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Journal of Organometallic Chemistry 557 (1998) 243–249

Journal of Organo metallic Chemistry

Pyrazine bridged organodicobaloximes: a convenient one pot synthesis and *cis* influence studies

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Received 9 October 1997

Abstract

Twenty six complexes, pyrazine bridged organodicobaloximes of the type $RCo(L_2)$-pyrazine-$Co(L_2)R$ where R is alkyl group and L is $dmgH^-/dpgH^-$ have been synthesised. It was found that one could synthesise such complexes in one pot directly from the alkyl(aquo)cobaloximes without converting it to the alkylcobaloxime dimer, as reported in the literature. ^{1}H-NMR studies have revealed that the pyrazine ring protons experience considerably more *cis* influence than the H_α protons of the pyridine in simple alkylcobaloximes. This is presumably because the pyrazine ring protons are in close proximity to two metallabicycles while the H_α protons of the simple alkylcobaloximes are influenced by only one metallabicycle. The trends in the Co–C charge transfer transition and N–O, N–O′ frequencies are similar to the alkyl (pyridine) cobaloximes. Low resolution x-ray crystal structure of one of the dicobaloximes, $[EtCo(dpgH)_2]$ μ-Pz indicates that the two subunits of the molecule rotate around the two Co–N single bonds with the result that the two metallabicycles are completely staggered with respect to each other. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Organodicobaloximes; Pyrazine; *cis*-influence

1. Introduction

Numerous fascinating bimetallic complexes have been reported in the literature with a wide variety of bridging ligands after their early recognition that they play an important role in the innersphere electron transfer processes [1]. Of late, their photoinduced electron and energy transfer, optical and thermal back-electron transfer and their versatile redox behaviour are being extensively studied [2]. These simple systems hold the key to the understanding of the electronic interactions in the bigger and more complex supramolecules which have promising applications [2].

On the other hand, the organocobaloximes[1], $RCo(dmgH)_2Py$, the well known Vit. B_{12} coenzyme model compounds [3] serve as templates in many organic reactions [4] and are known to catalyse a wide variety of chemical processes [5]. As small structural changes in the molecule have a profound effect on the cobalt–carbon bond reactivity [6], there has been a continued interest in the synthesis of new organocobaloximes [7]. A few reports of cyano and azido bridged organocobaloximes [8], neutral cyano, thiocyanato bridged and anionic selenocyanato-bridged cobaloximes [9], cobaloxime–chromium complex bridged bimetallic systems [10], polymeric pyrazine bridged inorganic cobaloximes with dpgH/dmgH ligands [11], and doubly alkylated binuclear cobalt complexes with bridging carbonyls [12] have appeared in the literature. A large number of organo(alkyl)bridged dicobaloximes, $PyCo(L_2)$-$(CH_2)_n$-$Co(L_2)Py$, have been reported by us [13].

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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

PII S0022-328X(97)00777-8

We have recently published [14] a detailed account of our investigations on the *cis* influence in simple monooganocobaloximes. We were able to arrange the equatorial ligands in order of their *cis* influencing ability as dpgH > chgH > dmgH. In order to test the generality of our findings in the related systems we wish to report our studies on the ligand bridged organocobaloximes of the type, $[RCo(L)_2]_2$-μ-Pz, where R is alkyl L is dmgH and dpgH. These are the ideal systems for studying the *cis* influence as they have two metallabicycle with their electronic and anisotropic effects [15] in close proximity to each other. The literature survey reveals that Herlinger and Ramakrishna [16] have reported the synthesis of two such complexes, $[RCo(dmgH)_2]_2$-μ Pz where R = Me and CH_2Cl but there is no report on the corresponding dpgH complexes. Besides we find that Herlinger's method is too tedious and lengthy.

In this paper we report a very simple and general one pot synthesis of the ligand bridged dicobaloximes of the type, $[RCo(L)_2]_2$-μ Pz and the *cis* influence studies on these systems by NMR and UV–vis. Low resolution x-ray crystal structure of one of the dicobaloximes, $[EtCo(dpgH)_2]$ μ-Pz is also reported.

