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Synthesis, Characterization and Electrochemical Investigation of Cobalt(III) Complexes of 3,8-Dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione Dioxime with Sulfur Ligands in the Axial Sites

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Abstract

Cobalt(III) complexes of the tetraaza quadridentate chelate, 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2.9-dione dioxime with a sulfur ligand such as 2-mercaptoethanol, ethanethiol, thiourea, thiocyanate and thiophenol in one of the axial coordination sites of cobalt have been synthesized to study the lability of the Co–S bond and the reactivity of the lower valent cobalt ion. These complexes have been characterized by C, H, N, Co analysis, conductivity measurements, magnetic susceptibility and IR, UV–Vis and ^{1}H NMR spectroscopy. The thiocyanato and 2-mercaptoethanolato complexes exhibit pseudo-octahedral geometry whereas the others undergo tetragonal distortion. All these complexes exhibit two polarographic one electron reduction waves corresponding to the reductions, Co(III) to Co(II) and Co(II) to Co(I). The cyclic voltammograms on a GC disk electrode consist of two cathodic waves corresponding to the reductions, Co(III) to Co(II) and Co(II) to Co(I) and two anodic waves corresponding to the oxidations, Co(I) to Co(II) and Co(II) to Co(III). Both Co(III)/Co(II) and Co(II)/Co(I) redox couples are irreversible as evidenced by the ΔE_p and i_{pa}/i_{pc} values. The i_{pa}/i_{pc} ratio of 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 polarographic and cyclic voltammetric $E_{1/2}$ values lie at less negative potentials when compared to that of the complexes of nitrogenous bases despite the fact that the field strength, Dq^z, of the axial sulfur ligands are comparable to that of the nitrogenous bases. This indicates that the Co–S bond is thermodynamically less stable than the Co–N bond. Electrochemical evidence is sought for the π-back bonding tendency of sulfur ligands.

Introduction

It has been well recognized that the facile cleavage and formation of the Co–C bond in alkylcobalamins under biological conditions is the key role of coenzyme B_{12} and methylcobalamin in mediating biochemical reactions [1]. Methane is evolved from the methylated corrin through the reductive cleavage of the Co–C bond [2]. This reaction occurs readily under non-enzymic conditions by the axial attack of cobalt by thiols or dithiols. At lower pH, complexes are formed between aquacobalamin and cysteine [3], glutathione [3b, c, 4] or other thiols in which mercaptide acts as the ligand. Thioproteins, dihydrolipoic acid and other thiols reduce vitamin B_{12a} to B_{12r} and B_{12s} forms in alkaline solution and hence may be the common biological reducing agents for vitamin B_{12} [5]. In the process of generation of B_{12r} and B_{12s} by thiols, mercaptocobalamin with a Co–S bond seems to be the intermediate. Schrauzer and Windgassen [6] in their model studies on cobamide dependent methyl transfer reactions found that the Co–S bond in mercaptocobaloximes is easily cleaved by a variety of reducing agents to yield cobaloxime$_r$ or cobaloxime$_s$. These reactions of mercaptocobaloximes closely resemble that of mercaptocobalamins. This demonstrated the utility of B_{12} models in understanding the properties of the Co–S bond in mercaptocobalamins. It has been observed that the affinity of the cobalt atom to sulfur is independent of the electronic structure of corrin.

Cyclic voltammetry seems to be the most versatile tool for evaluating the redox chemistry of vitamin B_{12}* and its model compounds** because of its ability to reproduce the interconversion between the

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*Cyclic voltammetry has been used to study the electrochemical behaviour of B_{12} [7a–c], B_{12a} [7b, c], B_{12r} [7a, d], B_{12s} [7a] and methyl B_{12} [7b, c]. The extensive electrochemical investigations carried out by Saveant and his co-workers [7e–l] on vitamin B_{12} and its derivatives unravelled the complexities deriving from the interplay between electron transfer and changes in the axial ligation in the reactions of B_{12} derivatives. Their work provides an operational electrochemical definition of a satisfactory B_{12} mimic.

**The cobaloximes [8a–f] and the alkyl- and (non-alkyl)-cobalt(III) complexes of the Costa-type models [8a, b, 8g–j] have been subjected for extensive electrochemical studies.

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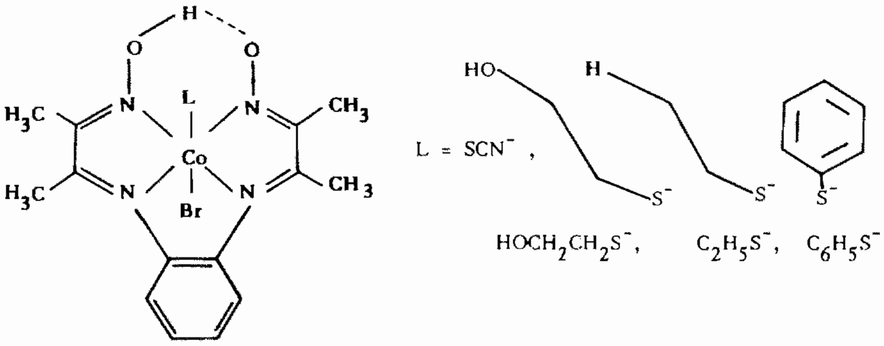

I

[LCo(DODOHbzo)Br]

