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Cobaloximes with mixed dioximes having C and S side chains: Synthesis, structure and reactivity

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1. Introduction

Organocobaloximes¹ have been known for more than four decades [1–12] and have extensively been used to mimic the B_{12} coenzyme [13–18] and the studies have continued to compliment those on the more complex cobalamin and B_{12} based protein [19]. However, organocobaloximes with mixed dioximes have virtually been unknown until recently. The first mention of these complexes was made by Schrauzer and Windgassen in 1966 who proposed that the following ligand exchange reaction undoubtedly proceeded by stepwise displacement of the dmgH₂ ligand and the reaction did not involve an ionic intermediate like CH₃–Co²⁺. However, they failed to isolate the intermediate mixed ligand complex, MeCo(dmgH)(chgH)B (B = Py or H₂O) [20].

$$MeCo(dmgH)_{2}H_{2}O + chgH_{2} \xrightarrow[toulene,Py]{140^{\circ}C} MeCo(chgH)_{2}Py$$

Subsequently, Johnson et al. in 1977 reported the kinetics and mechanistic details of the apparent alkyl transfer from alkylcobaloximes to cobaloxime (I), cobaloxime (II) and cobaloxime (III) reagents [21]. They proposed the formation of mixed ligand species,

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ABSTRACT

Ten mixed dioxime complexes RCo(L)(dmgH)Py [R = Cl, Me, Et, Bu, Benzyl] [L = dSPhgH (1–5) and dSEtgH (**6**–10)] have been synthesized and characterized by NMR. Formation of **1** and **6** is very fast and takes only 5 and 15 min in ethanol. Molecular oxygen insertion in **5** and **10** is monitored and forms mixture of products within 5 min. The crystal structure of **1**, **4**, **5**, **6**, **8** and **10** is reported. Benzyl ring is oriented over dmgH wing in both **5** and **10** and has a weak C–H... π interaction (3.33 Å and 3.22 Å) and this causes high upfield shift of the dmgH protons. Electrochemical study on **1**, **4**, **5**, **6**, **8** and **10** is also reported. Because of increased electron donation by SEt group, **6** is more difficult to reduce than **1**.

RCo(dmgH) (chgH)B in solution but did not isolate this intermediate. Only solution NMR values of the mixtures were reported.

The synthesis of RCo(L)(L')Py complexes [L = dpgH] and L' = dmgH, gH, chgH; R = Cl, alkyl, benzyl] using different methods has recently been published from our group [22–26]. A mixture of three products, RCo(L)₂Py, RCo(L')₂Py, and RCo(L)(L')Py was always formed and an equilibration between these products occurred in solution and was time dependent. Both the dioximes in all the reported complexes have carbon side chain. Since the nature of dioximes and solvent affect the equilibration process we have extended the study to mixed dioxime complexes having two dissimilar dioximes, one with C side chain(dmgH) and the other with S side chain (SPh or SEt). The study will allow us to make direct comparison with the previously reported mixed dioxime complexes in terms of synthesis, spectroscopy, structure and reactivity.

We herein report the synthesis and spectroscopic study of RCo(L) (dmgH)Py [R = Cl, Me, Et, Bu, Bn] [L = dSPhgH (1-5); dSEtgH (6-10)] complexes (Chart 1). The formation of 1 and 6 in different solvents has also been monitored with time. Molecular oxygen insertion in the benzyl complexes, 5 and 10 is carried out and carefully monitored. The X-ray structure of 1, 4, 5, 6, 8 and 10 is reported for the first time. Electrochemical study of some complexes is also reported.

2. Experimental section

2.1. Materials and physical measurements

Cobalt chloride hexahydrate (SD fine, India), glyoxime (Caution! it is highly flammable and explosive when dry) (Alfa Aesar,





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¹ Organocobaloximes have the general formula $\text{RCo}(L)_2\text{B}$, where R is an organic group σ -bonded to cobalt. B is an axial base trans to the organic group, and L is a monoanionic dioxime ligand (e.g. glyoxime (gH), dimethylglyoxime (dmgH), 1,2-cyclohexanedione dioxime (chgH), diphenylglyoxime (dpgH), dimesitylglyoxime (dmestgH), dithiophenylglyoxime (dSPhgH) and dithioethylglyoxime (dSEtgH).

