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Organocobaloximes with mixed dioxime equatorial ligands: a convenient one-pot synthesis. X-ray crystal structures of $BnCo^{III}$(dmgH)(dpgH)Py and $BnCO^{III}$(chgH)(dpgH)py☆

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Abstract

A simple and general route to the synthesis of organocobaloxime with mixed dioxime ligands, RCo(dmgH)(dpgH)Py and RCo(chgH)(dpgH)Py, has been described. The ^{13}C-NMR chemical shifts have been analysed to see whether one dioxime wing has any effect on the other dioxime wing. The first crystal structure of an organocobaloxime with mixed dioxime ligand in the same complex, BnCo(dmgH)(dpgH)Py and BnCo(chgH)(dpgH)Py, is reported. © 2001 Published by Elsevier Science B.V.

Keywords: Cobalt; Cobaloxime; Dioxime; Organocobaloxime

1. Introduction

Organocobaloximes,[1] originally proposed as models of Vitamin B_{12} nearly three decades ago, have been studied extensively and reviewed [1]. This was prompted by the need to understand the factors behind the cleavage of the Co–C bond in B_{12}-dependent enzymatic reactions [1f]. In particular, a lot of study on the steric factors that lead to the weakening of the Co–C bond in vitamin B_{12} model compounds has been made [1d]. This has been done in order to evaluate whether a conformational change in the B_{12}-coenzyme-enzyme complex is responsible for the Co–C bond cleavage step in catalysis by B_{12}-dependent enzymes [2]. Most of these studies have involved dmgH as the dioxime ligand in organocobaloximes. The studies involving other oximes with varying steric and electronic properties such as gH [2,3], chgH [4,22] and dpgH [5] have been few. Recently we have shown that the variation in the equatorial dioxime ligand field has a pronounced *cis* influence on the axial ligands [6].

The recent work on organocobaloximes shows that it has outgrown its initial relevance of B_{12} model and it has acquired an independent research field because of its rich chemistry. The use of organocobaloximes has been exploited in free-radical chemistry [7] and these find numerous applications in organic reactions [8–13]. It is also observed that a slight variation in the equatorial ligand brings out profound changes in the Co–C bond reactivity, for example in Diels–Alder reaction [11], alkyl–alkenyl cross-coupling reaction [14] and in the oxygen insertion reaction into the Co–C bond [15]. The key feature of these reactions is the fragility of the Co–C bond [6,16,17] and hence a fine-tuning of its strength has been a continuing challenge. Approaches to this problem have mainly been via changes in the steric and electronic properties of axial ligands [1d]. Therefore, there has been a sustained interest in the synthesis of new organocobaloximes with new or modified equatorial ligands [5,11,18–22].

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[1] General formula $RCo(L)_2B$ where R, an organic group σ bonded to cobalt; B, axial base *trans* to the organic group; L, dioxime ligand, e.g. gH, glyoxime; dmgH, dimethylglyoxime; chgH, 1,2 cyclohexanedione dioxime; dpgH, diphenylglyoxime (all monoanions).

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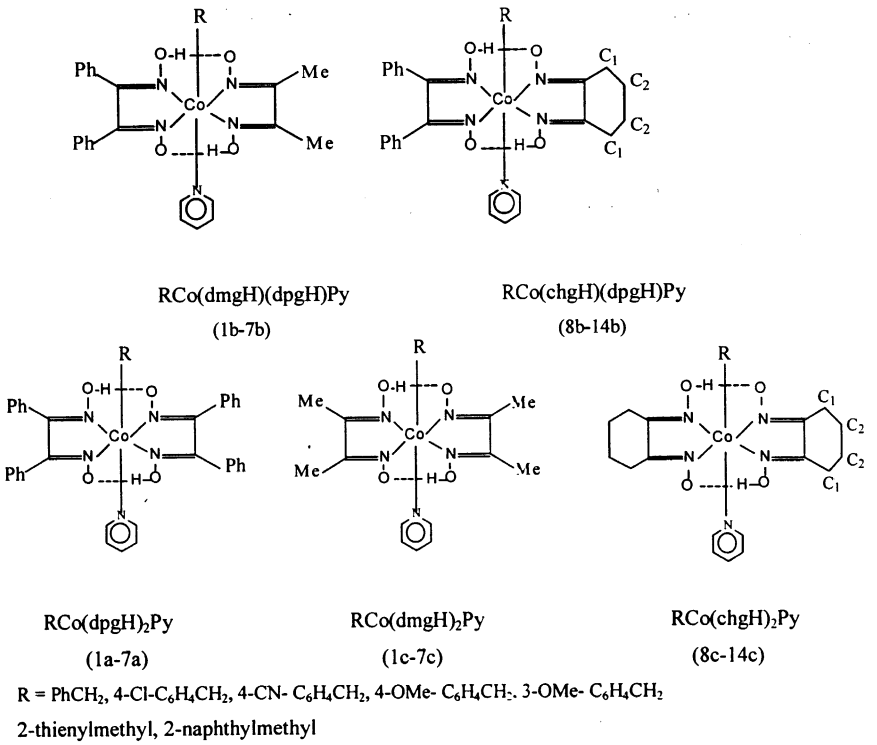


Fig. 1.

Keeping the above in view, we report here simple and general route to the synthesis of organocobaloximes of the type $ArCH_2Co^{III}(L)(L')B$ with mixed equatorial dioxime ligands. The synthesis is confirmed by the crystal structure of BnCo(dmgH)(dpgH)Py and BnCo(chgH)(dpgH)Py. These become the first structures of an organocobaloxime with two different dioximes in the same complex. After having synthesised these new complexes, we have analysed the ^{13}C-NMR resonance to see whether one equatorial wing has any effect on the other equatorial wing in the same plane (Fig. 1).

2. Results and discussion

2.1. Synthesis

A thorough literature survey reveals that such organocobaloximes with mixed dioxime ligands have never been isolated before.[2] In the light of the lack of preparative procedures we initially attempted synthetic procedures that had been successful for the analogous bis(dimethylglyoximato)cobalt(III) complexes. Organocobaloximes, though, have been synthesised by several methods [1e], but Schrauzer's disproportionation method [23] and the oxidative alkylation of cobaloxime(I) [24] find a much wider use in the synthesis. We have used Schrauzer's method, modified Schrauzer's method and oxidative alkylation of cobaloxime(I) generated from chlorocobaloxime for the synthesis

Method A: Disproportionation

$$CoCl_2.6H_2O/dmgH_2/dpgH_2/Py/NaOH \xrightarrow[RX\ [3\ Eq]]{NaOH[2.5\ Eq]} Products(1a\text{-}c) \quad (1)$$
[1:1:1:1:2]

Method B: Reduction by $NaBH_4$

$$CoCl_2.6H_2O/dmgH_2/dpgH_2/Py/NaOH \xrightarrow[RX\ [3\ Eq]]{NaBH_4} Products(1a\text{-}c) \quad (2)$$
[1:1:1:1:2]

