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Redox and Spectroscopic Properties of Heterobinuclear Complexes of Cobalt(III) Schiff Bases and Chloronitrosyl Molybdenum Fragments

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Abstract

A series of new heterobinuclear complexes obtained by the reaction of [Mo(NO){HB(dmpz)$_3$} Cl$_2$]; [HB(dmpz)$_3$ = tris(3,5-dimethylpyrazolyl)borate] with Cobalt(III) Schiff-base complexes derived by condensation of 1mol equiv. of 2,4-dihydroxylbenzaldehyde and salicylaldehyde with α,ω-diamines [$NH_2(CH_2)_nNH_2$, n = 2-4, 1,2-$C_6H_4(NH_2)_2$] were synthesized. The complexes were studied by electrochemistry and UV/VIS/NIR spectroelectrochemistry in DCM and MeCN to evaluate how the Schiff base donors affect the properties of the complexes. The coordination of the Schiff base appeared to occur through the two azomethine nitrogens and the two *o*-OH groups, while the molybdenum complex coordinated through the terminal *m*-OH of the Schiff bases. From cyclic and differential pulse voltammetric data it was shown that the $E_{1/2}$ values for monometallic Co(III)/(II) redox couple shifted to less cathodic values as the ethylene backbone increased. The corresponding bimetallic complexes had two reduction waves associated with the cobalt(III)/(II) and Mo (NO) (III)/ (II) redox couples. A comparison of the reduction peak potentials of these complexes in DCM and MeCN solvents revealed that the potentials in dichloromethane DCM are more cathodic than in MeCN suggesting that the type of solvent used has a significant effect on the electron distribution of the two metal centres.

Key words: tris (pyrazolyl) borate, nitrosyl, cobalt (III), bimetallic, redox-active

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Introduction

Complexes of transition metal ions with polydentate Schiff bases containing nitrogen and oxygen donor atoms play an important role in biological systems and represent interesting models for metalloenzymes that catalyze the reduction of dinitrogen and dioxygen (Sharma, Shipra and Ankita, 2005). Studies done by El-Medani (2004) showed that tetradentate ligands having N_2O_4 donor sets such as bis(salicylaldehyde)phenylenediimine (salphenH$_2$) have been found to have catalytic activity for epoxidation reactions. El-Medani further reports that electrochemical and spectrochemical studies of Co(salphen) revealed that the compound formed adducts with oxygen and exhibited catalytic activities for oxygen reduction. Other studies report that complexes of chromium, manganese, nickel and ruthenium with Schiff bases having N_2O_2 donor atoms were found to be catalytic for epoxidation reactions [Zhou *et al.,* 1999].

In this context, several Schiff bases and the relevant transition metal complexes have become of great interest to inorganic Chemistry and have been studied extensively (Tas, Aslanoglu, Ulusoy and Temel, 2004). Our interest is in the study of the redox properties of heterobinuclear complexes containing Mo(NO){HB(dmpz)$_3$}Cl$^-$ fragment 4**,** [dmpz = tris(3,5-dimethylpyrazolyl) hydroborate] connected to the *meta* terminal phenolic position of a series of cobalt(III) Schiff base fragments **2**. Since there is usually no direct overlap between two metal centres, the electron transfer pathway is mediated by a conjugated bridging ligand. Several methods for evaluating the degree of redox behaviour between the metal centres exist in the literature and have been found to be influenced by among other factors, nature of Schiff base ligand and type of solvent [Tao, Zang, Cheng, Wang, Niu and Liao, 2006; Pandiyan, Perla and Toscano, 2005; El-Medani, 2004; Tas *et al.*, 2004]. The ability of the conjugated series of multatom bridging ligand to mediate intramolecular electron transfer across it from one metal center to the other is a reasonable guide to its ability to permit redox activity in a nanoscopic circuit device.

Thus, it was thought worthwhile to synthesize a series of heterobinuclear Schiff base complexes of 3, code named CoL1-Mo to CoL4-Mo containing cobalt(III) implanted in the tetradentate Schiff base cavity and connected to a molybdenum mononitrosyl moiety *via* a phenolic *meta* position of the Schiff base (Lutta and Kagwanja, 2000). Such complexes play an important role in coordination Chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures [Fabbrizzi, Licchelli and Pallavicini, 1999]. Transition metal complexes of Schiff bases containing tetradentate ligands have also shown microbial activity [Raman *et al.*, 2003].

Although the redox behaviour of a number of bimetallic complexes containing Schiff base ligands is known, the electrochemical properties of some transition metal complexes are not completely clear. In this article, we would like to report that a Mo(NO){HB(dmpz)$_3$}Cl$^-$ moiety [dmpz = tris (3,5-dimethylpyrazolyl) hydroborate] connected to the *meta* terminal phenolic position of a series of cobalt(III) Schiff base fragments yields a binuclear system that is a good candidate for the role of molecular electronics.

