

Pyrazine bridged benzyl dicobaloximes: Competition between π -interaction and steric crowding in crystal structure

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Dedicated to Prof. S.S. Krishnamurthy, IPC, IISC Bangalore, India

Abstract

Pyrazine (Pz) bridged benzyl dicobaloximes $[\text{ArCH}_2\text{Co}(\text{dioxime})_2]_2\text{-}\mu\text{-Pz}$ [dioxime = dmgH, dpqH] have been synthesized and characterized with ^1H and ^{13}C NMR. The complexes have been synthesized by a simple procedure in one-pot directly from the corresponding benzyl aqua cobaloxime. In the crystal structure of $[\text{PhCH}_2\text{Co}(\text{dpqH})_2]_2\text{-}\mu\text{-Pz}$, two cobaloxime units are in eclipsed form whereas they were completely staggered in the reported $[\text{EtCo}(\text{dpqH})_2]_2\text{-}\mu\text{-Pz}$. This is due to the π - π interaction between the axial benzyl group and phenyl ring of the equatorial dpqH group. Both *cis* and *trans* isomer crystallized together in the crystal structure of $[\text{PhCH}_2\text{Co}(\text{dpqH})(\text{dmgH})]_2\text{-}\mu\text{-Pz}$. The cyclic voltammetry study in $[\text{PhCH}_2\text{Co}(\text{dioxime})_2]_2\text{-}\mu\text{-Pz}$ [dioxime = dmgH, dpqH] shows two cobalt center mixed together due to electron delocalization through pyrazine and behaves like a monocobaloxime and the reduction potentials are much higher than the monocobaloximes.

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1. Introduction

There has been an enormous study on the mononuclear transition metal complexes in view of their interesting electrochemical, photophysical and photochemical studies [1]. The situation becomes more interesting in the binuclear complexes because one can study properties of the whole molecule in addition to the properties related to each metal. A suitable choice of the mononuclear building block, the bridging ligand and an appropriate design of the structure of the binuclear complex can in fact allow the elucidation of the structural properties of the complex [2]. Therefore numerous bimetallic complexes have been reported in the literature. Ligand

bridged complexes are of particular interest in view of their role as reaction intermediates in inner sphere electron transfer processes [3].

Organocobaloximes have been extensively studied in the last four decades but the reports on the organo or ligand bridged dicobaloximes are limited [4,5]. Johnson et al. [6] were the first to report the bridged anionic complexes of organocobaloximes. Since then the synthesis of neutral cyano, thiocyanato and selenocyanato bridged cobaloximes [7], cyano bridged anionic and cationic di and tri-nuclear cobaloximes [8], cobaloxime-chromium bridged bimetallic systems [9], polymeric pyrazine bridged inorganic cobaloximes [10], doubly alkylated binuclear cobalt complexes with bridging carbonyl [11] and self-assembly in cobaloximes [12] have appeared in the literature. Herlinger et al have reported the synthesis of $[\text{RCo}(\text{dmgH})_2]_2\text{-}\mu\text{-Pz}$ and $[\text{RCo}(\text{dmgH})_2]_2\text{-}\mu\text{-4,4'}$ -bipyridyl $[\text{R}=\text{Me}, \text{CH}_2\text{Cl}]$ by a very tedious procedure [13].

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We have recently reported the synthesis and *cis* influence studies in pyrazine bridged alkyl dicobaloximes [5]. We could not make an extensive structural study on these complexes since we could not get a good quality crystal structure. However, the preliminary data in [Et-Co(dpgH)₂]₂- μ -Pz showed that the two cobaloxime units were in staggered conformation, thus allowing it to accommodate the sterically demanding phenyl groups. This prompted us to undertake the present study on the pyrazine bridged benzyl dicobaloximes, [ArCH₂Co(dioxime)₂]₂- μ -Pz [dioxime = dmgH, dpgH]. The synthesis of benzyl derivatives is more challenging as compared to alkyl as these are much more unstable in solution than the corresponding alkyl analogues. Since the benzyl group can have π - π interaction with the equatorial dpgH group, its solid-state structure might not be staggered as found in the alkyl case. Also the orientation of two benzyl groups can adopt either *cis* or *trans* form.

The benzyl group has been seen to orient over the dpgH group in the recently reported X-ray structure of PhCH₂Co(dioxime)(dpgH)Py complexes [dioxime = gH, dmgH, chgH] [14]. Keeping this in view, we have also synthesized [PhCH₂Co(dpgH)(dmgH)]₂- μ -Pz and reported its X-ray structure. The crystal structure reveals interesting and useful information on the competition between π -interaction and steric crowding by the dpgH groups.

2. Experimental

Silica gel (100–200 mesh) and distilled solvents were used in all chromatographic separations. ClCo(dioxime)₂Py, RC₆H₄CH₂Co(dioxime)₂Py [dioxime = dmgH, dpgH; R=H, 4-Cl, 4-CN, 4-OMe, 3-OMe] [15] and PhCH₂Co(dmgH)(dpgH)Py were synthesized by the literature procedure [14a]. The synthesis work was carried out in subdued light and under a blanket of argon or nitrogen.

