2-Substituted *m*-Xylylene-Bridged Dicobaloximes: Structure−Property Relationship Using Variable-Temperature ^{1}H NMR Study†

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m-Xylylene-bridged dicobaloximes with a substituent at the 2-position having varying electronic and steric properties have been synthesized and characterized by ^{1}H and ^{13}C NMR spectroscopy. The variable-temperature ^{1}H NMR study of these complexes shows that the electronic *cis* influence is an important phenomenon for the Co−C bond rotation. The coalescence temperature of the dioxime protons correlates well with the *ortho* substituent constant. The crystal structure of a 2-nitro-*m*-xylylene-bridged dicobaloxime, Py(dmgH)$_2$Co-CH$_2$-(2-NO$_2$-1,3-C$_6$H$_3$)-CH$_2$-Co(dmgH)$_2$Py, is reported. The X-ray structural data support the ^{1}H NMR findings.

Introduction

The character of the Co−C bond in organocobaloximes has been the center of study ever since the discovery that the coenzyme B_{12} contained such a linkage. Organocobaloximes have been extensively studied and reviewed in the last four decades.[1] Because of the inherently weak Co−C bond, these complexes are photolabile and have been utilized in organic synthesis and in polymer chemistry. The weakening of the Co−C bond in cobaloximes RCo(L)$_2$B has been interpreted as a function of steric as well electronic properties of R, L, and B ligands.[1]

Although numerous examples of mononuclear organocobaloximes have been described, the examples of organo-bridged dicobaloximes are rather scarce. We have recently reported the synthesis and characterization of organo-bridged dicobaloximes of the type PyCo(L)$_2$-R-Co(L)$_2$Py [L = gH, dmgH, chgH, and dpgH, R = *ortho*-, *meta*-, and *para*-xylylene].[2] The results suggest that the restriction to rotational freedom around the Co−C bond exists in such complexes. For example, the two cobaloxime units are far away from each other in the *para*-xylylene complex; each one behaves as an independent benzyl cobaloxime unit such that the rotational freedom is not restricted in any way at any temperature. On the other extreme, the rotation is fully restricted in the *ortho*-xylylene complex at room temperature. In the *meta* isomer the free rotation of the Co−C bond occurs at room temperature but becomes restricted at low temperature. This rotation is further affected substantially by the substituent present on the dioxime moiety, with the result that the coalescence temperature for the CH$_2$ signal follows the order dpgH > dmgH > gH.

The case study of *m*-xylylene-bridged dicobaloximes becomes significant since the restricted rotation is easily controlled externally by varying the temperature and can be studied by ^{1}H NMR. In the previous article, we could not rationalize whether the restriction to Co−C bond rotation was due to steric or electronic factors or a combination of both. Also in the absence of a crystal structure we could, at best, propose a tentative structure of the dicobaloxime.

Since the orientation of the benzyl group is such that the plane of the aromatic ring lies above the dioxime moiety in all the known crystal structures, PhCH$_2$Co(dmgH)$_2$Py,[3] PhCH$_2$Co(dmgH)(dpgH)Py,[4] PhCH$_2$Co(chgH)(dpgH)Py,[4] and (*o*-vinyl)C$_6$H$_4$CH$_2$Co(dmgH)$_2$Py,[2] the ring current in the phenyl group preferentially and significantly affects only one of the dioxime units in the cobaloxime moiety. It is, therefore, envisaged that any change in the steric and/or electronic properties of the bridging phenyl group should effect not only the degree of freedom of Co−C bond rotation but also the chemical shift in the dioxime and CH$_2$ bound to cobalt. We have therefore synthesized and characterized 2-substituted-*meta*-xylylene-bridged dicobaloximes, Py(dioxime)$_2$CoCH$_2$-(2-X-1,3-C$_6$H$_3$)-CH$_2$Co(dioxime)$_2$Py [dioxime = dmgH, dpgH]. The X-ray structure of 2-nitro-*meta*-xylylene dicobaloxime is reported. This is done to see if the structural details support the low-temperature NMR data. The low-temperature ^{1}H NMR data have been correlated with the substituent constant of X in the bridging phenyl group.

