

Biphenyl-Bridged Dicobaloximes: Synthesis, NMR, CV, and X-Ray Study[†]

Mouchumi Bhuyan, Moitree Laskar, and B. D. Gupta*

Department of Chemistry, Indian Institute of Technology Kanpur, India 208016

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4,4'-Disubstituted biphenyl-bridged dicobaloximes, $\text{Py}(\text{L})_2\text{Co-CH}_2\text{-Ar-CH}_2\text{-Co}(\text{L})_2\text{Py}$ [$\text{L} = \text{dmgH}$, dpgH], have been synthesized and characterized. The cobalt-bound CH_2 is diastereotopic and the dmgH (Me) shows nonequivalence in the ^1H NMR. This may occur due to atropisomerism and/or restricted rotation of the C-Ph/Co-C bond. Two X-ray structures of the biphenyl-bridged dicobaloximes, reported for the first time, show no direct or indirect interaction between the two cobaloxime units [$\text{Co}(\text{dioxime})_2\text{Py}$]. The NMR spectra and X-ray structural details complement each other. Three redox processes, $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$, $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$, and $\text{Co}^{\text{IV}}/\text{Co}^{\text{III}}$, are observed in the CV study. Two cobalt centers are oxidized at different potentials as two discrete units even though these are symmetrically located with respect to each other with no interaction between them.

Introduction

Although the cobaloximes [cobaloximes have the general formula $\text{RCo}(\text{L})_2\text{B}$, where R is an organic group σ -bonded to cobalt, B is an axial base *trans* to the organic group, and L is a monoanionic dioxime ligand (e.g., glyoxime (gH), dimethylglyoxime (dmgH), diphenylglyoxime (dpgH))] have been extensively studied over the past four decades,¹ the dinuclear complexes containing bridging ligands are of continuing interest since the presence of the bridging ligand has been shown to affect the geometry of the complex and the redox properties of the metal.^{2a} The study of these complexes helps us in understanding the electronic interaction in the supramolecules that have promising applications.^{2b} Though numerous ligand bridged bimetallic complexes have been reported,^{3a} little is known about the neutral organo-bridged bimetallic complexes.^{3b} Organo-bridged dicobaloximes of the type $\text{B}(\text{L})_2\text{Co-R-Co}(\text{L})_2\text{B}$ ($\text{L} = \text{dioxime}$) were virtually unknown until recently.⁴ In our recent studies we saw that the *ortho* and *meta* xylylene-bridged dicobaloximes exhibited very interesting NMR behavior in

solution; the cobalt-bound CH_2 became diastereotopic and the dioxime protons showed nonequivalence at subzero temperature.⁵ This was attributed to the restricted rotation of the Co-C and/or C-Ph bond. Many inherent problems are associated with the synthesis of such compounds since these are much more unstable in solution as compared to the corresponding monocobaloximes. Because of the presence of two inherently weak Co-C bonds, it was hoped that these might find better use as precursors in homolytic displacement reactions, more than the monocobaloximes derivatives.⁶ Also there is very little information on the structural and electrochemical behavior of the organo-bridged dicobaloxime complexes, in general. The idea is to play with the steric factor of the bridging ligand and to use the steric bulk as a handle to cause restricted rotation in the organo-bridged dicobaloximes; the biphenyl-bridged analogues become suitable systems for such a study.

Since the appropriately substituted biphenyl derivatives give rise to *axial chirality-atropisomerism*⁷ the study of biphenyl-bridged dicobaloximes having the *ortho* positions substituted by bulky groups like $-\text{CH}_2\text{Co}(\text{dmgH})_2\text{Py}$ is undertaken. Baddeley⁸ and Harris et al.⁹ have reported that while the major part of the origin of the energy barrier to inversion in the biphenyl derivatives is the steric strain at the transition state due to nonbonded interactions between atoms (or groups) at the *orthopositions*, it is also considerably affected by the *para* substituents. In view of this we have also studied the effect of substitution at 4,4'-positions in the biphenyl-bridged dicobaloximes.

[†] Dedicated to Prof. Karen Eichstadt, Department of Chemistry and Biochemistry, Ohio University.

* Corresponding author. Tel: +91-512-2597046. Fax: +91-512-2597436. E-mail: bdg@iitk.ac.in.

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Table 1. Crystal Data and Structure Refinement Details for **3a** and **7a**

	3a	7a · 2C ₆ H ₆ · C ₂ H ₅ OH
empirical formula	C ₄₀ H ₅₂ Cl ₂ N ₁₀ O ₁₀ Co ₂	C ₁₀₈ H ₁₀₀ Cl ₂ N ₁₀ O ₁₂ Co ₂
fw	1021.68	1918.74
temp (K)	100(2)	100(2)
diffraction measurement device/scan method	Smart CCD area detector/ φ - ω	Smart CCD area detector/ φ - ω
cryst syst	tetragonal	monoclinic
space group	<i>P</i> 4 ₂ 2 ₁ 2	<i>C</i> 2/ <i>c</i>
unit cell dimens		
<i>a</i> (Å)	14.763(5)	21.412(6)
<i>b</i> (Å)	14.763(5)	19.172(2)
<i>c</i> (Å)	21.544(5)	24.722(10)
α (deg)	90	90
β (deg)	90	113.537(3)
γ (deg)	90	90
<i>V</i> (Å ³)	4695(2)	9304(11)
<i>Z</i>	8	4
ρ (calcd) (Mg/m ³)	1.394	1.370
μ (mm ⁻¹)	0.879	0.484
<i>F</i> (000)	2040	4008
cryst size (mm ³)	0.35 × 0.25 × 0.20	0.30 × 0.25 × 0.22
index ranges	-19 ≤ <i>h</i> ≤ 13, -19 ≤ <i>k</i> ≤ 16, -28 ≤ <i>l</i> ≤ 28	-15 ≤ <i>h</i> ≤ 28, -25 ≤ <i>k</i> ≤ 24, -33 ≤ <i>l</i> ≤ 32
no. of reflns collected	31 223	30 106
no. of indep reflns	5845	11 531
GOOF on <i>F</i> ²	1.077	0.969
final <i>R</i> indices (<i>I</i> < 2 σ (<i>I</i>))	<i>R</i> 1 = 0.0652, <i>wR</i> 2 = 0.1594	<i>R</i> 1 = 0.0859, <i>wR</i> 2 = 0.1998
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0910, <i>wR</i> 2 = 0.1730	<i>R</i> 1 = 0.1841, <i>wR</i> 2 = 0.2449
data/restraints/param	5845/0/289	11531/0/612