¹H and ¹³C spectra were recorded on a JEOL JNM LA 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. UV–Vis spectra (methanol) were recorded on a Shimadzu 160 A spectrometer. Elemental analysis was carried out at the Regional Sophisticated Instrumentation Center, Lucknow. 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 workstation with platinum working electrode, Ag/AgCl reference electrode (3 M KCl), and a platinum wire counter electrode. All the measurements were performed in 0.1 M ⁿBu₄NPF₆ in CH₂Cl₂ (dry), at a concentration of 1 mM of each complex. In addition, in a separate series of experiments, an internal reference system (ferrocene/ferrocenium ion) was used. Under the conditions

used, the reversible Fc/Fc⁺ potential occurred at 0.51 V vs. Ag/AgCl electrode.

3. X-ray structural determination and refinement

Orange crystals were obtained by slow evaporation of the solution of **6** in CH₂Cl₂, methanol and *n*-hexane (for **11** CHCl₃, methanol and *n*-hexane) mixture. Single-crystal X-ray data were collected at 100 K on a “Bruker SMART APEX CCD” diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The linear absorption coefficients, scattering factors for the atoms and the anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* [16a]. The data integration and reduction were processed with SAINT [17] software. An empirical absorption correction was applied to the collected reflections with SADABS [18] using XPREP [19]. The structure was solved by the direct method using SIR-97 [20] and was refined on *F* [2] by the full-matrix least-squares technique using the SHELXL-97 [16b] program package. All non-hydrogen atoms were refined anisotropically in both the structure. One benzene ring of the axial benzyl group in **11** (*cis*-form) has disorder of 52:48 occupancies. The hydrogen atoms of the OH group of oxime were located on difference maps and were constrained to those difference map positions. The hydrogen atom positions or thermal parameters were not refined but were included in the structure factor calculations. The pertinent crystal data and refinement parameters are compiled in Table 1.

3.1. Benzyl-aqua cobaloximes: general procedure

The benzyl (aqua) cobaloximes were prepared from the corresponding benzyl (pyridine) cobaloxime complexes using Dowex 50WX8-100 ion-exchange resin (H⁺ form) in methanol in 78–85% yield according to the literature procedure [21]. In the case of dpgH complexes, the solvent used was 1:1 methanol and acetone and during its preparation we observed that a small amount of white substance was also formed. This was sparingly soluble in methanol and the extent of its formation depended upon the quantity of the Dowex used in the reaction. No attempt was made to characterize this compound.

3.2. PhCH₂Co(dmgH)(dpgH)(H₂O)

PhCH₂Co(dmgH)(dpgH)Py (0.150 g, 0.260 mmol) and Dowex 50WX8-100 ion-exchange resin (0.200 g) were mixed together with stirring in 60 ml acetone:methanol (1:1 mixture). 15 ml water was added and the stirring was continued for 17 h at ambient temperature during which the colour changed from light to dark

Table 1
Crystal data and structure refinement details for **6** and **11**

	[PhCH ₂ Co(dpgH) ₂] ₂ Pz · 2CH ₂ Cl ₂	[PhCH ₂ Co(dmgH)(dpgH) ₂ Pz · 0.5CHCl ₃
Empirical formula	C ₇₆ H ₆₆ Cl ₄ N ₁₀ O ₈ Co ₂	C ₁₀₉ H ₁₀₉ Cl ₃ N ₂₀ O ₁₆ Co ₄
Formula weight	1507.04	2297.23
Temperature (K)	100(2)	100(2)
Radiation λ (Å)	Mo Kα 0.071073	Mo Kα 0.071073
Diffractometer	CCD area detector	CCD area detector
Crystal system	Monoclinic	Triclinic
Space group	P2 ₁ /c	P $\bar{1}$
<i>Unit cell dimension</i>		
<i>a</i> (Å)	8.186(7)	13.954(14)
<i>b</i> (Å)	15.994(15)	18.373(18)
<i>c</i> (Å)	25.297(2)	27.777(3)
α (°)	90	86.533(2)
β (°)	90.536(2)	75.728(2)
γ (°)	90	70.353(2)
<i>V</i> (Å ³)	3312(4)	6498(9)
<i>Z</i>	2	2
ρ _{calc} (Mg/m ³)	1.511	1.174
μ (mm ⁻¹)	0.731	0.625
<i>F</i> (000)	1556	2380
Crystal size (mm ³)	0.28 × 0.21 × 0.18	0.40 × 0.24 × 0.22
Index ranges	-10 ≤ <i>h</i> ≤ 10, -21 ≤ <i>k</i> ≤ 21, -15 ≤ <i>l</i> ≤ 33	-16 ≤ <i>h</i> ≤ 18, -24 ≤ <i>k</i> ≤ 22, -36 ≤ <i>l</i> ≤ 37
No. of reflections collected	21981	43245
No. of independent reflections	8175	30794
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
GOF on <i>F</i> ²	1.054	0.906
Final <i>R</i> indices (<i>I</i> > 2σ <i>I</i>)	<i>R</i> ₁ = 0.0773 <i>wR</i> ₂ = 0.1718	<i>R</i> ₁ = 0.0784 <i>wR</i> ₂ = 0.1804
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1271 <i>wR</i> ₂ = 0.1938	<i>R</i> ₁ = 0.1680 <i>wR</i> ₂ = 0.2049
Data/restraints/param.	8175/0/451	30794/220/1432

orange. After completion of reaction Dowex was filtered off and the volume was reduced to 5–10 ml using rotary-vacuum evaporator. The solution containing solid precipitates was kept for 1 h in the refrigerator for complete precipitation. The compound was pure enough to proceed to the next step. Yield (0.130 g) 92%.

