a concomitant increase in Co^{III}–N bond strength and stretching frequency. Yamazaki and Hohokabe [53] also observed the appearance of a few bands in the 420–500 cm^{-1} region due to Co–N stretching vibrations in cobaloximes. In the dihalo complexes the metal–halogen bonds are only terminal. For divalent metal ions the ν(M–Cl) vibration appears in the 400–200 cm^{-1} region and ν(M–Br) in the 300–200 cm^{-1} region. The dichloro and dibromo complexes exhibit ν(Co–Cl) and ν(Co–Br) vibrations at 242 and 245 cm^{-1}, respectively. The ν(Co–N) vibration appears in the dichloro complex at 350 cm^{-1}. The weak bands appearing below 100 cm^{-1} are attributed to the IR active lattice vibrations [88].

Far-infrared spectra of Lewis base complexes

The far-IR spectral data for the Lewis base complexes are presented in Table 4. The far-IR spectrum of

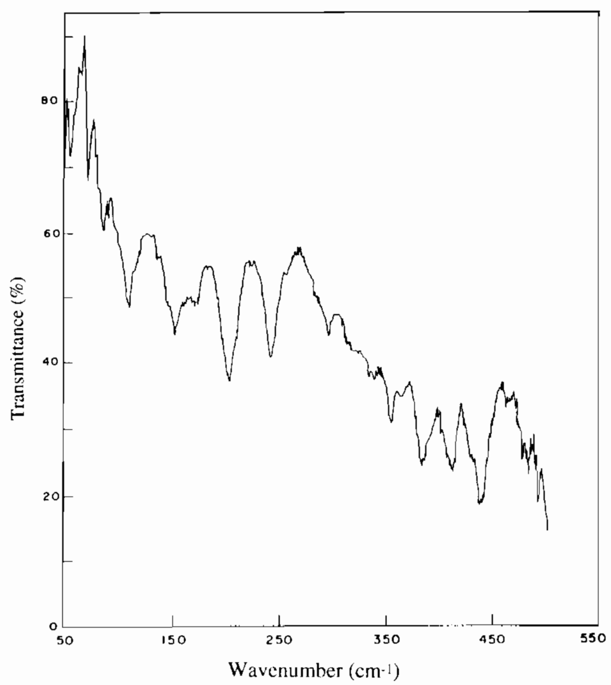

Fig. 5. Far-IR spectrum of $[Co((DO)(DOH)bzo)Br_2]$ on polyethylene disk.

$[pyCo((DO)(DOH)bzo)Br]ClO_4$ consists of a medium intensity band at 356 cm^{-1} assignable to ν(Co–N) (equatorial ligand). The weak band occurring at 240 cm^{-1} may be due to ν(Co–Br). The ν(Co–py) vibration occurs as a strong band at 274 cm^{-1}. The far-IR spectrum of $[pyCo((DO)(DOH)bzo)Br]ClO_4$ is depicted in Fig. 6(A). $[4\text{-}CH_3pyCo((DO)(DOH)bzo)Br]PF_6$ exhibits strong bands at 354 and 215 cm^{-1} due to ν(Co–N) and ν(Co–Br), respectively, and a broad band at 306 cm^{-1} assignable to $\nu(Co\text{–}4\text{-}CH_3py)$ [89]. Among the methyl substituted pyridines only the 4-methyl substitution produces a significant effect on the metal–4-methylpyridine stretching frequency. Hyperconjugative electron release by this group discourages metal $t_{2g} \rightarrow \pi^*$ electron transfer thereby reducing the metal–4-methylpyridine bond strength and IR absorption frequency [90]. But the energy of the $\nu(Co\text{–}4\text{-}CH_3py)$ vibration is higher than that of the ν(Co–py) and ν(Co–Iz) vibrations. This indicates that the 4-methylpyridine is a better σ-donor to cobalt(III) than pyridine and imidazole. (The higher field strength of 4-methylpyridine (1642 cm^{-1}) than pyridine (1625 cm^{-1}) and imidazole (1594 cm^{-1}) also indicates that it is a better σ-donor to cobalt(III).) The greater σ-donating ability of 4-methylpyridine than pyridine and imidazole reduces the energy of the ν(Co–N) vibration in $[4\text{-}CH_3pyCo((DO)(DOH)bzo)Br]PF_6$ more than that of the corresponding vibration in the pyridine and imidazole analogs since greater electron donation by the axial base discourages electron donation by the equatorial chelate to the metal center. Thus $[4\text{-}CH_3pyCo((DO)(DOH)bzo)Br]PF_6$ exhibits the ν(Co–N) vibration at lower energy (354 cm^{-1}) than the pyridine and imidazole complexes. The methyl group in 4-methylpyridine causes significant effect on the Co–Br vibration by transmission of the π-electronic substituent effect across the metal d-orbitals and consequently, the ν(Co–Br) vibration occurs in $[4\text{-}CH_3pyCo((DO)(DOH)bzo)Br]PF_6$ at lower energy (215 cm^{-1}) than that in the pyridine and imidazole complexes. This observation is best exemplified by the lowering of the M–SCN stretching vibration in complexes of the type, *trans*-$[ML_4(NCS)_2]$ [90] (where M = Co, Ni, Cu, Zn, Mn; L = 4-methylpyridine). Thus the hyperconjugative electronic transmission of 4-methylpyridine has a pronounced effect on the bonding of the equatorial and the *trans* axial ligands. The far-IR spectrum of