We have chosen two different dioximes, dmGH and dpGH, to see the effect of steric bulk in the dioxime moiety in -CH₂Co(dioxime)₂Py. We also report the first crystal structures of biphenyl-bridged dicobaloximes. The electrochemical studies have also been done for the first time.

Experimental Section

General Methods. 2,2'-Bis(bromomethyl) biphenyl was purchased from Aldrich and was used as received. 4,4'-Difluoro,¹⁰ 4,4'-dichloro,¹¹ 4,4'-dibromo-[2,2'-bis(bromomethyl)]biphenyl,¹² ClCo(dmGH)₂Py, and ClCo(dpGH)₂Py^{13a,3b} were synthesized according to the literature procedure. Silica gel (100–200 mesh) and distilled solvents were used in all chromatographic separations. The synthetic work was carried out in subdued light and under a blanket of argon or nitrogen.

¹H and ¹³C NMR spectra were recorded on a JEOL JNM LAMBDA 400 FT NMR spectrometer (400 MHz for ¹H and 100 MHz for ¹³C) in CDCl₃ with TMS as an internal standard. NMR data are reported in ppm. Elemental analysis was carried out using a Thermoquest CE Instruments CHNS-O elemental analyzer. 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 in dichloromethane (dry) at a concentration of 1 mM of each complex with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (ⁿBu₄NPF₆) as the supporting electrolyte. All the measurements were performed with a BASi platinum disk or glass carbon working electrode, a Ag/AgCl reference electrode (3 M NaCl), and a platinum-wire counter electrode. The reversible ferrocene/ferrocenium ion (Fc/

Fc⁺) couple occurs at *E*_{1/2} = +0.43 (71) V versus the Ag/AgCl electrode under the same experimental conditions.

X-ray Crystal Structure Determination and Refinements. We could obtain single crystals of **3a** from slow diffusion of pentane in a dichloromethane solution. The crystals of **7a** are found by slow evaporation of a mixture of benzene and ethanol in dichloromethane. The structure **3a** was solved in noncentric chiral space group *P*4₂2₁2. The space group for the structure **7a** is *C*2/*c*. Single-crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo K α radiation (λ = 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*.¹⁴ Cell parameters were retrieved using SMART software and refined using SAINT on all observed reflections. The data integration and reduction were processed with SAINT¹⁵ software. An empirical absorption correction was applied to the collected reflections with SADABS¹⁶ using XPREP.¹⁷ The structures were solved by the direct methods using SHELXTL¹⁸ and were refined on *F*² by the full-matrix least-squares technique using the SHELXL-97¹⁹ program package. All non-hydrogen atoms were refined anisotropically. 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 positional 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.

A CIF file is deposited with the Cambridge Crystallographic Data Center (CCDC number for **3a** is 660482 and for **7a** is 660483).

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Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EX, U.K. (fax +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk/).

Synthesis of Biphenyl-Bridged Dicobaloximes: General Procedure. One milliliter of aqueous sodium hydroxide (1 pellet in 2 mL of water) was added to a suspension of $\text{Co}(\text{dioxime})_2\text{Py}$ (1 mmol in 15 mL of methanol). The reaction mixture was purged with argon for 20 min while cooling it to 0 °C. A deaerated aqueous solution of sodium borohydride (0.04 g, 1 mmol in 0.5 mL of water) was added dropwise. The solution turned blue in color and showed the presence of cobaloximes(I). An argon-purged solution of dihalide (0.5 mmol in ca. 1 mL of diethyl ether) was added to it dropwise. The stirring was continued in the dark for 2–3 h, during which the solution became yellow-orange. The reaction mixture was poured into 100 mL of ice-cold water containing a few drops of pyridine. The orange-yellow precipitate was filtered on a sintered funnel, washed with water until the filtrate was pale yellow in color, and dried over P_2O_5 in the dark, and the crude product was subjected to column chromatography.

Chromatographic Separation. Since dicobaloximes decompose readily in solution and in the presence of visible light, the entire process of column chromatography including the evaporation of solvent and crystallization were carried out in diffused light. It is recommended that the rate of elution must be kept fast during the column chromatography.

dmgH Complexes 1–4. The crude product containing a mixture of monocobaloxime and biphenyl-bridged dicobaloxime was dissolved in a minimum amount of dichloromethane and was loaded on a silica gel column, pre-eluted with dichloromethane. The polarity of the solvent was carefully and slowly increased with an ethyl acetate/dichloromethane mixture (10–40%) until an orange-red band corresponding to monocobaloxime was distinctly visible. This band was completely eluted out with ethyl acetate/dichloromethane (80:20). The dicobaloxime was eluted out with 100% ethyl acetate and an ethyl acetate/methanol (90:10) mixture.

dpgH Complexes 5–8. The polarity of the solvent was carefully increased with an ethyl acetate/dichloromethane (2–4%) mixture when the orange band corresponding to monocobaloximes was eluted out. The dicobaloxime was eluted out with an ethyl acetate/dichloromethane (10:90) mixture.