Fig. 1. I, [LCo((DO)(DOH)bzo)Br]$^+$, L = SCN$^-$, HOCH$_2$CH$_2$S$^-$, C$_6$H$_5$S$^-$ or C$_2$H$_5$S$^-$.

pertinent oxidation states of cobalt in these complexes. As models for vitamin B$_{12}$, the cobaloximes [8a–f] and the alkyl and the (non-alkyl)cobalt(III) complexes of the Costa-type models [8a, b, g–j] have been subjected to extensive electrochemical studies. A new coenzyme B$_{12}$ model built upon the quadridentate tetraaza ligand, 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime has been reported recently [9]. In an attempt to study the lability of the Co–S bond and to examine the reactivity of the axial sites of lower valent cobalt ion, cobalt(III) complexes of this chelate with 2-mercaptoethanol, ethanethiol, mercaptophenol, thiocyanate or thiourea in one of the axial sites of cobalt (Fig. 1) have been synthesized and electrochemical investigations have been carried out by polarography and cyclic voltammetry. The results are reported herein.

Experimental

Reagents

Dimethyl sulfide (Fluka), 2-mercaptoethanol (SISCO-Chem., Bombay) and thiophenol and ethanethiol (Koch Light) were used as received. Thiourea and sodium thiocyanate (Laboratory Reagent, BDH) were recrystallized from water.

The other chemicals used and the methods employed to purify them are reported in our preceeding paper (see page 25 of this volume).

Synthesis of the Complexes

The synthesis of the ligand, (DOH)$_2$bzo and its dibromo complex, [Co((DO)(DOH)bzo)Br$_2$] have been reported elsewhere [9].

[HOCH$_2$CH$_2$SCo((DO)(DOH)bzo)Br] (1)

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 2-mercaptoethanol (0.39 g, 5 mmol). The resulting dark brown solution was refluxed on a water bath for 1 h and then the volume reduced to 10 ml by slow evaporation on a water bath and cooled to 0 °C. The black compound which separated out was filtered, washed with cold methanol (0 °C) and dried in air. Recrystallization from hot methanol yielded a brown crystalline compound. Yield 50%. *Anal.* Calc. for $C_{16}H_{22}N_4O_2BrSCo$: C, 39.22; H, 453; N, 11.44; Co, 12.02. Found: C, 39.45; H, 4.71; N, 10.85; Co, 12.20%. ^{1}H NMR (dmso-d$_6$)δ (Me$_4$Si) 1.35 (m, 2 H), 1.5 (m, 2 H), 2.35 (s, 12 H), 7.2 (m, 4 H).

[C$_2$H$_5$SCo((DO)(DOH)bzo)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 cooled to 5 °C in a round bottom flask. To this cold solution was added a slight excess of ethanethiol and the resulting brown solution stirred by a Teflon coated magnetic paddle for about 30 min at 5 °C and for another 30 min at room temperature (30 °C). The solution was transferred to a beaker and the volume reduced to 10 ml by slow evaporation of the solvent on a water bath and cooled to 0 °C. The black crystalline compound which separated out was filtered, washed with cold acetone (0 °C) and dried in air. Recrystallization from dry methanol yielded a brown crystalline compound. Yield 25%. *Anal.* Calc. for $C_{16}H_{22}N_4O_2SBrCo$: C, 40.60; H, 4.69; N, 11.84; Co, 12.45. Found: C, 40.97; H, 4.50; N, 12.05; Co, 12.50%. ^{1}H NMR (dmso-d$_6$)δ (Me$_4$Si) 1.15 (t, 3 H), 1.47 (m, 2 H), 2.2 (s, 6 H), 2.25 (s, 6 H), 7.55 (m, 4 H).

[C$_6$H$_5$SCo((DO)(DOH)bzo)Br] (3)

To 200 ml of brown aqueous methanolic solution of [Co((DO)(DOH)bzo)Br$_2$] (4.92 g, 10 mmol) at room temperature (30 °C) was added thiophenol (1.10 g, 10 mmol) with stirring. The resulting reddish brown solution was transferred into a round bottom flask and allowed to stand for nearly 1 h. The black crystals which deposited on the sides of the container were collected by filtration and dried under vacuum over anhydrous calcium chloride. Recrystallization from warm methanol yielded dark brown crystals. Yield 20%. *Anal.* Calc. for $C_{20}H_{22}N_4O_2SBrCo \cdot H_2O$: C, 44.53; H, 4.48; N, 10.39; Co, 10.93. Found: C, 45; H, 4.71; N, 10.20; Co, 11%.

[(H$_2$N)$_2$CSCo((DO)(DOH)bzo)Br]Br (4)

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 2 ml of an aqueous solution of thiourea (0.38 g, 5 mmol) with vigorous stirring. The brownish yellow crystalline compound which separated out was filtered immediately through a G3 sintered funnel, washed with dry alcohol followed by diethyl ether and dried under vacuum. Yield 70%. *Anal.* Calc. for $C_{15}H_{21}N_6O_2Br_2SCo$: C, 31.7; H, 3.73; N, 14.79; Co, 10.73. Found: C, 30.90; H, 3.80; N, 15; Co, 11.0%. ^1H NMR (dmso-d_6) δ (Me_4Si) 2.1 (s, 2 H), 2.36 (s, 12 H), 7.83 (m, 4 H).