Experimental Section

General Comments. Cobalt chloride hexahydrate, dimethylglyoxime (SD Fine, India), diphenylglyoxime, 2-fluoro-

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Table 1. Crystal Data and Structure Refinement Details for 5

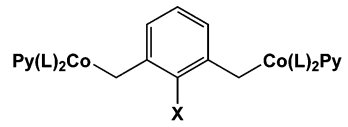
	2-NO_2-1,3-C_6H_3-[$CH_2Co(dmgH)_2$-Py]$_2$·C_2H_5OH
empirical formula	$C_{36}H_{51}N_{11}O_{11}Co_2$
fw	931.74
temperature (K)	100(2)
radiation λ (Å)	Mo Kα 0.071073
diffractometer	CCD area detector
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	
a (Å)	8.495(7)
b (Å)	15.544(12)
c (Å)	16.264(12)
α (deg)	73.740(10)
β (deg)	85.911(2)
γ (deg)	77.530(10)
V (Å^3)	2013(3)
Z	2
r(calc) (Mg/m^3)	1.537
μ (mm^{-1})	0.898
F(000)	972
cryst size (mm^3)	0.26 × 0.23 × 0.17
index ranges	$-11 \le h \le 11$ $-20 \le k \le 11$ $-21 \le l \le 18$
no. of reflns collected	13 615
no. of indep reflns	9627
refinement method	full-matrix least squares on F^2
GOF on F^2	1.050
final R indices ($I > 2\sigma(I)$)	R1 = 0.0685 wR2 = 0.1584
R indices (all data)	R1 = 0.0894 wR2 = 0.1705
no. of data/restraints/param	9627/0/550

1,3-dimethylbenzene, 2-chloro-1,3-dimethylbenzene, 2-bromo-1,3-dimethylbenzene, 2-nitro-1,3-dimethylbenzene, 2-methoxy-1,3-dimethylbenzene, *n*-butyllithium, and ethyl bromide were purchased from Aldrich or Fluka and were used as such. 1,3-Bis(bromomethyl)-2-fluorobenzene,[5] 1,3-bis(bromomethyl)-2-chlorobenzene,[6] 1,3-bis(bromomethyl)-2-bromobenzene,[7] 2,6-bis(bromomethyl)nitrobenzene,[8] 1,3-bis(bromomethyl)-2-methoxybenzene,[9] 1,3-bis(bromomethyl)-2-ethylbenzene,[10] and ClCo(dioxime)$_2$Py[11−13] were synthesized according to the literature reports. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a JEOL-JNM LAMBDA 400 model spectrometer in $CDCl_3$. For ^{1}H and ^{13}C NMR spectra, TMS was used as an internal reference. For ^{19}F NMR spectra, $CFCl_3$ was used as a reference. Elemental analysis was carried out using a thermoquest CE Instruments CHNS-O elemental analyzer. All the dicobaloxime complexes were characterized by elemental analyses and ^{1}H and ^{13}C NMR spectroscopy (Tables 2−4). The complexes synthesized are given in Scheme 1.

X-ray Structural Determination and Refinement. Orange crystals were obtained by slow evaporation of the solution of **5** in dichloromethane/ethanol/hexane. Single-crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα 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.[14a] The data integration and reduction were processed with SAINT[15] software. An empirical absorption correction was applied to the collected reflections with SADABS[16] using XPREP.[17] The structure was solved by the direct method using SHELXTL[18] and was refined on F^2 by the full-matrix least-squares technique using the SHELXL-97[14b] 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 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.

A cif file is deposited with the Cambridge Crystallographic Data Center (CCDC number for **5** is 271724). 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/).

