Inorganica Chimica Acta, *163* (1989) 25–40

Synthesis, Characterization and Spectrochemistry, Electrochemistry and Spectroelectrochemistry of Bromo (Lewis base) Cobalt(III) Complexes of 3,8-Dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione Dioxime*

V. ALEXANDER

Department of Chemistry, Loyola College, Madras 600 034 (India)

(Received January 9, 1989)

Abstract

A series of six coordinate cobalt(III) complexes of the type $[LCo((DO)(DOH)bzo)Br]^+$ (for abbreviations see V. Alexander and V. V. Ramanujam, *Inorg. Chim. Acta, 156* (1989) 125), where L = 4-methylpyridine, 1-methylimidazole, benzimidazole, 5,6-dimethylbenzimidazole, 2-aminopyridine, triphenylphosphine, ethylamine, diethylamine and triethylamine, have been synthesized with the tetraaza quadridentate chelate 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime. The quadridentate ligand coordinates with cobalt in the equatorial position as a monoanion with the concomitant formation of an intramolecular hydrogen bond. The Lewis base and the bromide coordinate in the axial sites of cobalt. The synthesis of these complexes has been accomplished by making use of the lability of the axial sites of the dibromo complex, $[Co((DO)(DOH)bzo)Br_2]$. These complexes have been characterized by C, H, N and Co analysis, conductivity measurements, magnetic susceptibility and IR, ^1H NMR and UV–Vis spectroscopy. Indirect evidence for the presence of a hydrogen bond in these complexes has been obtained by replacing the H-bonded proton by the BF_2 group. All these complexes exhibit three d–d transitions, two in the visible region and one in the near UV region, assignable to ${}^1A_{1g} \rightarrow {}^1E_g^a$, ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and ${}^1A_{1g} \rightarrow ({}^1E_g^b + {}^1B_{2g})$, characteristic of tetragonally distorted octahedral cobalt(III) complexes and have been assigned a D_{4h} microsymmetry in analogy with the crystal field model of Wentworth and Piper. The ligand field parameters such as Dq^{xy}, Dq^z and D_t have been computed and the field strength of the in-plane ligand is higher than that of the axial ligand. The electronic absorption spectra of low spin cobalt(III) in pseudo O_h symmetry and in a D_{4h} microsymmetry when $Dq^{xy} > Dq^z$, $Dq^z > Dq^{xy}$ and $Dq^{xy} \simeq Dq^z$ are explained with the aid of a qualitative energy level diagram. The observed spectrochemical series of the Lewis bases for Co^{3+} is $Iz < py < 4\text{-}CH_3py < Et_2NH < MeIz < EtNH_2 < Et_3N < BIz < PPh_3$. They exhibit two polarographic reduction waves corresponding to the Co(III) → Co(II) and Co(II) → Co(I) reductions. The cyclic voltammograms in DMF at a GC disk electrode consist of two cathodic waves corresponding to the reductions, Co(III) → Co(II) and Co(II) → Co(I) and two anodic waves corresponding to the oxidations, Co(I) → Co(II) and Co(II) → Co(III). Both Co(III)/Co(II) and Co(II)/Co(I) redox couples are irreversible as indicated by the ΔE_p and i_{pa}/i_{pc} values. ΔE_p for the former couple is much higher than that of the latter indicating a slow rate of electron transfer for the reduction of Co(III) to Co(II) due to the strong binding of the Lewis base to the Co^{3+} ion. The i_{pa}/i_{pc} for the Co(II)/Co(I) couple is 0.5 indicating a 50% Co(I) yield. This suggests the involvement of a coupled chemical reaction such as an ECE mechanism. The mechanisms of the electrode processes are explained in the light of recent electrochemical investigations on similar Co(III) complexes. The generation of five coordinate $[LCo^{II}((DO)(DOH)bzo)]^+$ during the reduction of the Co(III) complex and the generation of the four coordinate Co(I) complex, $[Co^I((DO)(DOH)bzo)]$, during the reduction of the Co(II) complex are envisioned. The cyclic voltammetric $E_{1/2}$ value for the Co(III)/Co(II) redox couple depends on the spectrally determined field strength of the axial ligand in a predictable manner. The plot of Dq^z versus $E_{1/2}$ is linear with a slope of 0.56 ± 0.02 cm^{-1} mV^{-1}. The Co(II)/Co(I) $E_{1/2}$ is independent of the axial ligand and reflects the nature of the in-plane ligand. The dependence of the Co(III)/Co(II) $E_{1/2}$ value on the axial ligand reflects the transfer of an electron during the reduction of the Co(III) complex to the d_{z^2} orbital which is sigma antibonding with respect to both axial and in-plane ligands while the independence of the Co(II)/Co(I) $E_{1/2}$ value on the axial ligand reflects the transfer of an electron during the reduction of the five

---

*This paper is dedicated to Dr V. V. Ramanujam, Professor of Inorganic Chemistry (retired), University of Madras, for his 40 years of dedicated service to the cause of teaching and research.

0020-1693/89/$3.50

coordinate Co(II) complex to the $d_{x^2-y^2}$ orbital which is sigma anti-bonding with respect to the equatorial ligand only.

Introduction*

Model studies in search of the mechanisms for the enzymic reactions catalysed by coenzyme B_{12} and methylcobalamin (methyl B_{12}), the only known organocobalt compounds of nature, exceeded this objective and has become a general contribution to coordination chemistry [1]. The field encompassed by this research is characterized by important contributions in terms of distinctive compounds and reactions. It has brought together in a highly creative and productive context the important lines of research in biochemistry and organometallic chemistry as commented upon by Halpern [2]. It is well recognized that the (non-alkyl)- and alkylcobalt(III) complexes of the bis(dimethylglyoximato) dianion, collectively called cobaloximes [3], have made rich contributions to the field of B_{12} chemistry and to inorganic chemistry in general [1, 4]. These compounds are interesting on the one hand because of their extensive coordination chemistry [1] and on the other hand because of the parallels between the chemistry of organometallic derivatives and organocobalamins [1, 3, 4b, 5]. As models for coenzyme B_{12}, cobaloximes have been subjected to extensive studies including electrochemical [6], kinetic [7], and structural [4b, 7s, t, 8] properties. Studies on models built upon the monoanionic chelates like corrin, championed by Costa and his co-workers, are a complement to the field of B_{12} chemistry [6a, 7r, s, 9, 10]. Costa's modified model, (C_2(DO)(DOH)pn)**, being an excellent electrochemical mimic of cobalamins [6a, b], seems to promote better types of reactions involved in B_{12}-dependent enzymic processes [10b, c, 11]. The enormous strides made recently through the organocobalt(III) compounds of the credible cobaloxime and Costa-type models provided valuable insight into the elegant chemistry orchestered by the primary bioinorganic system. Nevertheless, the related chemistry of the (non-alkyl)cobalt complexes is intriguing and informative transition metal chemistry.

A new coenzyme B_{12} model built upon the quadridentate ligand, 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime, (Fig. 1, Structure **I**) has been reported recently [12]. This chelate coordinates with cobalt in the equatorial position as a monoanion. The detailed electrochemical investigations carried out very recently on the alkyl- and (non-alkyl)cobalt(III) complexes of this chelate indicate that this is a closer electrochemical mimic of B_{12} than the cobaloxime and lies in between Costa's modified derivative, (C_2(DO)(DOH)pn), and cobaloxime [13]. Since this model affords a rich variety of (non-alkyl)- and alkylcobalt(III) complexes owing to the potentialities of the axial coordination sites of cobalt, it seems to be another convenient vehicle to study the intriguing relationship that exists between structure, axial ligands, spectral properties, and redox behaviour displayed by several other related quadridentate equatorial chelates. Therefore, the synthesis and physicochemical studies of a series of complexes of this new chelate with a closely related family of axial ligands would be of significance for exploring these properties. Herein the synthesis, characterization, and spectrochemical, electrochemical and spectroelectrochemical properties of (non-alkyl)cobalt(III) complexes of chelate **I** with a series of Lewis bases and a bromide ion in the axial sites (Fig. 1, Structure **II**) are reported.

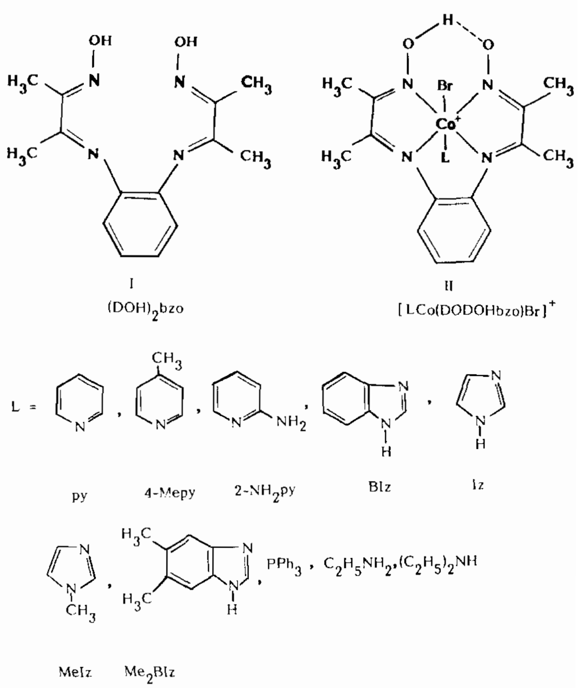

Fig. 1. **I**, (DOH)$_2$bzo (3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime); **II**, [LCo((DO)(DOH)bzo)Br]$^+$, L = py, 4-CH_3py, 2-NH_2py, BIz, Iz, MeIz, Me$_2$BIz, PPh$_3$, EtNH$_2$, Et$_2$NH or Et$_3$N.

---

*For abbreviations used in this paper see ref. 13. The equatorial chelate is represented by ((DO)(DOH)bzo) to be consistent with that employed by Costa.

**(C_2(DO)(DOH)pn) is Costa's modified model wherein the oxime methyl groups in ((DO)(DOH)pn) are replaced by ethyl groups (see refs. 9c, d). This derivative is also abbreviated as (EMO)(EMOH)pn (see ref. 10c).

Experimental

Materials

Triphenylphosphine, imidazole and boron trifluoride etherate (BDH); benzimidazole, potassium hexafluorophosphate and 1-methylimidazole (Fluka); 5,6-dimethylbenzimidazole and sodium fluoborate (Riedel); and sodium perchlorate (E. Merck) were used as received. Diethylamine and triethylamine (BDH, Laboratory Reagent) were dried over KOH pellets for several days, distilled twice and kept over KOH. Ethylamine (40 wt.% solution in water) and 4-picoline (4-methylpyridine) (IDPL, India) were used as received. 2-Aminopyridine (Koch Light) was recrystallized from ethanol.

Double distilled water, obtained by distilling distilled water over alkaline permanganate, was used throughout. Diethylether was dried by distilling over sodium metal. Commercial grade ethanol and methanol were purified by refluxing over lime for 7 h, and then distilled. Acetone (BDH, Analar Reagent) was used without further purification.

The supporting electrolyte, internal standard and the solvents used for electrochemical investigations have been reported recently [13].

Synthesis of the Ligand

The ligand, 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime, $(DOH)_2bzo$, was synthesized by the recently reported method [12].

Synthesis of the Complexes

All the complexes reported herein were synthesized starting from the dibromo complex $[Co((DO)(DOH)bzo)Br_2]$, reported recently [12].