Results and Discussion

Synthesis. Biphenyl-bridged dicobaloximes (**1a–8a**) were synthesized following a procedure published recently by us on the xylylene-bridged dicobaloximes.^{5b} In addition to the required product a small amount of methyl-substituted monocobaloxime (**1b–8b**) was also formed as a side product. The combined yield of mono- and dicobaloxime is around 70–80%. However their ratio depends upon many factors such as reaction time, the dihalide:Co^I ratio, and the nature of the dihalide used. For example (a) for Y = H the yield of dicobaloxime (**1a** or **5a**) is around 55% with reaction time 5 min to 1 h; however it falls to 15–20% when the reaction time is longer (> 5 h). (b) For Y = H or F the yield is always higher than when Y = Cl or Br, where it is 30–40%. (c) when the ratio of biphenyl dibromide: Co^I is 3:1, monocobaloxime is the major product (~70%); however with 1:3 ratio, no improvement in yield of dicobaloxime is observed.

The overall observations suggest that the best conditions for preparing the biphenyl-bridged dicobaloximes are 0 °C, dihalide: Co^I ratio 1:2, and the reaction time 2–3 h. The dicobaloximes are orange-red colored solids and are stable under nitrogen atmosphere. However, decomposition occurs in solution over a period of time, even under N_2 atmosphere. We have even noticed the decomposition of the dicobaloximes in the NMR tube. Since column

chromatography is the best way to separate the dicobaloxime from monocobaloxime, in certain cases the compounds decomposed on the silica gel column. In such cases these were purified by repeated fractional crystallization under argon atmosphere. In fact, one should first try to separate the products by partial crystallization (dicobaloximes are much less soluble than the monocobaloximes in common organic solvents), and if that fails, only then should column chromatography be tried.

The ¹H NMR of the mono- and dicobaloximes **1–8** is given in Table 2, and the elemental analysis, ¹³C NMR, and ratio of mono- and dicobaloximes under different conditions are given as Supporting Information as Tables S1, S2, and S3.

Spectroscopy. All the complexes have primarily been characterized with ¹H and ¹³C NMR. In the ¹H NMR spectra, Co–CH₂, dioxime, O–H···O, and pyridine resonances and in the ¹³C NMR C=N, Co–CH₂, and pyridine are clearly distinguished and are easily assigned on the basis of their chemical shifts. The assignments are consistent with the related organo-bridged complexes reported from our group.^{4d,5}

The CH₂ protons in the dicobaloximes **1a–8a** appear as double-doublets, suggesting that these protons are diastereotopic. The *J* value corresponds to the geminal coupling.

H_a is located close (3.268 Å) to one of the phenyl rings of the biphenyl and is affected by its ring current; it is upfield shifted as compared to H_b. Therefore, the substituent in the 4,4' position affects the chemical shift of H_a. On the other hand the chemical shift of H_b remains almost constant (see **2a**, **3a**, and **4a**). A similar pattern is observed in the dpgH complexes (**5a–8a**) also; the proximity of H_a to the phenyl ring is almost the same (3.292 Å) as in the corresponding dmgH complex. The strong downfield shift of CH₂ in the dpgH complexes is as expected and is due to the higher cobalt anisotropy in these complexes. The same has been observed earlier in the benzyl cobaloximes, BnCo(dioxime)₂Py (dioxime = dmgH, dpgH). The separation between the two doublets ($\Delta\delta$) is much smaller in the dpgH complexes (40–136 Hz) as compared to the dmgH complexes (145–180 Hz). It seems to be a general feature since the same was observed earlier in the xylylene-bridged dicobaloximes also. This might have occurred due to the change in the dihedral angle between the two phenyl groups of the biphenyl moiety, resulting due to the bulkiness of the [Co(dioxime)₂] moiety. This has been verified from the crystal structure details.

The dmgH(Me) appears as two singlets with a separation of about 0.13 ppm in all cases, and the substitution in the 4,4' position does not alter this value; however it is downfield shifted as compared to the parent dicobaloxime (Y = H).

Moving from dicobaloximes to the monocobaloximes (**1b–8b**), the Co–CH₂ remains diastereotopic and dmgH(Me) appears as two singlets. Interestingly, in the biphenyl complexes with only one *ortho* substituent such similar nonequivalence occurs at subzero temperature; for example the nonequivalence is observed at –15 °C (CH₂) and at –25 °C (dmgH) (Me) in 2-biphenyl CH₂Co(dmgh)₂Py.²⁰ This means that the barrier to rotation between the two phenyl rings in this molecule is small, but substitution by Me at the 2' position increases this barrier and facilitates the phenomenon of nonequivalence. This is expected and can be easily explained. The coplanar conformation for any biphenyl with a single *ortho* substituent has maximum destabilization from the steric interaction of the substituent with the nearer *ortho*-hydrogen on the second phenyl ring and maximum stabilization from the π – π interaction of

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Table 2. ^1H NMR Data for **1a–8a** and **1b–8b** at Room Temperature in CDCl_3^a