2. Results and discussion

2.1. Synthesis

In the process of the synthesis of these complexes following Brown's procedures [17], we found that their dehydrating step (heating the aquo complex in an vacuum oven at a temp > 100°C for 6 h, or azeotropic distillation of benzene suspensions for several hours) was both time consuming and tedious [18,19]. We could prepare the pyrazine bridged complex directly from the aquo complex, $RCo(L)_2H_2O$ simply by reacting it with slightly less than stoichiometric quantity of pyrazine in a suitable solvent.

$$2RCo(L)_2H_2O + Pz$$

$$\rightarrow RCo(L)_2 - Pz - Co(L)_2R + 2H_2O$$

R = Me, Et, Pr, ^{n}Bu, Pent, Hex, Hept, Oct, Non, Dec, ^{iso}Pr, ^{sec}But; L = dmgH, dpgH.

The use of excess pyrazine always lead to the formation of the monomer. The procedure was found to be quite general and was applicable to a wide variety of both primary and sec alkylcobaloximes having dmgH and dpgH as the equatorial ligands. The Herlinger's method, on the other hand, reports only two pyrazine bridged cobaloximes with dmgH as the equatorial ligands. Yields of 60–70% were obtained in all cases and all the complexes gave satisfactory elemental analyses.

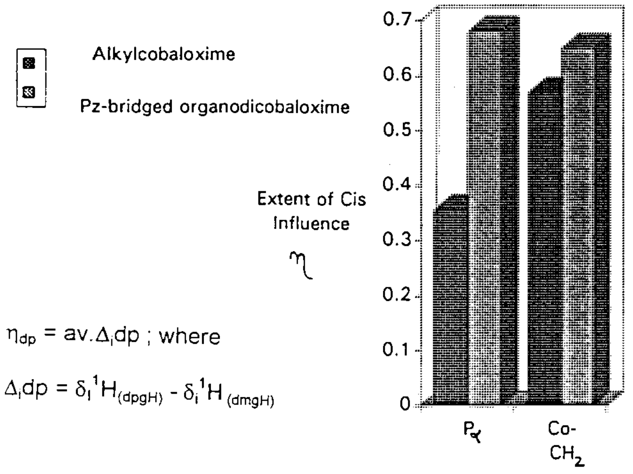
2.2. ^{1}H-NMR

The ^{1}H-NMR spectral data of the pyrazine bridged alkyl complexes **1**–**13a**,**b** are tabulated in Table 1. The species exists as six co-ordinated ligand bridged cobaloximes in $CDCl_3$ (the solvent used for NMR studies), as the cobalt bound methylene as well as the dmgH-Me/dpgH-Ph proton resonances did not shift even on addition of a large excess of pyrazine directly to the NMR sample.

The ^{1}H-NMR spectra of the alkyl series show the following general features,

1. Singlet/multiplet resonance due the eight equivalent methyl/phenyl groups,
2. Singlet, triplet or a quartet due to the cobalt bound methyl/methylene groups,
3. Multiplet due the rest alkyl chain and
4. Singlet due to the bridged pyrazine ring protons.

The pyrazine ring proton and cobalt bound methyl/methylene resonances all occur consistently down field in the dpgH complexes as compared to the analogous dmgH ones (*cis* influence). The *cis* influence on the pyrazine ring protons is comparable in magnitude to that on the cobalt bound methyl/methylene protons



This is in contrast to the simple alkyl(pyridine) cobaloximes where the pyridine H_α protons experience considerably less *cis* influence than the cobalt bound methylene protons [14].

The factors contributing to the *cis* influence detectable by ^{1}H-NMR are essentially the same as described for the simple alkyl cobaloximes, i.e. (a) changes in the anisotropy of the cobalt atom, (b) changes in the anisotropy brought about by the changes in the ring current in the metallabicycle, (c) the anisotropy of the C=N bonds and (d) anisotropy of the dpgH-Ph rings. In addition, in the pyrazine bridged dicobaloximes one should, in principle, expect anisotropic effects due to changes in the ring current of the bridging pyrazine ring. It can safely be assumed that any changes in the anisotropy of the pyrazine ring

Table 1
^{1}H-NMR of ligand bridged alkyl cobaloximes **1**–**13a**,**b** (δ ppm)