[Co((DO)(DOH)bzo)(OH$_2$)$_2$](ClO$_4$)$_2$ (5)

A solution of $[Co((DO)(DOH)bzo)Br_2]$ (4.92 g, 10 mmol) in 200 ml of aqueous methanol (1:5 vol./vol.) was treated with a dilute aqueous solution of silver perchlorate with stirring. The silver bromide which precipitated out was removed by filtration. The filtrate was again treated with a small amount of aqueous silver nitrate solution to ensure the complete removal of the axially bound bromide ions from the dibromo complex. The axial bromide ions in $[Co((DO)(DOH)bzo)Br_2]$ are highly labile and an aqueous alcoholic solution on treatment with $AgNO_3$ gives AgBr quantitatively [9]. The resulting dark brown solution was flash evaporated to dryness. The dark brown crude product was recrystallized twice from dry ethanol to get the brown diaqua complex. Yield 25%. *Anal.* Calc. for $C_{14}H_{21}N_4O_{12}Cl_2Co \cdot H_2O$: C, 28.73; H, 3.96; N, 9.57; Co, 10.07. Found: C, 28.69; H, 4.05; N, 9.85; Co, 10.28%. $\Lambda_M(CH_3OH)$ 205 ohm^{-1} cm^2 mol^{-1}.

[Co((DO)(DOH)bzo)(Me$_2$S)$_2$](ClO$_4$)$_2$ (6)

A solution of $[Co((DO)(DOH)bzo)(OH_2)](ClO_4)_2$ (5.67 g, 10 mmol) in 100 ml of dry methanol, taken in a 250 ml round bottom flask, was cooled to 10 °C and treated with a slight excess of dimethyl sulfide (15 mmol). The solution was stirred using a Teflon coated magnetic paddle at 10 °C for about 6 h. The volume of the solution was then reduced to 10 ml in a flash evaporator and cooled to 0 °C. The brown plates which separated out were filtered and washed rapidly with cold acetene (0 °C). The resulting transparent brown plates were stored in vacuum over anhydrous calcium chloride. Yield 20%. *Anal.* Calc. for $C_{18}H_{29}N_4O_{10}S_2Cl_2Co$: C, 32.98; H, 4.46; N, 8.55; Co, 8.99. Found: C, 32.78; H, 4.35; N, 8.78; Co, 9.21%.

[SCNCo((DO)(DOH)bzo)Br] (7)

This complex was synthesized by the reaction of $[Co((DO)(DOH)bzo)Br_2]$ with KSCN as previously reported [9].

Physical Measurements

The instruments used and the methods employed to study these complexes have been reported elsewhere [9] and in the preceeding paper*.

Results and Discussion

In the case of the mercapto complexes, the mercaptans, namely, 2-mercaptoethanol, ethanethiol and thiophenol act as monoanionic ligands. No pretreatment with base was needed to deprotonate the ligands. Among the mercapto complexes $[C_6H_5SCo((DO)(DOH)bzo)Br]$ is stable neither in the solid state nor in solution for a long time. The complex, $[Co((DO)(DOH)bzo)(Me_2S)_2](ClO_4)_2$ is stable in the solid state for several days but in solution (CH_3CN or CH_3OH) it emulates the odour of dimethyl sulfide, probably due to the replacement of dimethyl sulfide by the solvent molecules.

Infrared Spectra

The infrared spectrum of $[C_6H_5SCo((DO)(DOH)bzo)Br]$ consists of a strong as well as a sharp absorption band at 1470 cm^{-1} and a weak band at 1015 cm^{-1} which are not observed in $[Co((DO)(DOH)bzo)Br_2]$ [9] and hence these bands may be due to the coordinated theophenol. The complex, $[HOCH_2CH_2SCo((DO)(DOH)bzo)Br]$ exhibits a strong and broad band at 2940 cm^{-1} probably due to the ν(OH) vibration of the coordinated 2-mercaptoethanol. In $[Co((DO)(DOH)bzo)(Me_2S)_2]ClO_4)_2$ ν_a(CH) and ν_s(CH) of the dimethyl sulfide expected at 2900 cm^{-1} appear as a broad band at 2900 cm^{-1}. The broadness may probably be due to the coupling of these vibrations with the ν(OH) of the equatorial chelate. The asymmetric and symmetric deformation vibrations of the methyl groups of the coordinated dimethylsulfide appear as strong and sharp bands at 1440 and 1370 cm^{-1}, respectively, coupled with the same vibrations of the methyl groups of the equatorial ligand. The weak band at 1020 cm^{-1} and the strong sharp band at 975 cm^{-1} are attributed to the CH_3 rocking modes of vibration [10b].