$[4\text{-}CH_3pyCo((DO)(DOH)bzo)Br]PF_6$ (1)

To a solution of $[Co((DO)(DOH)bzo)Br_2]$ (2.46 g, 5 mmol) in 100 ml of hot aqueous methanol (1:5 vol./vol.) was added 2 ml of a saturated aqueous solution of potassium hexafluorophosphate followed by the addition of 4-methylpyridine (0.4656 g, 5 mmol) with stirring. The yellowish brown crystalline compound which separated out was filtered immediately through a G3 sintered funnel, washed twice with dry methanol followed by diethyl ether and dried under vacuum over anhydrous calcium chloride. Yield 80%. *Anal.* Calc. for $C_{20}H_{24}N_5O_2BrPF_6Co\cdot H_2O$: C, 35.95; H, 3.92; N, 10.48; Co, 8.82. Found: C, 36.07; H, 3.80; N, 10.67; Co, 9.21%. ^1H NMR (dmso-d_6) δ (Me_4Si) 2.23(s, 12H), 0.48(s, 3H), 7.26(m, 2H), 7.9(m, 6H). Λ_M (DMF) 68.2 ohm^{-1} cm^2 mol^{-1}.

$[MeIzCo((DO)(DOH)bzo)Br]Br$ (2)

A solution of $[Co((DO)(DOH)bzo)Br_2]$ (2.46 g, 5 mmol) in 100 ml of hot aqueous methanol (1:5 vol./vol.) was treated with 1-methylimidazole (0.4105 g, 5 mmol) and the resulting dark brown solution was refluxed on a water bath for an hour. The volume of the solution was then reduced to 10 ml by slow evaporation on a water bath and left at room temperature (30 °C) for 6 h. The dark brown product which separated out was filtered and washed repeatedly with cold methanol (0 °C) followed by diethyl ether to obtain the light brown tiny spongy needles. Yield: 60%. *Anal.* Calc. for $C_{18}H_{23}N_6O_2Br_2Co\cdot H_2O$: C, 36.51; H, 4.26; N, 14.9; Co, 9.90. Found: C, 36.72; H, 4.34; N, 13.98; Co, 9.81%. ^1H NMR (dmso-d_6) δ (Me_4Si) 1.45(s, 3H), 2.4(s, 12H), 6.8(m, 1H), 7.13(m, 1H), 7.5(m, 4H). Λ_M (DMF) 78.2 ohm^{-1} cm^2 mol^{-1}.

$[BIzCo((DO)(DOH)bzo)Br]BF_4$ (3)

This complex was synthesized by following the procedure employed for the synthesis of **1** using 5 ml of an alcoholic solution of benzimidazole (0.5 g, 5 mmol) and 3 ml of a saturated aqueous solution of sodium fluoborate. Yellowish brown crystals. Yield: 70%. *Anal.* Calc. for $C_{21}H_{23}N_6O_2BrBF_4Co\cdot H_2O$: C, 39.72; H, 3.97; N, 13.23; Co, 9.28. Found: C, 39.54; H, 3.75; N, 13.50; Co, 9.69%. ^1H NMR (dmso-d_6) δ (Me_4Si) 2.28(s, 12H), 7.30(m, 4H), 7.53(m, 4H), 8(m, 2H). Λ_M (DMF) 85.5 ohm^{-1} cm^2 mol^{-1}.

$[(Me_2BIzCo((DO)(DOH)bzo)Br]PF_6$ (4)

This complex was synthesized by following the procedure employed for the synthesis of **1** using 5 ml of an alcoholic solution of 5,6-dimethylbenzimidazole (0.74 g, 5 mmol) and 2 ml of a saturated aqueous solution of KPF_6. Brownish yellow crystals. Yield: 71%. *Anal.* Calc. for $C_{23}H_{27}N_6O_2BrPF_6Co$: C, 39.28; H, 3.87; N, 11.95; Co, 8.38. Found: C, 38.97; H, 3.60; N, 11.90; Co, 8.50%. ^1H NMR (dmso-d_6) δ (Me_4Si) 1.5(s, 6H), 2.3(s, 12H), 7.16(m, 4H), 7.83(m, 4H). Λ_M (DMF) 87.5 ohm^{-1} cm^2 mol^{-1}.

$[PPh_3Co((DO)(DOH)bzo)Br]Br$ (5)

To the brown solution of $[Co((DO)(DOH)bzo)Br_2]$ (2.46 g, 5 mmol) in 100 ml of hot aqueous methanol (1:5 vol./vol.) was added 10 ml of a hot alcoholic solution of triphenylphosphine (1.31 g, 5 mmol). The resulting reddish brown solution was vigorously stirred for 5 min. The brown shiny tiny needles which separated out were filtered through a G3 sintered funnel and washed repeatedly with dry alcohol followed by dry ether. Dried under vacuum oven at 60 °C overnight. Yield: 65%. *Anal.* Calc. for $C_{32}H_{32}N_4O_2Br_2PCo\cdot 0.5H_2O$: C, 50.35; H, 4.36; N, 7.34; Co, 7.72. Found: C, 50.45; H, 4.31; N, 7.30; Co, 7.98%. ^1H NMR (dmso-d_6) δ (Me_4Si) 1.97(s, 6H), 2.10(s, 6H), 7.56(m, 19H). Λ_M (DMF) 64.7 ohm^{-1} cm^2 mol^{-1}.

[EtNH$_2$Co((DO)(DOH)bzo)Br]ClO$_4$ (6)

To a solution of [(Co((DO)(DOH)bzo)Br$_2$] (2.46 g, 5 mmol) in 100 ml of hot aqueous methanol (1:5 vol./vol.) was added 2 ml of a saturated aqueous solution of NaClO$_4$. It was cooled to 10 °C and the cold solution was then treated with a 40 wt.% aqueous solution of ethylamine (0.5636 g, 5 mmol) with stirring. The resulting dark brown solution was kept undisturbed at room temperature (30 °C) for 2 h. The brown shiny crystals which separated out were filtered through a G3 sintered funnel, washed once with cold water (5 °C) and repeatedly with cold acetone (0 °C) followed by ether and dried under vacuum. Yield: 50%. *Anal.* Calc. for $C_{16}H_{24}N_5O_6BrClCo \cdot H_2O$: C, 33.44; H, 4.56; N, 12.19; Co, 10.25. Found: C, 33.65; H, 4.60; N, 12.03; Co, 10.50%. ^1H NMR (dmso-d$_6$) δ (Me$_4$Si) 0.83(m, 5H), 2.29(s, 12H), 7.35(m, 4H). Λ_M (DMF) 85.2 ohm^{-1} cm^2 mol^{-1}.

[Et$_2$NHCo((DO)(DOH)bzo)Br]ClO$_4$ (7)

To a solution of [Co((DO)(DOH)bzo)Br$_2$] (2.46 g, 5 mmol) in 100 ml of hot aqueous methanol was added 2 ml of a saturated aqueous solution of NaClO$_4$ followed by the addition of diethylamine (0.3657 g, 5 mmol). The resulting dark brown solution was refluxed for 2 h. The volume of the solution was then reduced to 10 ml by evaporation on a water bath and cooled to 0 °C. The black crude compound which separated out was filtered, washed once with water and twice with cold acetone (0 °C) and dried in air. Recrystallization from hot methanol yielded a dark brown crystalline complex. Yield: 50%. *Anal.* Calc. for $C_{18}H_{28}N_5O_6BrClCo \cdot 0.5H_2O$: C, 36.41; H, 4.92; N, 11.79; Co, 9.93. Found: C, 36.37; H, 4.87; N, 11.80; Co, 10.12%. ^1H NMR (dmso-d$_6$) δ (Me$_4$Si) 0.9(m, 10H), 2.3(s, 12H), 7.3(m, 4H). Λ_M (DMF) 69.5 ohm^{-1} cm^2 mol^{-1}.

[Et$_3$NCo((DO)(DOH)bzo)Br]ClO$_4$ (8)

This complex was synthesized by employing the procedure outlined for the synthesis of 7 using triethylamine (0.506 g, 5 mmol). Dark brown crystals were obtained. Yield: 60%. *Anal.* Calc. for $C_{20}H_{32}N_5O_6BrClCo$: C, 39.20; H, 5.26; N, 11.43; Co, 9.62. Found: C, 38.93; H, 5.19; N, 11.32; Co, 10.13%. ^1H NMR (dmso-d$_6$) δ (Me$_4$Si) 0.95(m, 15H), 2.32(m, 12H), 7.60(m, 4H). Λ_M (DMF) 75.5 ohm^{-1} cm^2 mol^{-1}.

[2-NH$_2$pyCo((DO)(DOH)bzo)Br]Br (9)

To a solution of [Co((DO)(DOH)bzo)Br$_2$] (2.46 g, 5 mmol) in 100 ml of hot aqueous methanol (1:5 vol./vol.) was added 5 ml of an alcoholic solution of 2-aminopyridine (0.47 g, 5 mmol). The resulting reddish brown solution was refluxed for 4 h on a water bath. The volume of the solution was then reduced to 25 ml by slow evaporation on a water bath and refrigerated at 0 °C overnight. The brown product which separated out was filtered, washed rapidly with cold acetone followed by diethyl ether and dried under vacuum over anhydrous calcium chloride. Recrystallization from warm ethanol yielded a light brown crystalline complex. Yield: 40%. *Anal.* Calc. for $C_{19}H_{23}N_6O_2Br_2Co$: C, 38.93; H, 3.95; N, 14.34; Co, 10.05. Found: C, 38.78; H, 4.11; N, 14.35; Co, 10.31%. Λ_M (CH$_3$OH) 110.7 ohm^{-1} cm^2 mol^{-1}.

[pyCo((DO)$_2$bzoBF$_2$)Br]ClO$_4$ (10)

The hydrogen bounded proton in [pyCo((DO)(DOH)bzo)Br]ClO$_4$ was replaced by the BF$_2$ group by following the procedure of Schrauzer and Windgassen [14]. A suspension of [pyCo((DO)(DOH)bzo)Br]ClO$_4$ (3.038 g, 5 mmol) in 100 ml of dry diethyl ether was stirred with a large excess of boron trifluoride etherate for 20 h using a magnetic stirrer in a stoppered round bottom flask. The yellowish brown complex turned dark brown as the reaction proceeded. The product was filtered, washed with dry alcohol followed by diethyl ether and dried under vacuum. Yield: 95%. *Anal.* Calc. for $C_{19}H_{21}N_5O_6ClBrBF_2Co$: C, 35.74; H, 3.32; N, 10.97; Co, 9.23. Found: C, 35.70; H, 3.50; N, 11.05; Co, 9.48%.

[pyCo((DO)(DOH)bzo)Br]ClO$_4$ (11) and [IzCo((DO)(DOH)bzo)Br]PF$_6$ (12)

The synthesis of these complexes has already been reported [12].

Physical Measurements

The instruments used and the method employed for C, H, N and Co estimations, for recording IR, ^1H NMR, UV–Vis spectra, for measuring the conductivity and for determining the magnetic susceptibility have been described elsewhere [12].

Thermo Gravimetric Analysis

TGA was carried out using a Dupont Thermogravimetric analyzer by heating the samples at a rate of 20 °C per minute under the atmosphere of dinitrogen. The loss of weight was recorded as a function of temperature.