Compound No.	H–O–H (s)	Pz (s)	L (s/m)	Co-(CH$_n$) (t)	Rest alkyl chain (m)
1a	18.08	8.37	2.18	0.82(s)	—
1b	18.75	9.15	7.25	1.56(s)	—
2a	18.03	8.37	2.13	—[a]	—[a]
2b	18.71	9.15	7.24	2.53(q)	0.78(t)
3a	18.03	8.43	2.12	1.75	0.68–1.00
3b	18.46	9.00	7.23	2.34	0.62–1.25
4a	18.02	8.40	2.13	1.81	0.35–1.40
4b	18.50	9.03	7.24	2.34	0.62–1.40
5a	18.24	8.40	2.14	1.76	0.31–1.37
5b	18.53	9.00	7.25	2.37	0.62–1.56
6a	18.56	8.42	2.11	1.67	0.37–1.40
6b	18.65	9.09	7.24	2.37	0.65–1.37
7a	18.13	8.39	2.13	1.73	0.36–1.37
7b	18.65	9.09	7.23	2.37	0.68–1.75
8a	18.15	8.42	2.12	1.73	0.46–1.34
8b	18.68	9.09	7.23	2.34	0.65–1.78
9a	18.13	8.34	2.13	1.65	0.62–1.40
9b	18.65	9.09	7.24	2.37	0.34–1.56
10a	18.31	8.35	2.11	1.73	0.53–1.43
10b	18.65	9.09	7.23	2.37	0.62–1.37
11a	18.13	8.44	2.13	—[a]	0.46(d)
11b	18.56	9.09	7.24	2.78(m)	1.03(d)
12a	18.36	8.37	2.11	1.71[a]	0.56–1.09
12b	18.68	9.12	7.24	2.40(d)	0.62–1.25
13a	—	8.42	2.12	1.71[a]	0.56–1.37
13b	18.53	9.06	2.43	2.43	0.9–1.87

(s), singlet; (d), doublet; (t), triplet; (m), multiplet, (q), quartet.

[a] Resonance merged or integrate together.

would not effect the cobalt bound methyl/methylene resonances significantly as these are far removed from the paramagnetic effects originating from the pyrazine ring.

Without a rigorous theoretical treatment it is difficult to determine the relative contribution of each of the above five factors to the overall *cis* influence detectable by ^{1}H-NMR. Qualitatively speaking, the reason for comparable *cis* influence on the H$_\alpha$ and the cobalt bound methylene protons in the bridged cobaloximes is that while two metallabicycles influence the H$_\alpha$ protons, the cobalt bound methylene protons are influenced by only one metallabicycle. With the result there is a substantial increase of the *cis* influence on the H$_\alpha$ protons in the bridged complex as compared to the H$_\alpha$ in the simple alkylcobaloximes [14].

2.3. UV–vis spectra

The $\lambda_{\max}$ values of the complexes **1**–**13a**,**b** in methanol (the Co–C CT band) are tabulated in Table 2. Our studies show that the pyrazine bridged cobaloximes show similar UV–vis behaviour as the alkyl(pyridine)cobaloximes [14]. That the compounds exist largely as solvated penta co-ordinated species was inferred on the basis of the spectral changes noticed in the Co–C CT band. It was observed on adding increasing quantities of pyrazine to a solution of the ligand bridged complex in methanol that the Co–C CT band changes shape from hump like to shoulder (saturation curve Fig. 1a). Similar changes were observed by

Table 2
$\lambda_{\max}$ (nm) of cobaloximes **1**–**13a**,**b** and their log ϵ values of the Co–C CT band in methanol

Compound Nos.	L = dmgH (**a**)		dpgH (**b**)	
	$\lambda_{\max}$ (nm)	log ϵ	$\lambda_{\max}$ (nm)	log ϵ[a]
1	444.2	—	454.1	—
2	454.3	3.49	466.9	—
3	454.2	3.48	465.7	—
4	455.0	3.49	466.9	—
5	454.3	3.46	467.3	—
6	455.0	3.49	467.6	—
7	454.1	3.50	467.4	—
8	455.3	3.51	467.1	—
9	454.3	3.47	467.2	—
10	455.2	3.51	467.2	—
11	466.8	3.38	479.3	—
12	458.1	3.42	469.1	—
13	454.3	3.45	467.5	—

[a] ϵ values could not be determined because of poor solubility in methanol.