Method C: All reagents in one pot

$$CoCl_2.6H_2O/dmgH_2/dpgH_2/Py/NaOH/RX \xrightarrow{NaBH_4} Products(1a\text{-}c) \quad (3)$$
[1:1:1:1:2:3]

Method D: From Chlorocobaloxime

$$ClCo(dmgH)_2Py + ClCo(dpgH)_2Py \xrightarrow[NaOH\ (trace)\ RX\ [3\ Eq]]{NaBH_4} Products(1a\text{-}c) \quad (4)$$
[1:1]

Method E: From $ClCo(dmgH)_2Py$ and $dpgH_2$ in the presence of BnCl and $NaBH_4$

$$ClCo(dmgH)_2Py + dpgH_2 \xrightarrow[ii)\ RX\ (1\ eq)]{i)\ NaBH_4} Products\ (1a\text{-}c) \quad (5)$$
[1:10]

Method F: From $ClCo(dpgH)_2Py$ and $dmgH_2$ in the presence of BnCl and $NaBH_4$

$$ClCo(dpgH)_2Py + dmgH_2 \xrightarrow[ii)\ RX\ (1\ eq)]{i)\ NaBH_4} Products\ (1a\text{-}c) \quad (6)$$
[1:10]

1a= $BnCo(dpgH)_2Py$; 1b = BnCo(dmgH)(dpgH)Py ; 1c = $BnCo(dmgH)_2Py$; RX= BnCl

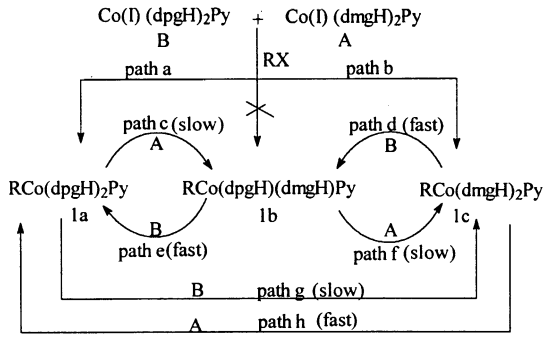
Scheme 1.

[2] Johnson et al. have mentioned the formation of similar complexes in solution [5a].

Table 1
Product distribution with BnCl using methods (A-F)

Method [a]	Molar distribution (%)		
	1a	**1b**	**1c**
A	83	17	–
B	73	10	17
C	62	15	22
D	35	42	23
E	94	6	–
F	84	7	9

[a] Reaction time is 3 h in all cases.



Scheme 2.

of mixed-ligand complexes. In all, six different methods (A–F) have been used (Scheme 1). A mixture of three products (**1a**–**1c**) is formed in every case, however, the method D gives the best yield of the mixed-ligand complex (**1b**) (Table 1). The yield of **1a** is always more than **1b** and **1c** in every case.

In order to know more about the synthesis, the reaction pathway and to maximise the yield of **1b** using method D, a series of reactions with varying reaction conditions have been carried out. An examination of the product distribution in Table 2 points to the following observations:

1. The formation of the mixed-ligand complex (**1b**) is a function of time. The yield reaches a maximum (entry 6) and then declines (entries 7–9).
2. The yield of **1b** is low at the initial stages of the reaction (entries 1–3) and is practically independent of the residence time of cobalt(I) (entries 1–3). This indicates that the following reaction is either very slow or does not occur in the reaction time scale otherwise we would have seen the formation of **1b** in the beginning of the reaction itself (entries 1–3).

   $Co^{I}(dmgH)_2Py + Co^{I}(dpgH)_2Py$

   $\rightarrow 2Co^{I}(dmgH)(dpgH)Py$

   Thus **1b** is not formed by direct alkylation of $Co^{I}(dmgH)(dpgH)Py$.[3]
3. $BnCo(dpgH)_2Py$ (**1a**) or $BnCo(dmgH)_2Py$ (**1c**), once formed in solution by direct alkylation of $Co^{I}(dpgH)_2Py$ or $Co^{I}(dmgH)_2Py$ (path a and b, Scheme 2), reacts further with $Co^{I}(dmgH)_2Py$ or $Co^{I}(dpgH)_2Py$, respectively, (path c and d) to yield the mixed dioxime complex (**1b**). This has been confirmed by independent experiments using equimolar quantities of each reactant (see Section 3). It is observed that path d is more facile than path c. Nearly all of the $BnCo(dpgH)_2Py$ (**1a**) is recovered back in the latter reaction while most of the $BnCo(dmgH)_2Py$ (**1c**) is consumed in the former (Scheme 2).
4. It is noticed that in all these reactions the yield of $BnCo(dpgH)_2Py$ (**1a**) is always more as compared to $BnCo(dmgH)_2Py$ (**1c**). This suggests that processes other than simple alkylation of $Co^{I}(dpgH)_2Py$ are also responsible for its formation, for example the independent reactions (see Section 3) show that: (i) $BnCo(dpgH)_2Py$ (**1a**) is formed by *trans*-alkylation reaction of $BnCo(dmgH)_2Py$ (**1c**) with $Co^{I}(dpgH)_2Py$ (path h); (ii) BnCo(dmgH)(dpgH)Py (**1b**) on reaction with $Co^{I}(dpgH)_2Py$ forms $BnCo^{III}(dpgH)_2Py$ (**1a**) in high yield (path e) while the reaction with $Co^{I}(dmgH)_2Py$ produces $BnCo(dmgH)_2Py$ (**1c**) in low yield (path f) in the same reaction. This also explains the depletion of the mixed dioxime complex (**1b**) in the later stages of the reaction (Table 2).

We have synthesised seven new mixed-ligand complexes, RCo(dmgH)(dpgH)Py (**1b**–**7b**) following method D. A mixture of three products is formed in each case. The molar distribution ratio is shown in Table 3. The general features of these reactions are similar to benzyl case as described above.

Since the yield of the mixed ligand complex (**1b**–**7b**) is poor in all cases, the next aim was to improve its yield. We have been able to achieve this via oxidative alkylation of $Co^{I}(dmgH)(dpgH)Py$, generated in situ, by sodium borohydride reduction of ClCo(dmgH)-(dpgH)Py (**15b**) (see Section 3 for its synthesis). The desired mixed-ligand complex (**1b**–**7b**) is formed as the major product in high yield (32–51%). The corresponding side products (**1a**–**7a**) and (**1c**–**7c**) are formed in less than 10% yield. Following this procedure we have extended the studies to other mixed-ligand combinations and have synthesised seven new complexes of the type RCo(chgH)(dpgH)Py (**8b**–**14b**) (55–80%) (Table 4). However, when the studies are extended to the dmgH/chgH combination, we find that three products are formed, as inferred from ^{1}H-NMR, but all efforts to separate these products by column chromatography, crystallisation, failed. This observation is similar to the earlier observation by Johnson et al. [5a].

[3] In the absence of rates, it is assumed that the rates of oxidative alkylation of Co I $(dmgH)_2Py$, $Co^{I}(dpgH)_2Py$ and Co(dmgH)-(dpgH)Py are similar.