If thiourea coordinates through nitrogen, the CS stretching frequency would be expected to increase with a concomitant decrease in the CN stretching frequency. On the other hand, if coordination occurs through sulfur, the CS stretching frequency would be expected to decrease with an appreciable change in NH stretching frequency [11]. The thiourea complex, $[(H_2N)_2CSCo((DO)(DOH)bzo)Br]Br$ exhibits a very strong band of medium

TABLE 1. Characteristic infrared absorption bands (cm^{-1}) of complexes of sulfur ligands[a]

Complex	Assignment					Absorption of sulphur ligands	
	ν(CH)	ν(C=N)	ν(NO)	ν'(NO)	ν(Co–N)	Band (cm^{-1})	Assignment
$[C_6H_5SCo((DO)(DOH)bzo)Br]$	3030mb,w	1570s,mb	1235vs,sp	1095vs,sp	520s,sp	1470s,sp	
	2930vw,sp					1015w	
$[HOCH_2CH_2SCo((DO)(DOH)bzo)Br]$	2940vb,s	1570b,s	1230vs,sp	1080s,b	520s,sp	2940vs,b	ν(OH)[b]
$[Co((DO)(DOH)bzo)(Me_2S)_2](ClO_4)_2$	2940vb,s	1570mb,s	1230vs,sp	1090s,mb	525vs,sp	2940	$\nu_a(CH) + \nu_s(CH)$ [b]
						1440s,sp	asy. defor. vib. of CH_3 [c]
						1370s,sp	sy. defor. vib. of CH_3 [c]
$[(H_2N)_2CSCo((DO)(DOH)bzo)Br]Br$	3190sp,w	1550s,mb	1230vs,sp	1085vs,mb	520vs,sp	3325vs,mb	ν(NH)
						1610s	NH_2 bending
						715sp,w	ν(C=S)
$[(H_2O)_2Co((DO)(DOH)bzo)](ClO_4)_2$	3420b,w	1570s,b	1240vs,mb		530vs,sp	2940s,b	ν(OH)
	3040b,w					750s,mb	ν(OH)

[a] Medium: KBr disk; abbreviations: *s* = *strong*, sp = *sharp*, vs = *very strong*, b = *broad*, *m* = *medium*, w = *weak*, *mb* = *medium board*, vw = *very weak*. [b] This vibration couples with the ν(OH) of the ligand framework. [c] The asymmetric and symmetric deformation vibration of the methyl groups of the coordinated Me_2S couple with the respective vibration of the methyl groups of the equatorial ligand.

TABLE 2. Electronic spectral band assignments ($cm^{-1} \times 10^3$) and the ligand field parameters of the ethanethiolato and thiourea complexes[a]

Complex	$^1A_{1g} \rightarrow {}^1E_g^a$	$^1A_{1g} \rightarrow {}^1A_{2g}$	$^1A_{1g} \rightarrow ({}^1E_g^b + {}^1B_{2g})$	Co^{III}–S CT band	Other bands	Ligand field parameters[c] (cm^{-1})		
						Dq^{xy}	Dq^z	D_t
$[C_2H_5SCo((DO)(DOH)bzo)Br]$	17.86	22.73	26.66	34	42.70	2653	1680	556
$[(H_2N)_2CSCo((DO)(DOH)bzo)Br]Br$	18.12	22.83	30.50	33.33	41.66	2663	1721	538

[a] Spectra were recorded by using ~10^{-3} M solution of the complex in DMF in the visible region and in methanol in the UV region. [b] The change-transfer transitions and/or the $\pi \rightarrow \pi^*$ transition of the ligand framework. [c] Computed according to the crystal field model of Wentworth and Piper [9] and our preceeding paper, see p. 25 of this volume.

broadness at 3325 cm^{-1} assignable to ν(NH). This band is sharper than that found in free thiourea which indicates that the coordinated thiourea does not form hydrogen bond [11b]. The strong band appearing at 1610 cm^{-1} is assigned to the NH_2 bending mode. The strong band appearing at about 1083 cm^{-1} in thiourea, assignable to ν(CS), is either much weakened or disappears upon coordination through the sulfur donor. Due to the presence of the ν'(NO) band in this region, the ν(CS) band could not be observed as a 'pure' band. The band appearing at 730 in thiourea, characteristic of the ν(CS) vibration, appears at 715 cm^{-1} in the complex. This lowering of frequency may be attributed to the reduced double bond character of the C=S bond due to the coordination of sulfur to cobalt as observed by Yamaguchi *et al.* [11b]. The characteristic infrared absorption bands of the complexes of sulfur ligands are presented in Table 1. All these complexes exhibit absorptions such as ν(C=N), ν(NO), ν'(NO), ν(CO–N), and symmetric and asymmetric deformation vibrations of the methyl groups characteristic of the ligand framework. The characteristic infrared absorption bands of the axial sulfur ligand and that of the equatorial ligand are given in Table 1.

Molar Conductivity

The molar conductances of [(SCNCo((DO)(DOH)bzo)]Br, $[HOCH_2CH_2SCo((DO)(DOH)bzo)Br]$ and $[C_2H_5SCo((DO)(DOH)bzo)Br]$ in DMF are very low indicating that they are non-electrolytes. The Λ_M of $[(Me_2S)_2Co((DO)(DOH)bzo)](ClO_4)_2$ in CH_3CN was found to vary with time probably due to the replacement of the coordinated dimethyl sulfide by the solvent molecules. However, the conductance was found to be constant after 12 h of preparing the solution and the calculated molar conductance is characteristic of a 1:2 electrolyte [12]. This indicates the formation of the complex $[(CH_3CN)_2Co((DO)(DOH)bzo)](ClO_4)_2$ in solution.

Magnetic Susceptibility

The weight of each one of the complexes reported herein decreased in the magnetic field and the χ_M^{corr} is a negative quantity ranging from -721×10^{-12} to -1834×10^{-12}. This indicates the diamagnetic nature of these complexes [9].