Experimental

Chemicals

All reagents used were of analytical reagent grade, obtained from Fluka and Aldrich and used without further purification. All reactions except for the preparation of Schiff bases were carried out under dry nitrogen. Preparation of the tetradentate Schiff base ligands 1 (L1 to L4) was done by the condensation of 1:1 mole equivalents of 2,4-dihydroxybenzaldehyde and salicylaldehyde with α,ω-diamines [1,2-$C_6H_4(NH_2)_2$ and $H_2N(CH_2)_nNH_2$, n = 2 - 4] as shown in Scheme 1 [Lutta and Kagwanja, 2000].

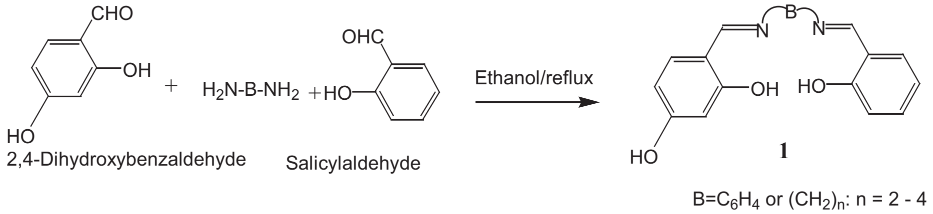
*Synthesis of the monometallic Co(III) Schiff base complexes CoL1 – CoL4 [**2,** B = $(CH_2)_n$, n = 2 – 4 and C_6H_4]*

The cobalt Schiff base complexes [2, B = $(CH_2)_n$, n = 2 – 4 and C_6H_4] were prepared by refluxing a mixture of cobalt(III) acetate and the appropriate Schiff base (L1 to L4) in absolute ethanol for a period of 3 days under dry nitrogen as shown in Scheme 2. A solution of cobalt(III) acetate (1.757mmoles) in 30ml absolute ethanol was added dropwise to a solution of Schiff base L1 to L4 (1.757mmoles) in 30ml absolute ethanol. The mixtures turned to wine red within thirty minutes of refluxing. Refluxing continued for three days followed by filtration while hot. The excess solvent in the filtrate was evaporated *in vacuo* to afford brown solids which were washed with ethanol (3 x 50ml) and diethyl ether (3 x 50ml) then dried in air for one day to afford brown solids.

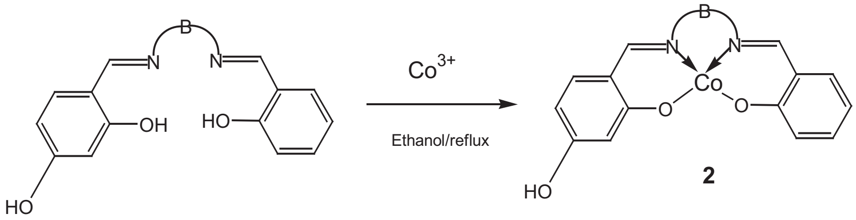
Synthesis of dichloromolybdenum nitrosyl tris(3,5-dimethylpyrazolyl) hydroborate [Mo(NO){HB(3,5-Me$_2$N$_2$C$_3$H)$_3$}Cl$_2$] precursor complex

The synthesis of molybdenum precursor complex 4 was, according to the synthetic route shown in Scheme 3 (McCleverty and Ward, 1998). Starting with a mixture of potassium borohydride (2.65g) and 3,5-dimethylpyrazole (20g) was heated by means of a hot plate in a 250ml refluxing flask connected to a bubbler. The reaction temperature was raised to 238°C, the melting temperature of the mixture, and maintained above 255°C until bubbling stopped. The melt was then cooled to 100°C, poured into 100ml of freshly distilled toluene and stirred with a glass rod until it attained the room temperature. The white precipitate formed was filtered and washed in freshly distilled toluene, giving colourless crystals [K{HB(3,5-Me$_2$N$_2$C$_3$H)$_3$}] which were washed with *n*-hexane (3x50ml) and left to dry on the filter paper overnight. A solution of potassium KHB[Me$_2$N$_2$C$_3$H$_3$] (10g, 29.77mmoles) and Mo(CO)$_6$, (7.86g, 29.77mmoles) in freshly distilled toluene (100ml) was refluxed in a 250ml refluxing condenser while stirring for 6 hours. The resulting yellow suspension was allowed to cool to room temperature and 0.57mL glacial acetic acid added. It was stirred again for two more hours while refluxing.