3.3. [ArCH₂Co(dmgH)₂]₂-μ-Pz (**1–5**): general procedure

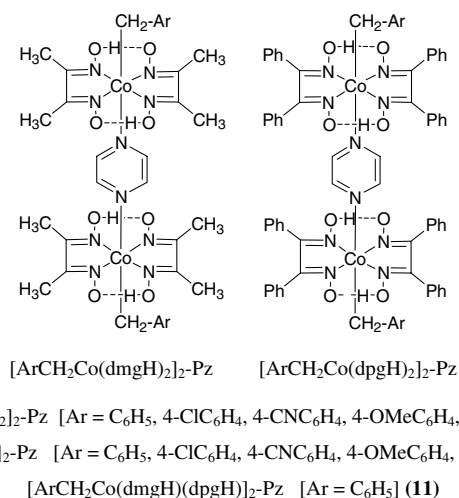
Pyrazine (0.08 g, 1 mmol) in methanol (2 ml) was added drop wise to a nitrogen flushed solution of benzyl (aqua) cobaloxime, PhCH₂(dmgH)₂(H₂O) (0.800 g, 2.00 mmol) in methanol (9 ml). The colour changed from wine-red to orange within minutes and the orange-yellow precipitates were formed. The reaction mixture was stirred in diffused light under nitrogen atmosphere. The completion of the reaction was checked with TLC on silica gel using CH₂Cl₂:ethyl acetate (1:9). The precipitates were filtered, washed with methanol (2 × 2 ml) and then with diethyl ether (2 ml) and dried over P₂O₅ under vacuum. Yield (0.684 g) 86%.

3.4. [ArCH₂Co(dpgH)₂]₂-μ-Pz (**6–10**): general procedure

The same procedure as described above for (**1–5**) was followed except that acetone was used as solvent instead of methanol. The progress of the reaction was monitored with TLC using CHCl₃:ethyl acetate (9:1). Yield 60–70%. The yield of the product is much less (30%) when methanol is used as solvent.

3.5. [PhCH₂Co(dmgH)(dpgH)₂]-μ-Pz (**11**)

Pyrazine (0.008 g, 0.100 mmol in 1 ml acetone) was added to a solution of PhCH₂Co(dmgH)(dpgH)(H₂O) (0.105 g, 0.200 mmol in 4 ml acetone:methanol, 1:1 mixture) and the solution was stirred for 2 h. The progress of the reaction was checked with TLC using CH₂Cl₂. No precipitate was formed during this time. The solution was concentrated to about 2 ml by evaporation of the solvent and 5 ml of diethyl ether was added. Orange precipitates thus obtained were filtered, washed twice with 2 ml diethyl ether and dried over P₂O₅ in vacuum. Yield (0.150 g) 70% (see Scheme 1, Table 2).



Scheme 1. Cobaloximes.

Table 2
Elemental analysis data for **1–11**

No.	Formula	C found (calculated)	H found (calculated)	N found (calculated)
1	C ₃₄ H ₄₆ Co ₂ N ₁₀ O ₈	48.58 (48.54)	5.52 (5.49)	16.66 (16.64)
2	C ₃₄ H ₄₄ Cl ₂ Co ₂ N ₁₀ O ₈	44.92 (44.86)	4.88 (4.89)	15.40 (15.37)
3	C ₃₆ H ₄₄ Co ₂ N ₁₂ O ₈	48.55 (48.58)	4.98 (4.98)	18.87 (18.85)
4	C ₃₆ H ₅₀ Co ₂ N ₁₀ O ₁₀	48.02 (47.95)	5.60 (5.67)	15.55 (15.57)
5	C ₃₆ H ₅₀ Co ₂ N ₁₀ O ₁₀	48.00 (48.01)	5.60 (5.62)	15.55 (15.52)
6	C ₇₄ H ₆₂ Co ₂ N ₁₀ O ₈	66.49 (66.41)	4.65 (4.70)	10.47 (10.46)
7	C ₇₄ H ₆₀ Cl ₂ Co ₂ N ₁₀ O ₈	63.21 (63.19)	4.30 (4.26)	9.96 (9.91)
8	C ₇₆ H ₆₀ Co ₂ N ₁₂ O ₈	65.80 (65.80)	4.35 (4.38)	12.12 (12.06)
9	C ₇₆ H ₆₆ Co ₂ N ₁₀ O ₁₀	65.33 (65.36)	4.76 (4.71)	10.02 (10.00)
10	C ₇₆ H ₆₆ Co ₂ N ₁₀ O ₁₀	65.33 (65.34)	4.76 (4.70)	10.02 (10.00)
11	C ₅₄ H ₅₄ Co ₂ N ₁₀ O ₈	59.56 (59.49)	5.00 (4.95)	12.86 (12.90)

4. Results and discussion

Synthesis: The literature survey shows that Herlingler et al. [13] were the first to report the synthesis of two complexes of pyrazine bridged dicobaloximes with dmgh as the equatorial ligand. We found their dehydration step (heating the aqua complex in vacuum oven at a temperature >100 °C for 6 h or the azeotropic distillation of benzene suspension for several hours) too tedious and time consuming. We have prepared the complexes in a one-pot by a simple procedure in which the aqua complex was reacted with slightly less than half the stoichiometric amount of pyrazine in a suitable solvent. The same product forms even if we use excess pyrazine in the reaction with dmgh complexes. However in the dpgH case, the use of excess pyrazine led to the formation of some impurity that was difficult to remove even by column chromatography.