Table 2
Molar distribution at various reaction times

$ClCo(dmgH)_2Py$ $Clco(dpgH)_2$-Py one equivalent each	BnCl (equivalents)	Residence time of Co^I (min) [a]	Reaction time (min) [b]	% molar distribution (after column)		
				$BnCo(dpgH)_2Py$	BnCo(dmgH)-(dpgH)Py	$BnCo(dmgH)_2Py$
Entry 1	3	30	15	73	3	23
Entry 2	3	5	15	63	0.4	36
Entry 3	3	5	30	63	0.8	36
Entry 4	3	5	60	61	17	21
Entry 5	3	5	120	45	31	24
Entry 6	3	10	180	35	42	23
Entry 7	3	5	240	44	30	26
Entry 8	3	5	300	55	20	25
Entry 9	3	10	400	63	0.8	36

[a] The time before the addition of benzyl chloride to Co(I).
[b] Refers to the time between the addition of benzyl chloride and the work up. The Julabo refrigerated circulator was turned off after the addition of the halide.

Table 3
Method D molar distribution [a]

Reactants $ClCo(dmgH)_2Py$ $ClCo(dpgH)_2Py$ (1:1)	Compound number	RX (three equivalents)	Molar distribution (%) (after column)		
			$RCo(dpgH)_2Py$	RCo(dmgH)-(dpgH)Py	$RCo(dmgH)_2Py$
Entry 1	**1**	$PhCH_2Cl$	35	42	23
Entry 2	**2**	4-Cl-C_6-CH_2Cl	35	29	35
Entry 3	**3**	4-CN-$C_6H_4CH_2Br$	54	16	44
Entry 4	**4**	4-OMe-$C_6H_4CH_2Cl$	59	31	10
Entry 5	**5**	3-OMe-$C_6H_4CH_2C1$	61	10	29
Entry 6	**6**	2-Thiophene CH_2Cl	43	42	–
Entry 7	**7**	2-NaphthylCH_2Br	54	11	34

[a] Reaction time is 3 h in all cases. The Julabo refrigerator circulator was switched off after the addition of the halide.

Table 4
Molar distribution [a] (after column): reaction time 3 h [a]

Reactant ClCo(chgH)(dpgH)Py	RX (three equivalents)	Compound number	% molar distribution		
			$RCo(dpgH)_2Py$	RCo(chgH)(dpgH)Py	$RCo(chgH)_2Py$
Entry 1	$PhCH_2Cl$	**8**	3	89	8
Entry 2	4Cl-$C_6H_4CH_2Cl$	**9**	4	92	
Entry 3	4-CN-$C_6H_4CH_2Br$	**10**	8	84	8
Entry 4	4-OMe-$C_6H_4CH_2Cl$	**11**	8	87	5
Entry 5	3-OMe-$C_6H_4CH_2Cl$	**12**	5	95	–
Entry 6	2-thiophene CH_2C1	**13**	5	90	5
Entry 7	2-naphthylCH_2Br	**14**	4	96	–

[a] **8a**–**14a** are the same as **1a**–**7a**.

The spectral characteristics of compounds **1b**–**14b** and **1a**–**7a** are given in Tables 5 and 6. The details of compounds **1a**–**7a** and **1c**–**14c** have been described earlier by us [15]. All the compounds give satisfactory elemental analysis.

In light of the lack of preparative procedures for the synthesis of ClCo(dmgH)(dpgH)Py (**15b**) and ClCo-(chgH)(dpgH)Py (**16b**), we initially attempted synthetic procedures that had been successful for the synthesis of analogous $ClCo(L)_2Py$ (L = dmgH, dpgH, chgH) com-

Table 5
^{1}H-NMR and λ_{max} values of **1b**–**14b** [a]

Compound number	O–HO (s)	Pyridine [b]			Aromatic	dmgH (s)/chgH	dpgH (m)	Co–CH_2 (s)	λ_{max} (log ε) (methanol)
		α (d)	β (t)	γ (t)					
1b	18.47	8.72	7.37	7.75	6.87–6.99 (m)	2.02	7.05–7.29	3.16	470.7 (3.15), 242 (4.50)
2b	18.44	8.68	7.34	7.73	6.88–6.94 (m), 6.98–7.03 (m)	2.03	7.05–7.23	3.06	473 (3.27), 239 (4.62)
3b	18.41	8.69	[c]	7.77	6.88 (d) [7.4]	2.09	7.18–7.49 [c]	3.02	469 (3.49), 239 (4.60)
4b [d]	18.48	8.71	7.34	7.74	6.63 (d) [1.6], 7.10 (d) [1.6]	2.00	6.88–6.96, 7.14–7.22	3.17	238 (4.59)
5b [d]	18.48	8.71	7.35	7.75	6.72–6.77 (m)	2.00	6.91–6.99, 7.14–7.23	3.18	460 (3.16), 239 (4.55)
6b	18.41	8.73	7.34	7.76	6.78–6.90 (m)	2.08	6.92–7.02, 7.10–7.27	3.33	239 (4.51)
7b	18.52	8.70	[c]	7.74	6.79 (d) [6.8], 7.05–7.70 (m)	1.93	[c]	3.31	–
8b	18.17	8.72	7.36	7.76	6.95–6.7 (m)	2.46 (d) [2.8] 1.45 (s)	7.05–7.30	3.16	472 (3.22), 244 (4.49)
9b	–	8.70	7.36	7.76	6.93–6.95 (m)	2.50 (s), 1.49 (s)	7.02–7.22	3.06	471 (3.22), 244 (4.48)
10b	18.15	8.65	7.36	7.78	6.92 (d)	2.42 (s), 1.51 (s)	7.20–7.29	3.02	472 (3.12)
11b [d]	18.23	8.71	7.35	7.75	6.64 (d) [8.4], 6.96 (d) [8.0]	2.48 (s),	7.01–7.22	3.17	239 (4.15)
12b [d]	18.19	8.72	7.36	7.76	6.73–6.79 (m)	2.47 (s), 1.45 (s)	6.96–6.98, 7.18–7.23	3.18	475 (3.20), 244 (4.43)
13b	18.14	8.71	7.36	7.76	6.78–7.01 (m)	2.50–2.63 (m), 1.53–1.55 (m)	7.16–7.21	3.37	244 (3.83)
14b	18.26	8.72	[c]	7.75	6.88–7.41 (m)	2.33–2.39 (m), 1.27 (t) [6.4], 1.08 (t) [6.4]	[c]	3.36	–

[a] R_f 0.374–0.54 (EtOAc–$CHCl_3$) (1:9); all the compounds give satisfactory elemental analyses. The coupling constants (J) in pyridine are $\alpha = 4.8$–5.6 Hz, $\beta = 6.0$–7.5 Hz and $\gamma = 6.9$–7.6 Hz.
[b] Free Py appears as $\alpha = 8.57$; $\beta = 7.05$; $\gamma = 7.43$.
[c] Merge with aromatic.
[d] OMe appears at 3.73.