Electronic Absorption Spectra

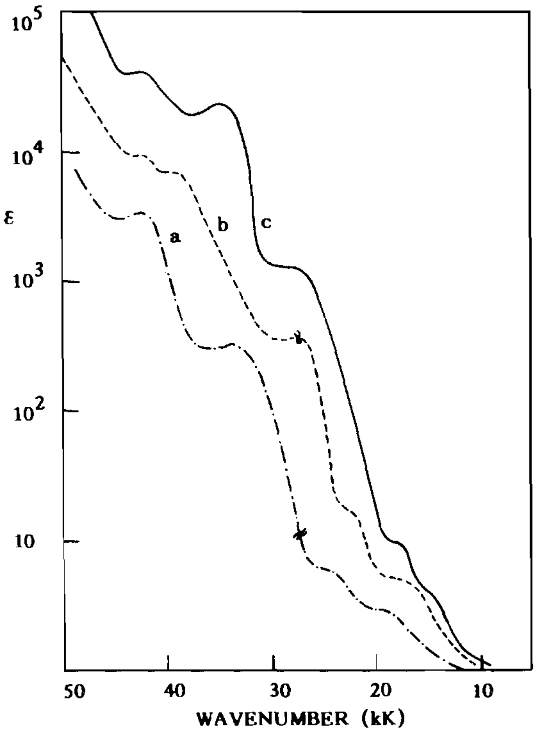

Fig. 2. Electronic absorption spectra of (a) $[(H_2N)_2CSCo((DO)(DOH)bzo)Br]Br$, (b) $[C_2H_5SCo((DO)(DOH)bzo)Br]$ and (c) $[HOCH_2CH_2SCo((DO)(DOH)bzo)Br]$ in DMF (visible region) and in methanol (UV region) at 25 °C.

The complexes $[(H_2N)_2CSCo((DO)(DOH)bzo)Br]$-Br and $[C_2H_5SCo((DO)(DOH)bzo)Br]$ exhibit three d–d transitions, two in the visible and one in the near UV region, characteristic of tetragonally distorted octahedral cobalt(III) complexes as do the (non-alkyl)cobalt(III) complexes of the same equatorial ligand reported elsewhere [9] and in the preceeding paper*. The electronic spectral band assignments and the ligand field parameters of these complexes are presented in Table 2. The electronic absorption spectra of $[(H_2N)_2CSCo((DO)(DOH)bzo)Br]Br$ and $[C_2H_5SCo((DO)(DOH)bzo)Br]$ are depicted in (a) and (b) respectively, of Fig. 2. The field strength of the equatorial ligand is very close to the value computed from the spectral data of the Lewis base complexes. The field strengths of ethanethiol and thiourea are comparable to that of the nitrogenous bases (see Table 3 of our preceeding paper, p. 25 of this volume). The intensity of the lowest spin allowed transition, $^1A_{1g} \rightarrow {}^1E_g^a$ varies from 4.5–7 l mol^{-1} cm^{-1} while that of the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition varies from 7.5–20 l mol^{-1} cm^{-1} and that of the $^1A_{1g} \rightarrow ({}^1B_{2g} + {}^1E_g)$ transition lies in the range of 350–900 l mol^{-1} cm^{-1}. The higher intensity of the third transition may be due to intensity stealing arising from the nearby occurring highly intense Co–S charge transfer transition (*vide infra*). The geometry of [SCNCo((DO)(DOH)bzo)Br] and $[HOCH_2CH_2SCo((DO)(DOH)bzo)Br]$ is accidently close to O_h as they exhibit the two predicted bands, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, characteristic of pseudo-octahedral cobalt(III) complexes [13]. The low lying transition, $^1A_{1g} \rightarrow {}^1T_{1g}$, occurs for these complexes at 15.95 and 14.38 kK, respectively, whereas the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition occurs at 22.72 and 17.36 kK, respectively. All these complexes exhibit an intense absorption band in the region 280–300 nm. This band is diagnostic of the Co^{III}–S bond and has been assigned to the ligand to metal change transfer (LTMCT) arising from the coordination of sulfur to a potentially oxidizing centre [14].