Solubility: The orange solid compounds are soluble in solvents like CH₂Cl₂, CHCl₃, but are sparingly soluble in methanol, ethanol, acetonitrile, tetrahydrofuran, ethyl acetate, toluene and ether.

4.1. Spectroscopy

The ¹H and ¹³C NMR spectral data for **1–10** have been tabulated in Tables 3 and 4. The ¹H NMR spectra of these complexes are easily assigned based on the chemical shifts. The signals are assigned according to their relative intensities and are consistent with the literature values on the related pyrazine bridged alkyl cobaloximes reported from our group [5]. All the complexes exist as six coordinate in CDCl₃, (the solvent used for NMR study) since the cobalt bound CH₂ and dmgh/dpgH resonance did not shift on the addition of pyrazine to the NMR sample. Also, in the UV–Vis spectra in CHCl₃, the shape and the λ_{max} value did not change with the addition of pyrazine to the complexes. This is similar to the observation made earlier in pyrazine bridged alkyl dicobaloximes [5].

4.1.1. ¹H NMR

All the four protons in the unligated pyrazine are equivalent and appear as a singlet at 8.59 ppm. The resonance shifts upfield on coordination to cobalt by

Table 3
¹H NMR data for 1–9 in CDCl₃

No.	O–H···O	Pz (s)	dmgH(s)/dpgH	Co–CH ₂ (s)	Aromatic	OMe	Yield (%)
1	18.07	8.35	1.99	2.97	6.95(d), 7.02(t), 7.18(t)	–	86
2	18.05	8.34	2.01	2.88	6.88(d), 6.98(d)	–	63
3	18.05	8.31	2.03	2.83	7.00(d) 7.28(d)	–	94
4	18.13	8.36	1.99	2.98	6.59(d), 6.90(d)	3.72	65
5	18.12	8.36	2.00	2.94	6.55(s), 6.58(d), 6.74(d), 6.91(d)	3.76	97
6	18.62	8.99	6.87(d), 7.08(t), 7.22(t)	3.56	7.13(d), 7.26(t), 7.31(t)	–	70
7	18.59	8.97	6.87(d), 7.10(t), 7.24(t)	3.47	6.95(d), 7.07(t), ^a	–	60
8	18.58	8.93	6.85(d), 7.11(t), 7.25(t)	3.42	^a , 7.28(d)	–	56
9	18.64	8.98	6.88(d), 7.08(t), 7.22(t)	3.58	6.66(d), 7.27(d)	3.73	86
10	18.64	8.99	6.88(d), 7.08(d), 7.22(t)	3.54	6.82(s), 6.83(d), 6.95(d), ^a	3.62	58
11	18.30	8.70	1.99 ^b	3.27	6.86(d), 6.90(t), 7.04–7.13(m), 7.21(t), 7.26(s)	–	70

^a Merge with dpgH protons.

^b dpgH protons merge with aromatic protons.

Table 4
¹³C NMR data for 1–11 in CDCl₃

No.	C=N	Pz	dmgH/dpgH	Co–CH ₂	Aromatic	Other
1	150.46	146.63	12.23	27.67	138.05, 128.81, 127.71, 124.87, 104.79	
2	150.49	146.62	12.28	29.20	145.22, 136.00, 129.89, 127.66	
3	150.81	146.67	12.42	30.83	153.54, 131.24, 129.05, 105.82	120.01
4	150.24	146.57	12.15	33.21	157.26, 138.50, 130.62, 129.89, 113.26, 108.67	55.25
5	150.47	146.59	12.18	–	157.26, 145.52, 129.89, 129.45, 113.08,	
6	151.62	146.78	^a	–	129.64, 129.23, 128.52, 127.76, 125.32	
7	151.34	146.80	^a	34.49	145.14, 130.86, 130.33, 129.56, 129.46, 129.38, 129.28, 129.10, 128.50, 127.86	
8	152.00	146.84	^a	33.29	132.02, 129.67, 129.47, 128.81, 127.96, 108.33	120.08
9	151.44	146.75	^a	36.25	159.67, 130.37, 129.65, 129.31, 129.19, 127.75, 114.12	55.30
10	151.66	146.77	^a	35.60	159.67, 147.95, 129.65, 129.22, 127.73, 122.03, 113.98, 111.69	55.08
11	151.34 150.75	146.68	12.32 ^a	35.08	129.77, 129.54, 129.26, 129.05, 128.11, 127.78, 123.91	

^a Merge with aromatic region.