Scheme 1: Preparation of the free *m*-Schiff bases ligands



Scheme 2: Preparation of the monometallic Schiff bases complexes

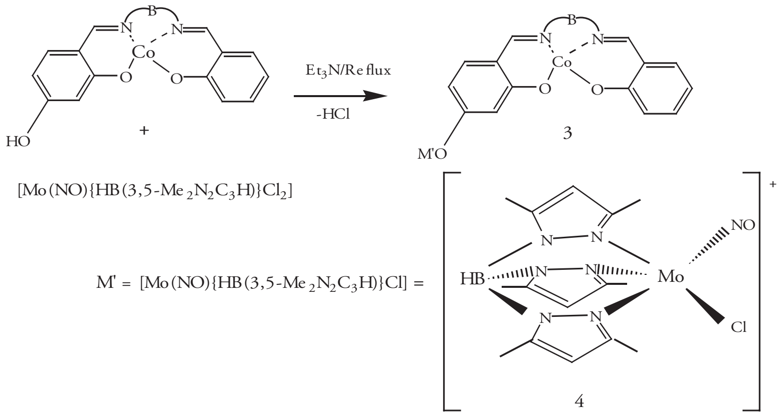


Scheme 3: Synthetic route for synthesis of the Molybdenum mononitrosyl precursor complex

$$\mathrm{BH_4^- + 3(dmpz)} \xrightarrow{\sim 240^{o}\mathrm{C}} \mathrm{HB(dmpz)_3^-} \xrightarrow[\text{toluene/reflux under } \mathrm{N_2}]{\mathrm{Mo(CO)_6}} \mathrm{K[Mo\{HB(dmpz)_3\}(CO)_3]}$$

$$\xrightarrow[\text{diazald}]{\text{ethanoic acid}} \mathrm{Mo\{HB(dmpz)_3\}(NO)(CO)_2} \xrightarrow[\text{Benzyl chloride}]{\text{halogenation}} \mathrm{Mo\{HB(dmpz)_3\}(NO)(Cl_2}$$

Scheme 4: Preparation of the bimetallic complexes



A solution of N-methyl, N-nitrosotoluene-*p*-sulphonamide (Diazald) (6.38g, 29.77mmoles) in 30ml freshly distilled toluene was added and the mixture was stirred by means of a magnetic stirrer at room temperature overnight. The solvent was evaporated *in vacuo* to give an orange solid. The solid was redisolved in chloroform (100ml) and the solution filtered to remove undissolved toluene sulphomamide. All the chloroform was removed using a rotavapour and the final solid product was purified with diethyl ether. It was then filtered and left briefly on the vacuum pump to dry. The semi-dry orange solid was then dried overnight in a vacuum dessicator to yield [Mo(NO){HB(3,5-$Me_2N_2C_3H)_3$}$(CO)_2$]. A solution of [Mo(NO){HB(3,5-$Me_2N_2H)_3$}$(CO)_2$] (8.00g, 12.68mmoles), iodine (3.23g, 12.68mmoles) and benzyl chloride (2.95mL, 25.36mmoles) in 60ml of freshly distilled toluene was stirred and refluxed under nitrogen for 21 hours. The reaction mixture was cooled and evaporated *in vacuo* to form a dark brown solid which was then washed with n-hexane (100ml) followed by diethyl ether (100mL). This yielded a yellow solid Mo(NO){HB(3,5-$Me_2N_2H)_3$}Cl_2 which was left to dry in air for six hours.

Synthesis of the heterobimetallic Complexes **3** *(Co-L1-Mo to Co-L4-Mo)*

In general, these complexes were prepared following Scheme 4 by reaction of equal moles of the cobalt Schiff base complexes, with the preformed [Mo(NO){dmpz}$_3Cl_2$] complex; in dry toluene to which a few drops of triethylamine had been added. The mixture was then refluxed for a period of seven days. On evaporation of the solvent *in vacuo*, followed by chromatographic separation and purification of the residue over silica gel, 60 grade (70-230mesh) using *n*-hexane, *n*-hexane/dichloromethane, dichloromethane and/or dichloromethane/THF mixtures as eluants, various fractions were collected. The solvent was evaporated *in vacuo* and the desired compound washed in *n*-hexane.

Voltammetric experiments were performed using an EcoChemie Autolab Potentiostat-12 with GPES 4.9 electrochemical software. Electrochemical properties of all the monometallic and bimetallic complexes were investigated by cyclic voltammetry in DMSO for the Schiff base complexes, DCM and MeCN for bimetallics respectively at room temperature. A three electrode system was used: a glassy carbon as the working electrode (WE), a Ag/AgCl reference electrode and a Pt wire counter-electrode in the potential window of -1.6 to +1.6V. The working electrode was polished with 0.05μm alumina prior to each experiment. Throughout the experiment, solutions were well stirred and purged with N_2 gas purified with chromous perchloric acid scrubber for about five minutes then left to settle before measurements were done. Tetrabutylammoniumtetrafluoroborate (n-Bu_4NBF_4) was used as supporting electrolyte.