TABLE 4. Characteristic far-IR spectral assignments of the dihalo and Lewis base complexes[a]

Complex	Assignments[b]			Lattice vibrations[b]	Bands[b] due to the axial base[c]
	ν(Co–N)	ν(Co–base)[c]	ν(Co–Br)		
$[Co((DO)(DOH)bzo)Br_2]$[e]	355s		245s	85w	110sp,w
$[Co((DO)(DOH)bzo)Cl_2]$[d]	350s		242s		
$[PyCo((DO)(DOH)bzo)Br]ClO_4 \cdot H_2O$[e]	356s	274w,b	240w	90s,b	202b; 175s,b; 146w
$[IzCo((DO)(DOH)bzo)Br]PF_6$[e]	374w,mb	290b,ms	242b,ms	65b	195
$[MeIzCo((DO)(DOH)bzo)Br]Br \cdot H_2O$[e]	345s,b	270s,mb	238s,b	95b	140w,mb; 125w,b
$[BIzCo((DO)(DOH)bzo)Br]BF_4 \cdot H_2O$[e]	358s,mb	270w	233s,mb	80, 62	205, 160, 130
$[Me_2BIzCo((DO)(DOH)bzo)Br]PF_6$[e]	364s,mb	335s,mb	236w		
$[PPh_3Co((DO)(DOH)bzo)Br]Br \cdot 0.5H_2O$[e]	327b	222w	275b	70w	145w,mb
$[EtNH_2Co((DO)(DOH)bzo)Br]Br \cdot H_2O$[d]	350s,mb	245b,w	235s,b	80w	120w,mb
$[Et_2NHCo((DO)(DOH)bzo)Br]ClO_4 \cdot 0.5H_2O$[d]	365s,mb	270b,w	240s,b	75w	130w,mb
$[Et_3NCo((DO)(DOH)bzo)Br]ClO_4$[e]	335s,b	290s,b	235s	90w,b	110
$[4\text{-}CH_3PyCo((DO)(DOH)bzo)Br]PF_6 \cdot H_2O$[e]	354s,b	306s,mb	215s		176b; 120b

[a] Abbreviations: s = strong, w = weak, b = broad, mb = medium broad. [b] For references see text. [c] The axially coordinated Lewis base. [d] Medium: polyethylene disk. [e] Medium: nujol mull plastered on a polyethylene plate.

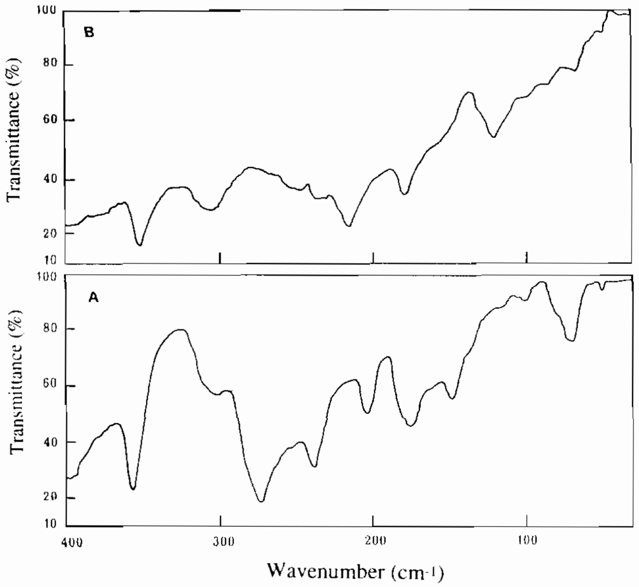

Fig. 6. Far-IR spectra of [pyCo((DO)(DOH)bzo)Br]ClO$_4$ (A) and [4-CH$_3$pyCo((DO)(DOH)bzo)Br] (B) on nujol mull plastered on polyethylene plate.