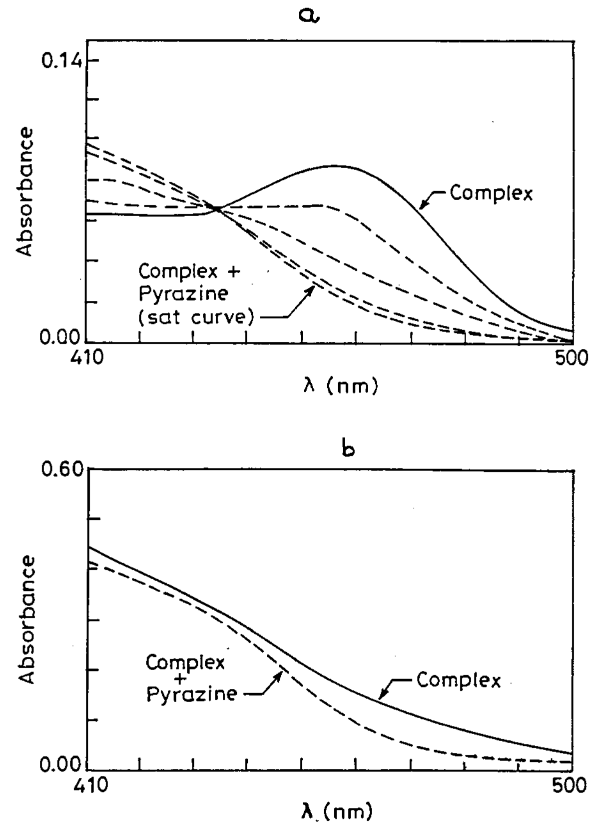


Fig. 1. Qualitative changes observed in the Co–C band of $[MeCo(dpgH)_2]$-μ-Pz on adding increasing quantities of pyrazine to a solution of $[MeCo(dpgH)_2]$-μ-Pz in: (a) methanol, (b) chloroform.

Table 3
Selected IR frequencies of cobaloximes (**1**–**13a**,**b**) (ν cm^{-1})

Compound No.	ν(C=N)	ν(N–O)	ν(N–O′)
1a	1553	1093	973
1b	1522	1078	923
2a	1547	1090	970
2b	1520	1077	920
3a	1550	1090	970
3b	1522	1074	922
4a	1543	1090	970
4b	1530	1075	925
5a	1555	1093	970
5b	1530	1074	925
6a	1543	1093	972
6b	1520	1079	925
7a	1554	1095	973
7b	1530	1077	923
8a	1552	1095	973
8b	1529	1076	923
9a	1549	1094	970
9b	1520	1079	922
10a	1555	1096	972
10b	1527	1076	925
11a	1550	1095	973
11b	1530	1077	925
12a	1548	1094	972
12b	1523	1076	924
13a	1550	1087	970
13b	1525	1078	920

Brown et al. [19] for simple alkylcobaloximes in aqueous solutions. It is obvious that the shape of the saturation curve (Fig. 1a) is similar to the one in chloroform (Fig. 1b). Furthermore the band in chloroform does not change in shape significantly on the addition of a large excess of pyrazine. This clearly shows that the species exists largely as a dimer in chloroform. Similar conclusions were drawn from the ^{1}H-NMR studies (discussed above). However, whether the species dissociates completely or partially cannot be ascertained.

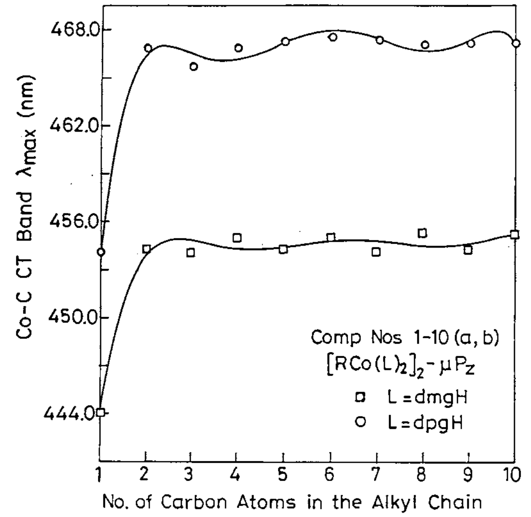


Fig. 2. Variation of Co–C CT band with increasing alkyl chain length.

$$[RCo(L)_2]_2 - \mu Pz \Leftrightarrow RCo(L)_2 - Pz + RCo(L)_2 \text{ (solvated)}$$

$$RCo(L)_2 - Pz \Leftrightarrow RCo(L)_2 \text{ (solvated)} + Pz$$

or

$$[RCo(L)_2]_2 - \mu Pz \Leftrightarrow 2RCo(L)_2 \text{ (solvated)} + Pz$$

The trends in the λ_{max} values (outlined below), are similar to that of the alkylcobaloximes [14]. See Table 2 for the following observations.