Me

Mo



Chart 1. Cobaloximes under consideration.





Lancaster), iodomethane, ethyl, butyl and benzyl bromide (Aldrich chemical company) were purchased and used as received. Bis(thiophenyl)glyoxime and Bis(thioethyl)glyoxime were prepared from dichloroglyoxime following the reported procedure [10]. Silica gel (100–200 mesh) and distilled solvents were used in all reactions and chromatographic separations. A julabo UC-20 low temperature refrigerated circulator was used to maintain the desired temperature. Cyclic voltammetry measurements were carried out using a BAS Epsilon electrochemical work station with a platinum working electrode, Ag/AgCl reference electrode (3 M KCl) and a platinumwire counter electrode. All the measurements were performed in 0.1 M ⁿBu4NPF₆ in dichloromethane (dry) at a concentration of 1 mM of each complex.



Fig. 2. Equilibration of 1, 1a and 1b in acetone.



Fig. 3. Monitoring of oxygen insertion of 5 in dichloromethane at 0 °C under oxygen.

¹H and ¹³C Spectra were recorded on a JEOL JNM LAMBDA 400 FT NMR Spectrometer (400 MHz for ¹H and 100 MHz for ¹³C) in CDCl₃ solution with TMS as internal standard. NMR data are reported in ppm. Elemental analysis was carried out at IIT Kanpur.

The molar percentage of the species in Figs. 1 and 2 has been calculated from the integration of ¹H NMR signals of Py_{α} whereas in Figs. 3 and 4 it is calculated from the integration of ¹H NMR signals of CH₂ group bound to CoO₂. **1a**, **1b**, **6a**, **2a**–**5a**, **7a**–**10a**, **7b**–**10b**, **5c**, **5d**, **10c**, **10d** are characterized by ¹H NMR (Table S1).

2.2. X-ray crystal structure determination and refinements

A slow evaporation of solvent from the solution of complexes **1**, **4**, **5**, **6**, **8**, **10** (CH₂Cl₂/MeOH for **4**, **5**, **8** and **10** and CH₂Cl₂/MeOH/ Hexane for **1** and **6**) in the refrigerator resulted in the formation of orange crystals. Single-crystal X-ray data were collected using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 100 K for **1**, **4**, **5**, **6** and **10**; at 273 K for **8**. The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* [27]. The data integration and reduction were processed with SAINT Software [28]. An empirical absorption correction was applied to the collected reflections with SADABS [29] using XPREP [30]. The structure was solved by direct methods



Fig. 4. Monitoring of oxygen insertion of 10 in dichloromethane at 0 °C under oxygen.

Table 1

Crystal data and structure refinement details for compounds 1, 4 and 5.

Parameters	1	4	5
Empirical formula	C23H23ClCoN5O4S2	C ₂₇ H ₃₂ CoN ₅ O ₄ S ₂	C ₃₀ H ₃₀ CoN ₅ O ₄ S ₂
Formula weight	591.98	613.65	647.64
Temp (K)	100(2)	100(2)	100(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	P 21 21 21	C2/c	P 21/n
Unit cell dimensions			
a (Å)	12.205(5)	38.662(5)	10.629(5)
b (Å)	12.599(5)	11.222(5)	14.453(5)
c (Å)	16.347(5)	13.434(5)	19.109(5)
α (deg)	90.000(5)	90.000(5)	90.000(5)
β (deg)	90.000(5)	91.521(5)	103.404(5)
γ (deg)	90.000(5)	90.000(5)	90.000(5)
$V(Å^3)$	2513.7(16)	5826(3)	2855.6(18)
Ζ	4	8	4
ρ (calc), mg/m ³	1.564	1.399	1.506
μ (Mo- $K\alpha$) (mm ⁻¹)	0.996	0.773	0.794
F (000)	1216	2560	1344
Crystal size (mm ³)	0.40 imes 0.35	0.47×0.34	$0.32 \times 0.27 \times 0.22$
	× 0.30	× 0.22	
Index ranges	$-15 \le h \le 16$	$-33 \le h \le 46$	$-12 \le h \le 11$
	$-10 \le k \le 16$	$-12 \le k \le 13$	$-15 \leq k \leq 17$
	$-21 \leq l \leq 21$	$-16 \leq l \leq 16$	$-19 \le l \le 23$
No. of rflns collected	16389	15323	15084
No. of indep rflns	6244	5413	5301
GOOF on F ²	1.112	0.985	0.998
Final R indices	R1 = 0.0578	R1 = 0.0603	R1 = 0.0552
$(I > 2\sigma(I))$	WR2 = 0.1283	WR2 = 0.1432	WR2 = 0.1388
R indices (all data)	R1 = 0.0806	R1 = 0.0919	R1 = 0.0719
· ·	WR2 = 0.1693	WR2 = 0.1662	WR2 = 0.1572
Data/restraints/param	6244/0/325	5413/0/352	5301/0/379