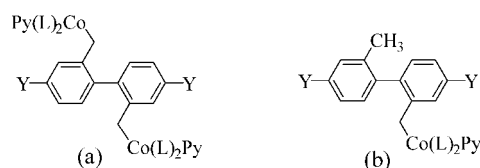
no.	$\text{CH}_2\text{-Co}$	dmgH/dpgH	pyridine			O–H \cdots O	aromatic	CH_3
			α (d)	β (t)	γ (t)			
1a	2.75(d) (6.4) 3.02(d) (6.4)	1.78, 1.91	8.37 (4.8)	* (7.6)	7.57 (7.6)	17.76	6.49(d) (7.2), 6.89(d) (6.8), 7.13–7.31(m)	
1b	2.66(d) (6.8) 3.04(d) (7.2)	1.87, 1.92	8.43 (5.2)	* (7.6)	7.62 (7.6)	17.94	6.72(d) (7.6), 6.90–6.96(m), 7.16–7.22(m)	2.10
2a	2.52(d) (6.4) 2.89(d) (6.8)	1.83, 1.96	8.36 (5.2)	7.18* (6.8)	7.61 (7.6)	17.75	[6.18(d) (2.8), 6.20(d) (2.4) $J = 8.0$], 6.98–7.03(m), 7.12–7.14(m)	
2b	2.41(d) (7.0) 2.91(d) (6.8)	1.92, 1.98	8.41 (4.8)	7.22* (6.8)	7.65 (7.6)	17.99	[6.37(d) (2.8), 6.40(d) (2.8) $J = 12.0$], 6.80–6.95 (m), 7.27–7.31(m)	2.06
3a	2.43(d) (6.6) 2.87(d) (6.8)	1.84, 1.99	8.35 (4.8)	7.18* (6.8)	7.61 (7.6)	17.77	6.43(d) (2.0), 7.14–7.16 (d) (8.0), 7.30 (d) (2.0)	
3b	2.39(d)(5.9) 2.89(d) (6.0)	1.93, 2.00	8.40 (5.2)	7.22 (6.8)	7.65 (7.6)	17.98	6.61(d) (2.4), 6.82(d) (8.4), 7.15–7.17(m)	2.07
4a	2.43(d) (6.8) 2.88(d) (7.2)	1.84, 1.99	8.35	*	7.60 (7.6)	17.75	6.43 (d) 7.08–7.44	
4b	2.40(b) 2.89(b)	1.91, 2.00	8.40		7.64 (7.6)	17.88	6.61(d)6.81–7.17	2.07
5a	3.44 (6.0) 3.74 (5.6)	*	8.74 (5.2)	7.73* (7.2)	7.32 (6.8)	18.40	6.69(d) (7.2), 6.91(d) (6.8), 7.05–7.19(m), 7.44–7.46(m), 7.55(d) (7.2)	
5b	3.74(6.4) 3.45(6.0)	*	8.74 (6.0)	7.75 (6.0)	*	18.38	6.69(d), 6.91(d), 7.05–7.33(m), 7.43–7.55(m), 7.72(d)	2.04
6a	3.24(b) 3.58(b)	*	8.72(b)	*	7.76(b)	18.38	6.73(b), 6.91(b), 7.13–7.26(m), 7.33, 7.47	
6b	3.03(d) (6.0) 3.55(d) (6.4)	*	8.74 (4.8)	7.37* (6.8)	7.80 (8.0)	18.52	6.77(d) (7.2), 6.84(d) (6.4), 6.79–7.02(m), 7.11–7.25(m), 7.49–7.53(m)	2.13
7a	3.29(d) (6.8) 3.56(d) (6.8)	*	8.59 (5.2)	*	7.39 (6.8)	18.27	6.68–7.28	
7b	3.23(d) (6.4) 3.50(d) (6.4)	*	8.63 (4.8)	*	7.68 (7.6)	18.32	6.65–7.30	1.97
8a	3.31(d) (5.6) 3.56(d) (5.8)	*	8.69	*	7.75	18.33	6.73–7.34	
8b	3.31(d)(5.2) 3.44(d) (5.4)	*	8.71	*	7.82	18.38	6.72–7.36	2.01

^a * = Merge with aromatic protons, b = broad.

the two rings. In the orthogonal conformation, these opposing contributions to the molecular energy are both at a minimum, so the overall lowest energy conformation for the biphenyl will be somewhere between these extremes, more or less near orthogonal, depending on the size of the substituent. This is an interesting observation since many groups have been trying to design organic biphenyl systems that show chirality at room temperature.

The separation between the two doublets ($\Delta\delta$) is much larger in the monocobaloximes [200–240 Hz in the dmgH complexes (**1b–4b**) and 108–208 Hz in the dpgH complexes (**5b–8b**)] than the corresponding dicobaloxime complexes (**1a–4a** and **5a–8a**). This suggests that the dicobaloximes are more rigid than the monocobaloximes and the orientation of two [Co] centers in the dicobaloximes is fixed in such a way as to eliminate or partly reduce the steric interactions between the two cobaloxime units (the dihedral angle between the two phenyl rings around the C–C bond defines the torsion) and thus results in a smaller separation in the peaks. Similarly, the large $\Delta\delta$ value in the monocobaloximes indicates a smaller dihedral angle and hence greater interaction between the two geminal hydrogens.²¹ The ^1H NMR data in the corresponding gH complex (Scheme 1; L = gH; Y = H) [the ^1H NMR data of gH complex (δ in ppm) 2.94, 3.36(CH_2Co), 8.40 (4.8) (Py_a), 7.65 (7.2) (Py_b), 6.99–7.13 (m); the ligand protons and Py_b are merged with the aromatic protons] support these arguments. Here the less bulky dioxime exerts fewer steric interactions and should have a small dihedral angle. Thus the separation of the peaks should be large. This is what is observed also ($\Delta\delta = 168$ Hz).