Table 6
^{13}C values of **1b**–**14b** and **1a**–**7a**

Compound number	C=N [a]	Pyridine [b]			Aromatic + dpgH	dmgH or chgH [c]	Co–CH_2
		α	β	γ			
lb	150.78, 149.71	150.24	125.35	137.68	130.21, 129.73, 129.59, 128.92, 128.67, 127.75, 127.69, 127.64	12.05	–
2b	150.83, 149.79	150.15	125.39	137.80	130.09, 130.04, 130.00, 127.71, 129.68, 129.49, 128.75, 127.70	12.12	31.02
3b [d]	151.13, 150.15	150.19	125.51	138.00	131.44, 130.06, 129.79, 129.41, 129.19, 129.08, 128.96, 128.78	12.23	–
4b [e]	150.60, 149.53	150.21	125.32	137.62	130.24, 129.99, 129.94, 129.58, 128.61, 127.69, 127.62, 113.48	12.02	32.37
5b [e]	150.82, 149.78	150.23	125.35	137.70	130.23, 129.60, 129.52, 128.64, 128.56, 127.64, 127.56, 121.66, 113.53, 111.03	12.07	29.70
6b	150.88, 149.87	150.29	125.35	137.71	130.24, 129.62, 128.72, 128.66, 128.59, 127.75, 127.55, 122.21	12.13	24.12
7b	150.81, 149.76	150.24	125.36	137.69	131.37,130.10,129.56, 129.50, 128.84, 128.65, 127.78, 127.58, 126.84, 124.28	11.99	–
8b	150.84, 150.48	150.29	125.35	137.68	130.31, 129.59, 128.97, 128.65, 127.91, 127.74, 127.70	25.26, 21.24	–
9b	150.87, 150.51	150.18	125.39	137.80	130.09, 130.04, 130.00, 127.71, 129.68, 129.49, 128.75, 127.70	25.31, 21.11	
10b [d]	151.21, 150.88	150.19	125.53	138.01	131.48, 129.90, 129.50, 129.45, 129.21, 128.99, 127.84	25.43,21.19	–
11b [e]	150.69, 150.24	150.24	125.33	137.63	130.32, 129.96, 129.59, 128.61, 127.68, 113.54	25.24, 21.21	32.28
12b [e]	150.84, 150.54	150.25	125.35	137.68	130.29, 129.56, 128.59, 127.66, 121.68, 113.57, 110.87	25.28, 21.08	–
13b	150.94, 150.68	150.30	125.35	137.71	130.24, 129.62, 128.72, 128.66, 128.59, 127.75, 127.55, 122.21	25.34 21.28	
14b	150.89, 150.51	150.27	125.37	.137.70	131.35, 130.23, 129.62, 129.54, 128.89, 128.63, 127.78, 127.67, 126.89, 126.79	25.16, 20.90	32.71
1a	151.03	150.14	125.52	137.96	147.35, 129.96, 129.66, 129.13, 128.89, 128.29, 127.66, 124.71	–	34.11
2a	151.13	150.14	125.59	138.05	146.02, 130.23, 130.12, 129.81, 129.59, 129.03, 128.24, 127.76	–	32.66
3a [d]	151.40	150.08	125.70	138.28	131.81, 129.56, 129.50, 129.35, 129.25, 127.84, 120.26, 107.23	–	31.70
4a [e]	150.86	150.14	125.50	137.89	139.27, 130.15, 129.98, 129.67, 128.86, 127.64, 113.92	–	34.11
5a [e]	151.09	150.15	125.53	137.98	148.85, 129.96, 129.68, 129.04, 128.89, 127.64, 121.94, 113.85	–	33.72
6a	151.16	150.16	125.53	137.98	130.07, 129.99, 129.80, 129.71, 129.30, 128.86, 128.06, 127.78	–	26.42
7a	151.08	150.12	125.53	137.97	145.32, 134.06, 131.64, 129.82, 129.57, 128.99, 128.84, 127.81, 127.59, 127.32, 127.04, 125.85, 125.78, 124.41	–	34.50

[a] The first value is C=N (dpgH) and the second value is C=N (dmgH) or (chgH).
[b] Free Py $\alpha = 149.82$; $\beta = 123.73$; $\gamma = 135.89$.
[c] The first value corresponds to C1 and the second to C2 carbons in cyclohexane (for numbering see Fig. 1).
[d] CN appears at (154.61, 154.79, 154.41 ppm) for **3b**, **10b** and **3a**, respectively.
[e] OMe appears at 55.32, 55.12, 55.29,55.16, 55.30, 55.10 for **4b**, **5b**, **11b**, **12b**, **4a** and **5a**, respectively.

plexes [5b,22,23]. The compounds were synthesised and purified as detailed in Section 3. Interestingly, their synthesis is always accompanied by the formation of $ClCo(dmgH)_2Py$/$ClCo(dpgH)_2Py$ and $ClCo(chgH)_2Py$/$ClCo(dpgH)_2Py$, respectively. The crystal structure of BnCo(dmgH)(dpgH)Py (**1b**) and BnCo(chgH)(dpgH)Py (**8b**) have been determined and the details are given later.

The exact mechanism of the reaction can be deciphered by detailed kinetic experiments. However, in the absence of kinetic data our preliminary studies showed that the randomisation of the dioxime ligand along with alkyl transfer in the presence of cobalt(I) is taking place.

The major concern with the cobaloxime(I) promoted alkyl exchange reactions is to establish whether cobaloxime(I) or traces of cobaloxime(II) is the reactive species. Usually, excess sodium borohydride is used in the reaction and it reduces cobaloxime(II) to cobaloxime(I). Also, we did not get any ESR signal of the blue cobaloxime(I) solution. We, therefore, believe that there is no cobaloxime(II) impurity present in cobaloxime(I). The latter has a very labile fifth ligand, Py or the solvent methanol, and exists in equilibrium with significant proportion of the four-coordinate species. The randomization might occur by any/all of the following pathways.

The exchange of equatorial ligand: (a) may take place directly between **1a** and **1c** and free ligand; (b) may occur via Co(I)(dmgH)(dpgH)Py as mentioned before; (c) may occur by routes outlined in Scheme 2. We have ruled out certain of these possibilities by independent reactions as outlined above. The experiments have shown further that **1b** is formed albeit in low yield when $ClCo(dmgH)_2Py/dpgH_2$ [1:10] or $ClCo(dpgH)_2Py/dmgH_2$ [1:10] is reduced with borohydride in presence of benzyl chloride (see methods E and F, Scheme 1). It is very difficult to comment on whether the dissociation of the equatorial ligand, i.e. randomization occur before or after the alkyl transfer.

2.2. Spectroscopy

Assignment of ^1H and ^{13}C resonance. The ^1H-NMR spectra of these complexes are easy to assign and the assignment is similar to the $RCo(dmgH)_2Py$ and $RCo(dpgH)_2Py$ complexes that have been reported earlier by us [15]. However, the ^{13}C values have been assigned for only a few organocobaloximes in the literature [26] and therefore further comments are warranted on its assignment.