Results and Discussion

Infrared Spectra

The characteristic infrared absorption bands of the ligand framework and the coordinated base are presented in Table 1. The characteristic absorption bands due to the axially bound Lewis base are observed besides the bands characteristic of the ligand framework. Upon complex formation, the pyridine vibrations in the high frequency region are not shifted appreciably whereas the out-of-plane

TABLE 1. Characterictic infrared absorption bands of the Lewis base complexes[a]

Complex	Assignments							Absorption of the Lewis base	
	ν(CH)	ν(C=C)	ν(C=N)	ν(NO)	ν'(NO)[b]	ν(Co–N)	ν(NH)	Band (cm^{-1})	Assignment[c]
$[4\text{-}CH_3pyCo((DO)(DOH)bzo)Br]PF_6$	3040w, sp 3110w, sp	1620s, sp	1560s, mb	1235s, mb	1090s, sp	520s, sp		1040w 1000w	unsym. ring breathing mode tot. sym. ring breathing mode
$[MeIzCo((DO)(DOH)bzo)Br]Br$			1565s, mb	1240vs, sp	1100	525			
$[BIzCo((DO)(DOH)bzo)Br]BF_4$	3280w, b	1625w, sp	1550w, sp	1235vs, sp	1095sh, sp	520s, sp	3120s, sp	3120sp	ν(NH)
								1500sp 1310sp 1280sp	ring stretching
								635w	ring torsion
$[Me_2BIzCo((DO)(DOH)bzo)Br]PF_6$	3380w, b 3235w, b	1615w, sp	1560s, mb	1230vs, sp	1090s, sp	530s, sp	3140w, sp		
$[PPh_3Co((DO)(DOH)bzo)Br]Br$	3060w, mb		1560s, sp	1235vs, sp	1080s, sp	540vs, sp		1620sp 1850sp	Ph ring vib.
								700s, sp	PPh_3 vibration
$[EtNH_2Co((DO)(DOH)bzo)Br]ClO_4$			1560vs, mb	1230vs, sp	1085s, mb	520vs, sp	3100w, sp 3200vs, sp		
$[Et_2NHCo((DO)(DOH)bzo)Br]ClO_4$			1570s, mb	1235vs, sp	1085vs, sp	525vs, sp			
$[Et_3NCo((DO)(DOH)bzo)Br]ClO_4$			1570s, mb	1225vs, sp	1090s, sp	515s, sp			
$[2\text{-}NH_2pyCo((DO)(DOH)bzo)Br]Br$	3300b, w	1620s, sp	1565s, b	1230vs, mb	1100s, mb	520s, sp	3160w, b 3080w, b		

[a] Medium: KBr disks; abbreviations: s = strong, sp = sharp, sh = shoulder, vs = very strong, b = broad, m = medium, w = weak, mb = medium broad. [b] 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^-. [c] For the references, see text.

ring deformation vibration at 405 cm^{-1} and the in-plane deformation vibration at 604 cm^{-1} suffer significant shifts towards higher frequencies [17]. Thus the in-plane deformation vibration of the coordinated pyridine ring occurs at 700 cm^{-1} while the out of plane deformation vibration occurs at 425 cm^{-1} in $[pyCo((DO)(DOH)bzo)Br]ClO_4$. The coupled C=C and C=N stretching and the CH deformation of the pyridine ring occur at 1610 and 770 cm^{-1}, respectively [18]. The 4-methylpyridine complex $[4\text{-}CH_3pyCo((DO)(DOH)bzo)Br]PF_6$ exhibits ν(CH) vibrations at 3040 and 3110 cm^{-1}. ν(C=C) appears as a strong sharp band probably due to the coupling with the HOH bending mode of lattice water. The unsymmetric ring breathing mode and the totally symmetric ring breathing mode appear as weak bands at 1040 and 1005 cm^{-1}, respectively [19]. ν(NH) appearing in solid imidazole as a very broad band due to intermolecular hydrogen bonding appears as a sharp band at 3140 cm^{-1}. The NH in-plane deformation vibration occurring at 1540 cm^{-1} in free imidazole [20] is not observed as a separate band in the complex. This may probably couple with the ν(C=N) of the ligand framework. Similarly, the ring stretching modes appearing at 1473 and 1445 cm^{-1} in the free imidazole appear as shoulders at 1490 and 1500 cm^{-1} as has been observed by Cordes and Walter [21]*. The very weak band appearing at 920 cm^{-1} may be attributed to the ring mode of coordinated imidazole which appears at 935 cm^{-1} in the free imidazole.

The ν(NH) absorption occurring at 3140 cm^{-1} in $[(IzCo((DO)(DOH)bzo)Br]PF_6$ is absent in [MeIz-Co((DO)(DOH)bzoBr]Br indicating the absence of the imino hydrogen in the latter. The sharp band appearing at 3120 cm^{-1} may be assigned to the methyl group vibration of the coordinated 1-methylimidazole since it is absent in the complex of imidazole. In $[BIzCo((DO)(DOH)bzo)Br]BF_4$ the weak bands above 3250 cm^{-1} are apparently due to the imidazole CH vibrations and those at 2980 and 3040 cm^{-1} are assignable to the CH vibration of the benzene portion of benzimidazole and the equatorial ligand. The strong band appearing at 3120 cm^{-1} may be due to the ν(NH) of the ligand. Several ring stretching bands are expected in the region 1700–1200 cm^{-1}. Thus the sharp bands at 1500, 1310 and 1280 cm^{-1} are assigned to the aromatic ring stretching and the sharp bands at 1625, 1440 and 1370 cm^{-1} are attributed to the ν(C=C), ν(C=N) and asymmetric and symmetric deformation vibrations of the methyl groups, respectively. Based on the infrared studies of Cordes and Walter [22] on the bis(benzimidazolato)metal complexes, the sharp band at 1280 cm^{-1} is assigned to the CH bending vibration which is not found in the dibromo complex, $[Co((DO)(DOH)bzo)Br_2]$. In analogy with the above work [22], the weak band at 635 cm^{-1} is assigned to ring torsion because of its consistent appearance in all the complexes of both imidazole and benzimidazole.

The spectrum of the 5,6-dimethylbenzimidazole complex, $[Me_2BIzCo((DO)(DOH)bzo)Br]PF_6$, resembles that of the benzimidazole complex except for the appearance of a sharp band at 1470 cm^{-1} assignable to the methyl group vibration. One common feature observed in the complexes of the imidazole group ligands is the appearance of a sharp band in the region 1310–1330 cm^{-1}. Since this band is not found in the complexes of 1-methylimidazole, it is assigned to NH bending vibration [21]. 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 infrared spectrum of the triphenylphosphine complex, $[PPh_3\text{-}Co((DO)(DOH)bzo)Br]Br$ is the appearance of a number of sharp bands in the 1620 cm^{-1} region probably due to the phenyl ring vibrations and a sharp as well as strong band at 700–705 cm^{-1}. Since the latter band is absent in the dibromo complex and in all other Lewis base complexes, it can be attributed to the vibration of coordinated triphenylphosphine.

The infrared spectrum of $[EtNH_2Co((DO)(DOH)\text{-}bzo)Br]ClO_4$ consists of sharp as well as strong bands at 3100 and 3200 cm^{-1}. The primary amines have the tendency to form hydrogen bonds with another molecule or with solvent molecule. Steric hindrance would not favour the formation of hydrogen bonds in this complex, however. The analytical data rules out the formation of associated molecule. The strong sharp bands appearing at 3100 and 3200 cm^{-1} can therefore be ascribed to the symmetric and asymmetric NH stretching frequencies [23], respectively. In the case of $[2\text{-}NH_2pyCo((DO)(DOH)\text{-}bzo)Br]Br$ it is difficult to describe unequivocally the mode of bonding of 2-aminopyridine since it is a potential ambidentate ligand. It can coordinate to a metal either through the nitrogen present in the ring (endocyclic N) or through the nitrogen of the amino group (exocyclic N). Summers *et al.* [8b] in their study on coenzyme B_{12} models invoked the endocyclic binding mode of 2-aminopyridine from the crystal and molecular structure of $[2\text{-}NH_2\text{-}pyCo(DH)_2i\text{-}Pr]$ supported by spectral and solution studies. Yet, these authors did not rule out the fluxional behaviour of 2-aminopyridine forming

---

*The authors report that the band at 1328 cm^{-1} in the imidazole complexes is assignable to the CH or NH bending mode. If this were due to the CH bending mode, [MeIzCo-((DO)(DOH)bzo)Br]Br would also give a band around 1328 cm^{-1} which is not observed. Therefore the band appearing in the 1310–1330 cm^{-1} region for the complexes of imidazole, benzimidazole and 5,6-dimethylbenzimidazole is attributed to the NH bending mode.

complexes through the endocyclic and exocyclic nitrogens which are present in equilibrium. Very recently, Marzilli *et al.* [8f] extensively studied the dynamic behaviour of 2-aminopyridine by kinetic, spectroscopic and structural studies. The absence of a sharp band characteristic of the free amino [24] group in the 3300–3500 cm^{-1} region in the infrared spectrum of $[2\text{-}NH_2pyCo((DO)(DOH)bzo)Br]Br$ indicates that 2-aminopyridine coordinates through its exocyclic nitrogen.

While complexes of ethylamine and 2-aminopyridine exhibit strong and sharp bands in the 3080–3200 cm^{-1} region, $[Et_2NHCo((DO)(DOH)bzo)Br]ClO_4$ exhibits a broad band at about 3250 cm^{-1} probably due to the coupling of ν(NH) and ν(CH) vibrations. The triethylamine complex, $[Et_3NCo((DO)(DOH)bzo)Br]ClO_4$, also exhibits a strong as well as broad band in this region due to ν(CH). All the Lewis base complexes exhibit absorption bands characteristic of the ligand framework besides the bands characteristic of the coordinated Lewis bases as described above. Among the bands characteristic of the macrocycle, the ν(OH) band merits discussion since it appears in a wider energy region in these complexes. The complexes of imidazole, 1-methylimidazole, 2-aminopyridine, ethylamine, diethylamine and triethylamine exhibit this absorption as a broad band of medium intensity in the region 2280–2450 cm^{-1} whereas in the complexes of benzimidazole and 5,6-dimethylbenzimidazole, it is very weak and broad and in the complexes of pyridine, 4-methylpyridine and triphenylphosphine it is obscured.

ν(Co–N) (nitrogen donors of the equatorial ligand) appears in all the complexes in the region 520–530 cm^{-1} except for $[PPh_3Co((DO)(DOH)bzo)Br]Br$ in which it occurs at 540 cm^{-1}. This indicates that the energy of the Co–N bond in this complex is higher than that in all other complexes due to the greater π-accepting tendency of triphenylphosphine. The sharp band, assignable to ν(C=C), occurring at 1630 and 1605 cm^{-1} in the free ligand and in the dibromo complex, respectively, appears in the complexes of pyridine, 4-methylpyridine, benzimidazole, 5,6-dimethylbenzimidazole and 2-aminopyridine as a sharp band probably as a coupled ν(C=C) vibration of the equatorial ligand and that of the coordinated Lewis base, whereas it overlaps with ν(C=N) in the complexes of imidazole, 1-methylimidazole, ethylamine and triphenylphosphine and appears as a broad band.

In broad agreement with the analytical composition, the complexes of pyridine, 4-methylpyridine, 1-methylimidazole, benzimidazole, 5,6-dimethylbenzimidazole, triphenylphosphine, ethylamine and diethylamine exhibit infrared absorption bands characteristic of lattice water. In general, lattice water absorbs at 3550–3200 cm^{-1} corresponding to antisymmetric and symmetric OH stretchings and at 1630–1600 cm^{-1} corresponding to HOH bending [25]. It also exhibits absorption bands in the region 600–300 cm^{-1} [25, 26]. All these complexes exhibit a strong as well as broad band in the region 3420–3540 cm^{-1} due to the antisymmetric and symmetric OH stretchings. The HOH bending vibration expected to occur in the 1630–1600 cm^{-1} region may probably be overlapping with ν(C=C). The complex $[Me_2BIzCo((DO)(DOH)bzo)Br]PF_6$ exhibits a sharp shoulder at 1630 cm^{-1} probably due to the 'pure' HOH bending of the lattice water. All those complexes which crystallize with lattice water exhibit another band at 440 cm^{-1}. Infrared absorption bands characteristic of ionic perchlorate, fluoborate and hexafluorophosphate are well observed [12].