using SIR-97 [31] and were refined on F^2 by the full-matrix least squares technique using the SHELXL-97 [32] program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom positions or thermal parameters

were not refined but were included in the structure factor calculations. The equatorial SEt groups in complex **8** were found to be disordered and were modelled satisfactorily. The pertinent crystal data and refinement parameters are compiled in Tables 1 and 2.

Table 2

Crystal data and structure refinement details for compounds 6, 8 and 10.

Parameters	6	8	10
Empirical formula	C ₁₅ H ₂₃ ClCoN ₅ O ₄ S ₂	C ₁₇ H ₂₈ CoN ₅ O ₄ S ₂	C ₂₂ H ₃₀ Co N ₅ O ₄ S ₂
Formula weight	495.90	489.49	551.58
Temp (K)	100(2)	273(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	C c	P21/n	P 21 21 21
Unit cell dimensions			
a (Å)	14.527(4)	16.150(5)	8.357(5)
b (Å)	8.554(4)	9.423(5)	9.274(5)
<i>c</i> (Å)	17.152(6)	16.573(5)	31.861(5)
α (deg)	90.000	90.000(5)	90.000(5)
β (deg)	109.441(9)	113.722(5)	90.000(5)
γ (deg)	90.000	90.000(5)	90.000(5)
V (Å ³)	2009.8(12)	2309.0(16)	2469(2)
Ζ	4	4	4
ρ (calc), mg/m ³	1.639	1.408	1.484
μ (Mo- $K\alpha$) (mm ⁻¹)	1.227	0.955	0.903
F (000)	1088	1024	1128
Crystal size (mm ³)	0.46 imes 0.35	0.32 imes 0.24	0.42×0.36
	× 0.21	× 0.18	× 0.22
Index ranges	$-19 \leq h \leq 18$	$-19 \leq h \leq 15$	$-10 \leq h \leq 10$
	$-11 \leq k \leq 9$	$-11 \le k \le 11$	$-11 \leq k \leq 7$
	$-18 \le l \le 22$	$-18 \leq l \leq 20$	$-38 \le l \le 38$
No. of rflns collected	6346	11820	13092
No. of indep rflns	3755	4254	4580
GOOF on F ²	1.135	0.978	0.979
Final R indices	R1 = 0.0617	R1 = 0.0585	R1 = 0.0525
$(I > 2\sigma(I))$	wR2 = 0.1414	wR2 = 0.1535	wR2 = 0.1383
R indices (all data)	R1 = 0.0803	R1 = 0.0974	R1 = 0.0556
	wR2 = 0.1833	wR2 = 0.1995	wR2 = 0.1416
Data/restraints/param	3755/2/253	4254/4/289	4580/0/307



Scheme 2.

2.3. Synthesis

2.3.1. Synthesis of ClCo(dmgH)(dSPhgH)Py (1)

Pyridine (0.265 ml, 0.0032 mol) was added with constant stirring to a refluxing solution of $CoCl_2 \cdot 6H_2O$ (0.391 gm, 0.0016 mol), dmgH₂ (0.190 gm, 0.0016 mol), dSPhgH₂ (0.500 gm, 0.0016 mol) in 95% ethanol. The solution was allowed to cool to room temperature and air was bubbled through the reaction mixture for 5 min. The residue obtained after evaporation of solvent was extracted with dichloromethane and the organic layer was dried over anhydrous sodium sulphate. The solid product obtained after evaporation of dichloromethane was chromatographed on silica gel column (100–200 mesh). ClCo(dSPhgH)₂Py (**1a**) (0.037 gm, 3%) eluted out first with dichloromethane, ClCo(dmgH)(dSPhgH)Py (**1**) (0.757 gm, 80%) came out with 10–15% ethyl acetate–dichloromethane mixture and finally ClCo(dmgH)₂Py (**1b**) (0.0645 gm, 10%) came out with 100% ethyl acetate.