Scheme 1. Biphenyl-Bridged Cobaloximes



Y = H, F, Cl, Br; L = dmgH (1–4)

Y = H, F, Cl, Br; L = dpgH (5–8)

A comparison of ^1H NMR in the di- and monocobaloximes (**1a–4a** and **1b–4b**) shows that the dmgH (Me) appears as two singlets in both cases. However, one singlet has an almost constant chemical shift, whereas the other one is downfield shifted by 0.1 ppm in the monocobaloximes as compared to the dicobaloximes. This is in contrast to the CH_2 protons, where one set of doublets was upfield shifted in the monocobaloximes.

The diastereotopic nature of CH_2 can occur due to atropisomerism and/or restricted rotation of the C–Ph/Co–C bond, as observed recently in the xylylene-bridged dicobaloximes^{5b} and in the *ortho*-substituted benzyl cobaloximes.²⁰ It is very difficult to distinguish between the two processes at this stage (Figure 1).

X-ray Crystal Structures. The diamond diagram of the molecular structures for **3a** and **7a** along with the selected numbering scheme is shown in Figures 2 and 3. The selected bond lengths and bond angles are given in Table 3. The geometry around each cobalt atom in **3a** and **7a** is distorted octahedral with four nitrogen atoms of the dioxime in the equatorial plane, with pyridine and biphenyl moieties in the axial positions. The crystal structure of **7a** shows one disorder:

(21) Mazzanti, A.; Lunazzi, L.; Minzoni, M.; Anderson, J. E. *J. Org. Chem.* **2006**, *71*, 5474.

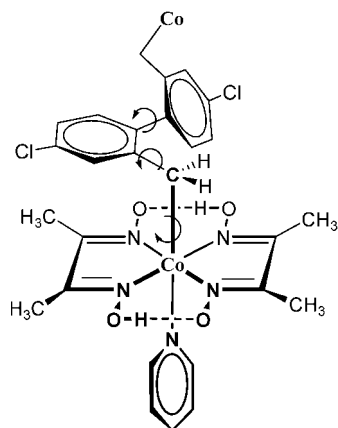


Figure 1. Biphenyl-Bridged Dicobaloximes: Possible C–Ph and C–C Bond Rotation.

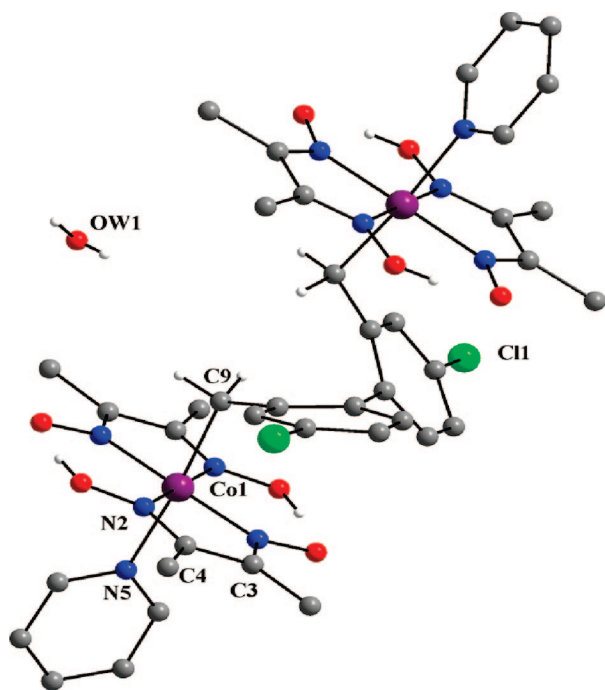


Figure 2. Molecular structure of **3a**.

the O (OW1) atom of one H₂O molecule is attached to one of the Co–CH₂ protons and the H···O distance is found to be 1.09 Å.

In view of the recent structural studies on cobaloximes we have focused mainly on (i) the axial Co–N and the Co–C bond lengths, (ii) the puckering of the equatorial dioxime ligand, i.e., butterfly bending angle (α),²² (iii) the torsion angle (τ)²³ between the axial base pyridine and equatorial ligand, (iv) the deviation of the cobalt atom from the mean equatorial N₄ plane (d), and (v) the dihedral angle between the two phenyl rings of the biphenyl. These points assist in defining the *cis* or *trans* influence of axial as well as equatorial ligands.

Two distinct cobaloxime units, Co(dioxime)₂Py, are axially bridged by the biphenyl group to form the dicobaloxime moiety

(22) The dihedral angle (butterfly bending angle, α) is the angle between two dioxime planes of each cobaloxime unit.

(23) The torsion angle (τ) is the angle between two virtual planes that bisects the cobaloxime plane. Each plane is formed considering the middle point of the C–C bond of two oxime units that passes through cobalt and the pyridine nitrogen.