Thermal Studies

Thermogravimetric analysis was carried out for all the twelve complexes. All these complexes decompose in the temperature range of 250–300 °C. In the case of $[IzCo((DO)(DOH)bzo)Br]PF_6$, $[Me_2BIzCo((DO)(DOH)bzo)Br]PF_6$, $[Et_3NCo((DO)(DOH)bzo)Br]ClO_4$, $[pyCo((DO)_2bzoBF_2)Br]ClO_4$ and $[2\text{-}NH_2pyCo((DO)(DOH)bzo)Br]Br$ no loss in weight was observed upto 250 °C indicating the absence of water or solvent molecules (CH_3OH) in the crystal lattice. The other complexes indicate loss of lattice water in the temperature range of 60–80 °C. $[PPh_3Co((DO)(DOH)bzo)Br]Br$ and $[Et_2NHCo((DO)(DOH)bzo)Br]ClO_4$ lose 0.5 molecules of water per molecule of the complex whereas $[pyCo((DO)(DOH)bzo)Br]ClO_4$, $[MeIzCo((DO)(DOH)bzo)Br]Br$, $[BIzCo((DO)(DOH)bzo)Br]BF_4$, $[4\text{-}CH_3pyCo((DO)(DOH)bzo)Br]PF_6$ and $[EtNH_2Co((DO)(DOH)bzo)Br]ClO_4$ loss 1 molecule of water per molecule of the complex. These data confirm the exact molecular composition of these complexes as inferred from the analytical data.

Magnetic Susceptibility

The weight of each of these complexes decreased in the magnetic field and the χ_M^{corr} is a negative quantity ranging from -985×10^{-12} to -2167×10^{-12} indicating the diamagnetic nature of these complexes [12].

Intramolecular Hydrogen Bond

The OH stretching vibration appearing in the free ligand at 2900 cm^{-1} is shifted to 2400 cm^{-1} in the dihalo, pseudohalogeno and alkylcobalt(III) complexes indicating the formation of hydrogen bonding during the complexation of the ligand [12]. The OH bond weakens in the complexes due to hydrogen bonding and consequently ν(OH) appears at lower energy. The Lewis base complexes also exhibit ν(OH) at around 2400 cm^{-1}. These complexes also exhibit two strong as well as sharp bands at 1220 and 1075 cm^{-1} assignable to ν(NO) and ν'(NO). The appearance of only one band at 1220 cm^{-1}, assignable to ν(NO), in the free ligand shows that the two –NOH groups are identical while the appearance of two bands, assignable to ν(NO), in the complexes indicates the presence of two unequal –NO– linkages. Indeed, upon complexation there are two –NO– linkages, C=N–O–H and C=N–O---H, due to the formation of the hydrogen bond. Studies on cobaloximes by Schrauzer and Windgassen [27] and by Yamazaki and Hohokabe [18] as well as the work of Blinc and Hadzi [28] also confirm the presence of two unequal –NO– linkages due to hydrogen bonding. Disappearance of the δ(OH) band in the complexes is further evidence for O–H...O bond formation [29]. The hydrogen bonded proton can be chemically innocent [9d] and it escaped experimental detection by proton NMR spectroscopy, but it can be replaced by a BF$_2$ group. Thus, indirect evidence for the presence of a hydrogen bond is obtained by replacing the hydrogen bonded proton in [pyCo((DO)(DOH)bzo)Br]ClO$_4$ by the BF$_2$ group by treating the complex with BF$_3$·OEt$_2$. The infrared spectrum of [pyCo((DO)$_2$bzoBF$_2$)Br]ClO$_4$ consists of sharp bands at 1190 and 815 cm^{-1} assignable to ν(BO) and weak and sharp bands at 1025 and 1005 cm^{-1} assignable to ν(BF) [30]. The ν(OH) and ν'(NO) bands appearing in [pyCo((DO)(DOH)bzo)Br]ClO$_4$ disappear in the BF$_2$ derivative and the presence of the sharp as well as strong band assignable to ν(NO) in the BF$_2$ derivative indicates the presence of only one –NO– linkage, C=N–O–B. The BF$_2$ derivatives of similar hydrogen bonded complexes have demonstrated quite unusual structural, spectroscopic and chemical properties [31].

Electronic Absorption Spectra

Six coordinate complexes of cobalt(III) are invariably low spin and diamagnetic with $^1A_{1g}$ ground term. Thus their behaviour parallels low-spin Fe(II), but shifted to higher energy for comparable ligands, because of the higher oxidation state [32, 33]. The crystal field model predicts that the electronic spectra of complexes of metal ions having low-spin d^6 configuration will be characterized by two low lying spin allowed crystal field transitions, assignable to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, as shown in part A of Fig. 2. When the symmetry is lowered from O_h to D_{4h} (tetragonal centric) or C_{4v} (tetragonal acentric), corresponding to a tetragonal distortion, the excited $^1T_{1g}$ level of the pseudo O_h symmetry is split into $^1E_g^a$ and $^1A_{2g}$ while the $^1T_{2g}$ level is split into $^1B_{2g}$ and $^1E_g^b$ according to the crystal field model of Wentworth and Piper [34]. The splitting of the $^1T_{2g}$ band is predicted by theory to be too small to be experimentally observed [35]. Thus on lowering the symmetry to D_{4h} from O_h, more than two bands, usually three, are observed, two in the visible region and one in the near UV region assignable to $^1A_{1g} \rightarrow {}^1E_g^a(\nu_E)$, $^1A_{1g} \rightarrow {}^1A_{2g}(\nu_A)$ and $^1A_{1g} \rightarrow (^1B_{2g} + {}^1E_g^b)$ (ν_{II}). The spin allowed crystal field transition in pseudo O_h symmetry is shown in part A of Fig. 2. The splitting of the excited states of low-spin d^6 cobalt(III) in a D_{4h} microsymmetry and the spin allowed crystal field transitions when $Dq^{xy} > Dq^z$ are shown in part B of Fig. 2.

When the field strength, Dq^{xy}, of the equatorial ligand is less than that of the axial ligand, i.e. when D_t is negative, the $^1A_{2g}$ level drops in energy below the $^1E_g^a$ level as illustrated in part C of Fig. 2. Busch and his co-workers [36], in their study on cobalt(III) complexes of tetraaza macrocycles, observed falling of the $^1A_{2g}$ level below the $^1E_g^a$ level in dicyano

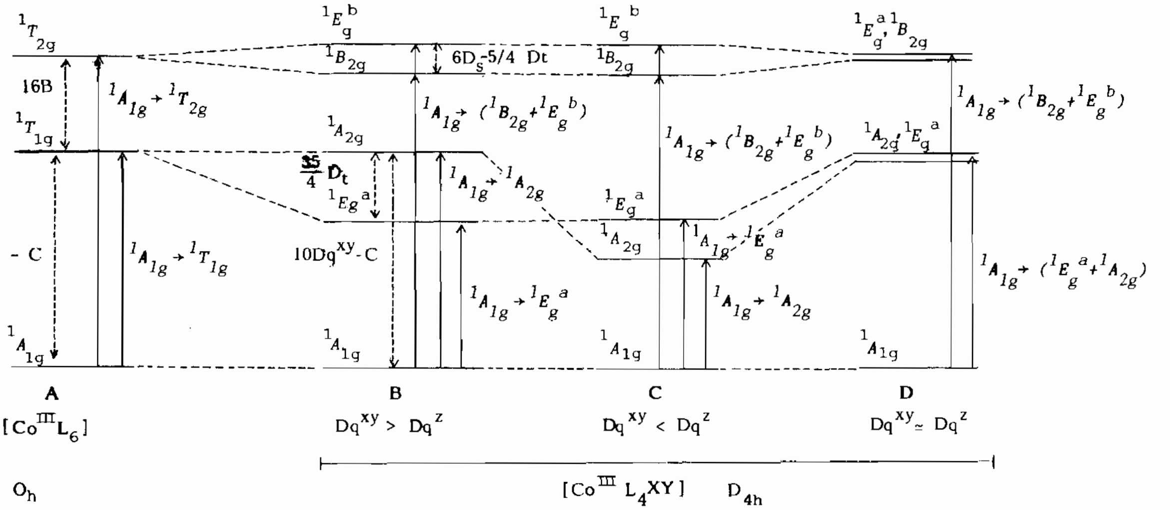

Fig. 2. Energy level diagram (not to scale) and the d–d transitions for a low spin d^6 ion in pseudo O_h symmetry (A); the splitting of the excited states in D_{4h} microsymmetry when $Dq^{xy} > Dq^z$ (B); when $Dq^{xy} < Dq^z$ (C); and when $Dq^{xy} \simeq Dq^z$ (D).

TABLE 2. Electronic spectral band assignments for the Lewis base complexes[a]

Complex	$^1A_{1g} \to {}^1E_g^a(\nu_E)$ (kK)	$^1A_{1g} \to {}^1A_{2g}(\nu_A)$ (kK)	$^1A_{1g} \to ({}^1E_g^b + {}^1B_{2g})(\nu_{II})$ (kK)	Other bands[b]
$[4\text{-CH}_3\text{pyCo((DO)(DOH)bzo)Br}]\text{PF}_6$	17.80	22.98	27.62	37.73
$[\text{MeIzCo((DO)(DOH)bzo)Br}]\text{Br}$	17.86	23	27.55	38.17
$[\text{BIzCo((DO)(DOH)bzo)Br}]\text{BF}_4$	18	23	27.62	37.73
$[\text{PPh}_3\text{Co((DO)(DOH)bzo)Br}]\text{Br}$	18	22.83	30.30	38.17
$[\text{EtNH}_2\text{Co((CO)(DOH)bzo)Br}]\text{ClO}_4$	17.80	22.83	27.62	33.98, 38
$[\text{Et}_2\text{NHCo((DO)(DOH)bzo)Br}]\text{ClO}_4$	17.83	22.98	27.40	37.30
$[\text{Et}_3\text{NCo((DO)(DOH)bzo)Br}]\text{ClO}_4$	18	23.15	27.78	38

[a] Spectra were recorded using ~10^{-3} M solution in DMF in the visible region and in methanol in the UV region at 30 °C. [b] The charge transfer transition and/or $\pi \to \pi^*$ transition of the ligand framework.

complexes where Dq^z is greater than Dq^{xy}. When Dq^z is very close to Dq^{xy}, the symmetry becomes closer to O_h and the splitting of the $^1T_{1g}$ excited state of the pseudo O_h symmetry is too small to be experimentally detected and the low lying band is the composite of the $^1E_g^a$ and $^1A_{2g}$ transitions as illustrated in part D of Fig. 2.