2.3.2. Synthesis of ClCo(dmgH)(dSEtgH)Py (6)

The procedure is exactly the same as that of **1** except that the air was passed through the solution for 15 min to maximize yield and three products were isolated after chromatography, ClCo(dmgH) (dSEtgH)Py (**6**) (65%), $ClCo(dSEtgH)_2Py$ (**6a**) (5%) and $ClCo(dmgH)_2Py$ (**1b**) (21%).

2.3.3. Preparation of RCo(dmgH)(dSPhgH)Py and RCo(dmgH) (dSEtgH)Py (**2–5**, **7–10**)

The same procedure, as described earlier for the preparation of mixed dioxime complexes, RCo(dpgH) (dioxime)Py, was used [25]. In this study **1** and **6** have been used as the starting material. The reaction took 15 min for completion and a mixture of products was formed in each case and the ratio of these products remained constant up to reaction time of 1 h (Scheme 2). Two products, RCo(dmgH)(dSPhgH)Py (**2**–**5**) (76–80%) and RCo(dSPhgH)₂Py (2–5%) were formed in the reaction with (**1**) whereas three products, RCo(dmgH) (dSEtgH)Py (**7–10**) (65–68%), RCo(dmgH)₂Py

Table 3	3
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Molar distribution ((%) of 1	. 1a	and	1b i	in	ethanol	and	acetone.
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Time (min)	1/1	a/1b
	Ethanol	Acetone
5	83/5/12	19/2/79
15	71/2/27	44/1/55
30	56/1/43	51/2/47
45	55/2/43	53/3/44
60	57/1/42	55/2/43

(6-8%) and RCo(dSEtgH)₂Py (4-7\%), were formed in the reaction with (**6**).

2.3.4. Reaction monitoring: formation of (1) and (6)

Pyridine was added with constant stirring to a refluxing solution of CoCl₂·6H₂O, dmgH₂, dSPhgH₂ (or dSEtgH₂) in 95% ethanol or acetone. The solution was allowed to cool to room temperature and the air was bubbled through the reaction mixture. Aliquots from reaction mixture were taken out at time intervals of 5 min, 15 min, 30 min and 45 min and 60 min for **1** and 15 min, 30 min and 60 min for **6**. Water was added to each aliquot followed by extraction with dicholoromethane. Three products were formed in each case (Scheme 1) and their molar ratio was calculated from the integration of the ¹H NMR signals of Py_α for **1** and from the isolated products after column chromatography for **6**. The molar ratios are given in Tables 3 and 4.

2.3.5. Oxygen insertion reaction monitoring of 5 and 10

Oxygen gas was bubbled through a solution of PhCH₂Co(dmgH) (dSPhgH)Py (**5**) or PhCH₂Co(dmgH)(dSEtgH)Py (**10**) (100 mg) in 10 ml of dichloromethane at 0 °C while the solution was irradiated with a 200 W tungsten lamp. The aliquots from the reaction mixture were taken out at time intervals of 5 min, 30 min, 60 min, 120 min and 150 min for **5** and 5 min, 15 min, 30 min, 45 min and 60 min for **10**. The aliquot solution was evaporated to dryness and its NMR was recorded in CDCl₃. Oxygen insertion in **5** results in formation of two products; whereas it gives three products in case of **10** (Scheme 3) and their molar ratio was calculated from the integration of the ¹H NMR signals of CH₂ group bound to CoO₂ (Tables 5 and 6).

3. Results and discussion

3.1. Synthesis

The mixed dioxime cobalt complexes, RCo(dpgH)(dioxime)Py(dioxime = gH, dmgH, chgH) were first reported from our

Table 4
Molar distribution (%) of 6 , 6a and 1b in ethanol and acetone.