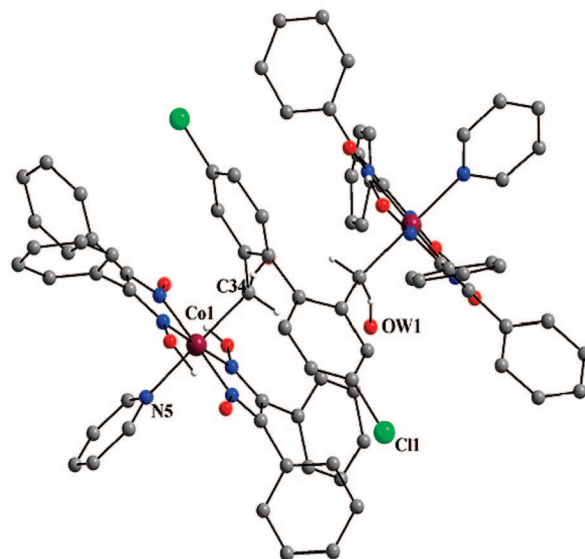


Figure 3. Molecular structure of **7a**.

in each structure. Each cobaloxime unit has many structural similarities and can be looked at as an independent benzyl cobaloxime; for example, in structure **3a**, the Co–C bond length, the butterfly bending angle (α) between the two dioxime units, the CH··· π and π ··· π interactions, and the orientation of the benzyl group over the dmgH(Me) are very similar to those found earlier in the benzyl and *ortho*-substituted benzyl cobaloximes.²⁰ A similar trend follows in the dpgH complex, **7a**, except that the α is much higher (6.37°) as compared to the benzylCo(dpgH)₂Py complex (1.75°). The high α value can be explained by the C–H··· π interaction [(3.307(11) and 3.693(8) Å)] between one of the aromatic rings of biphenyl and the H atom of the equatorial aromatic ring.

The number of crystal structures of the organo-bridged dicobaloximes is limited; a few structures on the alkyl-bridged⁴ and only one structure on the xylylene-bridged dicobaloximes^{5b} have been reported so far. Some important differences are observed from the reported *m*-xylylene-bridged dicobaloxime (**A**); the dicobaloxime units are symmetrical and the distance between the cobalt atoms [7.148(1) and 7.106(21) Å for **3a** for **7a**] is shorter than the corresponding distance in **A** (7.871 Å); α is identical (1.63°) for both Co1 and Co2 in **3a**, whereas these are different (2.99° and 8.81°) in structure **A**. The displacement (d) from the mean equatorial N₄ plane for both the cobalt atoms in **3a** is the same (+0.014) and is toward pyridine, whereas it is +0.029(9) for Co1 and –0.0063 (8) for Co2 in **A**. [For cobaloximes, RCo(dioxime)₂Py, the positive sign of α and d indicates bending toward R and displacement toward B and *vice versa*.] These differences point to many more observations; for example, no direct or indirect interaction between the two cobaloxime units [Co(dioxime)₂Py] in **3a** and **7a** is observed since the structural parameters in the two units are identical. This is in contrast to the *m*-xylylene complex (**A**), where the sign of d and different value of α suggest that one dioxime unit on Co1 pushes the other dioxime unit toward Co2, with the result that one cobalt atom is displaced toward pyridine and the other toward the benzyl group. This interaction cannot occur directly between the two dioxime units since these are too far away. This occurs via the aromatic ring.

The pyridine ring is practically planar and parallel to the dioxime C–C bonds, its conformation being defined by a twist angle of 85.045(8)° in **3a** and 89.501(1)° in **7a**. The bridging biphenyl in **3a** is sandwiched between the two dmgH wings,

Table 3. Selected Bond Lengths (Å), Bond Angles (deg), Torsion Angles (deg), and Structural Data for **3a** and **7a** (**X₁** and **X₂** for comparison)^a

	3a	7a	X₁	X₂
Co–Co (Å)	7.148(1)	7.106(21)		
biph twist angle (deg)	57.85	64.35		
Co–C (Å)	2.065(4)	2.046(5)	2.064(15)	2.056(5)
Co–N _{ax} (Å)	2.068(3)	2.041(5)	2.056(14)	2.061(4)
C–Co–N _{ax} (deg)	175.01(19)	174.81(18)	177.1(1)	176.8(2)
Co–C–C(Ph) (deg)	117.1(3)	120.1(4)	116.6(3)	117.9(3)
N5–Co–C–C	130.68	155.27	158.8	155.1
N _{eq} –Co–C–C _b	–20.12	–6.99	–20.1	–12.7
Co–C–C–C	–83.61	–78.66	–93.94	–91.65
<i>d</i> (Å)	+0.014	0.0	–0.0371	–0.0275
α (deg) (dihedral angle)	1.63	6.80	1.86	1.75
τ (deg)	85.045(8)	89.501(1)	86.454	88.96
π···π (Å)			3.564(19)	3.748(3)
C–H···π (Å)	3.421(0), 3.861(0)	3.307(11), 3.693(8)	3.183(22)	2.880(4), 3.189

^a **X₁** = C₆H₅CH₂Co(dmgh)₂Py;³¹ **X₂** = C₆H₅CH₂Co(dpgH)₂Py.^{20b}

and the directly linked aromatic ring of the biphenyl unit forms an angle of 26.47° with the cobaloxime plane.²⁴ However, this angle is 36.94° in **7a**. The values point to how crowded or flattened the cobaloximes are; **3a** is much more flattened as compared to **7a**. The equatorial planes (the plane of four nitrogens of dioxime) of the two cobaloxime units are staggered with respect to each other in **3a**, whereas they are partially staggered in **7a**.

Both the dioxime planes in the cobaloxime units in each structure are bent toward the biphenyl moiety, and α is the same for both the dioxime units (1.63°, 1.63° in **3a** and 6.80°, 6.80° in **7a**). Both the cobalt atoms (Co1 and Co2) are displaced (*d*) equally by 0.014 Å from the equatorial N4 plane of the two dioximes in **3a**, and the displacement is toward pyridine.

However in **7a** each Co is coplanar with the N4 plane of the dioxime unit and the *d* value is zero.

A critical value for biphenyl derivatives lies in the dihedral angle around the central C–C bond, and this angle between the two phenyl rings is 57.85° and 64.35° in **3a** and **7a**, respectively. That means that the phenyl units are in a *cisoid* conformation (the two [Co] units are located on the same side of the biphenyl scaffold). This conformation is comparable to the reported 2,2'-dimethoxy-substituted biphenyl derivatives.²⁵ As a consequence, the two biphenyl moieties are approximately arranged orthogonally in the crystal.