Conductivity measurements were done for all the monometallic and bimetallic complexes to establish whether they are electrolytes or not. This was carried out in DMSO, DMF and acetonitrile as solvents using a JENWAY model 4310 General Purpose Conductivity Meter. IR spectra were recorded at room temperature for all compounds using FTIR – 8400 SHIMADZU spectrometer. Solid IR spectra were recorded using KBr pellets. About 1:50mg (sample:KBr) were mixed and ground together in an agate mortar to produce a fine powder that was then hard pressed to form disks in a hard press. The discs were mounted to the IR spectrophotometer and the spectra read and recorded directly.

UV/visible electronic spectra were recorded using CECEIL CE 2041 spectrophotometer using rectangular *einmel-kuvette* (10x10x45mm, 4ml) cells. The electronic spectra for Schiff bases were run in ethanol, while those of monometallic complexes and bimetallic complexes were run in DMSO.

Results and discussion

Synthetic studies and physical properties: The analytical data are presented in Table 1. The reaction steps for the synthesis of the free Schiff bases L1, L2, L3, and L4 (1) and their corresponding cobalt complexes CoL1, CoL2, CoL3 and CoL4 (2) are given in Schemes 1 and 2. The bimetallic species CoL1-Mo, CoL2-Mo, CoL3-Mo, and CoL4-Mo (3) were obtained by reaction of the cobalt Schiff base complexes (2) with the preformed $[Mo(NO)\{HB(dmpz)_3\}Cl_2$ in a 1:1 molar ratio in the presence of triethylamine Schemes 3 and 4. The amine can act in two ways: either by reduction of $[Mo(NO)\{HB(dmpz)_3\}Cl_2$ to a labile monoanion that readily undergoes substitution or by facilitating elimination of HCl in the reaction (Kagwanja *et al.,*1996).

There was evidence for the formation of other compounds during these reactions, and it has been reported that these compounds could be $[Mo(NO)\{HB(dmpz)_3\}(OH)_2]$ and/or $Mo(NO)\{HB(dmpz)_3\}(\mu\text{-}OH)_2$ and $Mo(NO)\{HB(dmpz)_3\}Cl_2(\mu\text{-}O)$ [Kagwanja *et al.,* 1996]. The first two species are coloured pink/red and the last green. None were specifically isolated for purification, and there is probably also decomposition of the Schiff base species, although we did not isolate identifiable fragments. The bimetallic species were obtained as wine-red solids in yields ranging from 38-57%. Elemental analysis and FTIR data (Table 1 & 2) were in general agreement with our formulations.

Conductivity measurements indicated that all complexes behaved as non-electrolytes in DMSO, DMF and Acetonitrile ($\Lambda m = 0.4 – 8.4$ $ohms^{-1}$ cm^2 mol^{-1}) at room temperature. In general the values obtained for all compounds were far less than those quoted by Sear and co-workers (Lutta, 1997) for 1:1 electrolyte suggesting that the complexes were non-electrolyte. It has been found previously that cobalt mononuclear and binuclear complexes of a type similar to those discussed here are non-electrolytes in methanol $\Lambda m = 0.5 – 5.0$ $ohms^{-1}$ cm^2 mol^{-1} (Syamal and Ghanekar, 1975). This was in good agreement with our expected structures [Tas *et al.*, 2004]. The influence of the solvent on the molar conductivity values was significant as well. As it can be seen in table 1, molar conductivity was highest in DMSO then DMF and lowest in acetonitrile as a general trend for all monometallic and bimetallic complexes.

For example, cobalt monometallic complexes had molar conductivity of between 9.3 and 6.5 $ohms^{-1}$ cm^2 mol^{-1} in DMSO, whereas in DMF it was between 4.1 and 2.1 $ohms^{-1}$ cm^2 mol^{-1}. In acetonitrile the same complexes had molar conductivity of less than 2.8 $ohms^{-1}$ cm^2 mol^{-1}.

Table 1: Elemental analyses and some physical properties of the solid free Schiff base ligands and complexes