Time (min)	6/6	a/1b
	Ethanol	Acetone
15	69/7/24	38/9/53
30	67/7/26	24/13/63
60	54/6/40	49/11/40

$$\begin{array}{ccc} PhCH_{2}Co(dmgH)(dSPhgH)Py & \frac{hv/O_{2}}{0 \ ^{o}C} & PhCH_{2}(O_{2})Co(dmgH)(dSPhgH)Py + PhCH_{2}(O_{2})Co(dmgH)_{2}Py \\ & \mathbf{5} & \mathbf{5c} & \mathbf{5d} \\ PhCH_{2}Co(dmgH)(dSEtgH)Py & \frac{hv/O_{2}}{0 \ ^{o}C} & PhCH_{2}(O_{2})Co(dmgH)(dSEtgH)Py + PhCH_{2}(O_{2})Co(dSEtgH)_{2}Py \\ & \mathbf{10} & \mathbf{10c} & \mathbf{10d} \\ & + PhCH_{2}(O_{2})Co(dmgH)_{2}Py \\ & \mathbf{5d} \end{array}$$

Scheme 3.

Table 8

1_F

Table 5Molar distribution (%) of 5c and 5d in DCM.

Time (min)	5c	5d
5	31	1
30	32	3
60	34	4
120	70	17
150	87	11

Table 6				
Molar distribution	(%) of 10c	, 10d and	5d in DCM.	

Time	10c	10d	5d
5 min	52	2	3
15 min	61	2	3
30 min	84	2	3
45 min	91	2	3
1 h	95	2	3

laboratory and a reaction scheme was proposed based on many independent reactions. The formation of ClCo(dpgH) (dioxime)Py was slow and took 2 h–2days depending upon the nature of the dioxime and the yields varied between 25% and 58% [25,26]. In contrast, in the present systems it takes only 5 and 15 min to form **1** and **6** in very high yield. The monitoring of the formation of **1** and **6** in ethanol and acetone gives the following useful information.

1. There is an equilibration between (1) and (1b), for example, the amount of (1) is highest at 5 min and gradually decreases up to 15 min and then becomes almost constant. On the other hand the amount of (1b) gradually increases up to 15 min and becomes constant (Fig. 1). A different scene emerges when the reaction is monitored in acetone, instead of ethanol. Now (1b) forms first and its amount is highest at 5 min which slowly decreases and becomes constant at 30 min. At the same time the formation of (1) is slow in the beginning but it gradually increases with time and becomes constant at 30 min (Fig. 2). The amount of (1a) is slight (1–5%) and does not change much with time, in ethanol or acetone. The product ratios are calculated from the chemical shift ratio of Py_{α} in (1), (1a) and (1b).

Table 7			
¹ H NMR data	(ppm)	for	1-5.

Compd no.	Руα	Ρуβ	Руү	Aromatic proton	H-1	dmgH	0-H0	Other proton
1 2 3 4	8.17 8.45 8.48 8.48	7.24 7.27 7.31 7.32	7.76 7.74 7.80 7.79	7.12–7.24 6.85–7.19 6.89–7.10 6.91–7.10	0.97 1.95 1.83	2.42 2.08 2.13 2.13	17.70 17.95 17.92 17.93	0.39 1.22, 0.95, 0.80
5	8.44	7.29	7.78	6.94-7.28	3.09	1.73	17.76	

I NMR data (ppm) for 6–10.								
Compd no	Руα	Ρуβ	Руү	H-1	dSEtgH	dmgH	0-H0	Other proton
6	8.26	7.24	7.71		3.52(m),3.12(m), 1.22(t)	2.41	18.17	
7	8.59	7.37	7.73	0.94	3.19(m),3.04(m), 1.06(t)	2.14	18.31	
8	8.57	7.32	7.71	1.86	3.11(m), 1.05(t)	2.13	18.21	0.39
9	8.57	7.31	7.72	1.75	3.11(m), 1.05(t)	2.13	18.21	0.81, 0.96,1.22
10	8.51	7.29	7.69	2.98	3.14(m), 1.07(t)	1.75	18.17	6.97-7.14

2. The product ratios in (**6**) cannot be monitored from the chemical shift of Py_{α} since the values are almost identical for (**6**) and (**1b**) [8.25 & 8.26 ppm]. So the product ratios are based on the isolated products after the column chromatography. However, the information is similar, as described for (**1**).