In a recent study [12] on vitamin B_{12} and coenzyme B_{12} models built upon the equatorial ligand under study, the crystal field model of Wentworth and Piper [34] has been usefully employed to interpret the electronic absorption bands and to compute the ligand field parameters of the (non-alkyl)cobalt(III) complexes since they exhibited the three predicted bands. The Lewis base complexes under study also exhibit the three predicted bands, two in the visible region and one in the near UV region indicating their close approximation to the D_{4h} microsymmetry. This amounts to assuming that the four donor atoms of the macrocyclic ligand are coordinated in a square planar array and impose equivalent field strength on the metal ion. Thus the site symmetry of the cobalt atom is considered to be D_{4h}. Other low-spin cobalt(III) complexes of macrocyclic and nonmacrocyclic ligands have been usefully treated by assuming the D_{4h} symmetry [36–39]. The electronic spectral band assignments and the ligand field parameters of these complexes are given in Tables 2 and 3, respectively. The electronic absorption spectra of $[4\text{-CH}_3\text{pyCo((DO)(DOH)bzo)Br}]\text{PF}_6$, $[\text{MeIzCo((DO)(DOH)bzo)Br}]\text{Br}$, $[\text{PPh}_3\text{Co((DO)(DOH)bzo)Br}]\text{Br}$ and $[\text{EtNH}_2\text{Co((DO)(DOH)bzo)Br}]\text{ClO}_4$ are depicted in parts (a), (b), (c) and (d), respectively, of Fig. 3. In general,

TABLE 3. Ligand field parameters for the Lewis base complexes[a]

Complex	Ligand field parameters (cm^{-1})		
	Dq^{xy}	Dq^z	D_t
$[\text{pyCo((DO)(DOH)bzo)Br}]\text{ClO}_4$	2663	1625	593
$[\text{IzCo((DO)(DOH)bzo)Br}]\text{PF}_6$	2674	1594	617
$[4\text{-CH}_3\text{pyCo((DO)(DOH)bzo)Br}]\text{PF}_6$	2678	1642	592
$[\text{MeIzCo((DO)(DOH)bzo)Br}]\text{Br}$	2680	1652	587
$[\text{BIzCo((DO)(DOH)bzo)Br}]\text{BF}_4$	2680	1680	571
$[\text{PPh}_3\text{Co((DO)(DOH)bzo)Br}]\text{Br}$	2663	1697	552
$[\text{EtNH}_2\text{Co((DO)(DOH)bzo)Br}]\text{ClO}_4$	2663	1657	575
$[\text{Et}_2\text{NHCo((DO)(DOH)bzo)Br}]\text{ClO}_4$	2678	1647	589
$[\text{Et}_3\text{NCo((DO)(DOH)bzo)Br}]\text{ClO}_4$	2695	1664	589

[a] Computed according to the crystal field model of Wentworth and Piper [34]. See also ref. 12.

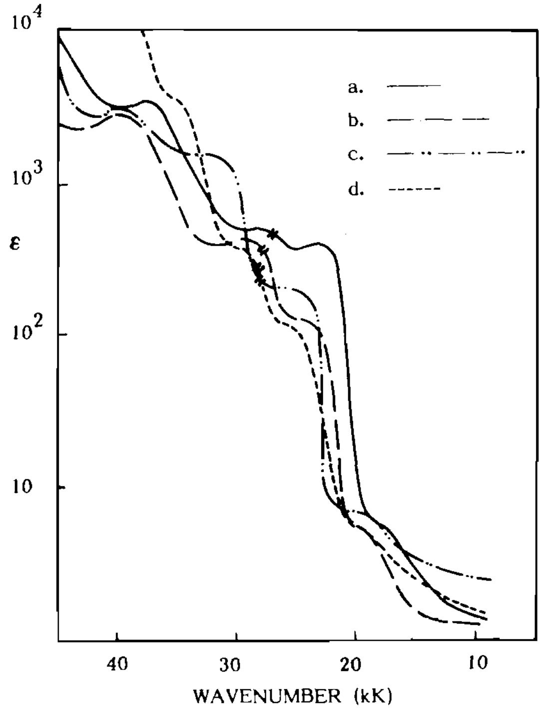

Fig. 3. Electronic absorption spectra of (a) $[4\text{-CH}_3\text{pyCo((DO)(DOH)bzo)Br}]\text{PF}_6$, (b) $[\text{MeIzCo((DO)(DOH)bzo)Br}]\text{Br}$, (c) $[\text{PPh}_3\text{Co((DO)(DOH)bzo)Br}]\text{Br}$, (d) $[\text{EtNH}_2\text{Co((DO)(DOH)bzo)Br}]\text{ClO}_4$ in DMF (visible region) and in methanol (UV region) at 25 °C.

molar absorptivities will be higher for tetragonal than for octahedral complexes [40]. Another factor which enhances the intensity of d–d transitions is the ligand field strength. The stronger the ligand field, the more intense is the absorption [41]. The intensity of the crystal field transitions of the complexes under study is slightly higher due to tetragonal distortion and strong ligand fields. The intensity of the lowest spin allowed ${}^1A_{1g} \rightarrow {}^1E_g^a$ transition varies from 40 to 70 l mol^{-1} cm^{-1} while that of the ν_A transition, ${}^1A_{1g} \rightarrow {}^1A_{2g}$ varies from 140–300 l mol^{-1} cm^{-1} and that of the ν_{II} transition, ${}^1A_{1g} \rightarrow ({}^1B_{2g} + {}^1E_g^b)$, lies in the range of 300–600 l mol^{-1} cm^{-1}.

The ligand field parameters of [pyCo((DO)(DOH)bzo)Br]ClO_4 and [IzCo((DO)(DOH)bzo)Br]PF_6 have been reported elsewhere [12]. The Dq^{xy}, Dq^z and D_t values of the former are 2663, 1625 and 593 cm^{-1}, respectively, while the corresponding values of the latter are 2674, 1594 and 617 cm^{-1}, respectively. The complex [4-CH_3pyCo((DO)(DOH)bzo)Br]PF_6 exhibits the ν_E transition at 17.8 kK and the ν_A transition at 22.98 kK with molar absorptivities of 73 and 556 l mol^{-1} cm^{-1}, respectively. The ν_{II} band occurs at 27.62 with an ϵ value of 720 l mol^{-1} cm^{-1}. These assignments lead to Dq^{xy}, Dq^z and D_t values of 2678, 1642 and 592 cm^{-1}, respectively. The field strength of 4-methylpyridine is thus greater than pyridine as expected from the hyperconjugative electron release by the methyl group. The greater availability of the lone pair electron density on the 4-methylpyridine nitrogen enhances its field strength. The field strengths of 1-methylimidazole, 5,6-dimethylbenzimidazole, ethylamine, diethylamine and triethylamine are very nearly the same indicating their comparable coordinating ability. The field strength of benzimidazole is 1680 cm^{-1}, higher than that of other bases, indicating its stronger bonding to the cobalt(III) ion. This is reflected in the Co(III)/Co(II) $E_{1/2}$ values of the benzimidazole complex which are higher than those of others (*vide infra*). The field strength of triphenylphosphine is worthy of comment. The field strength of triphenylphosphine, being a better π-acceptor, is expected to be high. Indeed, it exhibits the highest field strength of 1697 cm^{-1}. The observed spectrochemical series of the Lewis bases for Co^{3+} is in the following increasing order: $Iz < py < 4\text{-}CH_3py < Et_2NH < MeIz < EtNH_2 < Et_3N < NIz < PPh_3$.

The reliability of the spectral assignments lies on the near constancy of the field strength of the equatorial ligand which falls in the range of 2663 to 2680 cm^{-1} for the 10 complexes for which all ligand field parameters have been computed. Note, however, that the Dq^{xy} calculated for [Et_3NCo((DO)(DOH)bzo)Br]ClO_4 is 2695 cm^{-1}. The near invariance of the field strength of the equatorial ligand despite the presence of different axial ligands is of commendable chemical significance. Such a small variation of Dq^{xy} with different axial ligands is essentially due to the occurrence of the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition, crucial to the computation of Dq^{xy}, in a narrow energy region. It is very interesting and intriguing 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. Therefore, it is almost certain that the σ-donation of the axial ligand contributes to Dq^z while both σ- and π-bonding contribute to Dq^{xy}.

Electrochemical Behaviour of the Complexes

The DC polarograms of these complexes consist of two well defined reduction waves corresponding to the reduction of Co(III) to Co(II) and Co(II) to Co(I). The half-wave potentials and the diffusion current constants for both of these reduction processes are presented in Table 4. The near constancy of the ratio of the diffusion current to the concentration indicates that the reductions are diffusion controlled at DME and one electron transfer occurs for both reductions [6d, 13].

TABLE 4. Polarographic half-wave potentials[a] and diffusion current constants for the reduction of the Lewis base complexes in DMF containing ~0.1 M TEAP at 25 °C

Complex	Concentration $\times 10^{-3}$ M	First reduction wave Co(III) → Co(II)		Second reduction wave Co(II) → Co(I)	
		$E_{1/2}$ (V)	i_d/c (log units)	$E_{1/2}$ (V)	i_d/c (log units)
[4-CH_3pyCo((DO)(DOH)bzo)Br]PF_6	1.25	−0.25	2.02	−1.18	1.79
[MeIzCo((DO)(DOH)bzo)Br]Br	1.12	−0.24	1.90	−1.15	1.87
[BIzCo((DO)(DOH)bzo)Br]BF_4	1.08	−0.17	1.71	−1.13	1.74
[Me_2BIzCo((DO)(DOH)bzo)Br]PF_6	1.00	−0.26	1.90	−1.15	1.90
[PPh_3Co((DO)(DOH)bzo)Br]Br	0.65	−0.23	1.66	−0.84	1.71
[2-NH_2pyCo((DO)(DOH)bzo)Br]Br	1.10	−0.21	1.78	−1.00	1.75

[a] Potentials are reported in volts vs. Ag/AgCl.

TABLE 5. Cyclic voltammetric data for the reduction of Lewis base complexes at a glassy carbon disk electrode in DMF containing TEAP (0.1 M) at 22 °C[a]

Complex	Cobalt redox couple	E_{pc} (V) (vs. SCE)	E_{pa} (V) (vs. SCE)	$E_{1/2}$ (V) (vs. SCE)	$E_{1/2}$ (V) (vs. Fc/Fc$^+$)	i_{pc} (μA)	i_{pa} (μA)	i_{pa}/i_{pc}	ΔE_p (mV) (vs. SCE)	$i_{pc}/\nu^{1/2}$ (μA s$^{-1/2}$ mV$^{-1/2}$)
[4-CH$_3$pyCo((DO)(DOH)bzo)Br]PF$_6$	III/II	−0.66	−0.32	−0.490	−0.980	1.5	1.5	1.00	340	0.21
(1 × 10^{-3} M)	II/I	−1.17	−1.12	−1.145	−1.635	11.7	5.6	0.48	50	1.63
[BIzCo((DO)(DOH)bzo)Br]BF$_4$	III/II	−0.60	−0.40	−0.500	−0.990	12.6	12.7	1.00	200	1.78
(0.98 × 10^{-3} M)	II/I	−1.12	−1.05	−1.060	−1.550	20	10	0.50	70	2.82
[EtNH$_2$Co((DO)(DOH)bzo)Br]ClO$_4$	III/II	−0.66	−0.24	−0.450	−0.940	26	26	1.00	420	3.60
(1.124 × 10^{-3} M)	II/I	−1.12	−1.14	−1.180	−1.670	36	18	0.50	80	5.09
[Et$_2$NHCo((DO)(DOH)bzo)Br]ClO$_4$	III/II	−0.62	−0.25	−0.435	−0.925	30	31	1.03	370	4.24
(1.107 × 10^{-3} M)	II/I	−1.12	−1.14	−1.180	−1.670	40	21	0.52	80	5.65
[Et$_3$NCo((DO)(DOH)bzo)Br]ClO$_4$	III/II	−0.65	−0.27	−0.460	−0.950	33	33	1.00	380	4.67
(1.12 × 10^{-3} M)	II/I	−1.12	−1.13	−1.175	−1.665	86	46	0.53	90	12.16
[MeIzCo((DO)(DOH)bzo)Br]Br	III/II	−0.60	−0.30	−0.450	−0.950				300	
(0.92 × 10^{-3} M)	II/I	−1.15	−1.08	−1.100	−1.590				70	
[Me$_2$BIzCo((DO)(DOH)bzo)Br]PF$_6$[b]	III/II	−0.75	−0.20	−0.475	−0.965				550	
(1 × 10^{-3} M)	II/I	−1.23								
[PPh$_3$Co((DO)(DOH)bzo)Br]Br[c]	III/II	−0.75	−0.30	−0.525	−1.015				450	
(1.16 × 10^{-3} M)	II/I	−0.96	−0.87	−0.915	−1.415				90	

[a] Sweep rate: 50 mV s^{-1} unless otherwise stated. [b] The anodic and cathodic waves for both redox couples are sharp. [c] Well defined cathodic and anodic waves are observed at the sweep rate, 20 mV s^{-1} for both redox couples. When the voltammogram was recorded at 500 mV s^{-1}, a new cathodic wave appears at around − 1.25 V.