The ^{13}C resonance of dmgH (Me), chgH (C1 and C2), Co–CH_2, Py_β and Py_γ are easily assigned based on their chemical shifts. The difficult part has been the assignment of C=N (dmgH or chgH), C=N (dpgH) and Py_α as these occur very close to each other. The highest intensity peak is assigned to Py_α. The other two peaks having lower intensity belong to C=N. Their intensity is expectedly low because these are quaternary carbons. The peak with higher ppm (δ) is assigned to C=N (dpgH) and the other with lower ppm (δ) value is assigned to C=N (dmgH or chgH). Py_α lies in between C=N (dmgH) and C=N (dpgH) in **1b**–**7b** whereas it occurs upfield as compared to C=N (chgH) and C=N (dpgH) in **8b**–**14b**.

^1H and ^{13}C-NMR spectra of the complexes (**1b**–**14b**) (Tables 5 and 6) show some general trends that are discussed below.

We have recently shown that organocobaloximes, in general, are good systems for the study of *cis* and *trans* influence [6,25]. It was observed, based on spectral studies, that the *cis* influencing ability in alkylcobaloximes followed the order dpgH > chgH > dmgH and ^1H and ^{13}C-NMR studies indicated further that OH–O and Py_γ were the most affected followed by Py_γ. The *cis* influence studies in the present systems having mixed ligands throw further light on the phenomenon. The following observations are noteworthy.

1. The ^1H-NMR values for Py_α and Co–CH_2 are affected by the equatorial plane. For example, if we compare the values in **1b**–**7b** and **8b**–**14b** with the values in parent cobaloximes, $RCo(L_2)Py$ (L = dmgH, chgH, dpgH) [15] then they lie in between the **1a**–**7a** and **1c**–**7c** and **1a**–**7a** and **8c**–**14c**, respectively. This indicates that the *cis* influence by the equatorial plane on Py_α and Co–CH_2 depends on both the equatorial wings around the cobalt centre. The ^1H-NMR values for Py_α and Co–CH_2 in complexes **1b**–**7b** are almost same as in **8b**–**14b** which further means that the *cis* effect of (dmgH/dpgH) is similar to the (chgH/dpgH). This supports our earlier findings in which the *cis* influence of dmgH was found to be similar to chgH in $RCo(L_2)Py$ (L = dmgH, chgH) complexes [22].
2. The O–HO values in **1b**–**7b** and **8b**–**14b** lie in between the values for parent cobaloximes and the values in **1b**–**7b** are consistently down field as compared to the values in **8b**–**14b**.
3. The ^{13}C resonance of pyridine on coordination to the cobaloxime moiety shifts downfield and this coordination shift ($\Delta^{13}C = \delta_{complex} - \delta_{free\ pyridine}$) follows the order $\Delta^{13}C\ Py_\gamma > \Delta^{13}C\ Py_\beta > \Delta^{13}C\ Py_\alpha$ (Table 7). However, the order observed based on the coordination shift in ^1H-NMR values is $\Delta^1Py_\gamma \cong \Delta^1H\ Py_\beta > \Delta^1H\ Py_\alpha$ (Table 7)
4. We have considered whether one equatorial wing has any effect on the other equatorial wing, i.e. the effect of dmgH or chgH wing on dpgH wing. ^1H-NMR data does not give any information. For example, dmgH (Me) in $RCo(dmgH)_2Py$ and in RCo(dmgH)(dpgH)Py have the same chemical shift. However, the comparison of the ^{13}C values of the

Table 7
Coordination shift from ^{13}C- and ^{1}H-NMR values

Compound	$\Delta^{13}C$ Py_{α}	$\Delta^{13}C$ Py_{β}	$\Delta^{13}C$ Py_{γ}	$\Delta^{1}H$ Py_{α}	$\Delta^{1}H$ Py_{β}	$\Delta^{1}H$ Py_{b}
1b	0.40	1.62	1.79	0.15	0.32	0.32
2b	0.33	1.66	1.91	0.11	0.29	0.30
3b	0.37	1.78	2.11	0.12	–	0.34
4b	0.39	1.59	1.73	0.14	0.29	0.31
5b	0.41	1.62	1.81	0.14	0.30	0.32
6b	0.47	1.62	1.82	0.16	0.29	0.33
7b	0.42	1.63	1.80	0.13	–	0.31
8b	0.47	1.62	1.79	0.15	0.31	0.33
9b	0.36	1.66	1.91	0.13	0.31	0.33
10b	0.37	1.90	2.12	0.08	0.31	0.35
11b	0.42	1.60	1.74	0.14	0.30	0.32
12b	0.43	1.62	1.79	0.15	0.31	0.33
13b	0.48	1.62	1.82	0.14	0.31	0.33
14b	0.45	1.64	1.81	0.15	–	0.32

Table 8
Effect of one wing on the other wing (^{13}C-NMR)

Compound	$\delta_{C=N}$ (dpgH)	$\delta_{C=N}$ (dpgH wing)	Δ_{dmgH} [a]	Compound	$\delta_{C=N}$ (dpgH wing)	Δ_{chgH} [b]
1	151.03	150.78	−0.25	**8**	150.84	−0.19
2	151.13	150.83	−0.30	**9**	150.87	−0.26
3	151.40	151.13	−0.27	**10**	151.21	−0.19
4	150.86	150.60	−0.26	**11**	150.69	−0.17
5	151.09	150.82	−0.27	**12**	150.84	−0.25
6	151.16	150.88	−0.28	**13**	150.94	−0.22
7	151.08	150.81	−0.27	**14**	150.89	−0.19

[a] $\Delta_{dmgH} = {}^{13}C\ \delta_{\mathbf{1b-7b}} - {}^{13}C\ \delta_{\mathbf{1a-7a}}$.
[b] $\Delta_{chgH} = {}^{13}C\ \delta_{\mathbf{8b-14b}} - {}^{13}C\ \delta_{\mathbf{1a-7a}}$.

phenyl carbons of dpgH ligand in both wings in **1b**–**14b** might render some information. We cannot test this viewpoint in the present series of complexes since we are unable to make the precise assignment as these are very close to the phenyl carbons. However, the comparison of ^{13}C values for C=N (dpgH) in **1b**–**14b** with ^{13}C (C=N) in **1a**–**7a** shows that the ^{13}C value shifts upfield by about 0.2 ppm in all cases indicating that one wing has some effect on the other wing (Table 8). This further means that there is a higher charge density on C=N (dpgH) in the mixed-ligand complexes, **1b**–**14b**, as compared to the pure complexes, $RCo(dpgH)_2Py$ (**1a**–**7a**). This might be a general phenomenon, however, it requires confirmation by extending it to more systems with mixed ligands having both steric and electronic differences. The studies are in progress in this direction. We, however, cannot comment on the origin of this shift but it might be due to the electronic effect of one wing on the other.