The organo complexes (2-5) and (7-10) are formed by the reaction of Co^l(dmgH)(dSPhgH)Py or Co^l(dmgH)(dSEtgH)Py, generated *in situ* by the sodium borohydride reduction of the corresponding chlorocobaloxime (1) and (6), with alkyl halides. A mixture of two or three products is formed in each case depending upon the dioxime side chain. The scrambling of products occurs by a process similar to the previously described RCo(dpgH)(L)Py [L = dmgH, gH, chgH] complexes [25,26]. However, the process is much faster in the



Fig. 5. Molecular structure of 1.



Fig. 6. Molecular structure of 4.

present systems and takes only 15 min for completion which is much less compared to the time needed for RCo(dpgH)(L)Py complexes.

3.2. Oxygen insertion

Oxygen insertion in ArCH₂Co(L)(L')Py where L and L' are dioximes with carbon side chain, has been described from our group and it shows the formation of three products, $ArCH_2(O_2)Co(L)_2Py$, $ArCH_2(O_2)Co(L)(L')Py$ and $ArCH_2(O_2)Co(L')_2Py$ [33]. The ratios depend upon the nature of the dioxime. In the present study the oxygen insertion reaction in **5** and **10** gives the following information.



Fig. 8. Molecular structure of 6.

Two compounds **5c** and **5d** are formed within 5 min. The amount of **5d** remains constant up to 1 h and then increases and becomes constant again after 2 h. The amount of **5c** continuously increases with time (Fig. 3).

The insertion in **10** is faster compared to **5** and three products **10c**, **10d** and **5d** are formed during the course of the reaction. The amount of **10c** increases with time and becomes constant after 45 min. However the amount of **10d** and **5d** is very small and remains constant during the course of the reaction (Fig. 4).

4. Spectroscopy

All the complexes **1–10** have been characterized by ¹H (Tables 7 and 8) and ¹³C NMR and in addition **1**, **4**, **5**, **6**, **8** and **10** have also been characterized by X-ray. The NMR assignments are consistent with the previously described cobaloxime complexes. Bis(thiophenyl)glyoxime (dSPhgH₂) and bis(thioethyl)glyoxime (dSEtgH₂) are not completely soluble in CDCl₃ and a drop of DMSO-d⁶ is necessary to dissolve it.



Fig. 7. Molecular structure of 5.



Fig. 9. Molecular structure of 8.



Fig. 10. Molecular structure of 10.

A quartet for $-CH_2$ and a triplet for $-CH_3$ group is observed, as expected, in free dSEtgH₂ but CH₂ appears as two sets of multiplets in 1:1 ratio in **6–10** and their separation depends upon the axial R group, for example it is largest in **6** whereas these merge in **8**, **9** and **10**. This can happen only if the CH₂ protons become non-equivalent and have interaction with the methyl group. Interestingly, the chemical shift of the methyl group remains almost the same in all complexes.

 δPy_{α} is upfield shifted in **1–5** as compared to the unligated Py and its value lies in-between the parent complexes, RCo(dmgH)₂Py and RCo(dSPhgH)₂Py as observed earlier in RCo(dpgH)(L)Py [L = dmgH chgH, gH] [10,11]. It is possible that the upfield shift in **1–5** may be the result of the close proximity of Py_{\alpha} to the phenyl ring of the dioxime (see X-ray). Little or no upfield shift in Py_{\alpha} value in **6–10** supports this view.

The dmgH (Me) is significantly upfield shifted in the benzyl complexes **5** and **10** when compared with the corresponding alkyl complexes **2**–**4** and **7**–**9**. Two factors may be responsible for this (a) enhanced ring current in the metallabicycle when alkyl is replaced by the benzyl (b) C–H... π interaction between the benzyl centroid and dmgH protons. Since δ^{13} C (Py_{α}) and δ^{13} C(C–H) are similar in the alkyl and benzyl complexes, this rules out the first factor (Tables S2 and S3). X-ray structures of **5** and **10** also support the second factor; the benzyl group is oriented over the dmgH wing and has a weak C–H... π interaction (3.33 Å and 3.22 Å). A comparison of δ^{1} H dmgH (Me) in **5** and **10** with PhCH₂Co(dmgH) (dpgH)Py also supports the second factor; δ^{1} H dmgH (Me) is 0.29 and 0.27 ppm upfield shifted in **5** and **10** as compared to PhCH₂Co(dmgH)(dpgH)Py (Table S4). There is no C–H... π



Fig. 11. Cyclic voltammograms of 1 and 6 in CH_2Cl_2 with 0.1 M $({^nBu_4NPF_6})$ as supporting electrolyte at 0.1 V $s^{-1}at$ 25 $^\circ C.$

interaction in the latter, as revealed by X-ray, since the benzyl centroid lies over dpgH and not over dmgH wing.