The cyclic voltammograms of these complexes consist of two cathodic waves corresponding to the reductions, Co(III) → Co(II) and Co(II) → Co(I) and two anodic waves corresponding to the oxidations, Co(I) → Co(II) and Co(II) → Co(III). The cathodic and anodic waves are well developed for [4-CH_3py-Co((DO)(DOH)bzo)Br]PF_6, [BIzCo((DO)(DOH)bzo)-Br]BF_4, [$EtNH_2$Co((DO)(DOH)bzo)Br]ClO_4, [Et_2-NHCo((DO)(DOH)bzo)Br]ClO_4 and [Et_3NCo((DO)-(DO)bzo)Br]ClO_4 and all parameters are computed. The cyclic voltammetric data for the reduction of these complexes are presented in Table 5. In the case of the complexes of pyridine, imidazole, 1-methylimidazole, and triphenylphosphine, the waves are poorly defined and hence all parameters could not be accurately obtained. The parameters, namely, i_{pa}/i_{pc}, ΔE_p and $i_{pa}/\nu^{1/2}$, employed to evaluate the reversibility of the redox couple, are given in the last three columns of Table 5 [13, 42].

In the case of the complexes of 4-methylpyridine, benzimidazole, ethylamine, diethylamine, triethylamine, and triphenylphosphine i_{pa}/i_{pc} is 1 for the Co(III)/Co(II) redox couple indicative of reversible electron transfer. But the separation between the anodic and cathodic peak potentials, ΔE_p, is too large, ranging from 360 to 400 mV at the sweep rate of 50 mV s^{-1}, indicative of its electrochemical irreversibility. Also, both cathodic and anodic peaks of this couple lack the characteristic sharpness of a reversible electrode reaction. The cyclic voltammograms for the reduction of [$EtNH_2$Co((DO)-(DOH)bzo)Br]ClO_4, [Et_2NHCo((DO)(DOH)bzo)Br]-ClO_4 and [Et_3NCo((DO)(DOH)bzo)Br]ClO_4 are shown in parts (a), (b) and (c), respectively, of Fig. 4. Though the anodic and cathodic peaks shift farther apart with increasing scan rate, characteristic of the quasireversible couple [43], the peaks are widely separated (360–400 mV) indicating irreversible electrochemical reduction of [LCo((DO)(DOH)bzo)Br]$^+$ to the cobalt(II) state. The causes of irreversibility have already been explained [13]. This indicates extensive bond breaking [43] during the reduction of [LCo^{III}((DO)(DOH)bzo)Br]$^+$ and it is almost certain that the axial bromide, *trans* to the Lewis base, is lost and the formation of a five coordinate Co(II) complex, [LCo^{II}((DO)(DOH)bzo)]$^+$ is envisioned as shown in eqn. (1). The (non-alkyl)-cobalt(III) complexes of ((DO)(DOH)bzo) [13]

$$[LCo^{III}((DO)(DOH)bzo)Br]^+ + e \longrightarrow [LCo^{II}((DO)(DOH)bzo)]^+ + Br^- \quad (1)$$

and (C_2(DO)(DOH)pn) [6a] also exhibit a similar behaviour. De Tacconi *et al.* [44] in their studies on aquacobalamin have also observed a slow rate of electron transfer for the Co(III)/Co(II) couple, a behaviour which they ascribed to the benzimidazole moiety of the nucleotide being more strongly bonded to cobalt resulting in a larger vibrational contribution to the reorganization energy of the electron transfer. The near constancy of $i_{pa}/\nu^{1/2}$ indicates that the reduction of Co(III) to Co(II) is diffusion controlled at the working electrode [45].

In the case of the Co(II)/Co(I) redox couple the separation between the anodic and cathodic peak potentials spans between 50–100 mV at all sweep rates and the i_{pa}/i_{pc} ratio is ~0.5 indicating the electrochemical irreversibility of the couple. A very interesting feature of the cyclic voltammetry of these complexes is the relative insensitivity of the Co(II)/Co(I) redox couple to the axial ligands. The near invariance of the position of the cathodic peak corresponding to the reduction of Co(II) → Co(I) is indicative of the weak interaction of the axial ligand in the electrogenerated five coordinate cobalt(II) complex, [LCo^{II}((DO)(DOH)bzo)]$^+$. A similar observation was made by Endicott *et al.*

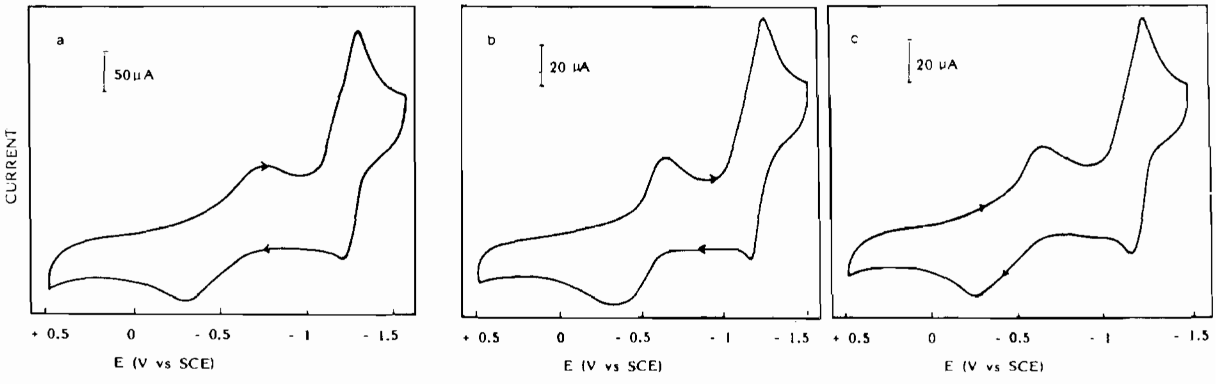

Fig. 4. Cyclic voltammograms for the reduction of (a) [$EtNH_2$Co((DO)(DOH)bzo)Br]ClO_4 (1.124 × 10^{-3} M), (b) [Et_2NHCo-((DO)(DOH)bzo)Br]ClO_4 (1.107 × 10^{-3} M), (c) [Et_3NCo((DO)(DOH)bzo)Br]ClO_4 (1.12 × 10^{-3} M) at a glassy carbon disk electrode in DMF containing 0.1 M TEAP at 22 °C. Sweep rate for (a), 200 mV s^{-1}; and for (b) and (c), 50 mV s^{-1}.

[46] who in their studies on the *trans* influence and axial interactions in low spin tetragonal cobalt(II) complexes of the type $[\mathrm{CoL_4(OH_2)_2}]^{2+}$ and $[\mathrm{CoL_4(ClO_4)_2}]$[*] have shown that the axial Co–ligand bond lengths are 0.3–0.5 Å longer than the equatorial Co–ligand bond. A similar observation was made by Schneider *et al.* [47] who in their studies on the kinetics of bis(dimethylglyoximato)cobalt(II) complexes of the type $[\mathrm{Co(DH)_2B_2}]$ and $[\mathrm{Co(DH)_2B}]$ have shown that in solution the former undergoes complete dissociation into $[\mathrm{Co(DH)_2B}]$ and B. The near invariance of the position of the anodic peak corresponding to the oxidation of Co(I) to Co(II) is attributed to the complete loss of the axial ligands during the generation of the Co(I) complex as shown in eqn. (2). The generation of four coordinate Co(I) complex was also observed by Alexander and Ramanujam in their electrochemical investigations on the halogeno- and pseudohalogenocobalt(III) complexes of $\mathrm{(DOH)_2bzo}$ [13] and by Swetik and Brown [48] and by Saveant and his coworkers [49] in their cyclic voltammetric studies on vitamin B_{12} derivatives. A weak axial interaction of the solvent molecules (DMF) with the electrogenerated Co(I), as observed by Elliott *et al.* [6a], cannot be ruled out however.

$$[\mathrm{LCo^{II}((DO)(DOH)bzo)}]^+ + e \longrightarrow [\mathrm{Co^{I}((DO)(DOH)bzo)}] + \mathrm{L} \qquad (2)$$

The magnitude of ΔE_p for the Co(II)/Co(I) redox couple (50–100 mV) is much lesser than that of the Co(III)/Co(II) couple (360–400 mV) indicating that the rate of electron transfer is much faster for the Co(II) → Co(I) reduction than that of the Co(III) → Co(II) reduction. The much slower rate of electron transfer for the reduction of the Co(III) complex than the subsequent reduction of the electrogenerated $[\mathrm{LCo^{II}((DO)(DOH)bzo)}]^+$ to $[\mathrm{Co^{I}((DO)(DOH)bzo)}]$ is due to the strong binding of the Lewis base to the $\mathrm{Co^{3+}}$ ion which results in a larger vibrational energy contribution to the electron transfer process. The faster rate of electron transfer during the reduction of the Co(II) complex is due to the weak axial binding of the Lewis base (*vide supra*) which results in a small vibrational energy contribution to the reduction process. A similar observation was made by de Tacconi *et al.* [44] who in their study on aquacobalamin observed a faster electron transfer in the case of the base-off B_{12r}/base-off B_{12s} couple than in the base-off B_{12a}/base-off B_{12r} couple.

In the case of the Co(II)/Co(I) redox couple the i_{pa}/i_{pc} ratio is 0.5 indicating a 50% Co(I) yield. This indicates the involvement of a coupled chemical reaction such as an ECE mechanism depicted below (eqns. (3)–(6)).

$$\underline{\mathrm{E}}\ [\mathrm{LCo^{III}((DO)(DOH)bzo)Br}]^+ + e \rightleftharpoons [\mathrm{LCo^{II}((DO)(DOH)bzo)}]^+ \qquad (3)$$

$$\underline{\mathrm{C}}\ [\mathrm{LCo^{III}((DO)(DOH)bzo)Br}]^+ + [\mathrm{LCo^{II}((DO)(DOH)bzo)}]^+ \rightleftharpoons [\mathrm{L_2Co^{III}((DO)(DOH)bzo)}]^{2+} + [\mathrm{Co^{II}((DO)(DOH)bzo)}]^+ \qquad (4)$$

$$\underline{\mathrm{E}}\ [\mathrm{LCo^{II}((DO)(DOH)bzo)}]^+ + e \rightleftharpoons [\mathrm{Co^{I}((DO)(DOH)bzo)}] \qquad (5)$$

This ECE mechanism also predicts a 50% cobalt(I) yield (eqn. (6)). The irreversibility of both the redox couples is also well accounted for by this mechanism.

$$2[\mathrm{LCo^{III}((DO)(DOH)bzo)Br}]^+ + 2e \rightleftharpoons [\mathrm{L_2Co^{III}((DO)(DOH)bzo)}] + [\mathrm{Co^{I}((DO)(DOH)bzo)}] \qquad (6)$$

Spectroelectrochemistry

While the polarographic half-wave potentials for the reduction of Co(III) to Co(II) spans between −0.14 and −0.25 V (versus Ag/AgCl) with a potential variation of only 0.11 V, the cyclic voltammetric $E_{1/2}$ values for the Co(III)/Co(II) couple span in an even narrower region of −0.43 to −0.525 V with a variation of 0.095 V (versus SCE). Despite the small variation of the Co(III)/Co(II) $E_{1/2}$ values for these complexes there is a dramatic dependence of the $E_{1/2}$ values on the field strength of the axial ligand as indicated by a linear plot of Dq^z versus $E_{1/2}$ with a slope of $0.56 \pm 0.02\ \mathrm{cm^{-1}\ mV^{-1}}$. The dependence of the cyclic voltammetric Co(III)/Co(II) $E_{1/2}$ values on the field strengths of the axial ligands is depicted in Fig. 5. The dependence of the Co(III)/Co(II) couple on the spectrally determined ligand field strength of the axial ligands was documented by Rillema *et al.* [50] in their studies on cobalt(III) complexes of $\mathrm{Me_6}$[14]4,11-diene$\mathrm{N_4}$ with a variety of axial ligands. The authors have observed a wide potential variation of over 1 V and obtained a linear plot of Dq^z versus $E_{1/2}$ with a slope of $1.7 \pm 0.2\ \mathrm{cm^{-1}\ mV^{-1}}$. This observation further substantiates that the Co(III)/Co(II) redox couple is very sensitive to the axial ligand. Complimentary studies by Rillema *et al.* [51] on a series of

---

[*] L_4 refers to a 14-membered tetraaza macrocyclic ligand. The following are the macrocyclic ligands employed: [14]ane$\mathrm{N_4}$, $\mathrm{Me_6}$[14]4,11-diene$\mathrm{N_4}$, $\mathrm{Me_8}$[14]4,11-diene$\mathrm{N_4}$, [14]tetraene$\mathrm{N_4}$, [14]4,7-diene$\mathrm{N_4}$, [14]py-diene$\mathrm{N_4}$ and [14]tetraeneoximato$\mathrm{N_4}$. For the expanded names of these ligands and their skeletal structures see ref. 46.