0.2 ppm in 1–5 whereas it shifts downfield by 0.4 ppm in 6–10 complexes. A similar trend was observed in the reported pyrazine bridged alkyl dicobloximes [5]. The dmG methyl resonance in 1–5 appears upfield by 0.12 ppm when compared with the value in pyrazine bridged alkyl dicobloximes. However there is no shift in the pyrazine resonance. The upfield shift is due to the interaction of the benzyl group with the equatorial dmG methyl through space. A similar interaction is also seen in X-ray structure of 6.

A comparison of the chemical shifts for O–H···O, Pz and CH₂ bound to cobalt in 1–5 with 6–10 shows that all shift downfield by about 0.6 ppm in 6–10. The data can be rationalized keeping in view the cobalt anisotropy and the metallabicyclic ring currents. We have recently discussed the detail of these effects [22]. Interestingly, a comparison of the coordination shift [22,23] $\Delta\delta(^1\text{H}, \text{Pz})$ in 1–10 with the coordination shift $\Delta\delta(^1\text{H}, \text{Py}_x)$ in the corresponding PhCH₂Co(dioxime)₂Py complexes [dioxime = dmG, dpgH] shows that the value is much higher in 1–10. This is expected since ring current from two-metallabicyclic rings affects δPz but only one in case of $\delta\text{Py}_{\text{H}\alpha}$.

4.1.2. ¹³C NMR

All the four carbons in the unligated pyrazine are equivalent and appear at 145.09 ppm. This on the formation of complex shifts downfield by 1.5–1.8 ppm in 1–11.

4.2. Cyclic voltammetry

In the cyclic voltammogram of any cobaloxime, say, PhCH₂Co(dioxime)₂Py, we expect three types of redox couple Co(III)/Co(II), Co(II)/Co(I) and Co(IV)/Co(III) [22]. Very little work has been reported on the CV studies in cobaloximes and hence there is a lack of information on these three redox systems. There is only one recent report of such study in organobridged dicobaloxime [4d]. The present work reports the first cyclic voltammogram study on a pyrazine linked dicobaloxime. CH₂Cl₂ is the only choice as solvent; there is no proper solvent system to get a good CV because of poor solubility in other solvents.

The cyclic voltammogram of 1 (Fig. 1(a)) shows two completely irreversible waves in the reductive half at –0.97 and –1.37 V corresponding to Co(III)/Co(II)

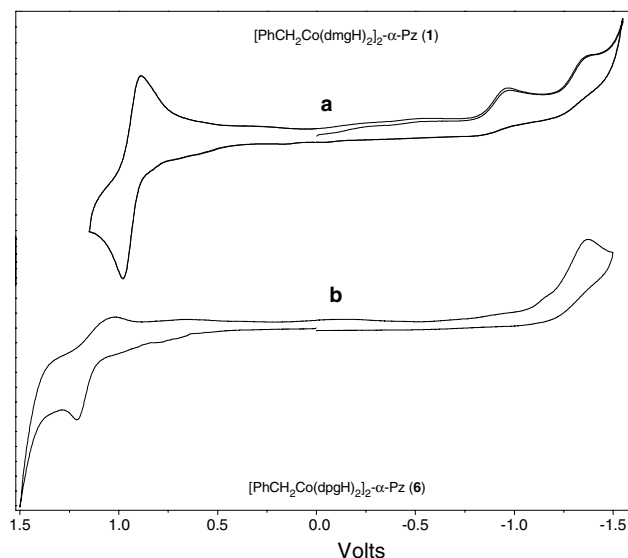


Fig. 1. Cyclic voltammograms of **1** (a) and **6** (b) in CH_2Cl_2 with 0.1 M TBAPF₆ as supporting electrolyte at 0.2 V s^{-1} at 25°C .

and Co(II)/Co(I), respectively. On the oxidation half only one reversible wave corresponding to Co(IV)/Co(III) (+0.94 V) is observed. Since the molecule is symmetrical both the cobalt centers behave similarly. This might be due to electron delocalization between two cobalt centers by a substantial overlap of cobalt and pyrazine orbitals.

The ΔE_p for Co(IV)/Co(III) wave is little higher than a quasi-reversible process and increases with increasing scan rate; thus indicating the quasi-reversible nature of the electron transfer. The oxidized product $[\text{PhCH}_2\text{Co}^{\text{IV}}(\text{dpgH})_2]_2\text{-}\mu\text{-Pz}$ (**6**) (Fig. 1(b)), is much more unstable than the corresponding dmgH complex (**1**) since the value of $i_{\text{pa}}/i_{\text{pc}}$ is 17 as compared to 2 in the latter. The more positive value in **6** is due to the electron withdrawing effect of dpgH ligand (see Table 5).