Electrochemical Study (Cyclic Voltammetry). The cyclic voltammogram (CV) of a cobaloxime shows three types of redox couples: Co^{III}/Co^{II}, Co^{II}/Co^I, and Co^{IV}/Co^{III}. Organo-cobaloximes, in general, give poor CV, and most of the time the Co^{III}/Co^{II} redox couple is not observed.²⁶ None of the studies have reported the values for all three redox systems. On the other hand, inorganic cobaloximes show relatively better CV and all the redox couples are prominent. The CV study of organocobaloximes becomes complicated due to the change in coordination number (cleavage of axial base and/or Co–C bond) during the redox process and therefore has not been studied that well. Finke and co-workers²⁷ found that the reduction of alkylcobaloximes was irreversible under all conditions of solvents and scan rate, whereas Le Hoang et al.²⁸ found that

these could be reversibly reduced in DMSO solution. Two common solvents used for the study are dichloromethane and acetonitrile. We have preferred to use dichloromethane because of the higher solubility of the cobaloximes. We have studied the electrochemical behavior of **1a**, **2a**, **3a**, **5a**, **8a**, **2b**, and **5b** in order to find out the effect of the bridging biphenyl group as well as the effect of the dioxime on the redox potentials of the metal centers. The ligand oxidation is also observed, but this occurs at higher potential (>1.6 V). Since the X-ray structural parameters have indicated that the two cobalt centers are almost identical and each unit resembles the isolated benzyl cobaloxime, it would be interesting to see if the electrochemical behavior also gives the same information or not. The cyclic voltammograms are given in Figure 4, and the redox potential data are given Tables 4 and 5.

In the reductive half, only one irreversible peak at –0.92, –1.23, and –1.43 V corresponding to one-electron reduction of Co^{II}/Co^I is observed in **1a**, **2a**, and **8a**. However in **3a** and **5a** both processes, Co^{III}/Co^{II} and Co^{II}/Co^I, are observed. The reduction of the dpgH complexes, as expected, is easier than the dmgh complexes because of the higher cobalt anisotropy in the former.²⁹

Two irreversible waves in the oxidation half are observed in the dmgh complexes **1a** and **2a**, whereas the peaks are reversible in **3a**. The oxidation becomes more difficult, as expected, with the substitution at the 4,4'- position in the biphenyl by the electron-withdrawing groups (**2a** and **3a**). The same phenomenon is observed in the dpgH complexes also.

The presence of two oxidation potentials in the dmgh as well as in the dpgH complexes indicates that two cobalt centers [Co] are oxidized at different potentials as two discrete units. A similar observation was made earlier in the xylylene-bridged dicobaloximes.^{5b} This, however, is surprising since the present systems, unlike the xylylene-bridged dicobaloximes, have two cobalt centers symmetrically located with respect to each other with no direct or indirect interaction between the two cobaloxime units as per the X-ray details. Therefore, only one oxidation potential was expected. In the *m*-xylylene-bridged dicobaloximes the two cobalt centers were unsymmetrically oriented with respect to each other. The present systems resemble the symmetrical pyrazine-bridged dicobaloximes, [RCo(dioxime)₂]₂-μ-Pz, where a single oxidation potential was observed due to the high electron delocalization between the two [Co] centers

(24) This plane is defined as the plane passing through N1 C8 C9 N2 and N3 C12 C13 N4 of the structure **3a**.

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(29) Cobalt anisotropy is the total field effect of the CoC₄N₄ system. The field effect is the combination of the inductive effect of cobalt and the effect of donation through Co→dioxime and Co→axial ligand and back-donation.