Scheme 1. Cobaloximes



L	X						
	H	F	Cl	Br	NO_2	OMe	Et
dmgH	**1**	**2**	**3**	**4**	**5**	**6**	**-**
dpgH	**7**	**8**	**9**	**10**	**11**	**12**	**13**

Results and Discussion

Synthesis. All the complexes reported in this work are new. The substituents have varying electronic and steric properties (Scheme 1). The dicobaloximes have been synthesized by a procedure described earlier for the synthesis of organo-bridged dicobaloximes.[2] A mixture of mono- and dicobaloxime is formed in each reaction. The dicobaloximes result due to a two-step oxidative alkylation of Co(I) with the corresponding dihalide, the second step being slower than the first. The formation of a small amount of monocobaloxime in each reaction supports this view. The yield of dicobaloxime depends on many factors such as the reaction time, dihalide:Co(I) ratio, and the nature of the dihalide. A high solvent:Co(I) ratio favors the formation of dicobaloxime. The mono- and dicobaloximes were separated on silica gel columns or by fractional crystallization by a procedure described earlier for xylylene-bridged dicobaloximes.[2] In general, the yield of dpgH complexes (**7**−**13**) is higher compared to the dmgH complexes (**1**−**6**)

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Table 2. Yield and Elemental Analysis Data for 1−13

no.	yield	formula	elemental analysis calc (found) C	H	N
1	55	$C_{34}H_{46}Co_2N_{10}O_8$	48.58 (48.56)	5.52 (5.55)	16.66 (16.66)
2	35	$C_{34}H_{45}Co_2N_{10}O_8F$	47.56 (47.56)	5.28 (5.24)	16.31 (16.34)
3	38	$C_{34}H_{45}Co_2N_{10}O_8Cl$	46.66 (46.65)	5.18 (5.15)	16.01 (16.05)
4	35	$C_{34}H_{45}Co_2N_{10}O_8Br$	44.41 (44.44)	4.93 (4.97)	15.23 (15.26)
5	39	$C_{34}H_{45}Co_2N_{11}O_{10}$	46.11 (46.13)	5.12 (5.10)	17.40 (17.43)
6	41	$C_{35}H_{48}Co_2N_{10}O_9$	48.28 (48.25)	5.56 (5.54)	16.09 (16.05)
7	69	$C_{74}H_{62}Co_2N_{10}O_8$	66.47 (66.44)	4.64 (4.67)	10.43 (10.47)
8	41	$C_{74}H_{61}Co_2N_{10}O_8F$	65.58 (65.55)	4.54 (4.53)	10.34 (10.31)
9	47	$C_{74}H_{61}Co_2N_{10}O_8Cl$	64.80 (64.82)	4.48 (4.45)	10.21 (10.24)
10	45	$C_{74}H_{61}Co_2N_{10}O_8Br$	62.76 (62.75)	4.34 (4.32)	9.89 (9.85)
11	44	$C_{74}H_{61}Co_2N_{10}O_{10}$	64.30 (64.34)	4.45 (4.43)	11.15 (11.18)
12	52	$C_{75}H_{64}Co_2N_{10}O_9$	65.88 (65.84)	4.72 (4.76)	10.25 (10.21)
13	49	$C_{76}H_{66}Co_2N_{10}O_8$	66.86 (66.89)	4.87 (4.83)	10.26 (10.24)