Electrochemical Behaviour of the Complexes

The complexes [SCNCo((DO)(DOH)bzo)Br], $[(H_2N)_2CSCo((DO)(DOH)bzo)Br]Br$, $[HOCH_2CH_2SCo((DO)(DOH)bzo)Br]$ and $[C_2H_5SCo((DO)(DOH)bzo)Br]$ exhibit two well defined polarographic reduction waves corresponding to the reductions, Co(III) to Co(II) and Co(II) to Co(I). The $E_{1/2}$ values and the diffusion current constants are presented in Table 3 and the polarograms for the reduction of $[(HOCH_2CH_2SCo((DO)(DOH)bzo)Br]$ and $[(H_2N)_2CSCo((DO)(DOH)bzo)Br]$ are depicted in (a) and (b), respectively of Fig. 3. The $E_{1/2}$ values for both reduction processes of all these complexes lie at less negative potentials than that of $[Co((DO)(DOH)bzo)Br_2]$ and the complexes of nitrogenous bases reported in our preceeding paper, see p. 25 this volume. The polarographic $E_{1/2}$ value for the Co(III) → Co(II) reduction is −0.13 V (versus Ag/AgCl) for [SCNCo((DO)(DOH)bzo)Br] and −0.26 V (versus Ag/AgCl) for $[Co((DO)(DOH)bzo)Br_2]$ and the $E_{1/2}$ values for the Co(II) → Co(I) reduction are −0.91 and −1.1 V (versus Ag/AgCl), respectively. Thus the reduction of the thiocyanato complex, for example, to the Co(II) form is easier by 0.13 V and the reduction of the Co(II) form to the Co(I) form is easier by 0.19 V than the corresponding reductions of the dibromo complex, $[Co((DO)(DOH)bzo)Br_2]$ [15]. The difference in reduction potentials of the complexes of sulfur ligands and the nitrogenous bases is still more pronounced in that the former ones undergo both reduction at much less negative potentials than the latter (see Table 3 of this paper and Table 4 of our preceeding paper, see p. 25 this volume). The variation of i_d with concentration is very nearly constant which indicates that the waves are diffusion controlled at the DME and the occurrence of one electron transfer for both reductions [8d, 15].

The cyclic voltammograms of these complexes consist of two cathodic waves corresponding to the reductions, Co(III) to Co(II) and Co(II) to Co(I) and two anodic waves corresponding to the oxidations Co(I) to Co(II) and Co(II) to Co(III). The cyclic voltammograms of [SCNCo((DO)(DOH)bzo)Br] and $[HOCH_2CH_2SCo((DO)(DOH)bzo)Br]$ are shown in parts (a) and (b), respectively, of Fig. 4 and the cyclic voltammetric data of all the four complexes are presented in Table 4. These complexes exhibit similar behaviour as do the (non-alkyl)cobalt(III) complexes discussed in our preceeding paper, see p. 25 this volume. Both the Co(III)/Co(II) and Co(II)/Co(I) redox couples are irreversible as evidenced from the ΔE_p and i_{pa}/i_{pc} values. The irreversible electron transfer encountered during the reduction of the Co(III) complex to the Co(II) form is due to the breaking of one of the axial ligands and the generation of a five coordinate Co(II) complex is envisioned. Since the E_{pc} value for the Co(II)/Co(I) couple is quite different for all these complexes, it is evident that the Co–S bond is not broken during the reduction of the initial Co(III) complex to the Co(II) complex, but the axial bromide is lost as shown in eqn. (1).

$$[S\text{–}Co^{III}((DO)(DOH)bzo)Br] + e \longrightarrow [S\text{–}Co^{II}((DO)(DOH)bzo)] + Br^- \qquad (1)$$

If the axially bonded sulfur ligand(S)* were lost, the E_{pc} values for the Co(II)/Co(I) couple of all these complexes would be the same since the same five coordinate Co(II) complex, $[Co^{II}((DO)(DOH)bzo)Br]$ would undergo reduction to cobalt(I). The generation of five coordinate cobalt(II) complexes was observed in the electrochemical investigation of the (non-alkyl)cobalt(III) complexes of the $(C_2(DO)(DOH)pn)$ [8a] and ((DO)(DOH)bzo) [15] chelates and with aquacobalamin [7b, e, f].

The E_{pa} values for the Co(II)/Co(I) couple of all these complexes are very nearly the same at all sweep rates. This indicates the loss of both the axial ligands

TABLE 3. Polarographic half-wave potentials[a] and diffusion current constants for the reduction of the complexes of sulfur ligands in DMF

Complex	Concentration ×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)
[SCNCo((DO)(DOH)bzo)Br]	1.32	−0.13	1.52	−0.91	1.55
$[HOCH_2CH_2SCo((DO)(DOH)bzo)Br]$	1,43	−0.14	1.99	−0.96	1.98
$[(H_2N)_2CSCo((DO)(DOH)bzo)Br]Br$	0.67	−0.14	1.91	−0.62	2.24
$[C_2H_5SCo((DO)(DOH)bzo)Br]$	1.02	−0.15	1.69	−0.98	1.78

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

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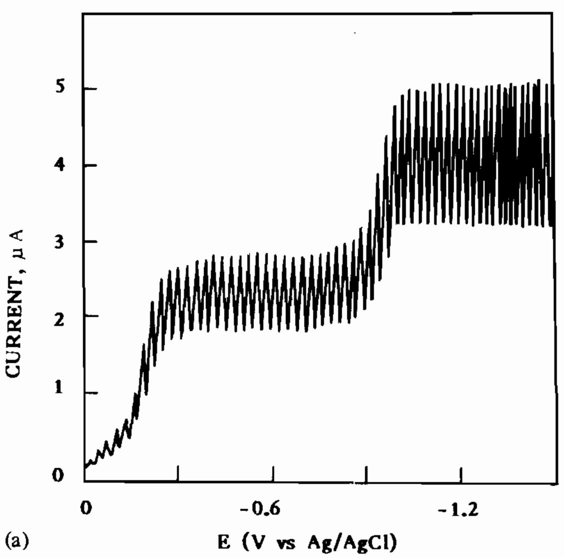
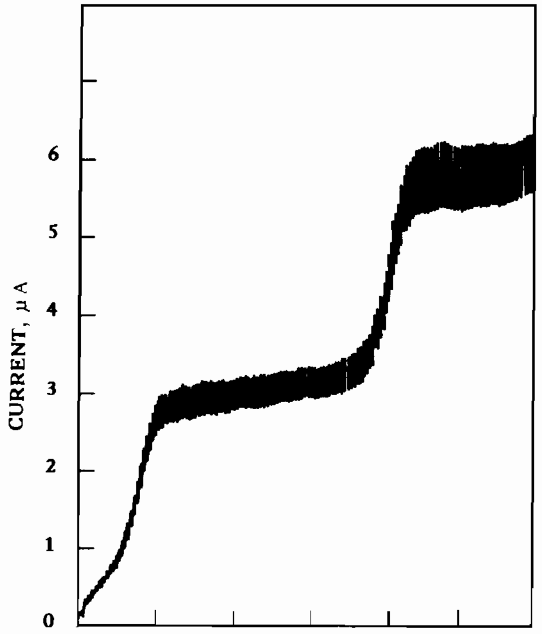
*The axially bound sulfur ligand is labelled as S in general for simplicity.