5. The coordination shift of the γ and β carbon of pyridine, $\Delta^{13}CPy_{\gamma}$ and $\Delta^{13}CPy_{\beta}$, in (**1a**–**7a** and **8b**–**14b**) correlate well and show a linear trend with the ^{13}C of $C{=}N_{oximinic}$.[4] However, no correlation is observed for a carbon. $\delta^{13}C$ $(C{=}N)_{\mathbf{1a-7a}} = 0.72$ (13) $\Delta^{13}C$ Py_{γ} -107.23 (1911) ($r = 0.93$, e.s.d = 0.05 ppm). $\delta^{13}C$ $(C{=}N)_{\mathbf{1a-7a}} = 0.38$ (9) $\Delta^{13}C$ Py_{β} -55.24(1313) ($r = 0.89$, e.s.d = 0.03 ppm). $\delta^{13}C$ $(C{=}N)_{\mathbf{8b-14b}} = 0.74$(14) $\Delta^{13}C$ Py_{γ} -110.34 (2154) ($r = 0.92$, e.s.d = 0.06 ppm). $\delta^{13}C$ $(C{=}N)_{\mathbf{8b-14b}} = 0.60$ (12) $\Delta^{13}C$ Py_{β} -89.42 (1871) ($r = 0.91$, e.s.d = 0.05 ppm).

2.3. UV–vis spectra

Organocobaloximes generally show a Co–C CT band between 440 and 470 nm and a CoDioxH CT band between 230 and 250 nm [15,25]. We are not able to observe the Co–C CT band in certain cases in the mixed-dioxime complexes (**1b**–**14b**). 2-Naphthylmethyl cobaloximes (**7b** and **14b**) do not give any band at all (Table 5).

[4] The least-square method and the programme 'origin' have been used.

Table 9
Crystal data collection and refinement parameters

Compound	**1b**	**8b**
Formula	$CoO_4N_5C_{30}H_{30}$	$CoC_{32}H_{32}N_5O_4$
Formula weight	583.53	609.56
Tempearture (K)	293	293(2)
Crystal size (mm)	$0.20\times0.38\times0.46$	$0.50\times0.30\times0.10$
Crystal colour	orange	orange
Unit cell dimensions		
a (Å)	17.1950(19)	17.9648(5)
b (Å)	9.5165(13)	32.0298(8)
c (Å)	18.170(4)	10.2559(9)
α (°)	–	90.00
β (°)	107.050(14)	90.00
γ (°)	–	90.00
V (Å^3)	2842.6(8)	5901.31(6)
Cell determination reflections	25	25
Cell determination, 2θ range (°)	18–20	18–20
D_{calc} (g cm^{-3})	1.36	1.372
Space group	$P2_1/c$	$Pnca$
Z	4	8
$F(000)$	1217.7	2544
Radiation	Mo–K_α, graphite monochromated	Mo–K_α, graphite monochromated
λ (Å)	0.7107	0.7107
Linear absorption coefficient (mm^{-1})	0.64	0.627
Diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
Scan technique	θ–2θ	Multi-scan
2θ range (°)	4–50	2.27–30.17
Index ranges (h, k, l)	−20, 20; −11, 0; −21, 0	−24, 24; 44, 44; −14, 13
Drift of standard deviation (%)	2.5	
Absorption correction	analytical	empirical
Absorption range	0.78–0.89	1.00–0.85
Reflections measured	5179	7647
Unique reflections	5002	7646
R for merge	0.016	0.038
Reflections in refinement, $I>2.0\sigma(I)$	2877	7646
Parameters refined	331	507
$R(F)$ [a], $Rw(F)$ [b]	0.054, 0.072	0.0668, 0.1655
R for $I>3.0\sigma(I)$	0.047	0.1142
Goodness-of-fit on F^2	1.26	1.144
p ($w^{-1}=[\sigma^2(I)+pI^2]/4F^2$)	0.04	–
Largest Δ/σ	0.00	0.857
Extinction correction	None	None
Final difference map (e Å^{-3})	−0.32(7), +0.64(7)	−0.563
Programs	NRC386 [c]	SHELXL-97 [d]
H atom treatment	idealised (C−H = 0.95 Å)	idealised (C−H = 0.95 Å)

[a] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[b] The value is for $Rw(F^2)$ and $wR=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)]]^{0.5}$, $w=[\sigma^2(F_o^2)+(0.05F_o^2)]$.

[c] NRCVAX — An Interactive Program System for Structure Analysis, E.J. Gabe, Y. Lepage, J.P. Charland, F.L. Lee, P.S. White, J. Appl. Crystallogr. 22 (1989) 383.

[d] Sheldrick, G.M. (1993). SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany.

2.4. Crystal structure determination and refinements

Orange crystals were obtained by slow evaporation of solutions of the complexes in methanol. A small crystal size (Table 9) was selected and mounted on a Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. The unit cell parameters were determined from 25 reflections (2θ range 18–20) and the cell parameters were refined by least-squares. Intensities were collected with Mo–K_α radiation, using the θ–2θ and multi-scan techniques. For compound **1b**, 5179 intensities were measured in the range (4–50°) and 2877 were considered as observed applying the condition $I>2.0\sigma(I)$, while 7647 reflections were measured for compound **8b** in the range (2.27–30.17), from which 7646 were considered as observed. Empirical absorption corrections based on ψ-scan data were applied to the reflection intensities for these two compounds.

The structures were isotropically refined by full-matrix least-squares method, using the NRC386 and the SHELXL-97 computer programs. The function minimised was $[\Sigma[w|F_o|-|F_c|^2]^{0.5}]$, where $w=[\sigma^2(F_o^2)+(0.05F_o^2)^2]$. The hydrogen atoms of the OH groups were located on difference maps and were constrained to these difference map positions. The orientations of the methyl H atoms were also determined from difference maps and refined with an overall isotropic temperature factor. The perspective views of the molecular structures together with the atom numbering schemes are shown in Figs. 2 and 3.

2.5. Description of the structures

The cobalt atom is linked to four nitrogen atoms belonging to the equatorial plane. Out of this, two nitrogen atoms belong to diphenylglyoximato (dpgH) ligand and the other two to dimethylglyoximato (dmgH) or 1,2-cyclohexanedionedioximato (chgH) ligand. The Co atom displays an approximately octahedral coordination. The Co atom in compound **1b** is 0.024(2) Å out of the mean plane of the four nitrogen atoms, while it is 0.044(2) Å in compound **8b**. The displacement is towards pyridine in both cases. These deviations from planarity are well within the range found in similar dmgh complex (0.05 Å) [27]. Pyridine ring is practically planar and parallel to the glyoxime C–C bonds, its conformation being defined by a twist of 80.3(5) and 79.0(3)° for the compounds **1b** and **8b**, respectively. The Co–C_{24} and Co–N_{ax} bonds arc perpendicular (90°) to the equatorial plane as seen in the N_{eq}–Co–C_{24}, N_{eq}–Co–N_{ax} and C_{24}–Co–N_{ax} bond angles. Co–N_5 bond distance in **1b** and **8b** are some what longer than the corresponding value in $ClCo(L_2)Py$, where L = dmgH, dpgH [5d,27]. The phenyl group of the benzyl unit in **1b** has disorder with 50–50 occupancy in the model with both phenyl rings refined as

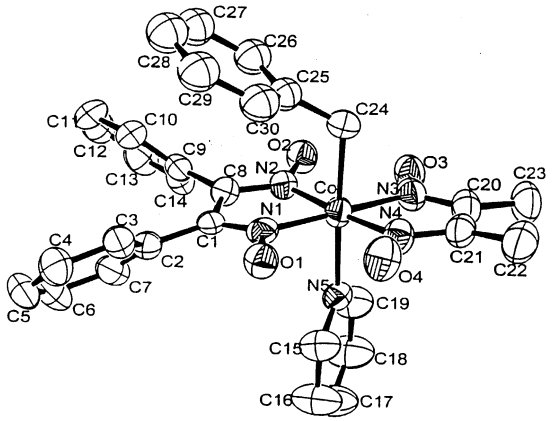


Fig. 2. ORTEP plot of structure benzylCo(dmgH)(dpgH)Py (**1b**).