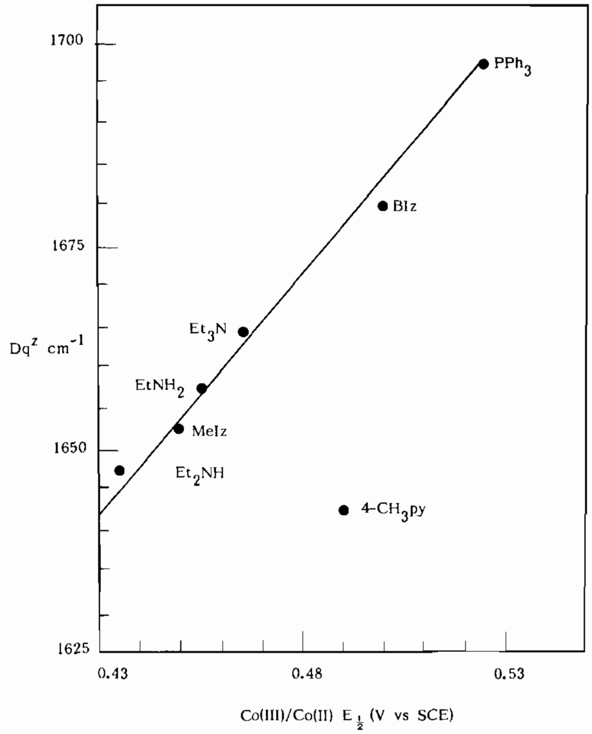

Fig. 5. Correlation between the field strength (Dq^z) of the Lewis bases and cyclic voltammetric $E_{1/2}$ values of the Co(III)/Co(II) redox couple.

cobalt(III) complexes of the type [$Co^{III}L_4(OH_2)_2$] with constant axial ligands and varying equatorial chelates, L_4, such as Me_4[14]1,3,8,10-tetraeneN_4, Me_6[14]4,11-dieneN_4, and Me_6[14]aneN_4 have shown a constant standard potential, E°, of 0.55 V for the Co(III)/Co(II) redox couple.

The polarographic and cyclic voltammetric $E_{1/2}$ values for the Co(II)/Co(I) redox couple span over 0.3 and 0.12 V, respectively. But, neither the polarographic nor the cyclic voltammetric $E_{1/2}$ values depends on the Dq^z systematically as indicated by the plot of $E_{1/2}$ versus Dq^z, which is scattered. This indicates that the Co(II)/Co(I) couple is quite insensitive to the axial ligand. The spectrochemical and electrochemical studies by Busch and his co-workers on cobalt(III) complexes of 13–16aneN_4macrocyclic ligands [36] and a series of 14-membered macrocycles varying in their degree and position of ligand unsaturation and substitution [3a] also indicated that the Co(II)/Co(I) $E_{1/2}$ value depends on the in-plane ligand in a predictable manner. A similar observation was made by Costa *et al.* [52] for cobalt(III) complexes of linear quadridentate ligands. The electrochemical study of Elliott *et al.* [6a] on coenzyme B_{12} models also reveals that the couple is insensitive to potential axial ligand or solvent and it measures primarily the electronic influence of the equatorial ligand. The differences between the $E_{1/2}$ values of the Co(III)/Co(II) and Co(II)/Co(I) redox couples of all these complexes are not constant. This indicates that electrons are not transferred to the same metal d-orbital during the reduction of the Co(III) and Co(II) complexes. This observation is clearly borne out on the dependence of the Co(III)/Co(II) $E_{1/2}$ value on the axial ligands and on the dependence of the Co(II)/Co(I) $E_{1/2}$ on the equatorial ligand.

In a complex of [CoL_4XY] of D_{4h} symmetry where X and Y occupy the principal axis, z, a pair of π-orbitals on the ligands X and Y will perturb d_{xz} and d_{yz} orbitals which then become π-antibonding (or π-bonding if the π-orbitals of X and Y are empty). These d_{xz} and d_{yz} pairs will then interact with the z-directed π-orbitals on L_4. The d_{xy} orbital interacts only in a π-sense with the π-orbitals of L_4 lying in the XY plane. The d_{z^2} orbital is sigma antibonding with respect to both L_4 and X and Y ligands, whereas $d_{x^2-y^2}$ is sigma antibonding to the L_4 only [see ref. 33, p. 50]. The dependence of the Co(III)/Co(II) redox couple on the axial ligand thus indicates the addition of electron to the d_{z^2} orbital during the electrolytic reduction of [LCo^{III}((DO)(DOH)bzo)-Br]$^+$ to the Co(II) form. Whereas the independence of the Co(II)/Co(I) redox couple on the axial ligand and its dependence only on the equatorial ligand is attributed to the addition of the electron to the $d_{x^2-y^2}$ orbital during the reduction of [LCo^{II}((DO)-(DOH)bzo)]$^+$ to [Co^{I}((DO)(DOH)bzo)]. In the extreme case of tetragonal distortion by the elongation of the axial ligands, a square planar bonding environment results, a situation not at all uncommon for d^8 metal ions. Under such a situation d_{z^2} falls in energy below the d_{xy} and d_{yz} orbitals and is no longer the lowest unoccupied orbital and the absence of an axial ligand field dependence on $E_{1/2}$ is readily understood.

Conclusion

The synthesis of macrocyclic complexes with modified structural features continues to be a fascinating field of chemistry. The cobaloximes represent a closely related family of Co complexes of $(DH)_2$ with the most diverse variety of axial ligands ever reported for any equatorial chelate. The (DO)(DOH)-bzo chelate, designed to synthesize suitable B_{12} models, affords a greater diversity of (non-alkyl)-Co(III) complexes than the (DO)(DOH)pn and C_2(DO)(DOH)pn models due to the potentiality of the axial coordination sites of Co. This is due to the enhanced field strength due to the constructive effect of the mechanically confining (DO)(DOH)bzo ligand which provides optimum central cavity to accommodate Co^{3+} and imposes equivalent coordination sites. The tetragonal distortion reflects the spectroscopic consequence of the equatorial ligand imposing a different coordination site from that of the axial ligands. These compounds are remarkable in having given insight into the contribution of σ-bonding to Dq^z and σ- and π-bonding to Dq^{xy} from electrochemistry in conjunction with the result of Busch and his co-workers [38]. The participation of t_{2g} orbitals in π-bonding with both axial and equatorial ligands and the antibonding nature of the e_g orbitals with respect to the axial or equatorial ligand provides a major impetus for these molecules to serve as a useful qualitative guide to construct an MO diagram from spectroelectrochemistry. It is conceivable that the formation of five coordinate Co(II) and four coordinate Co(I) complexes may probably be due to the lowered synergistic effect between the electron rich Co centre and the axial ligands. But more definite informations about the electrogenerated lower valent Co complexes are needed from controlled potential electrolysis, spectroscopy and solution studies to ascertain this effect with confidence. Since it affords six coordinate alkyl- and (non-alkyl)cobalt(III) complexes, characteristic of an intriguing B_{12} model, definite knowledge of the three dimensional structures of these complexes are needed to ascertain the site symmetry of Co^{3+} and the flexibility of the equatorial ligand for comparison with other B_{12} models and macrocycles.

References

1 P. J. Toscano and L. G. Marzilli, *Prog. Inorg. Chem., 31* (1984) 105.

2 J. Halpern, *Ann. N.Y. Acad. Sci., 239* (1974) 2.

3 G. N. Schrauzer, *Acc. Chem. Res., 1* (1968) 97.

4 (a) N. M. Samus and A. V. Ablov, *Coord. Chem. Rev., 28* (1979) 177; (b) N. Bresciani-Pahor, M. Forcolin, L. G. Marzilli, L. Randaccio, M. F. Summers and P. J. Toscano, *Coord. Chem. Rev., 63* (1985) 1.

5 (a) J. P. Glusker, in D. Dolphin (ed.), *B_{12}*, Vol. 1, Wiley, New York, 1982, p. 623; (b) K. L. Brown, p. 245; (c) H. P. C. Hogenkamp, p. 295; (d) J. Halpern, p. 501; (e) B. T. Golding, p. 543.

6 (a) C. M. Elliott, E. Hershanhart, R. G. Finke and B. L. Smith, *J. Am. Chem. Soc., 103* (1981) 5558; (b) R. G. Finke, B. L. Smith, M. Droege, C. M. Elliott and E. Hershenhart, *J. Organomet. Chem., 202* (1980) C25; (c) G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc., 88* (1966) 3738; (d) G. Costa, G. Mestroni, A. Puxeddu and E. Reisenhofer, *J. Chem. Soc. A,* (1970) 2870; (e) G. Costa, A. Puxeddu and G. Tauzher, *Inorg. Nucl. Chem. Lett., 4* (1968) 319; (f) D. G. Brown, *Prog. Inorg. Chem., 18* (1973) 177.