(a)



(b)

Fig. 3. Polarograms for the reduction of (a) [$HOCH_2CH_2SCo((DO)(DOH)bzo)Br$] ($1.43 \times 10^{-3}$ M) and (b) [$(H_2N)_2CSCo((DO)(DOHbzo)bzo)Br$]Br ($0.67 \times 10^{-3}$ M) in DMF containing 0.1 M TEAP at 25 °C. DME vs. Ag/AgCl. Sweep rate 4 mV s^{-1}.

when the five coordinate Co(II) complex is reduced to the Co(I) form as shown in eqn. (2). The generation of the four coordinate Co(I) complex was also observed in the cyclic voltammetric studies of vitamin B_{12} derivatives [7i] and B_{12} models [15]. The rate of electron transfer for the Co(II) → Co(I) reduction is much faster than for the Co(III) → Co(II) reduction

TABLE 4. Cyclic voltammetric data for the reduction of complexes of sulfur ligands at a glassy carbon 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)	$i_{pc}/\nu^{1/2}$ (μA $s^{-1/2}$ $mV^{-1/2}$)	$E_{pc} - E_{p/2}$ (mV)
[$SCNCo((DO)(DOH)bzo)Br$]	III/II	−0.62	−0.22	−0.42	−0.91	12	13	1.08	400	1.70	130
(0.85×10^{-3} M)	II/I	−1.12	−1.10	−1.10	−1.59	40	20	0.50	60	5.65	100
[$HOCH_2CH_2SCo((DO)(DOH)bzo)Br$]	III/II	−0.62	−0.22	−0.42	−0.91	14	16	1.14	400	1.98	130
(1.527×10^{-3} M)	II/I	−1.19	−1.10	−1.14	−1.63	30	30	1	90	4.24	110
[$C_2H_5SCo((DO)(DOH)bzo)Br$]	III/II	−0.59	−0.24	−0.415	−0.905	12	11	0.92	350	1.7	140
(1×10^{-3} M)	II/I	−1.10	−1.040	−1.07	−1.56	25	50	0.50	60	3.54	110
[$(H_2N)_2CSCo((DO)(DOH)bzo)Br$]Br	III/II	−0.60	−0.22	−0.41	−0.90	10	10	1	380	1.41	120
(1.12×10^{-3} M)	II/I	−1.11	−1.040	−1.075	−1.565	18	18	1	70	2.55	100

[a] Sweep rate: 50 mVs^{-1}.

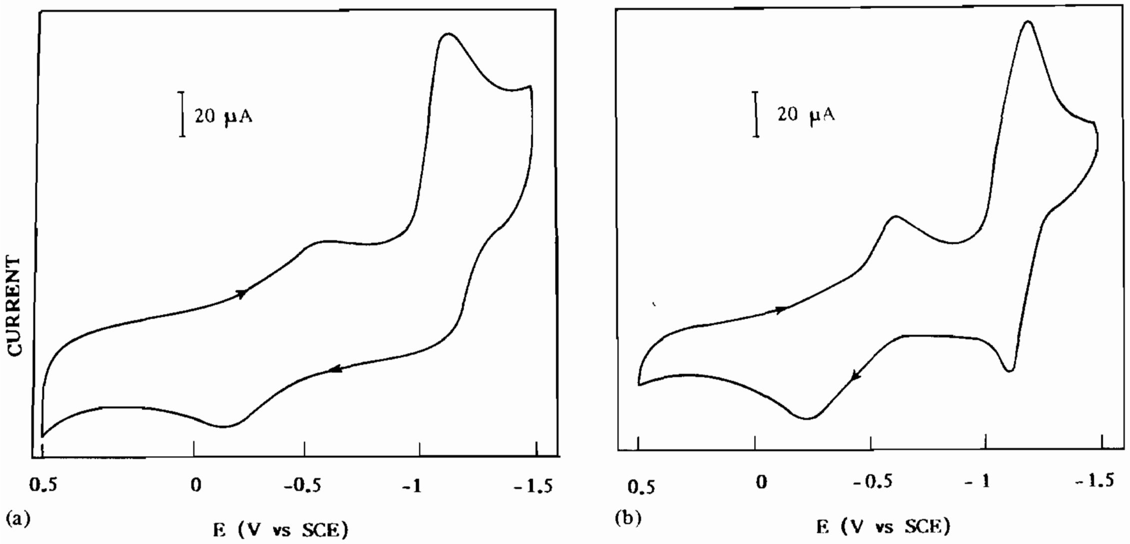


Fig. 4. Cyclic voltammograms of (a) [SCNCo((DO)(DOH)bzo)Br] (0.85×10^{-3} M) and (b) [$HOCH_2CH_2SCo((DO)(DOH)bzo)Br$] ($1.52 \times 10^{-3}$ M) at a glassy carbon electrode in DMF containing 0.1 M TEAP at 22 °C. Sweep rate 100 mV s^{-1}.