4.3. X-ray crystallographic studies: description of structure **6**

A slow evaporation of solvent from the solution of **6** (CH_2Cl_2 , methanol and *n*-hexane) in the refrigerator resulted in the formation of orange crystals. The X-ray analysis of these crystals showed the composition as $[\text{PhCH}_2\text{Co}(\text{dpgH})_2]_2\text{-}\mu\text{-Pz} \cdot 2\text{CH}_2\text{Cl}_2$. The ‘‘Diamond’’ diagram of the molecular structure for **6** along with se-

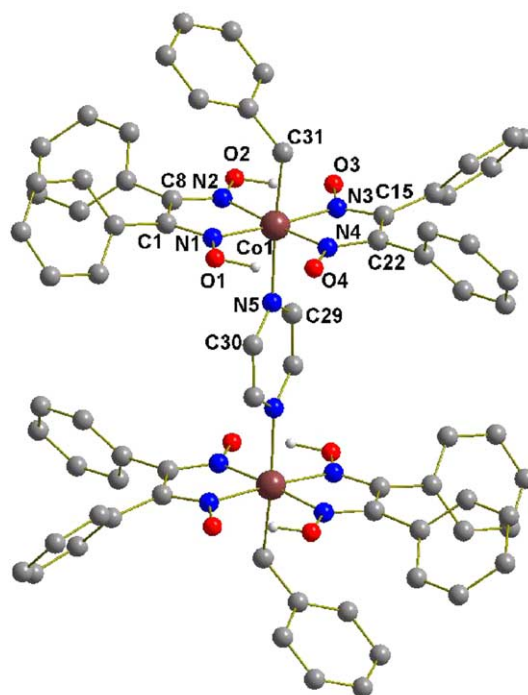


Fig. 2. Crystal structure of $[\text{PhCH}_2\text{Co}(\text{dpgH})_2]_2\text{-}\mu\text{-Pz}$ (**6**). Solvent molecule and Hydrogen atoms are omitted for clarity.

lected numbering scheme is shown in Fig. 2. The structure contains an inversion center located at the center of the pyrazine ring. Selected bond lengths and bond angles are given in Table 6.

Two distinct cobaloxime units are axially bridged together with two nitrogen of pyrazine at 1, 4 position to form the dicobaloxime unit and the distance between two cobalt atoms is 6.991 Å. The geometry around each cobalt atom is distorted octahedron with four nitrogen atoms of the dioxime (dpgH) in the equatorial plane. Pyrazine and benzyl groups are axially coordinated.

The Co–C and Co–N5 bond distance in **6** are 2.059(4) and 2.091(3) Å, respectively. The deviation of cobalt atom from the mean equatorial N₄ plane is +0.0682(7) Å and the deviation is towards axial pyrazine.

Let us look at the theoretically possible structures for $[\text{PhCH}_2\text{Co}(\text{dpgH})_2]_2\text{-}\mu\text{-Pz}$ before we discuss the actual X-ray structure. Pyrazine linked two cobaloxime units, $[\text{Co}(\text{dpgH})_2]$ can be in eclipsed or staggered conformation and two benzyl groups may take up either the *cis*

Table 5
CV data for **1** and **6** in CH_2Cl_2 with TBAPF₆ at 0.2 mV/s at 25°C

No.	Co(III)/Co(II)			Co(II)/Co(I)			Co(IV)/Co(III)			i_{pc} (μA)	i_{pa} (μA)	$i_{\text{pa}}/i_{\text{pc}}$
	E_{pc} (V, vs. Ag/AgCl)	E_{pc} (V, vs. Fc/Fc ⁺)	i_{pc} (μA)	E_{pc} (V, vs. Ag/AgCl)	$E_{1/2}$ (V, vs. Fc/Fc ⁺)	i_{pc} (μA)	$E_{1/2}$ (V, vs. Ag/AgCl)	$E_{1/2}$ (V, vs. Fc/Fc ⁺)	ΔE_p (mV)			
1	−0.97	−1.48	2.0	−1.37	−1.88	2.0	0.94	0.43	91	4.3	8.6	2.0
6	–	–	–	−1.41	−1.92	5.6	1.12	0.61	214	0.3	5.2	17.3

Table 6
Selected bond length, angle and structural data of **6** and **11**

	6	11-cis	11-trans	
Co–Co (Å)	6.991	6.840	6.882	
Bending between two cobaloxime planes		19.17(8)	15.32(11)	
Twist between two cobaloxime planes		26.51(3)	30.43(2)	
	Co1	Co2	Co3	Co4
Co–C (Å)	2.059(4)	2.034(5)	2.048(5)	2.044(5)
Co–N(ax) (Å)	2.091(3)	2.047(4)	2.058(4)	2.062(4)
C–Co–N(ax) (°)	174.51(15)	178.67(19)	175.16(17)	174.2(2)
d (Å)	+0.0682(7)	+0.0045(9)	+0.0201(7)	+0.0108(7)
α (°) (dihedral angle)	6.35(2)	8.82(16)	1.57(15)	4.57(22)
τ (°) (twist angle)	70.38(4)	86.34(3)	67.15(3)	87.03(2)

or *trans* form (Fig. 3). In the staggered form, one of the twist angles for one cobaloxime unit is 90° and another is 0° . A twist angle of 0° is uncommon in cobaloximes [25]. In the eclipsed form there will be a large steric interaction between 4-phenyl rings of dpgH group located on each side. However, the π – π interaction between the phenyl-dpgH and the phenyl of benzyl group would increase the bending angle (dihedral angle) and hence decrease the steric interaction. This may lead to the preferential formation of eclipsed over staggered conformation.