In general, the chemical shifts of dmgH (Me), Py_{α} and OH...O in **2–5** and **7–10** are upfield shifted as compared to the values in RCo(dmgH) (dpgH)Py and the upfield shift is much larger in **2–5**.

5. Structural studies

The diamond diagram of complexes **1**, **4**, **5**, **6**, **8** and **10** are shown in Figs. 5–10.

Selected bond angles and bond distances are presented in Table 9. The Cobalt atom is linked to four nitrogen atoms belonging to the equatorial plane. Out of this, two nitrogen atoms belong to dmgH ligand and the other two belong to dSPhgH or dSEtgH. The Co–Cl or Co–C bond distances [2.2368(16), 2.012(3), 2.056(3), 2.226(2), 2.040(6), 2.065(4) Å] and Co–N_{Py} bond distances [1.965(5), 2.083(3), 2.065(3), 2.002(7), 2.078(4), 2.058(4) Å] in **1**, **4**, **5**, **6**, **8** and **10** do not differ significantly from the reported value of mixed cobaloxime complexes. Cobalt atom deviates, 0.0225, 0.0029 and 0.0173 Å from mean equatorial CoN₄ plane [34] towards neutral pyridine in **4**, **6** and **8** respectively whereas the deviation is 0.0446, 0.0012 and 0.0314 Å towards R group in **1**, **5** and **10**. Pyridine attached to cobalt has a twist angle (τ) [35] of 85.755, 84.563, 83.905, 82.723, 87.045 and 83.412 in **1**, **4**, **5**, **6**, **8** and **10** respectively.

The orientation of SPh groups with respect to dioxime plane remains same in **1**, **4** and **5** but varies with change in R in $RCo(dSPhgH)_2Py$. The orientation of SEt group in **6** and **10** is same but different in **8**.

Although the distance between phenyl centroid and Py_{α} proton (4.014, 5.259 and 5.212 Å in **1**, **4** and **5** respectively) is relatively large to have any C–H... π interaction, it is the close proximity of the phenyl ring which causes upfield shift of Py_{α} in **1–5**.

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Selected bond lengths (Å), bond angles (deg) and structural data for 1, 4, 5, 6, 8 and 10.

	1	4	5	6	8	10
Co-Cl/Co-C	2.2368(16)	2.012(3)	2.056(3)	2.226(2)	2.040(6)	2.065(4)
Co-N	1.965(5)	2.083(3)	2.065(3)	2.002(7)	2.078(4)	2.058(4)
Cl-Co-N/C-Co-N	176.85(15)	176.46(14)	175.55(12)	179.2(2)	178.9(2)	176.89(17)
d (Å)	-0.0446(8)	+0.0225(5)	-0.0012(6)	+0.0029(11)	+0.0173(7)	-0.0314(6)
α (deg)	-5.354(168)	+3.191(110)	-8.146(109)	+4.576(301)	+8.316(150)	-2.717(101)
τ (deg)	85.755(156)	84.563(87)	83.905(89)	82.723(191)	87.045(124)	83.412(117)

For definition of *d*, α and τ see Refs. [34] and [35].



Fig. 12. Cyclic voltammograms of 4 and 8 in CH_2Cl_2 with 0.1 M ($^nBu_4NPF_6)$ as supporting electrolyte at 0.1 V s ^{-1}at 25 $^\circ C.$

Since bending angle [34] is a measure of interaction between the axial and equatorial ligand, a high α value for **5** (8.14) compared to **1** and **4** (5.35 and 3.19 respectively) is quite justified (because of C–H... π interaction). This is the highest α value observed among all the reported mixed benzyl cobaloxime structures so far. In spite of having similar type of C–H... π interaction in **10**, bending angle decreases as we go from **8** to **10**, which is quite surprising. We cannot offer any explanation right now for this.