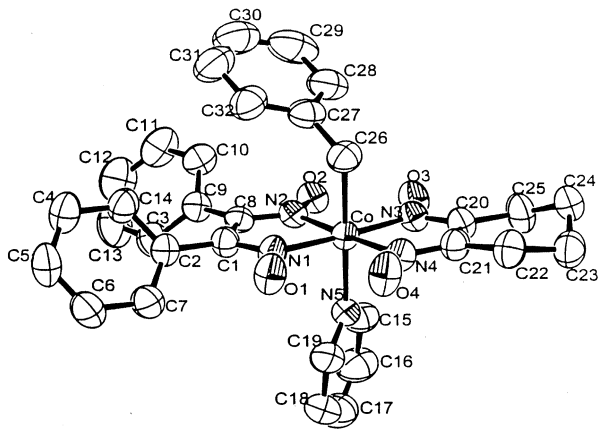


Fig. 3. ORTEP plot of structure benzylCo(chgH)(dpgH)Py (**8b**).

rigid groups (C–C = 1.395). The N_1–N_2 and N_3–N_4 equatorial bond distances are shorter than the N_2–N_3 and N_1–N_4 bonds. This allows the location of the oxime bridge hydrogen. The butterfly bending angle[5] (α) for **1b** is higher (4.90°) than in **8b** (3.8°). The selected bond lengths and bond angles are given in Table 10.

3. Experimental

Chlorocobaloxime, $ClCo^{III}(L)_2Py$ [L = dmgH, dpgH, chgH], were synthesised according to the literature procedure [5b,22,23]. The cobaloxime(I) was generated in situ by the sodium borohydride reduction of chlorocobaloxime under inert conditions at 0°C. Organocobaloximes have been synthesised by the reaction of $Co^{I}(L)_2Py$ with the corresponding benzyl halide under strict anaerobic conditions at 0°C. The general work-up procedure is similar to the organocobaloximes as detailed earlier. It was observed that in certain cases the precipitation of the cobaloxime did not occur on pouring the reaction mixture into water; instead an orange-red emulsion formed. In those cases the emulsion was extracted with dichloromethane, the solvent layer was washed several times with brine, dried over anhydrous sodium sulfate and the volume concentrated to a few ml. The precipitation was then achieved by pouring it dropwise into light petroleum with constant stirring. The solid was filtered and then dried in vacuum.

^1H and ^{13}C spectra were recorded on a JEOL JNM LA 400 PT NMR spectrometer (at 400 MHz for ^1H and at 100 MHz for ^{13}C) in $CHCl_3$-*d* solution with Me_4Si as internal standard. UV–vis spectra were recorded on a Shimadzu 160A spectrometer. The degassed solvent was used for recording spectra as these compounds undergo oxygen insertion very readily. The elemental analysis was carried out at the Regional Sophisticated Instrumentation Center, Lucknow.

3.1. Synthesis of BnCo(dmgH)(dpgH)Py (1b) (method D): general procedure

NaOH (1 pellet dissolved in 1.0 ml water) was added to a suspension of $ClCo^{III}(dmgH)_2Py$ (0.201 g, 0.5 mmol) and $ClCo^{III}(dpgH)_2Py$ (0.326 g, 0.5 mmol) in methanol (10 ml) and the reaction mixture was thoroughly purged with argon for 15 min. The temperature was brought down to 0°C by Julabo refrigerator circulator. The reaction mixture turned deep blue after the addition of $NaBH_4$ (0.048 g, 1.27 mmol, dissolved in 1

Table 10
Selected bond lengths and bond angles

Bond distances and angles	Compound **1b**	Compound **8b**
$Co–C_{24}$	2.045(60	2.063(4) [a]
$C–N_5$	2.086(4)	2.070(3)
$C–N_1$	1,882(4)	1.876(3)
$Co–N_3$	1.885(4)	1.893(3)
$C_1–C_8$	1.471(7)	1.473(4)
$C_{21}–C_{20}$	1.456(10)	1.465(5)
$N_1–O_1$	1.334(6)	1.336(3)
$N_5–Co–C_{24}$	175.56(22)	177.63(15) [a]
$N_1–Co–N_5$	89.83(17)	91.27(13)
$N_2–Co–C_{24}$	88.25(23)	93.65(14) [a]
$N_1–Co–N_2$	81.96(19)	81.91(12)
$O_1–O_4$	2.481(5)	2.496(4)
$O_2–O_3$	2.479(5)	2.488(4)
$N_1–N_2$	2.466(6)	2.457(4)
$N_1–N_4$	2.853(6)	2.867(4)
$N_3–N_4$	2.450(7)	2.457(4)
$N_2–N_3$	2.848(6)	2.859(4)
α [b]	4.9(5)	3.8(3)
τ [c]	80.3(5)	79.0(3)

[a] Corresponds to $Co–C_{26}$ in **8b**.
[b] Butterfly bending angle.
[c] Twist angle of pyridine with respect to the line joining the midpoints of $C_1–C_8$ and $C_{20}–C_{21}$.

[5] For definition and other details see Refs. [1c,6]

ml water). Benzyl chloride (0.189 g, 1.5 mmol) in methanol (5 ml) was added dropwise. The reaction mixture was stirred for 3 h in dark during which the reaction mixture was brought to ambient temperature and then the contents were poured into water. The orange-red solid was filtered, dried and chromatographed on a silica gel column with ethylacetate–chloroform as eluent yielding three cobaloximes **1a** (0.142 g), **1b** (0.145 g) and **1c** (0.063 g). The products **1a** and **1c** were compared with the authentic samples from this laboratory [22].

3.2. Synthesis of BnCo(chgH)(dpgH)Py (**8b**) (method D): general procedure

The same procedure as outlined above for the preparation of BnCo(dmgH))(dpgH)Py was used. The only difference is that now a mixture of $ClCo^{III}(chgH)_2Py$ (0.230 g, 0.5 mmol) and $ClCo^{III}(dpgH)_2Py$ (0.326 g, 0.5 mmol) was used. Three products were formed, which were separated by column chromatography: **8a** (0.280 g), **8b** (0.060 g) and **8c** (0. 120 g).