7 (a) D. N. Hague and J. Halpern, *Inorg. Chem., 6* (1967) 2059; (b) T. Sakurai, J. P. Fox and L. L. Ingraham, *Inorg. Chem., 10* (1971) 1105; (c) A. W. Herlinger and T. L. Brown, *J. Am. Chem. Soc., 94* (1972) 388; (d) K. L. Brown and R. G. Kallen, *J. Am. Chem. Soc., 94* (1972) 1894; (e) R. L. Courtright, R. S. Drago, J. A. Nusz and M. S. Nosari, *Inorg. Chem., 12* (1973) 2809; (f) W. C. Trogler, R. C. Stewart and L. G. Marzilli, *J. Am. Chem. Soc., 96* (1974) 3697; (g) K. L. Brown, D. Lyles, M. Pencovici and R. G. Kallen, *J. Am. Chem. Soc., 97* (1975) 7338; (h) L. Seibles and E. Deutsch, *Inorg. Chem., 16* (1977) 2273; (i) W. W. Reenstra and W. P. Jencks, *J. Am. Chem. Soc., 101* (1979) 5780; (j) P. J. Toscano and L. G. Marzilli, *Inorg. Chem., 18* (1979) 421; (k) N. Bresciani-Pahor, L. Randoccio, P. Toscano, A. C. Sandercocic and L. G. Marzilli, *J. Chem. Soc., Dalton Trans.,* (1972) 129; (l) R. Dreos-Garlatti, G. Tauzher and G. Costa, *Inorg. Chim. Acta, 70* (1983) 83; (m) R. Dreos-Garlatti, G. Tauzher and G. Costa, *Inorg. Chim. Acta, 71* (1983) 9; (n) R. Dreos-Garlatti, G. Tauzher and G. Costa, *Inorg. Chim. Acta, 82* (1984) 197; (o) L. Randaccio, N. Bresciani-Pahor, J. Orbell, J. D. M. Calligaris, M. F. Summers, B. Snyder, P. Toscano and L. G. Marzilli, *Organometallics, 4* (1985) 469; (p) N. Bresciani-Pahor, L. Randaccio, E. Zangrando and P. J. Toscano, *Inorg. Chim. Acta, 96* (1985) 193; (q) N. Bresciani-Pahor, L. Randaccio, E. Zangrano, M. F. Summers, J. H. Ramsden, P. A. Marzilli and L. G. Marzilli, *Organometallics, 4* (1985) 2086; (r) W. O. Parker, Jr., N. Bresciani-Pahor, E. Zangrando, L. Randaccio and L. G. Marzilli, *Inorg. Chem., 24* (1985) 3908; (s) L. G. Marzilli, N. Bresciani-Pahor, L. Randaccio, E. Zangrando, S. A. Myers and R. G. Finke, *Inorg. Chim. Acta, 107* (1985) 139; (t) E. Zangrando, N. Bresciani-Pahor, L. Randaccio, J. P. Charland and L. G. Marzilli, *Organometallics, 5* (1986) 1938; (u) K. L. Brown and T. F. Yang, *Inorg. Chem., 26* (1987) 3007.

8 (a) L. Randaccio, N. Bresciani-Pahor, P. J. Toscano and L. G. Marzilli, *J. Am. Chem. Soc., 103* (1981) 6347; (b) M. F. Summers, P. J. Toscano, N. Bresciani-Pahor, G. Nardin, L. Randaccio and L. G. Marzilli, *J. Am. Chem. Soc., 105* (1983) 6259; (c) M. F. Summers, L. G. Marzilli, N. Bresciani-Pahor and L. Randaccio, *J. Am. Chem. Soc., 106* (1984) 4478; (d) M. Rossi, J. P. Glusker, L. Randaccio, M. F. Summers, P. J. Toscano and L. G. Marzilli, *J. Am. Chem. Soc., 107* (1985) 1729; (e) L. G. Marzilli, M. F. Summers, N. Bresciani-Pahor, E. Zangrando, J. P. Charland and L. Randaccio, *J. Am. Chem. Soc., 107* (1985) 6880; (f) L. G. Marzilli, M. F. Summers, E. Zangrando, N. Bresciani-Pahor and L. Randaccio, *J. Am. Chem. Soc., 108* (1986) 4830.

9 (a) S. Costa and G. Mestroni, *Tetrahedron Lett., 41* (1967) 4005; (b) G. Costa, G. Mestroni and E. L. Savorgnani, *Inorg. Chim. Acta, 3* (1969) 323; (c) R. G. Finke and W. McKenna, *J. Chem. Soc., Chem. Commun.,* (1980) 460; (d) R. G. Finke, B. L. Smith, W. A. McKenna and P. A. Christian, *Inorg. Chem., 20* (1981) 687; (e) K. Farmery and D. H. Busch, *Inorg. Chem., 11* (1972) 2901; (f) E. Ochiai and D. H. Busch, *J. Chem. Soc., Chem. Commun.,* (1968) 905; (g) E. Ochiai, L. M. Long, C. R. Sperati and D. H. Busch, *J. Am. Chem. Soc., 91* (1969) 3201; (h) G. Costa, G. Mestroni and L. Stefani, *J. Organomet. Chem., 7* (1967) 493; (i) G. Costa, G. Mestroni and G. Pellizer, *J. Organomet. Chem., 11* (1968) 333; (j) A. Bigotto, G. Costa, G. Mestroni, G. Pillizer, A. Puxeddu, E. Reisenhofer, L. Stefani and G. Tauzher, *Inorg. Chim. Acta Rev., 4* (1970) 41; (k) G. Costa, G. Mestroni, G. Tauzher and L. Stefani, *J. Organomet. Chem., 6* (1966) 181; (l) G. Costa and G. Mestroni, *J. Organomet. Chem., 11* (1968) 325; (m) G. Costa, *Coord. Chem. Rev., 8* (1972) 63; (n) G. Costa, *Pure Appl. Chem., 30* (1972) 335; (o) D. Dolphin and A. W. Johnson, *J. Chem. Soc., Chem. Commun.,* (1965) 494.

10 (a) R. G. Finke, B. L. Smith, B. J. Mayer and A. A. Molinero, *Inorg. Chem., 22* (1983) 3677; (b) R. G. Finke, W. P. McKenna, D. A. Schiraldi, B. L. Smith and

C. Pierpont, *J. Am. Chem. Soc., 105* (1983) 7592; (c) R. G. Finke and D. A. Schiraldi, *J. Am. Chem. Soc., 105* (1983) 7605; (d) W. O. Parker, E. Zangrando, N. Bresciani-Pahor, L. Randaccio and L. G. Marzilli, *Inorg. Chem., 25* (1986) 3489; (e) W. O. Parker, Jr., N. Bresciani-Pahor, E. Zangrando and L. G. Marzilli, *Inorg. Chem., 25* (1986) 1303; (f) R. G. Finke and B. P. Hay, *Inorg. Chem., 23* (1984) 3043.

11 R. G. Finke, D. A. Schiraldi and B. J. Mayer, *Coord. Chem. Rev., 54* (1984) 1.

12 V. V. Ramanujam and V. Alexander, *Inorg. Chem., 26* (1987) 3124.

13 V. Alexander and V. V. Ramanujam, *Inorg. Chim. Acta, 156* (1989) 125.

14 G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc., 88* (1966) 3738.

15 (a) G. Gritzner and J. Kuta, *Pure Appl. Chem., 56* (1984) 461; (b) R. R. Gagne, C. A. Koval and G. C. Lisensky, *Inorg. Chem., 19* (1980) 2854.

16 G. A. Mabbott, *J. Chem. Educ., 60* (1983) 697.

17 R. J. H. Clark and C. S. Williams, *Inorg. Chem., 4* (1965) 350.

18 N. Yamazaki and Y. Hohokabe, *Bull. Chem. Soc. Jpn., 44* (1971) 63.

19 D. Cook, *Can. J. Chem., 42* (1964) 2523.

20 W. J. Davis and J. Smith, *J. Chem. Soc. A,* (1971) 317.

21 M. M. Cordes and J. L. Walter, *Spectrochim. Acta, Part A, 24* (1968) 237.

22 M. M. Cordes and J. L. Walter, *Spectrochim. Acta, Part A, 24* (1968) 1421.

23 J. Chatt, L. A. Duncanson and L. M. Venanzi, *J. Chem. Soc.,* (1956) 2712.

24 A. M. Ingham and R. C. Henson, *J. Chem. Educ., 61* (1984) 704.

25 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* Wiley, New York, 4th edn., 1986, p. 228.

26 B. K. Coltrain and S. C. Jackels, *Inorg. Chem., 20* (1981) 2032.

27 G. N. Schrauzer and R. J. Windgassen, *Chem. Ber., 99* (1966) 602.

28 R. Blinc and D. Hadzi, *J. Chem. Soc.,* (1958) 4536.

29 A. Gul and O. Bekaroglu, *J. Chem. Soc., Dalton Trans.,* (1983) 2537.

30 G. N. Schrauzer, *Chem. Ber., 95* (1962) 1438.

31 (a) B. K. Cottrain and S. C. Jackels, *Inorg. Chem., 20* (1981) 2032; (b) J. W. L. Martin, J. H. Timmons, A. E. Martell and P. Rudolf, *Inorg. Chem., 20* (1981) 814; (c) A. W. Addison, M. Carpenter, L. K. M. Lau and M. Wicholas, *Inorg. Chem., 17* (1978) 1545; (d) R. R. Gagne, J. L. Allison and D. M. Ingle, *Inorg. Chem., 18* (1979) 2767; (e) N. Aoi, G. Matsubayashi and T. Tanaka, *J. Chem. Soc., Dalton Trans.,* (1987) 241.

32 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry,* Wiley, New York, 5th edn., 1988, p. 733.

33 A. B. P. Lever, *Inorganic Electronic Spectroscopy,* Elsevier, Amsterdam, 2nd edn., 1984, p. 473.

34 R. A. D. Wentworth and T. S. Piper, *Inorg. Chem., 4* (1965) 709.

35 D. S. McClure, in S. Kirshner (ed.), *Advances in the Chemistry of Coordination Compounds,* Macmillan, New York, 1961, p. 498.

36 Y. Hung, L. Y. Martin, S. C. Jackels, A. M. Tait and D. H. Busch, *J. Am. Chem. Soc., 99* (1977) 4029.

37 G. R. Brubaker and J. J. Fitzgerald, *J. Coord. Chem., 4* (1974) 93.

38 A. M. Tait, F. V. Lovecchio and D. H. Busch, *Inorg. Chem., 16* (1977) 2206.

39 (a) E. Ochiai, L. M. Long, C. R. Sperati and D. H. Busch, *J. Am. Chem. Soc., 91* (1969) 3201; (b) S. C. Jackeles, K. Farmery, E. K. Barefield, N. J. Rose and D. H. Busch, *Inorg. Chem., 11* (1972) 2893; (c) K. M. Long and D. H. Busch, *J. Coord. Chem., 4* (1974) 113; (d) A. M. Tait and D. H. Busch, *Inorg. Chem., 15* (1976) 197.

40 R. S. Drago, *Physical Methods in Chemistry,* Saunders, Philadelphia, 1977, p. 391.

41 H. L. Schlafer and G. Gliemann, *Basic Principles of Ligand Field Theory,* Wiley-Interscience, New York, 1969, p. 87.

42 R. L. Lintvedt, G. Ranger and B. A. Schoenfelner, *Inorg. Chem., 23* (1984) 688.

43 G. A. Mabbott, *J. Chem. Educ., 60* (1983) 697.

44 N. R. de Tacconi, D. Lexa and J. M. Saveant, *J. Am. Chem. Soc., 101* (1979) 467.

45 D. H. Evans, K. M. O'Connel, R. A. Petersen and M. J. Kelly, *J. Chem. Educ., 60* (1983) 290.

46 J. F. Endicott, J. Lilie, J. M. Kuszaj, B. S. Ramaswamy, W. G. Schmonsees, M. G. Simic, M. D. Glick and D. P. Rillema, *J. Am. Chem. Soc., 99* (1977) 429.

47 P. W. Schneider, P. F. Phalden and J. Halpern, *J. Am. Chem. Soc., 91* (1969) 77.

48 P. G. Swetik and D. G. Brown, *J. Electroanal. Chem., 51* (1974) 433.

49 (a) D. Faure, D. Lexa and J. M. Saveant, *J. Electro. Chem., 140* (1982) 269; (b) D. Lexa and J. M. Saveant, *J. Am. Chem. Soc., 98* (1976) 2652.

50 D. P. Rillema, J. F. Endicott and E. Papaconstaninou, *Inorg. Chem., 10* (1971) 1739.

51 D. P. Rillema, J. F. Endicott and R. C. Patel, *J. Am. Chem. Soc., 94* (1972) 394.

52 G. Costa, A. Puxeddu and E. Reisenhoffer, *J. Chem. Soc., Dalton Trans.,* (1972) 1519.