The structure of **1** and **6** show some interesting properties. The crystal packing of **1** shows one-dimensional chain due to one C–H...Cl intermolecular hydrogen bond [C11(Py, C–H) acts as donor and the metal bound Cl1 acts as acceptor] (Figure S1). Compound **6** forms a two dimensional lamellar network involving two intermolecular C–H...Cl contacts. One-dimensional polymeric network is formed by C–H...Cl hydrogen bonds [C8 (Py, C–H) acts as donor and metal bound Cl1 acts as acceptor]. Two such polymeric networks are interconnected through one more C–H...Cl hydrogen bond [C15 (CH₃, C–H) acts as donor and Cl1 acts as acceptor] (Figure S2).

6. Cyclic voltammetry

CV study in cobaloximes is not very well defined because of the possibility of change in coordination number of cobalt during reduction/oxidation process [36–38]. Inorganic cobaloximes, in general, give a better cyclic voltammogram as compared to organo derivatives and three types of redox couples Co^{III}/Co^{II}, Co^{II}/Co^I, and Co^{IV}/Co^{III} are expected. The cyclic voltammograms of **1**, **4**, **6** and **8** are shown in Figs. 11 and 12 and CV data are given in Table 10.

The cyclic voltammogram of 1 shows an irreversible wave in the reductive half at -0.457 V, corresponding to Co^{III}/Co^{II} and a quasi-

Table 10

CV data for **1**, **4**, **5**, **6**, **8** and **10** in CH₂Cl₂ and TBAPF₆ at 0.1 V/s at 25 °C.

No	Co ^{III} /Co ^{II}		Co ^{II} /Co ^I		Co ^{IV} /Co ^{III}	
	$E_{pc} (V)^{a}$	$E_{pc} \left(V \right)^{b}$	$E_{1/2}(V)^{a}$	E _{1/2} (V) ^b	$E_{1/2}(V)^a$	$E_{1/2}(V)^{b}$
1	-0.457	-0.883	-0.734(153)	-1.16	1.344(156)	0.918
4	-1.441	-1.866	-	_	1.091(177)	0.664
5	-1.450	-1.876	-	_	1.112(181)	0.685
6	-0.522	-0.948	-0.930(202)	-1.35	1.258(208)	0.831
8	-1.51	-1.93	-	_	1.052(155)	0.625
10	-1.42	-1.84	-	-	0.999(102)	0.572

 Fc/Fc^+ ($E_{1/2} = 0.4269 V$).

^a (vs.Ag/AgCl). ^b (vs. Fc/Fc⁺). reversible wave at -0.734 V corresponding to Co^{II}/Co^I. In comparison **6** is difficult to reduce with values -0.522 V and -0.930 V respectively. One quasi-reversible wave at +1.34 V and +1.25 V is observed in **1** and **6** respectively. This may simply be due to the increased electron donation by SEt group in **6** which puts more negative charge on the cobalt.

In contrast **4**, **5**, **8** and **10** show a different behaviour. Only one completely irreversible reductive half corresponding to Co^{III}/Co^{II} at -1.44 V, -1.45 V, -1.51 V and -1.42 V is obtained. Due to enhanced σ donation by the R- group the Co^{III} state in **4**, **5**, **8**, and **10** is substantially stabilized. In other words, the Co^{III}/Co^{II} redox process in these complexes is considerably cathodically shifted. Due to this, the Co^{II}/Co^{I} response is further cathodically shifted and therefore is not observed even down to -1.6 V.

7. Conclusion

This is the first study of mixed dioxime complexes with two dissimilar dioximes with C and S side chain. Their formation is much faster compared to similar complexes having both dioximes with C side chain. Molecular oxygen insertion in the benzyl complexes is fast and forms mixture of products within 5 min. The upfield shift of Py_α in the alkyl complexes occurs due to its close proximity to the phenyl ring of the dioxime and the high upfield shift of dmgH proton in the benzyl complexes is due to the C–H...π interaction between the benzyl centroid and dmgH protons. This has been confirmed by the X-ray studies.

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Appendix. Supplementary material

CCDC 806944, 806946, 806947, 806948, 806949 and 806945 contains the supplementary crystallographic data for **1**, **4**, **5**, **6**, **8** and **10** respectively. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EX, UK (fax: +44 1223 336033. email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk/). Supplementary data associated with this article can be found, in the online version.

Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.02.033.

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