3.3. Synthesis of BnCo(dmgH)(dpgH)Py/BnCo(chgH)(dpgH)Py from $ClCo^{III}$(dmgH)(dpgH)Py/$ClCo^{III}$(chgH)(dpgH)Py: general procedure

The general procedure and work-up was similar to method D except that $ClCo^{III}$(dmgH)(dpgH)Py or $ClCo^{III}$(chgH)(dpgH)Py was used as the starting material. The yields (after column) of the products (**lb**–**7b**) and (**8b**–**14b**) are in the range 32–51 and 55–80%, respectively.

3.4. Synthesis of $ClCo^{III}$(dmgH)(dpgH)Py (**15b**)

Pyridine (0.79 g, 10 mmol) was added with constant stirring to a refluxing solution of cobalt(II) chloride hexahydrate (1.20 g, 5 mmol), dimethylglyoxime (0.58 g, 5 mmol) and diphenylglyoxime (1.20 g, 5 mmol) in 95% ethanol (25 ml). The solution was allowed to cool to RT and air was bubbled through the reaction mixture for 6 h. The solid residue obtained after the evaporation of the solvent on the rotavap was purified on the column. The residue, dissolved in a minimal amount of chloroform, was loaded on a silica gel column (100–200 mesh) pre-eluted with chloroform. Three distinct bands were visible with 10% ethylacetate. The first band corresponding to the $ClCo^{III}(dpgH)_2Py$ complex (1.02 g) came out completely with 10% ethylacetate in chloroform. The mixed-ligand complex, $ClCo^{III}$(dmgH)(dpgH)Py (1.12 g) came out with 10–50% ethyl acetate–chloroform mixture and finally the $ClCo^{III}(dmgH)_2Py$ complex (0.208 g) came out with 100% ethylacetate mixture. Any deviation in these ratios gives the contaminated products.

Note: the general procedure used for the preparation of $ClCo^{III}(dpgH)_2Py$ does not yield any product.

3.5. Synthesis of $ClCo^{III}$(chgH)(dpgH)Py (**16b**)

This has been synthesised by two methods.

(a) Solid cobalt(II) chloride hexahydrate (2.02 g, 5 mmol) was added to a suspension of diphenylglyoxime (2.02 g, 8.4 mmol) and Nioxime (1.20 g, 8.4 mmol) in acetone (100 ml). The mixture was stirred for 48 h at room temperature (r.t.) during which the reaction mixture gradually changed from deep blue to green. Pyridine (1.58 g, 16.80 mmol) was added dropwise and the solution slowly turned brownish-green. It was stirred for additional 1 h and the solvent was evaporated on the rotavap. The crude product so obtained was separated and purified on the column. The solvent system was similar to as outlined above for $ClCo^{III}$(dmgH)-(dpgH)Py complex. Three products were isolated $ClCo^{III}(dpgH)_2Py$ (0.184 g), $ClCo^{III}$(chgH)(dpgH)Py (1.149 g), $ClCo^{III}(chgH)_2Py$ (0.630 g).

(b) Pyridine (1.58 g, 16.80 mmol) was added with constant stirring to a refluxing solution of cobalt(II) chloride hexahydrate (2.02 g, 5 mmol), Nioxime (1.20 g, 8.4 mmol) and diphenylglyoxime (2.02 g, 8.4 mmol) in 95% ethanol (50 ml). The solution was allowed to cool to r.t. and air was passed through the reaction mixture for 6 h. The crude product obtained after evaporation of the solvent was separated and purified on the column. Three products were isolated $ClCo^{III}(dpgH)_2Py$ (0.740 g), $ClCO^{III}$(chgH)(dpgH)Py (1.782 g), $ClCo^{III}(chgH)_2Py$ (0.275 g).

3.6. Separation of products: column details

The separation of the products has posed a lot of problems. Various adsorbents (silica gel, basic alumina), solvent systems (carbon tetrachloride–ethylacetate, petroleum ether–chloroform–ethylacetate), column dimensions and flash chromatography were tried. The best separation could be achieved by the following procedure.

The orange–red powder containing the mixture of cobaloximes, dissolved in minimum amount of chloroform, was loaded on a silica gel (100–200 mesh) column pre-eluted with chloroform. The polarity was increased carefully with ethylacetate. Three distinct bands were visible with 1% ethylacetate in chloroform. The first band corresponding to the dpgH complex came out completely with 1% ethylacetate. The mixed-ligand complex came out with 1–10% ethyl acetate–chloroform mixture and the dmgH complex finally came out with 50–100% ethylacetate–chloroform mixture. Any deviation in these ratios gives the contaminated products.

3.7. Reaction of $BnCo^{III}(dpgH)_2Py$ with $Co^{I}(dmgH)_2Py$

In this reaction a suspension of $BnCo^{III}(dpgH)_2Py$ (0.350 g, 0.50 mmol in 10 ml methanol) is added to a blue solution of $Co^{I}(dmgH)_2Py$ [generated by the reduction of $ClCo(dmgH)_2Py$, 0.50 mmol in 10 ml methanol] at 0°C under nitrogen atmosphere and the mixture is stirred for 3 h. After the usual work-up, most of the $BnCo^{III}(dpgH)_2Py$ was recovered back (0.195 g). A small amount of **1b** (0.063 g) and **1c** (0.026 g) was formed.

3.8. Reaction of $BnCo^{III}(dmgH)_2Py$ with $Co^{I}(dpgH)_2Py$

The same procedure as stated above was used. Almost all the $BnCo^{III}(dmgH)_2Py$ was consumed and was transformed into **1a** and **lb**.

3.9. Reaction of $BnCo^{III}(dmgH)(dpgH)Py$ with $Co^{I}(dmgH)_2Py$

Cobaloxime(I), $Co^{I}(dmgH)_2Py$, (generated in situ by the alkaline sodium borohydride reduction of chlorocobaloloxime, $ClCo(dmgH)_2Py$, 0.101 g, 0.25 mmol in 10 ml methanol under nitrogen atmosphere at 0°C) was added to a suspension of mixed-ligand complex, $Bnco^{III}(dmgH)$, (dpgH)Py, (0.146 g, 0.25 mmol in 10 ml methanol). The stirring was continued for 3 h during which the reaction mixture was brought to ambient temperature. The product was extracted with chloroform after pouring the reaction mixture into water. After evaporating the solvent on the rotavap, the purification was carried out by column chromatography as described above. Three products were isolated [**1a** (0.016 g); **1b** (0.028 g) and **1c** (0.035 g)] in a molar distribution of 15, 32 and 52%]

3.10. Reaction of $BnCo^{III}(dmgH)(dpgH)Py$ with $Co^{I}(dpgH)_2Py$

The same procedure as outlined above was used except that now $Co^{I}(dpgH)_2Py$, generated in situ from $ClCo(dpgH)_2Py$ (0.163 g in 10 ml methanol), was added instead of $Co^{I}(dmgH)_2Py$. After column purification two products were obtained [**1a** (0.141 g) and **1b** (0.041 g)] in a molar distribution of 74 and 26%, respectively.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 135131 and 149630 for **1b** and **8b**, respectively. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 lEZ, UK (Fax +44-1223-336033; email: deposit@ccdc.com.ac.uk or www:http://www.ccdc.cam.ac.uk)

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