[4-CH$_3$pyCo((DO)(DOH)bzo)Br]PF$_6$ is shown in Fig. 6(B).

The imidazole complex exhibits a weak band of medium broadness at 374 cm^{-1} assignable to ν(Co–N). The broad bands of medium intensity at 242 and 290 cm^{-1} are attributable to ν(Co–Br) and ν(Co–Iz) vibrations, respectively. The ν(Co–Iz) vibration occurs at higher energy than the ν(Co–py) vibration of the pyridine complex. (The energy of the ν(Co–Iz) vibration found in the imidazole complex is higher than that of the octahedral and tetragonally distorted octahedral cobalt(III) complexes of imidazole as reported by Cornilsen and Nakamoto [91].) Similar observations were also made by Taylor and Underhill [92] in their studies on the complexes of imidazole and pyridine. Clark and Williams [72] have also observed the ν(Co–Iz) vibration occurring in a higher energy region (278–285 cm^{-1}) than the ν(Co–py) vibration (250–252 cm^{-1}) in their IR spectral studies of compounds of the type [CoL$_2$X$_2$] (where L=Iz or py). The benzimidazole complex exhibits four absorption bands in the lower energy region. The bands at 160 and 130 cm^{-1} could possibly be due to the ligand fundamentals. The bands at 358, 233 and 270 cm^{-1} may be assigned to ν(Co–N), ν(Co–Br) and ν(Co–BIz) vibrations, respectively. The energy of the ν(Co–Br) vibration in the benzimidazole complex is found to be lower than that of the pyridine, 4-methylpyridine and imidazole complexes. The far-IR spectrum of [BIzCo((DO)(DOH)bzo)Br]BF$_4$ is presented in Fig. 7(A). The spectrum of [Me$_2$BIzCo((DO)(DOH)bzo)-Br]PF$_6$ resembles that of the benzimidazole complex but for the weak absorptions below 200 cm^{-1}. The three bands of medium intensity appearing at 364, 335 and 236 cm^{-1} are assigned to ν(Co–N), ν(Co–Me$_2$BIz) and ν(Co–Br), respectively. In the triphenylphosphine complexes the M–PPh$_3$ vibrations are always found at lower energies than the M–py vibrations as expected from the relative masses of the ligands [93]. Thus the band at 222 cm^{-1} may be assigned to the ν(Co–PPh$_3$) vibration in [PPh$_3$Co((DO)(DOH)bzo)Br]Br. Triphenylphosphine, being a better π-acceptor, removes electron density from the metal ion which strengthens the Co–Br bond, *trans* to PPh$_3$, and consequently the ν(Co–Br) vibration is expected to occur at a higher frequency. The band at 275 cm^{-1} may therefore be ascribed to ν(Co–Br). The far-IR spectrum of [PPh$_3$Co((DO)-(DOH)bzo)Br]Br is depicted in Fig. 7(B). The complex of triethylamine exhibits strong bands at 335, 290 and 235 cm^{-1} assignable to ν(Co–N), ν(Co–NEt$_3$) and ν(Co–Br), respectively. The complexes of ethylamine and diethylamine exhibit the ν(Co–Br) vibration at 235 and 240 cm^{-1}, respectively. The ν(Co–EtNH$_2$) vibration occurs in the former at 245 cm^{-1} while the ν(Co–Et$_2$NH) vibration occurs in the latter at 270 cm^{-1} as expected from the relative masses of these ligands.