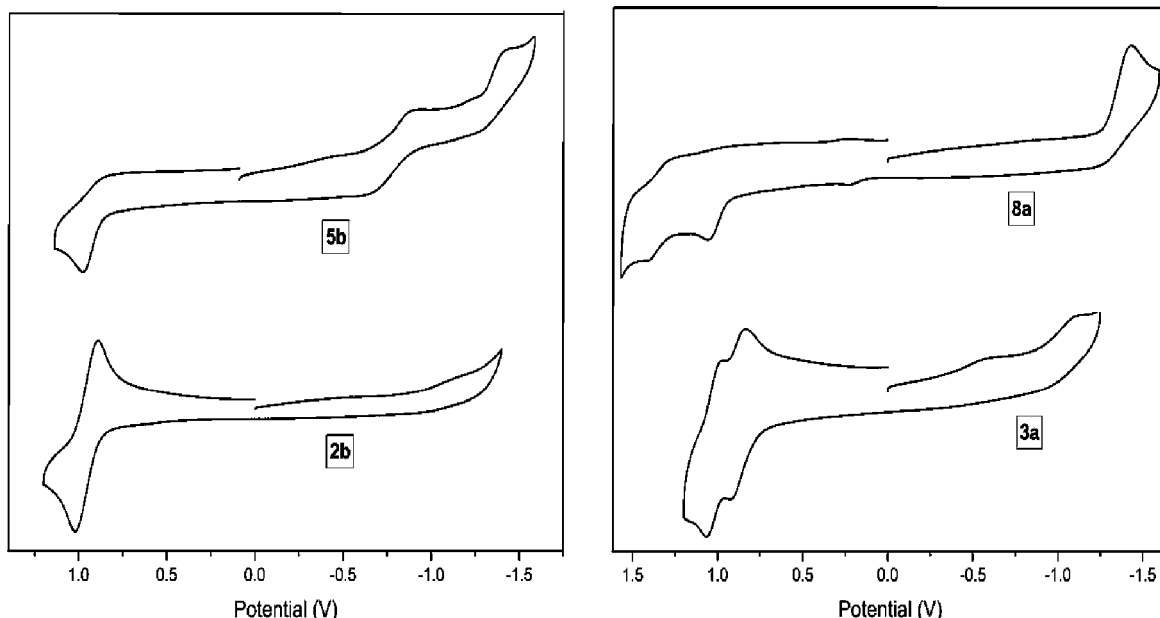


Figure 4. Cyclic voltammograms of (a) monocobaloximes and (b) biphenyl-bridged dicobaloximes in DCM with 0.1 M ($t\text{Bu}_4\text{NPF}_6$) as supporting electrolyte at 0.2 V s $^{-1}$ at 25 °C.

Table 4. CV Data of Cobaloximes in DCM and TBAPF $_6$ at 0.2V/s at 25 °C

no.	CoIII/CoII		CoII/CoI		CoIV/CoIII									
	E_{pc} (V)	i_{pc} (μA)	E_{pc} (V)	i_{pc} (μA)	E_{pc1} (V)	i_{pc} (μA)	E_{pa1} (V)	i_{pa} (μA)	$E_{1/2}^a$ (V)	E_{pc2} (V)	i_{pc} (μA)	E_{pa2} (V)	i_{pa} (μA)	$E^{1/2}$ (V)
1a			-0.92	4.89			0.74					0.87	3.49	
2a			-1.23				0.80	2.11				1.14	3.21	
3a	-0.56		-1.08		0.83	2.55	0.91	2.75	0.87	0.98	3.31	1.05	3.39	1.02
5a	-0.99		-1.49	16.4			0.96	11.5				1.39	16.1	
8a			-1.43	9.34			1.05	5.17				1.4	3.65	
2b			-1.12		0.89		1.02	3.01	0.95					

$^a E_{1/2} \text{Fc/Fc}^+ = 0.4269 \text{ V}$.

Table 5. Comparative CV Data Taken in DCM and TBAPF $_6$ at 0.2 V/s at 25 °C

compound	Co ^{III} /Co ^{II}	Co ^{II} /Co ^I	Co ^{IV} /Co ^{III}					ref
	E_{pc} (V)	E_{pc} (V)	E_{pc} (V)	$E_{pa(1)}$ (V)	$E_{1/2}$ (V)	E_{pc} (V)	$E_{pa(2)}$ (V)	
PhCH $_2$ Co(dmgH) $_2$ Py		-1.04	0.842	0.917	0.879			this work
PhCH $_2$ Co(dpgH) $_2$ Py	-0.88	-1.3	1.09	1.01	1.05			this work
[PhCH $_2$ Co(dmgH) $_2$] $_2$ - μ -Pz	-0.887	-1.28			1.023			30
[PhCH $_2$ Co(dpgH) $_2$] $_2$ - μ -Pz		-1.27			1.203			30
[Co(dmgH) $_2$ Py] $_2$ - μ -m xylene		-1.3		0.98			1.34	5b

through pyrazine.³⁰ The presence of two oxidative potentials in the present systems suggests that one cobaloxime unit affects the other cobaloxime unit in terms of its electrochemical behavior, and this occurs via the bridging biphenyl rings.

Since the X-ray structural parameters in **3a** and **7a** show that each cobaloxime unit behaves as an independent benzyl cobaloxime, the electrochemical data in the dicobaloximes should resemble the corresponding benzyl cobaloximes. However a comparison of the data with the benzyl cobaloximes shows that the dicobaloximes are more difficult to oxidize, and unlike the BnCo(dioxime) $_2$ Py, they do not show any reversible wave in the oxidation half. This difference further suggests the transmission of the effect of one cobaloxime unit on the other. Again the monocobaloxime **5b** shows an irreversible oxidation wave, whereas **2b** shows a single reversible oxidation wave just like in the simple benzyl cobaloximes. However, the oxidation is more difficult compared to the BnCo(dioxime) $_2$ Py.

Conclusion

4,4'-Disubstituted biphenyl-bridged dicobaloximes have been synthesized. Two crystal structures, reported for the first time, show two distinct cobaloxime units, Co(dioxime) $_2$ Py, bridged by biphenyl, that can be looked at as two independent benzyl cobaloximes. The two cobaloxime units are symmetrical and have no direct or indirect interaction between them. The NMR and electrochemical study, however, show it otherwise. The two cobalt centers are oxidized at different potentials as two discrete units. Also the oxidation of the cobalt centers becomes more difficult by the substitution of electron-withdrawing groups at the 4,4'-position in the biphenyl. The cobalt-bound CH $_2$ is diastereotopic and the J value in the ^1H NMR corresponds to the geminal coupling. The dioxime protons, dmgH(Me), also show nonequivalence in a 1:1 ratio. The chemical shift of one of the CH $_2$ protons is affected by the electron-withdrawing groups at the 4,4'-position in biphenyl. The NMR data suggest that the dicobaloximes are more rigid than the methyl-substituted biphenyl monocobaloxime and the orientation of two [Co] centers in the dicobaloximes is fixed in such a

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way as to eliminate or partly reduce the steric interactions between the two cobaloxime units. The nonequivalence may occur due to atropisomerism and/or restricted rotation of the C–Ph/Co–C bond.

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Supporting Information Available: Table of CHN analysis data, ¹³C NMR, yields of mono- and dicobaloximes under different conditions, representative figures, and the CIF files for X-ray crystal structures of **3a** and **7a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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