1. When R = methyl, the λ_{max} values are considerably lower than the rest of the series.
2. The sec cobaloximes have considerably higher λ_{max} values than the corresponding primary cobaloximes. This difference is much larger in the isopropyl cobaloximes (12–14 nm) (compare **11a**,**b** and **3a**,**b**) than in the sec butyl cobaloximes (2–3 nm) (compare **12a**,**b** and **4a**,**b**).

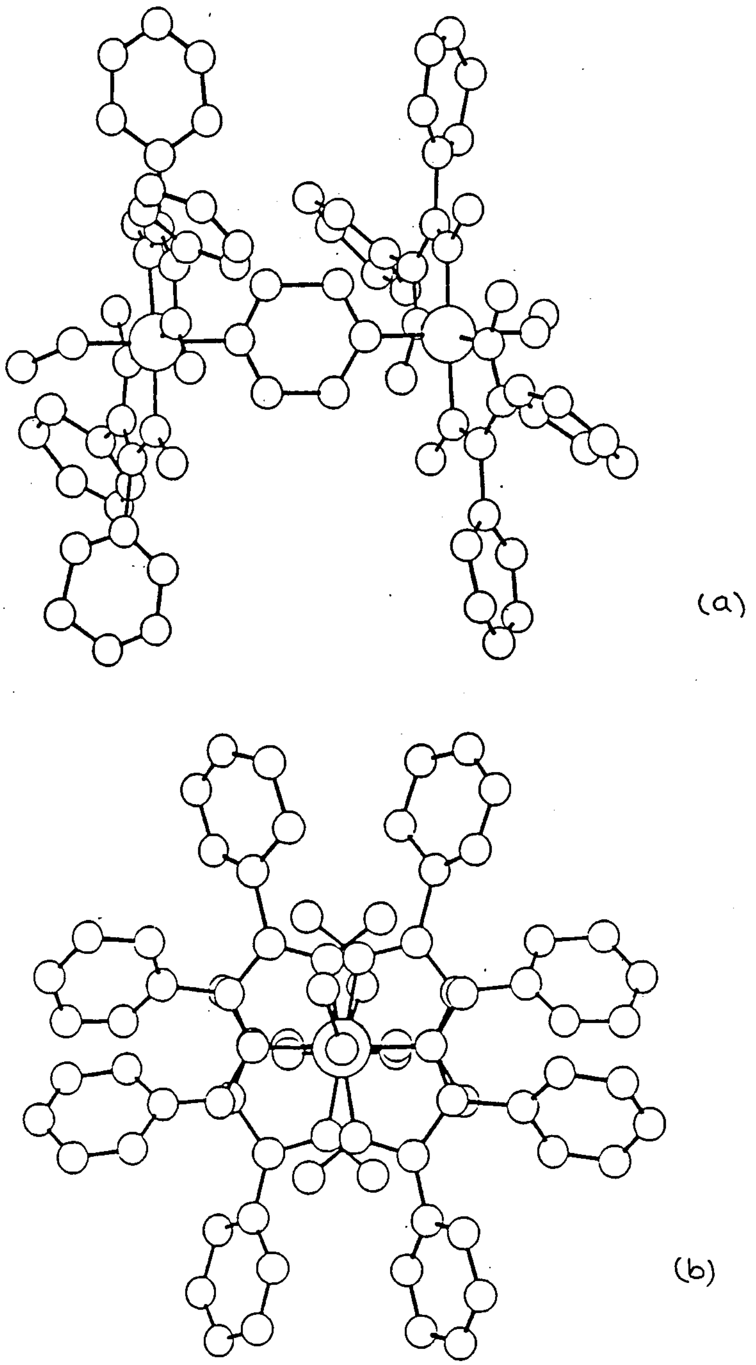


Fig. 3. The PLUTO plot showing the crystal structure of [EtCo(dpgH)$_2$]$_2$-μ-Pz: (a) as viewed perpendicular to the Co–NC$_4$N–Co axis. (b) as viewed long the Co–NC$_4$N–Co axis.

3. Branching in the alkyl chain on a carbon not directly attached to the cobalt atom has no significant effect on the λ_{max} of the Co–C CT band (compare **13a**,**b** and **5a**,**b**).
4. The similarity of the subtle variations of λ_{max} with the alkyl chain length for the two series of cobaloximes stand out clearly from the similar shapes of the best fit lines (polynomials of the order six) (Fig. 2).