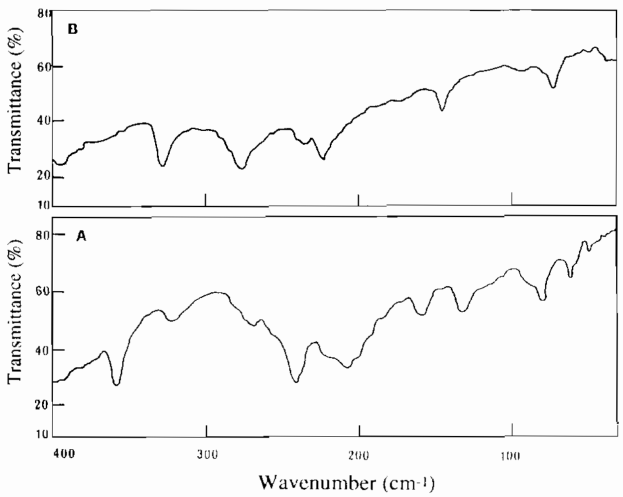

Fig. 7. Far-IR spectra of [BIzCo((DO)(DOH)bzo)Br]BF$_4$ (A) and [PPh$_3$Co((DO)(DOH)bzo)Br]Br (B) on nujol mull plastered on polyethylene plate.

Far-infrared spectra of alkylcobalt(III) complexes

The alkylcobalt(III) complexes exhibit a broad as well as strong band in the 334–320 cm^{-1} region. In analogy with the work of Yamazaki and Hohokabe [53] this band is assigned to ν(Co–C). The ν(Co–N) vibration occurring in the 327–410 cm^{-1} region for the (non-alkyl) derivatives is not resolved probably due to coupling with ν(Co–C). The far-IR spectrum of [pyCo((DO)-(DOH)bzo)CH$_3$]ClO$_4$ is shown in Fig. 8.

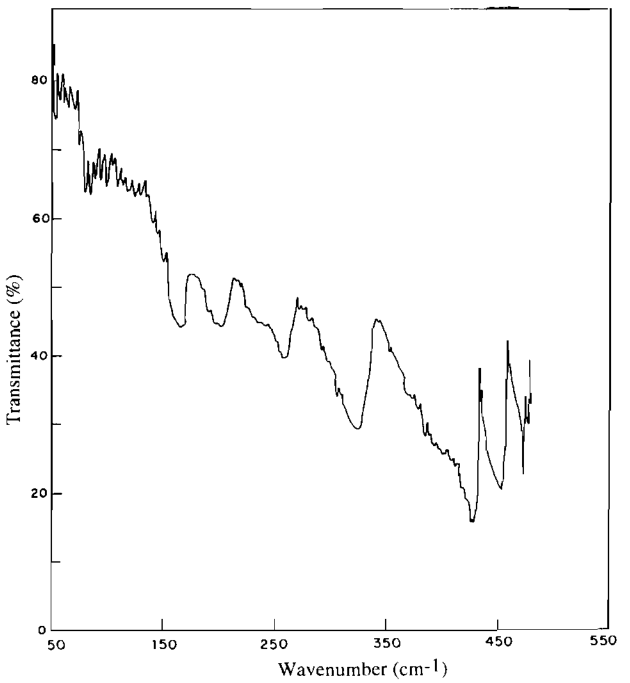

Fig. 8. Far-IR spectrum of [pyCo((DO)(DOH)bzo)CH_3]ClO_4 on polyethylene disk.

Electronic absorption spectra and the computation of the ligand field parameters

The crystal field model predicts that the electronic spectra of low-spin pseudooctahedral cobalt(III) complexes will be characterized by two bands assignable to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions [94]. On lowering the symmetry to D_{4h} due to tetragonal distortion the low lying excited state, $^1T_{1g}$, of the parent pseudooctahedral complex is split into $^1E^a{}_g$ and $^1A_{2g}$ and the higher energy excited state, $^1T_{2g}$, is split into $^1B_{2g}$ and $^1E^b{}_g$ according to the crystal field model of Wentworth and Piper [95]. Experimentally, this lowering of symmetry is manifested by the splitting of the $^1T_{1g}$ level. The splitting of the $^1T_{2g}$ level has escaped experimental detection, for it has been predicted by theory and proved by experiments that the energy difference between the $^1B_{2g}$ and $^1E^b{}_g$ levels is too small to be experimentally observed [96]. Thus the tetragonally distorted low-spin octahedral cobalt(III) complexes will be characterized by three absorption bands, two in the visible and one in the near UV region, assignable to $^1A_{1g} \rightarrow {}^1E^a{}_g$, $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow ({}^1B_{2g} + {}^1E^b{}_g)$ transitions. The dihalo, pseudohalogeno and Lewis base complexes of the (DO)(DOH)bzo chelate undergo tetragonal distortion [46, 47] since these complexes exhibit the three transitions characteristic of tetragonally distorted low-spin octahedral cobalt(III) complexes [97–101]. This amounts to assuming that the four nitrogen donors of the (DO)(DOH)bzo chelate coordinate to cobalt(III) in a square planar array and impose equivalent field strength on the metal ion. Low spin cobalt(III) complexes of other macrocycles which lack true D_{4h} symmetry have been usefully treated by assuming D_{4h} microsymmetry [102]. The field strength, Dq^{xy}, of the equatorial chelate, the field strength, Dq^z, of the axial ligand, and the tetragonal splitting parameter, D_t, have been computed by the application of the crystal field model of Wentworth and Piper [95].