Table 3. ^{1}H NMR Data for 1−13 in $CDCl_3$

no.	CH_2Co	L	pyridine α	pyridine β	pyridine γ	O−H···O	others
1	2.78	1.92	8.37 (5.2)	7.26	7.66 (7.6)	18.16	6.32 (s), 6.70 (t) (7.6), 6.86 (d) (7.2)
2	2.83 (bs)[a]	1.96	8.52 (5.2)	7.25 (7.6)	7.65 (7.2)	18.06	6.52 (t) (8.0), 6.86 (d) (7.6)
3	2.92 (bs)	1.96	8.52 (5.6)	7.26 (6.4)	7.66 (7.6)	18.19	6.62 (t) (7.6), 6.90 (d) (7.2)
4	3.03 (bs)	1.97	8.52 (5.2)	7.25 (6.8)	7.65 (8.0)	18.16	6.65 (t) (7.6), 6.90 (d) (8.0)
5	2.89 (bs)	2.01	8.43 (5.2)	7.23 (7.2)	7.64 (7.6)	18.00	6.83 (t) (6.8), 6.93 (d) (7.6)
6	3.02	1.95	8.54 (4.4)	7.25 (7.2)	7.65 (8.0)	18.26	3.87 (s), 6.38 (t) (7.6), 6.71 (d) (8.0)
7	3.45	6.96 (d) (6.4)	7.79 (8.0)	8.87 (5.2)	7.39 (6.8)	18.74	6.83 (t) (7.6), 7.45 (s)[b]
8	3.10 (bs), 3.84 (bs)	7.00 (d) (6.4), 7.13−7.20 (m)	8.88 (4.8)	7.40 (7.2)	7.80 (7.6)	18.71	6.57 (t) (7.2)[b]
9	3.44 (bs), 4.02 (bs)	6.96 (bs), 7.14−7.20 (m)	8.88 (5.6)	7.40 (6.8)	7.79 (7.6)	18.78	6.62 (t) (7.6), 7.11 (d) (6.0)
10	3.46 (bs), 4.02 (bs)	6.96 (bs), 7.15−7.21 (m)	8.89 (5.2)	7.42 (6.4)	7.81 (7.2)	18.78	6.63 (t) (7.2)[b]
11	3.72 (bs)	7.04 (d) (7.6), 7.18−7.21 (m)	8.80 (5.2)	7.38 (7.2)	7.79 (7.2)	18.64	6.71 (t) (7.6)[b]
12	3.40 (bs)	6.97 (d)(6.4), 7.11−7.25 (m)	8.88 (5.2)	7.40 (6.4)	7.79 (7.4)	18.72	3.86(s)
13	3.79	6.94 (d) (8.0), 7.14−7.20 (m)	8.90 (5.2)	7.41 (6.4)	7.80 (8.0)	18.82	1.55 (t) (6.8), 2.89 (q) (7.2), 6.58 (t) (7.6)

[a] bs = broad. [b] Merge with dpgH protons.

Table 4. ^{13}C NMR Data for 1−13 in $CDCl_3$

no.	CH_2Co	C=N	Py α	Py γ	Py β	aromatic	others
1	31.1	149.2	150.3	137.3	125.1	125.6, 127.0, 128.0, 145.9	11.9
2	28.6	149.5	150.2	137.3	125.1	122.5, 128.1, 131.2, 133.5, 133.7	11.9
3	27.0	149.5	150.0	137.2	125.0	124.5, 127.8, 131.1, 144.8	11.9
4	30.4	149.6	150.1	137.3	125.1	124.1, 127.8, 146.7	12.0
5	26.6	149.9	150.0	137.4	125.1	128.6, 141.1, 147.4	12.1
6	24.9	149.3	150.1	137.1	125.0	121.3, 128.8, 138.3, 156.7	11.8, 62.0
7	34.9	150.9	150.2	137.8	125.5	126.1, 127.6, 128.7, 129.8, 130.0, 146.8	
8	25.6	151.0	150.1	137.8	125.5	123.9, 127.6, 127.9, 128.6, 128.8, 129.8, 130.0, 134.2, 134.4	
9	29.7	151.1	150.0	137.8	125.5	126.2, 127.6, 127.8, 128.1, 128.8, 129.7, 130.0, 133.2, 145.6	
10	32.3	151.2	150.0	137.8	125.5	126.3, 126.9, 127.6, 127.9, 128.8, 129.8, 130.0, 147.6	
11	29.7	151.3	149.9	138.0	125.6	127.6, 127.9, 128.0, 128.9, 129.8, 129.9, 142.1, 148.8	
12	26.5	151.3	149.9	138.0	125.5	127.6, 127.7, 127.9, 129.0, 129.6, 129.8, 129.8	61.0
13	31.8	151.2	150.0	137.8	125.5	125.9, 127.7, 127.9, 128.8, 129.5, 129.7, 130.0, 145.3	15.1, 22.3

(Table 2). Also the yield of **1** and **7** is higher than the rest of the compounds. The dpgH complexes are more soluble in chloroform or dichloromethane than the corresponding dmgH complexes.