2.4. IR spectra

The IR data for the two series of complexes is tabulated in Table 3. The order of the C=N, N–O and

N–O′ stretching frequencies is found to dmgH > dpgH and it is same as that of the alkyl cobaloximes [14].

2.5. Crystal structure

We could at best obtain poor quality crystals for $[EtCo(dpgH)_2]_2$-μ-Pz from acetone which could only be isotropically refined to a *r* factor of 0.15. The PLUTO plot Fig. 3a, shows that the two $EtCo(dpgH)_2$ moieties are co-ordinated to the either ends of the pyrazine molecule and confirms our synthesis. When viewed along the Co–NC_4N–Co axis (Fig. 3b), the 'staggered' conformation of the metallabicycles becomes distinct. In contrast, the metallabicycles in the crystal structure of the polymeric 19-electron cobalt(II) complex $[Co(dmgH)_2(\mu\text{-Pz})]_\infty$ are eclipsed [11]a. Apparently, the staggered conformation in the dpgH complex allows it to accommodate the more sterically demanding phenyl groups.

It is of interest to note that the iodo cobalt (II) complex of corbyrinic acid-hepta methylester exists as a dimer with the two molecules linked face to face by the iodide [20]. The axial Co–C and the Co–$N_{(pz)}$ bond distances are 2.05(5) and 2.02(4) Å respectively. The equatorial Co–$N_{(C=N)}$ and the O–$N_{(C=N)}$ distances are 1.90(4) and 1.35(6) Å, while in the pyrazine moiety the C=N and the C=C bonds are 1.33(9) and 1.64(11) Å respectively. Though the bond distances are typical of organocobaloximes, the high r factor limits our comments on comparison with the known dpgH-organocobaloxime crystal structures in the literature.

3. Experimental

The alkyl(aquo)cobaloximes were prepared according to published procedure [18,21,22]. All synthesis/manipulations of cobaloximes have been carried out in subdued light under a blanket of argon or nitrogen. UV–vis spectra were recorded on a Shimadzu 160-A Spectrophotometer in methanol. ^{1}H-NMR were recorded on a Bruker WP-80 FT NMR Spectrometer in $CDCl_3$ using TMS as internal reference at ambient temperature. IR was recorded on a Perkin Elmer 1320 IR Spectrometer as nujol mulls calibrated with polystyrene. Elemental analysis were carried out at the Regional Sophisticated Instrumentation Centre, (RSIC) Lucknow.

X-ray studies were done on Enraf Nonius CAD-4 diffractometer at Fateyeville, AK, USA.

3.1. General procedure for the synthesis of $[RCo(dpgH)_2]_2$-μ-Pz

Typically, pyrazine (0.02 gm, 0.26 mmol) in acetone (1 ml) was added dropwise, to a solution of the ethyl(aquo)cobaloxime, $EtCo(dpgH)_2H_2O$ (0.34 gm, 0.58 mmol) in acetone (3 ml). The reaction mixture was stirred in diffused light under a blanket of argon (to prevent the cleavage of the Co–C bond). The reaction was checked for completion with TLC on silica gel using EtOAc:CCl_4, in 1:9 ratio. Visibly, the wine-red reaction mixture turned orange within minutes and the orange-yellow precipitates which formed were filtered, washed with acetone (2 × 2 ml) and dried in vacuo over P_2O_5. Yields 60–70%.

3.2. General procedure for the synthesis of $[RCo(dmgH)_2]_2$-μ-Pz

The same procedure as described in 3.1 was followed except that the alkyl(aquo)cobaloxime was dissolved in methanol rather than in acetone and the progress of the reaction was monitored with TLC using EtOAc. Yields 60–67%.

All the complexes were characterised by elemental analysis, ^{1}H-NMR, UV–vis and IR spectroscopy (see Tables 1–3). The details of the elemental analysis data are available on request from the authors.

Acknowledgements

This work is supported by grant in aid from the CSIR, New Delhi and KQ is grateful to the Department of Atomic Energy, Bombay for the K.S. Krishnan Fellowship. Thanks are due to Prof. Wally Cordes, University of Arkansas for x-ray analysis. The authors thank the RSIC, Lucknow for the elemental analysis.

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