Code	Schiff base nature of B	Colour	FW (g mol^{-1})	m.p °C	%Yield	Conductance $\Omega^{-1}cm^2mol^{-1}$			Elemental analyses % found (calculated)		
						DMSO	DMF	MeCN	C	H	N
L1	$-(CH_2)_2-$	Yellow	316.3	217	58	-	-	-	-	-	-
L2	$-(CH_2)_3-$	Yellow	330.3	192	79	-	-	-	-	-	-
L3	$-(CH_2)_4-$	Yellow	344.3	195	90	-	-	-	-	-	-
L4	C_6H_4	Orange	364.3	215	65	-	-	-	-	-	-
CoL1	$-(CH_2)_2-$	Brown	373.2	>300	76	7.6	3.3	2.5	51.3(51.5)	3.7(3.8)	7.3(7.5)
CoL2	$-(CH_2)_3-$	Brown	387.2	>300	66	5.5	2.1	4.7	53.2(52.7)	4.3(4.2)	7.4(7.2)
CoL3	$-(CH_2)_4-$	Brown	401.3	>300	78	4.7	2.2	5.7	53.9(53.9)	4.5(4.5)	7.1(7.0)
CoL4	C_6H_4	Brown	421.3	>300	78	8.2	6.4	0.4	57.0(57.5)	3.5(3.3)	6.7(6.7)
Co-L1-Mo	$-(CH_2)_2-$	Red	830.8	>300	63	2.5	3.7	0.5	44.9(44.7)	4.4(4.2)	14.8(15.3)
Co-L3-Mo	$-(CH_2)_3-$	Wine red	844.8	>300	64	4.7	3.1	2.1	45.5(45.1)	4.5(4.4)	14.9(14.8)
Co-L4-Mo	$-(CH_2)_4-$	Wine red	858.8	>300	57	5.7	0.5	0.5	46.1(46.3)	4.4(4.6)	14.7(14.6)
Co-L5-Mo	C_6H_4	Wine red	878.8	>300	65	0.4	0.5	0.5	47.3(47.8)	4.2(4.0)	14.3(14.5)

Spectroscopic studies: A comparison of the IR spectra of the free ligands with those of the metal complexes revealed the following:

> The solid IR spectra of the ligands L1, L2, L3, and L4 were similar with bands at 1639-1614, 1587-1542, and 1289-1269 cm^{-1} attributed to v(C=N) and v(C=C), and v(C-O) respectively (Table 2). Bonding of these Schiff bases to cobalt(III) has been suggested by a careful comparison of the infrared spectra of the complexes with those of the free ligands. The bands in the region 1298 and 1277 cm^{-1} in the IR spectra of the synthesized ligands were ascribed to the phenolic *v*C–O stretching vibrations. These bands were shifted to lower frequencies due to O–metal coordination [Tas *et al.*, 2004, Tao *et al.*, 2006]. A strong band observed in the IR spectra of the free ligands in the range of 1614 - 1639 cm^{-1} was attributed to the azomethine –C=N linkages for free Schiff bases L1, L2, L3, and L4. These bands showed a shift to *ca*. 1617–1596 cm^{-1} in the spectra of all Cobalt complexes as expected, indicating coordination of the azomethine nitrogen atom to cobalt(III) [Tas *et al.*, 2004, Tao *et al.*, 2006]. At 2548 – 2551 cm^{-1}, the bimetallic complexes showed characteristic B-H stretching frequency indicating that the tripodal ligand was still intact in the molybdenum complex (Figure 1). In the –C=N stretching frequencies of the bimetallic complexes, the shift of frequencies to higher energy wavelength compared to their corresponding monometallic complexes was in line with the observed infrared spectra of metal chelates of similar ligands studied earlier by Syamal and Ghanekar (1975).

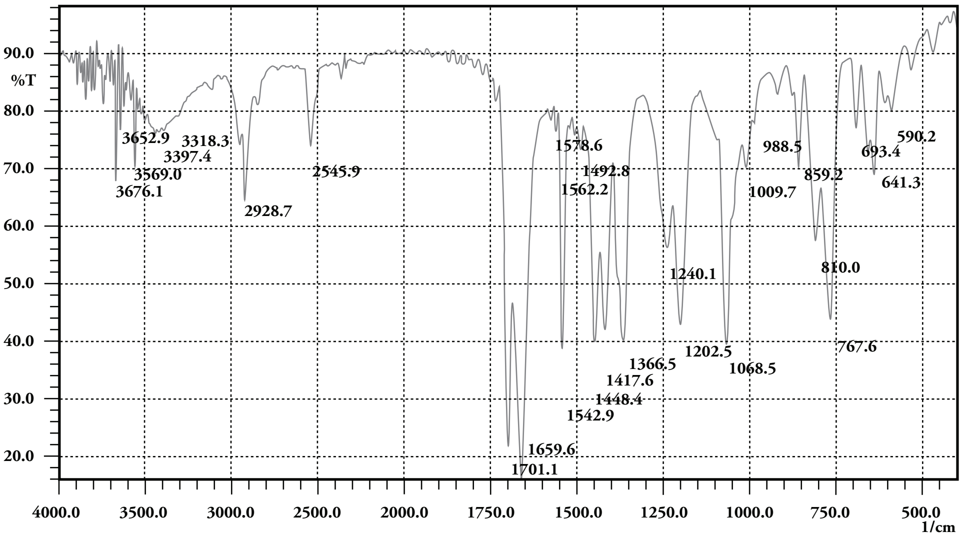
In this study, it was still not clear why this phenomenon was that way. A tentative explanation may be that the electron density in the azomethine linkage increases after addition of the molybdenum fragment due to a stronger electron withdrawing cobalt(III) ion than molybdenum fragment. Alternatively, it may also be due to a possible overlap of both the C=N and NO bands to give a broad unsymmetrical band between 1700cm-1 to 1650cm-1. Observation of the IR spectra of bimetallic complexes also showed that the NO stretching frequencies fall in a region typical of a [Mo(NO){HB(dmpz)3}Cl] fragment bonded to a phenolic ligand although they occur at values slightly lower than those in simple related monophenolate complexes [Kagwanja *et al.*, 1996]. This has been explained in terms of synergic bonding of NO ligand to the Mo2+ which suggests a substantial dπ⊠pπ back-bonding leading to a decrease in NO bond order and hence stretching frequency [Lutta, 1997].