as indicated by the ΔE_p values. This is attributable to the stronger binding of the sulfur ligand to cobalt(III) than to cobalt(II).

$$[\mathrm{S{-}Co^{II}((DO)(DOH)bzo)}] + e \longrightarrow [\mathrm{Co^{I}((DO)(DOH)bzo)}] + \mathrm{S^-} \quad (2)$$

The cyclic voltammetric $E_{1/2}$ values for both Co(III)/Co(II) and Co(II)/Co(I) redox couples lie at less negative potentials for these complexes than that of the Lewis base complexes. The $E_{1/2}$ values of the former couple ranges between −0.59 and −0.62 V for the sulfur complexes whereas it lies in the range of −0.60 to −0.75 V for the Lewis base complexes. Similarly, the $E_{1/2}$ values of the latter couple fall in the range of −1.10 to −1.19 V and −1.12 to −1.23 V for the sulfur complexes and the Lewis base complexes, respectively (see Table 4 of this paper and Table 5 of our preceeding paper, p. 25). The less negative $E_{1/2}$ potentials for the sulfur complexes indicate a lowered electron density on the cobalt centre which can be attributed to the enhanced tendency of the sulfur ligand to remove electron density from cobalt rather than the Lewis bases.

The i_{pa}/i_{pc} ratio of 0.5 for the Co(II)/Co(I) redox couple of all these complexes indicates a 50% Co(I) yield. This indicates the involvement of a coupled chemical reaction such as an ECE mechanism as observed with the cobalt(III) complexes of nitrogenous bases, discussed in our preceeding paper, p. 25.

$$\underline{E}\ [\mathrm{S{-}Co^{III}((DO)(DOH)bzo)Br}] + e \rightleftharpoons [\mathrm{S{-}Co^{II}((DO)(DOH)bzo)}] + \mathrm{Br^-} \quad (3)$$

$$\underline{C}\ [\mathrm{S{-}Co^{II}((DO)(DOH)bzo)}] + [\mathrm{S{-}Co^{III}((DO)(DOH)bzo)Br}] \rightleftharpoons [\mathrm{S_2Co^{III}((DO)(DOH)bzo)}] + [\mathrm{Co^{II}((DO)(DOH)bzo)}]^+ + \mathrm{Br^-} \quad (4)$$

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

This ECE mechanism also predicts a 50% Co(I) yield besides accounting for the electrochemical irreversibility of both Co(III)/Co(II) and Co(II)/Co(I) redox couples (eqn. (6)).

$$2[\mathrm{S{-}Co^{III}((DO)(DOH)bzo)Br}] + 2e \rightleftharpoons [\mathrm{S_2Co^{III}((DO)(DOH)bzo)}] + [\mathrm{Co^{I}((DO)(DOH)bzo)}] + 2\mathrm{Br^-} \quad (6)$$

In the case of the cobalt(III) complexes of nitrogeneous bases with the same equatorial ligand, reported in our preceeding paper, p. 25, there is a perfect correlation between the $E_{1/2}$ values and the field strength, Dq^z, of the axial ligands. It has been found that as the Dq^z increases, the $E_{1/2}$ moves to higher negative potential. But in the case of the complexes of sulfur ligands under study, it is very interesting to note that the polarographic and cyclic voltammetric $E_{1/2}$ values lie at less negative potentials than the complexes of nitrogenous bases despite the fact that the Dq^z values of the sulfur ligands are comparable with that of the nitrogeneous bases. This indicates that the $E_{1/2}$ value does not depend only on the electronic transmission of the axial ligand but on the thermodynamic and kinetic properties of the metal–ligand bond as well. Since the $E_{1/2}$ values reflect primarily the thermodynamic stability of the metal–ligand bond, the variation observed in the $E_{1/2}$ values of the complexes of nitrogeneous bases from that of the sulfur ligands indicates the lowered stability of the Co–S bond as compared with the Co–N bond.

Conclusions

The (DO)(DOH)bzo chelate forms stable Co(III) complexes with sulfur ligands in the axial sites of Co besides forming a wide variety of stable Lewis base complexes. The physical and electrochemical properties demonstrate the tendency of Co(III) to stabilize Co–S bond. The comparable Dq^z values of the axially bound sulfur ligands and the Lewis bases indicate their comparable σ-donating ability to Co(III). But the less negative $E_{1/2}$ potentials for the sulfur complexes reflect the lowered electron density on the Co centre and it is almost certain that it is due to the π-back bonding tendency of the sulfur ligands. This accounts for the lowered thermodynamic stability of the Co–S bond compared to the Co–N bond and the lowered stability of complexes formed between a hard acid (Co(III)) and soft bases (sulfur ligands) is readily understood.

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