The X-ray structure of $[\text{PhCH}_2\text{Co}(\text{dpgH})_2]_2\text{-}\mu\text{-Pz}$ shows that the two cobaloxime units are in the eclipsed conformation and the two benzyl groups attain the *trans* form. Since the pyrazine bridged alkyl dicobaloxime lacks the π – π interaction, hence the two-cobaloxime units are found to be in the staggered form. The dihedral angle (α) [26] in **6** [$6.35(2)^\circ$] is very high as compared to the value in monocobaloximes. The twist angle (τ) between cobaloxime and pyrazine plane is $70.38(4)^\circ$. The deviation is very high from the expected 90° .

We have recently observed in the X-ray structures of $\text{PhCH}_2\text{Co}(\text{dioxime})(\text{dpgH})\text{Py}$ complexes [dioxime = gH, dmgH, chgH] that the benzyl group leans towards the dpgH equatorial wing and the phenyl ring of the benzyl

group lies above one of the dpgH unit due to π – π interaction [14]. In view of this it would be interesting to study the X-ray structure of a pyrazine bridged benzyl dicobaloxime with mixed dioxime ligand, $[\text{PhCH}_2\text{Co}(\text{dmgH})(\text{dpgH})]_2\text{-}\mu\text{-Pz}$. If eclipsed form is the preferred structure (as found in **6**) then three possible structures may arise as shown below (Fig. 4). In structures **a** and **b** all the 4 phenyl rings of dpgH are on the same side and the orientation of the benzyl group leads to *cis* and *trans* structures. Structure **a**, the *cis* form is very strained. In structure **c**, two dpgH groups are on one side of a cobalt atom and the other two are on the opposite side of the second cobalt atom. This may arise to alleviate the steric crowding of four dpgH groups.

4.4. $[\text{PhCH}_2\text{Co}(\text{dmgH})(\text{dpgH})]_2\text{-}\mu\text{-Pz}$: crystal structure

The X-ray analysis of compound **11** gives interesting result and the composition found is $[\text{cis-}\{\text{PhCH}_2\text{Co}(\text{dpgH})(\text{dmgH})\}_2\text{-}\mu\text{-Pz}] \cdot [\text{trans-}\{\text{PhCH}_2\text{Co}(\text{dpgH})(\text{dmgH})\}_2\text{-}\mu\text{-Pz}] \cdot \text{CHCl}_3$. The structure is shown in Fig. 5 and the selected bond angles and structural parameters are tabulated in Table 6. We get both the *cis* and *trans* isomers in the same crystal. Two cobaloxime units are in the eclipsed conformation with slight deviation. The deviation is defined by the twist angle between two cobaloxime planes. The twist angle¹ in the *cis* form is $26.51(3)^\circ$ and in the *trans* form is $30.43(2)^\circ$. Also, the two-cobaloxime units attached to pyrazine are bent with respect to each other. The bending angle² between two cobaloxime planes are $19.17(8)^\circ$ and $15.32(11)^\circ$ in *cis* and *trans* form. The bending is clearly due to the π – π interaction.

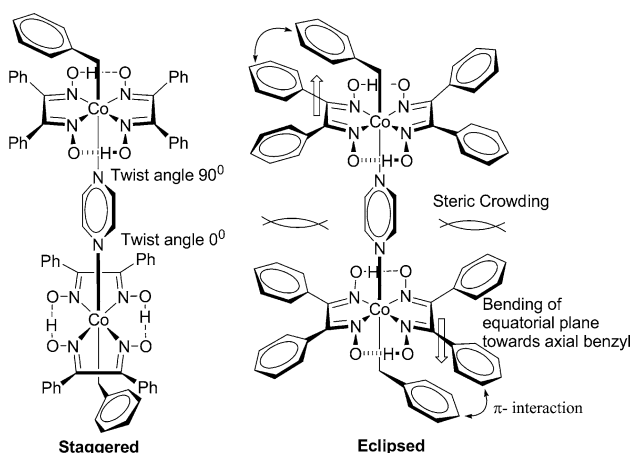


Fig. 3. Staggered and eclipsed conformation.

¹ Here the twist angle is the angle between two virtual planes that bisect cobaloxime plane. Each plane is formed considering the middle point of C–C bond of two oxime units that passes through cobalt and pyrazine nitrogen.

² The bending angle is the angle between two equatorial N_4 planes of each cobaloxime unit.

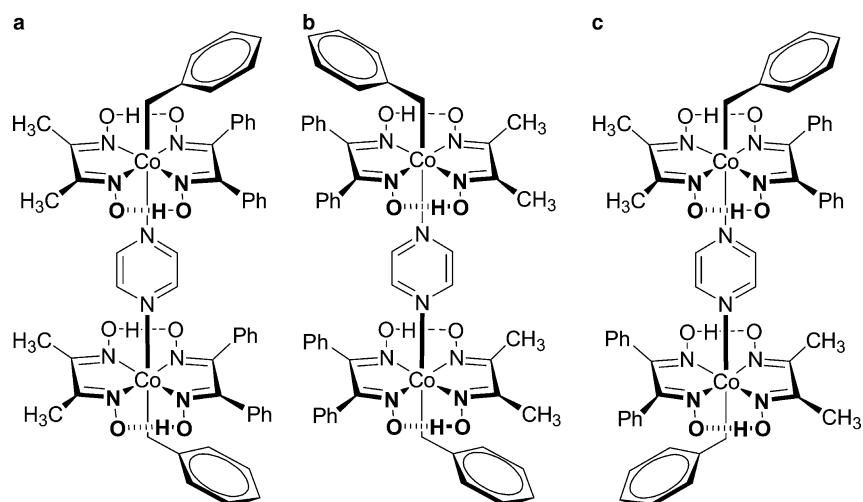


Fig. 4. Possible structures of dicobaloximes with mixed ligand cobaloximes.