The electronic spectra were recorded in the range 1100 – 200 nm (Table 2). In the electronic spectra of the Schiff bases (L1, L2, L3 and L4), intense intraligand $\pi - \pi^*$ and n - π^* bands due to benzene ring and imine group transitions were observed in the range of 269nm – 378nm region [Kagwanja *et al.*, 2000]. The electronic spectra of the monometallic complexes CoL1 to CoL4 showed no bands in the 369-378 nm range, thus confirming the fact that in the metal complexes the ligands exist mainly in the imine form [Martel and Heinert, 1963; Thankarajan and Mohanan, 1986]. Other than the missing bands, the monometallic complexes had similar spectral features as the Schiff base ligands although they were generally red shifted. They also exhibited very weak absorptions at 480 and 520 nm in DMSO which were assigned to *d-d* transitions as they were usually of very low intensity suggesting that these complexes may be diamagnetic in the distorted square-planar geometry [Tas *et al.*, 2004].

In the bimetallic complexes, other than peaks observed in the monometallic complexes, there were additional weak peaks in the 446–554nm region. These bands may originate from $e_g \rightarrow \pi^*$ metal to ligand charge-transfer transitions [Lutta, 1997] and the presence of $[Mo(NO)T_p^*ClO\text{-}Ar]$ chromophore associated with the metal to ligand charge transfer (MLCT) between the molybdenum centre and the phenoxide (OAr) moiety of the coordinated Schiff base. The electronic spectra of the complexes and the fact that tetradentate Schiff base ligands coordinate only as tetradentate ligands suggest that the tetrahedral geometry was most favoured for CoL1 to CoL4. It was possible that the length of B is sufficient to permit some flexibility within the tetradantate ligand system, leading to some distortion either towards a tetrahedral geometry or by formation of a five-coordinate species.

Table 2: IR and electronic spectral data for the compounds

Compound			**IR spectra**					**Electronic spectra Λ_{max}/nm in DMSO**
Code	**M'**	**B**	**νC=N**	**νC-O**	**νC=C**	**νBH**	**νNO**	
L1	H	$(CH_2)_2$	1635	1281	1587	-	-	269,307,376
L2	H	$(CH_2)_3$	1635	1278	1542	-	-	272,312,378
L3	H	$(CH_2)_4$	1639	1277	1542	-	-	281,311,367
L4	H	C_6H_4	1614	1289	1548	-	-	291,314,369
CoL1	H	$(CH_2)_2$	1604	1278	1557	-	-	277, 299, 351
CoL2	H	$(CH_2)_3$	1615	1274	1548	-	-	288, 298, 355
CoL3	H	$(CH_2)_4$	1617	1271	1548	-	-	270, 290, 353
CoL4	H	C_6H_4	1596	1269	1562	-	-	272, 301, 409
Co-L1-Mo	Mo(NO)L*Cl	$(CH_2)_2$	1662	-	1542	2551	1690	280, 307, 431, 549
Co-L3-Mo	Mo(NO)L*Cl	$(CH_2)_3$	1660	-	1542	2548	1699	274, 312, 422, 551
Co-L4-Mo	Mo(NO)L*Cl	$(CH_2)_4$	1660	-	1542	2548	1701	277, 289, 311, 422, 546
Co-L5-Mo	Mo(NO)L*Cl	C_6H_4	1659	-	1542	2548	1702	278.5, 313, 422, 548



JULIUSIR: sample 7 b2

Date:	**07/26/2006**	**Time:**	**11:44:14**	**NScans:**	**20**
Type:	**HYPER IR**	**User:**	**CHEMRE**	**Detector:**	**standard**
Abscissa:	**1/CM**	**Ordinate:**	**%T**	**Apodization:**	**Happ**
Min:	**400.20**	**Max:**	**3999.12**	**Range:**	**1/cm**
Ndp:	**3733**	**Data interval:**	**0.96434**	**Resolution:**	**2.0**
Gain:	**auto**	**Aperture:**	**auto**	**Mirror Speed:**	**2.8 (low)**

Figure 1: Solid i.r. spectrum of bimetallic complex Co-L3-Mo obtained as KBr pellet.