The σ-donation and field strength of Lewis bases

Studies of the spectroscopic effects on the *cis*- and *trans*-effects provide a major impetus to study the metal complexes. Parameters such as coupling constant, chemical shift and stretching frequency being measured on the probe ligand to study the *cis*- and *trans*-effects of the test ligands must be a sensitive function solely of the electronic property of the metal complexes. The influence of the test ligands on the probe ligand should be solely a measure of their electron donating ability to the central metal ion. Extraneous factors must be small or absent. Obviously it is unlikely that these conditions will be met completely. Therefore inherent errors are likely to exist in the spectroscopically determined measure of the electron donating ability of the test ligand [103].

For the (Lewis base)cobalt(III) complexes of the (DO)(DOH)bzo chelate under study the Dq^{xy} value of (DO)(DOH)bzo is nearly constant [46, 47]. The near invariance of the Dq^{xy} values despite the presence of different Lewis bases in the axial site indicates that the field strength of the axially bound Lewis base is independent of the field strength of the equatorial ligand. Thus the Dq^z value serves as a measure of the electron donating ability solely of the Lewis bases. It is interesting to note that the aliphatic amines, namely, ethylamine, diethylamine and triethylamine which do not possess π-orbitals also produce Dq^z values comparable to that of the aromatic Lewis bases possessing π-orbitals. This indicates that the σ-donation of the axial ligands contribute to Dq^z. Thus the Dq^z value serves as a quantitative measure of the σ-donation of the base, coordinated in the axial site [47].

The fact that Dq^{xy} and Dq^z are quantitative measures of the electron donating ability of the equatorial and axial ligands, respectively, is borne out from the spectroelectrochemical investigation of these complexes [47]. The cyclic voltammetric $E_{1/2}$ values for the Co(III)/Co(II) redox couple depends on the spectrally determined ligand field strength of the axially bound Lewis bases whereas the Co(II)/Co(I) $E_{1/2}$ values are quite insensitive to the axial ligands and depend only on the Dq^{xy}. The dependence of the Co(III)/Co(II) $E_{1/2}$ values on the Dq^z values was observed by Endicott and coworkers [104, 105] in their studies on cobalt(III) complexes of Me_6-[14]-4,11-diene-N_4. The dependence of

TABLE 5. Field strength[a] of the axial ligands and the Co–Br stretching frequencies of the Lewis base complexes

Complex	Field strength of the Lewis base, Dq^z (cm^{-1})	ν(Co–Br) (cm^{-1})
$[Co((DO)(DOH)bzo)Cl_2]$	1612	242
$[Co((DO)(DOH)bzo)Br_2]$	1615	245
$[pyCo((DO)(DOH)bzo)Br]ClO_4$	1625	240
$[IzCo((DO)(DOH)bzo)Br]PF_6$	1594	242
$[4\text{-}CH_3pyCo((DO)(DOH)bzo)Br]PF_6$	1642	215
$[MeIzCo((DO)(DOH)bzo)Br]Br$	1652	238
$[BIzCo((DO)(DOH)bzo)Br]BF_4$	1680	233
$[PPh_3Co((DO)(DOH)bzo)Br]Br$	1697	275
$[EtNH_2Co((DO)(DOH)bzo)Br]ClO_4$	1657	235
$[Et_2NHCo((DO)(DOH)bzo)Br]ClO_4$	1647	240
$[Et_3Co((DO)(DOH)bzo)Br]ClO_4$	1664	235

[a]Computed according to the crystal field model of Wentworth and Piper [95]. The values are taken from refs. 46 and 47.