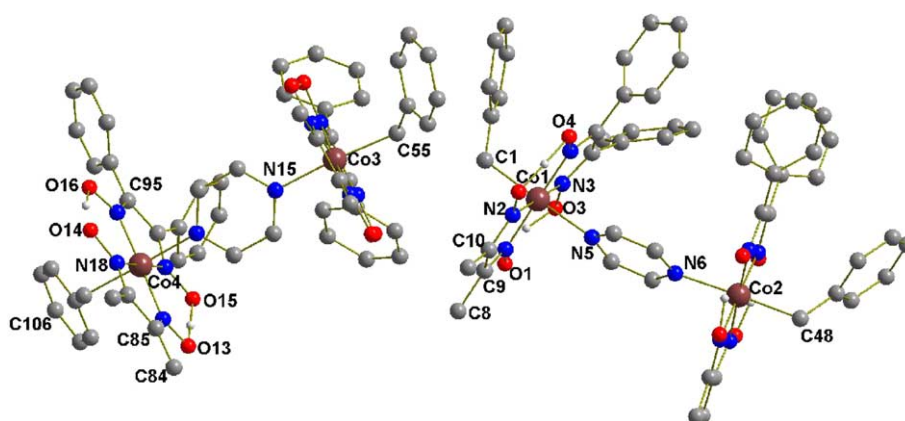


Fig. 5. Crystal structure of $[\text{PhCH}_2\text{Co}(\text{dmgH})(\text{dpgH})]_2-\mu\text{-Pz}$ (**11**). Solvent molecule and Hydrogen atoms are omitted for clarity.

The phenyl ring of the benzyl group lies above the equatorial dpgH group as expected. The intramolecular $\pi-\pi$ interaction overweighs steric crowding and forms the *cis* structure. In the *trans* form the orientation of one benzyl group is above the dmGh methyl. This reduces the intramolecular $\pi-\pi$ interaction.

cis: The butterfly angle (α) between two equatorial wings at Co1 is $8.82(16)^\circ$ (the highest value known so far). In contrast the value is very small $1.57(15)^\circ$ at Co2. The twist angle (τ) between pyrazine and cobaloxime planes are $86.34(3)^\circ$ with Co1 and $67.15(15)^\circ$ with Co2.

trans: The butterfly angles (α) are $4.57(22)^\circ$ at Co3 and $6.23(17)^\circ$ at Co4 and the twist angle (τ) between pyrazine and cobaloxime planes are $87.03(2)^\circ$ with Co3 and $62.78(2)^\circ$ at Co4.

There is strong intermolecular C–H– π and C–H \cdots O interaction that leads to supra molecular array in **6** and **11** (see supporting information).

Since the crystal structure shows the formation of both *cis* and *trans* isomers in the solid state in

$[\text{PhCH}_2\text{Co}(\text{dmgH})(\text{dpgH})]_2-\mu\text{-Pz}$ (**11**) the question arises is whether is it possible to achieve the restricted rotation around Co–C bond and see both the isomers at low temperature? The restriction on Co–C bond rotation due to $\pi-\pi$ interaction is a solid-state property and is not observed in solution even at -55°C in NMR.

5. Conclusion

Pyrazine bridged benzyl dicobaloximes $[\text{ArCH}_2\text{-Co}(\text{dioxime})_2]_2-\mu\text{-Pz}$ [dioxime = dmGh, dpgH] have been synthesized in one-pot by a simple procedure directly from the corresponding benzyl aqua complex. The $\pi-\pi$ interaction between the axial benzyl group and phenyl ring of the equatorial dpgH group forces the two cobaloxime units to attain the eclipsed form in the crystal structure of $[\text{PhCH}_2\text{Co}(\text{dpgH})_2]_2-\mu\text{-Pz}$. However, a competition between steric crowding and $\pi-\pi$ interaction in $[\text{PhCH}_2\text{Co}(\text{dmgH})(\text{dpgH})]_2-\mu\text{-Pz}$ results in the formation of two isomeric conformations, *cis*

and *trans*, in the crystal structure. The cyclic voltammogram of pyrazine bridged benzyl dicobaloximes is similar to other monocobaloximes with pyridine. This is due to the electron delocalization between two cobalt centers through pyrazine. The reduction potentials in pyrazine complexes are remarkably much higher than the monocobaloximes.

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Appendix A. Supplementary data

The cif files have been deposited with the Cambridge Crystallographic Data Centre, CCDC number for **6** and **11** are 260523 and 260524, 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 at doi:10.1016/j.jorganchem.2005.05.021.

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