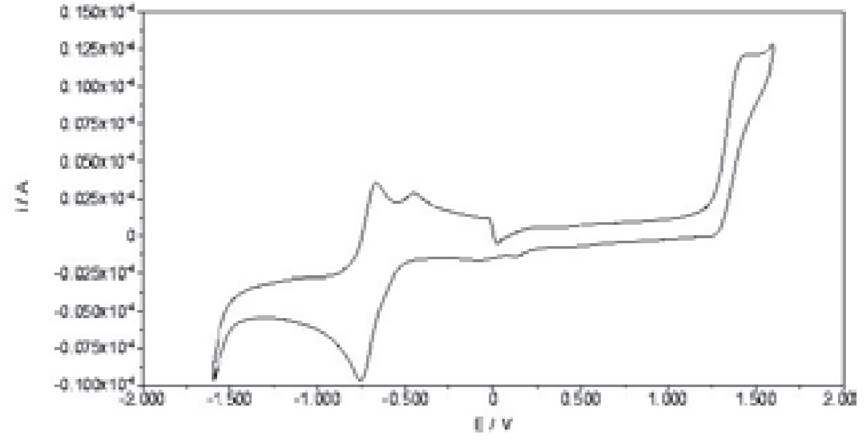


Figure 2: Cyclic voltammogram of Co-L2-Mo in MeCN at a scan rate of 200mV/s

The effective magnetic moments (3.95 – 5.00 BM) of the CoL_x complexes at room temperature fell in the range 4-5 BM, which suggests a spin quartet state S=3/2 in a tetrahedral geometry [Tas *et al.,* 2004].

Electrochemical studies: The monometallic complexes (CoL1 – CoL4) had relatively low solubility in dichloromethane and acetonitrile and so their electrochemical properties were investigated by cyclic (CV) and differential pulse while the bimetallics were investigated in both DCM and MeCN. Measurements were made at scan rates of 50mV/s, 100mV/s and 200mV/s with a current range of 100mA, 10mA and 1mA for comparison purposes.

Cyclic voltagrams exhibited mostly reversible cobalt(III)/cobalt(II) reduction peaks for monometallic complexes and a second molybdenum(III)/molybdenum(II) peak in the case of bimetallic complexes (Figure 2). One-electron reduction peak ($^2E_p^c$), corresponding to the cobalt(III)/cobalt(II) redox couple occurred in the potential range -0.496 to -0.461V, with an associated reoxidation peak (E_p^a) in the reverse scan, whose potential values fell within the range -0.376V to -0.342V (Table 3a). However, all complexes exhibited another irreversible peak at positive anodic potentials near 0.521V which may be assigned to the oxidation of ligands in DMSO or oxidation of cobalt(III)/cobalt(IV) pair.

It was interesting to observe that the $E_{1/2}$ values for Co(III)/Co(II) couple shifted anodically as the ethylene backbone lengthened. This property has been observed elsewhere (Averill and Broeman, 1978) in which it was found that similar compounds with cobalt as the central metal whose $E_{1/2}$ values for the Co(III)/Co(II) couple were observed to shift cathodically as the degree of substitution on the ethylene backbone increased.

The CVs of the molybdenated species revealed two reversible reduction peaks both in DCM and MeCN solvents. One reversible wave which may be attributable to reduction process Co(III) → Co(II) appear in the range of -0.858 to -0.787V in DCM but in the range -0.769 to -0.695V in MeCN, Table 3b. The corresponding oxidative wave that may be associated with Co(II) → Co(III) process occurred in the range -0.687 to -0.554V in DCM and -0.582 to -0.554V in MeCN. The second reduction wave which may be attributed to reduction process $Mo(NO)^{3+} + e^- \rightarrow Mo(NO)^{2+}$ occurred in the range -0.618 to -0.416V in DCM but -0.687 to -0.351V in MeCN.

However, its associated oxidative peak for $Mo(NO)^{2+}/Mo(NO)^{3+}$ couple was broad and ill formed. Comparison of the potentials of the monometallic complexes with the bimetallic species revealed red shift to higher values implying that the molybdenum nitrosyl complex had a large influence towards the central metal. This indicated significant stabilization of the cobalt(II) state in these complexes. In the positive potential, all bimetallic complexes exhibited another irreversible peak at 1.43 to 1.26V in DCM and 1.50 to 1.27V in MeCN, this may be associated with oxidation process Co(III) → Co(IV), oxidation of the ligands or an overlap of both.