Spectroscopy. All the complexes are primarily characterized with ^{1}H and ^{13}C NMR (Tables 3 and 4). The peaks are assigned by a comparison with the ^{1}H and ^{13}C NMR values in xylylene-bridged dicobaloximes reported recently by us.[2] ^{19}F NMR spectra have been recorded for the fluoro-substituted complexes (**2** and **8**), and they appear at −119.7 and −114.9 ppm, respectively. The dmgH methyl protons appear as a singlet, and the upfield shift follows the order NO_2 < Br ≈ Cl ≈ F < OMe < H. In the dpgH complexes (**7**−**13**) two sets of peaks are observed for the dioxime phenyl protons. The *ortho* hydrogens (16H in all) appear as a doublet around 6.90−7.10 ppm, and the remaining protons appear as a multiplet at further low field. The upfield shift of the *ortho* hydrogens follows the order NO_2 < F < Br ≈ Cl ≈ H ≈ OMe < C_2H_5. The CH_2 protons appear as a singlet in **1**, **5**, and **6** and as a broad peak in **4**. No peak is observed in **2** and **3** at room temperature; however a broad singlet is seen at 40 °C. The downfield chemical shift follows the order OMe ≈ Br > Cl > NO_2 > F > H. In the corresponding dpgH complexes, CH_2 protons appear as a singlet in **7**, **11**, **12**, and **13** and as