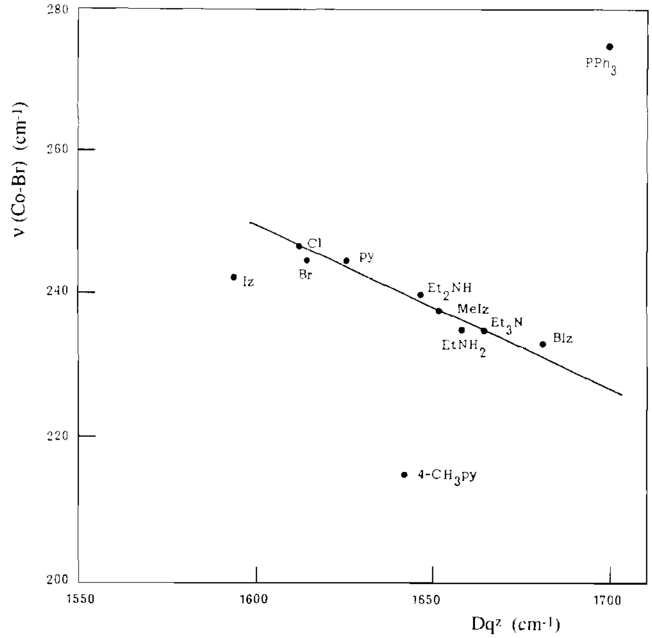

Fig. 9. Plot of Dq^z values of the Lewis bases vs. ν(Co–Br) frequencies (cm^{-1}) in bromo(Lewis base)cobalt(III) complexes of (DO)(DOH)bzo.

the Co(II)/Co(I) $E_{1/2}$ values on the Dq^{xy} values is well documented by Busch and co-workers [106, 107] Costa *et al.* [108], and Elliott *et al.* [109]. Marzilli and co-workers [110–112] have demonstrated that the relative donor ability of the organic ligands in the axial sites in organocobalt(III) complexes of macrocycles is nearly independent of the equatorial ligands.

In six-coordinate cobalt(III) complexes of the type $[CoL_4XY]$ having D_{4h} microsymmetry (tetragonal acentric) a pair of π-orbitals on the ligands X and Y in the axial sites will perturb the *xz* and *yz* orbitals which then become π-anti-bonding. These *xz*, *yz* pairs will π-interact with the *z* directed π-orbitals on the ligand L_4. The *xy* orbital interacts in a π-sense with the π-orbitals of L_4 lying in the *xy* plane. The z^2 orbital is σ-anti-bonding with respect to both axial and equatorial ligands while the x^2–y^2 orbital is σ-anti-bonding to L_4 only. It is now obvious that the Lewis base in the axial site transmits the electron density to the metal ion through the x^2–y^2 orbital. This observation is clearly borne out from the dependence of the Co(III)/Co(II) $E_{1/2}$ values on the Dq^z values and the dependence of the Co(II)/Co(I) $E_{1/2}$ values on the Dq^{xy} values indicating addition of an electron to the d_{z^2} orbital (which is σ-anti-bonding with respect to both L_4 and X, Y) during the reduction of Co(III) and the addition of an electron to the $d_{x^2-y^2}$ orbital (which is σ-anti-bonding with respect to L_4 only) during the reduction of Co(II). This ascertains that the Dq^z value is a quantitative measure of the σ-bonding ability of the Lewis bases.

Ground state trans-effect

The plot of Dq^z versus ν(Co–Br) is depicted in Fig. 9. As the field strength of the Lewis base increases there is a gradual lowering of the Co–Br stretching frequency and the plot of ν(Co–Br) versus Dq^z is linear. As the field strength of the Lewis base increases it transmits more electron density to cobalt(III) through $d_{x^2-y^2}$ by σ-donation and the metal ion in turn transmits the electron density to Br^-. This electronic transmission of the Lewis bases to the *trans* Br^- through the central metal ion renders the Co–Br bond weaker with a concomitant decrease in the Co–Br stretching frequency. This observation substantiates the enhanced synergistic effect between the cobalt(III) centre and the axial ligands, an observation that testifies the increased stability of six-coordinate cobalt(III) complexes.

Acknowledgements

I acknowledge with a deep sense of gratitude the generous help rendered by Professor Koya Aida and Dr Yoshika Imai, Department of Engineering Science, Tohoku University, for recording the far-IR spectra of many samples.

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