Comparing the reduction peak wave potentials of these complexes in MeCN to those in DCM revealed that the potentials in DCM were more cathodic than in MeCN with $E_{1/2}$ values of about 100mV difference showing that the effect of changing solvent on the electrochemical properties of these complexes is significant.

Table 3 a. Cyclic voltammetric data of the cobalt(III) Schiff base complexes

Code	**B**	**$^2E_p^c$**	**$^2E_p^a$**	**$^2E_{1/2}$**	**ΔE**	**$^2E_p^a$**
Co-L1	$(CH_2)_2$	-0.496	-0.376	-0.436	120	0.500
Co-L2	$(CH_2)_3$	-0.484	-0.376	-0.430	108	0.516
Co-L3	$(CH_2)_4$	-0.480	-0.365	-0.422	115	0.521
Co-L4	C_6H_4	-0.461	-0.342	-0.401	109	0.305

^{2}Reduction potential (in volts) for the process $Co^{3+} + e^- \rightarrow Co^{2+}$
$^2E_p^c$ = Cathodic (reduction) peak potentials (in volts)
E_p^a = Anodic (oxidation) peak potentials (in volts)
$^2E_{1/2} = 0.5(^2E_p^c + {}^2E_p^a)$
$\Delta E = (^2E_p^c - {}^2E_p^a)$

Table 3 b. Cylic voltammetric data of the bimetallic complexes of cobalt(III) in DCM and MeCN

Code	M'	B	$^2E_p^c$	$^2E_p^a$	$^2E_{1/2}$	ΔE	$^{pr}E_p^c$	E_p^a
	In DCM							
Co-L1-Mo	Mo(NO)L*Cl	$(CH_2)_2$	-0.849	-0.687	-0.768	162	-0.618	1.432
Co-L3-Mo	Mo(NO)L*Cl	$(CH_2)_3$	-0.858	0.666	-0.762	192	ND	1.438
Co-L4-Mo	Mo(NO)L*Cl	$(CH_2)_4$	-0.862	-0.649	-0.755	213	-0.568	1.262
Co-L5-Mo	Mo(NO)L*Cl	C_6H_4	-0.787	-0.554	-0.670	233	-0.416	1.291
	In MeCN							
Co-L1-Mo	Mo(NO)L*Cl	$(CH_2)_2$	-0.769	-0.582	-0.660	187	ND	1.382
Co-L2-Mo	Mo(NO)L*Cl	$(CH_2)_3$	-0.758	-0.581	-0.69	177	-0.351	1.270
Co-L3-Mo	Mo(NO)L*Cl	$(CH_2)_4$	-0.727	-0.554	-0.640	173	-0.687	1.506
Co-L4-Mo	Mo(NO)L*Cl	C_6H_4	-0.695	-0.568	-0.631	127	-0.402	1.284

$^2E_p^c$ = Cathodic (reduction) peak potentials (in volts) for the process Co(III) → Co(II)
$^2E_p^a$ = Anodic (oxidation) peak potentials (in volts) for the process Co(II) → Co(III)
$^2E_{1/2}$ = $0.5(^2E_p^c + {}^2E_p^a)$
$^{pr}E_p^c$ = Cathodic peak potentials (in volts) for the process Mo(NO)(III) → Mo(NO)(II)
E_p^a = Anodic (oxidation) peak potentials (in volts) for the process Co(III) → Co(IV)
ΔE = $(^2E_p^c - {}^2E_p^a)$
ND = Not Detected

Conclusion

The redox potentials ($E_{1/2}$) obtained from monometallic complexes of cobalt shifted cathodically by between 200 and 300mV on incorporating the $Mo(NO)^{3+}$ centre to produce bimetallic complexes. Likewise, from the differential pulse voltammetry data, similar results were obtained whereby the reduction potentials of the monometallic complexes associated with the reduction of Co(III) showed that they shift cathodically by about 300mV on incorporating the $Mo(NO)^{3+}$ centre. Although data for the monometallic complexes were obtained in DMSO, the results indicated that the molybdenum centre, being highly electron deficient, alters the electron distribution of the central metal ion complexed in the tetradentate Schiff base cavity by withdrawing an electron.

The electrochemical behaviour of the complexes was also ligand dependent. Studies showed that the length of polymethylene carbon chain of the ligand backbone had a slight effect on the interaction of the two metal centres in the complexes. Change of solvent between DCM and MeCN affected the electrochemical properties of these complexes significantly. The redox potentials of both chromium and cobalt bimetallic complexes generally shifted to less negative potentials on changing the solvent from DCM to MeCN by about 120 to 200mV showing that it was easier for the central metal ion complex to undergo oxidation process in DCM than it was in MeCN.

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