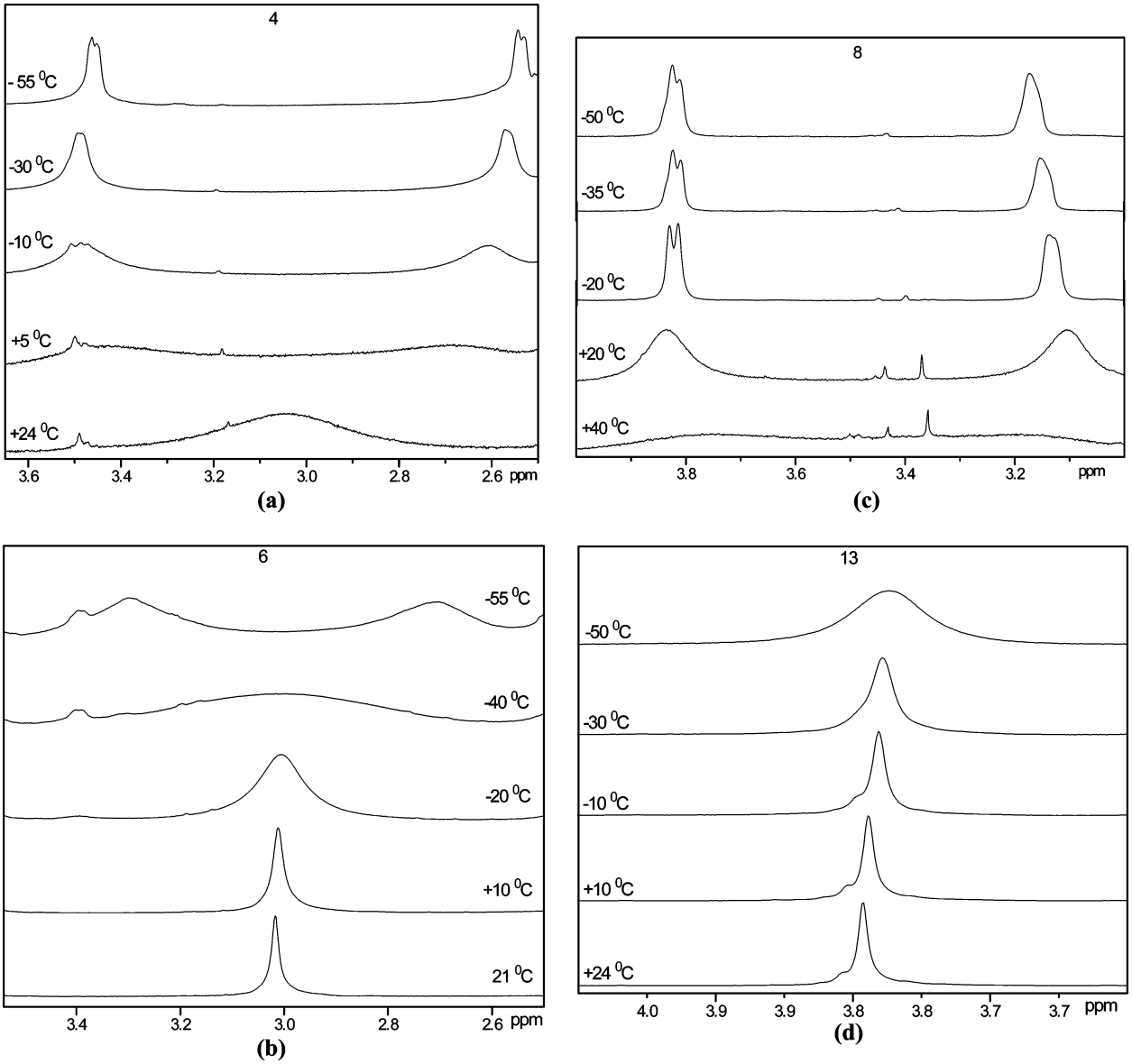

Figure 1. Variable-temperature ^{1}H NMR spectra of the CH_2−Co signal for (a) **4**, (b) **6**, (c) **8**, and (d) **13**.

two peaks in **8**, **9**, and **10**. The downfield chemical shift follows the order C_2H_5 > NO_2 > H. The room-temperature NMR spectra do not reveal the environment of CH_2 and dioxime methyl/phenyl protons. Therefore, a low-temperature NMR study was carried out on these samples.

^{1}H NMR spectra have been recorded for the complexes **1**−**13** in the temperature range +40 to −60 °C. The peaks considered for study are (a) the CH_2 resonance, (b) the dioxime methyl and phenyl resonance, (c) the pyridine resonance, and (d) the bridging phenyl ring resonance (see Figures 1, 2 and Table 5).

The dynamic process involving cobalt-bound CH_2 and dioxime methyl/phenyl signals (methyl in **1**−**6** and phenyl in **8**−**13**) are readily seen, but the other parts of the NMR spectrum are temperature invariant. For example, both CH_2 and dmgH methyl protons in **1** appear as singlets at room temperature. These peaks broaden at 0 °C and sharpen below this temperature, and finally at −60 °C CH_2 protons appear as a double doublet at 2.65 (J = 5.2 Hz) and 2.82 (J = 5.6 Hz) ppm with the chemical shift difference ($\Delta\delta$) of 68 Hz and dmgH methyl signals appear at 1.85 and 2.06 ppm ($\Delta\delta$ = 84 Hz). The CH_2 group in **7** shows a pattern similar to that in **1** except that the coalescence temperature is higher in **7** as compared to **1**.

Table 5. Coalescence Temperature (*A*) and $\Delta\delta$ in 1−13

CH_2Co (**1**−**6**)

	1	**2**	**3**	**4**	**5**	**6**
σ_o^-	0.00	0.29	0.50	0.55		−0.37
A (°C)	0	+30	+15	+10	+10	−40
$\Delta\delta$ (Hz)	68	380	400	384	380	236
dmgH-Me (**1**−**6**)						
A (°C)	0	−10	−15	−20	−15	
$\Delta\delta$ (Hz)	84	52	28	28	28	

CH_2Co (**7**−**13**)

	7	**8**	**9**	**10**	**11**	**12**	**13**
σ_o^-	0.00	0.29	0.50	0.55		−0.37	−0.15
A (°C)	+8	+40	+40	+25	0	+10	
$\Delta\delta$ (Hz)	16	220	200	160	108	230	
dpgH *o*-protons (**7**−**13**)							
A (°C)	0	0	+10	+10	+10	−10	−50
$\Delta\delta$ (Hz)	28	28	80	104	28	68	

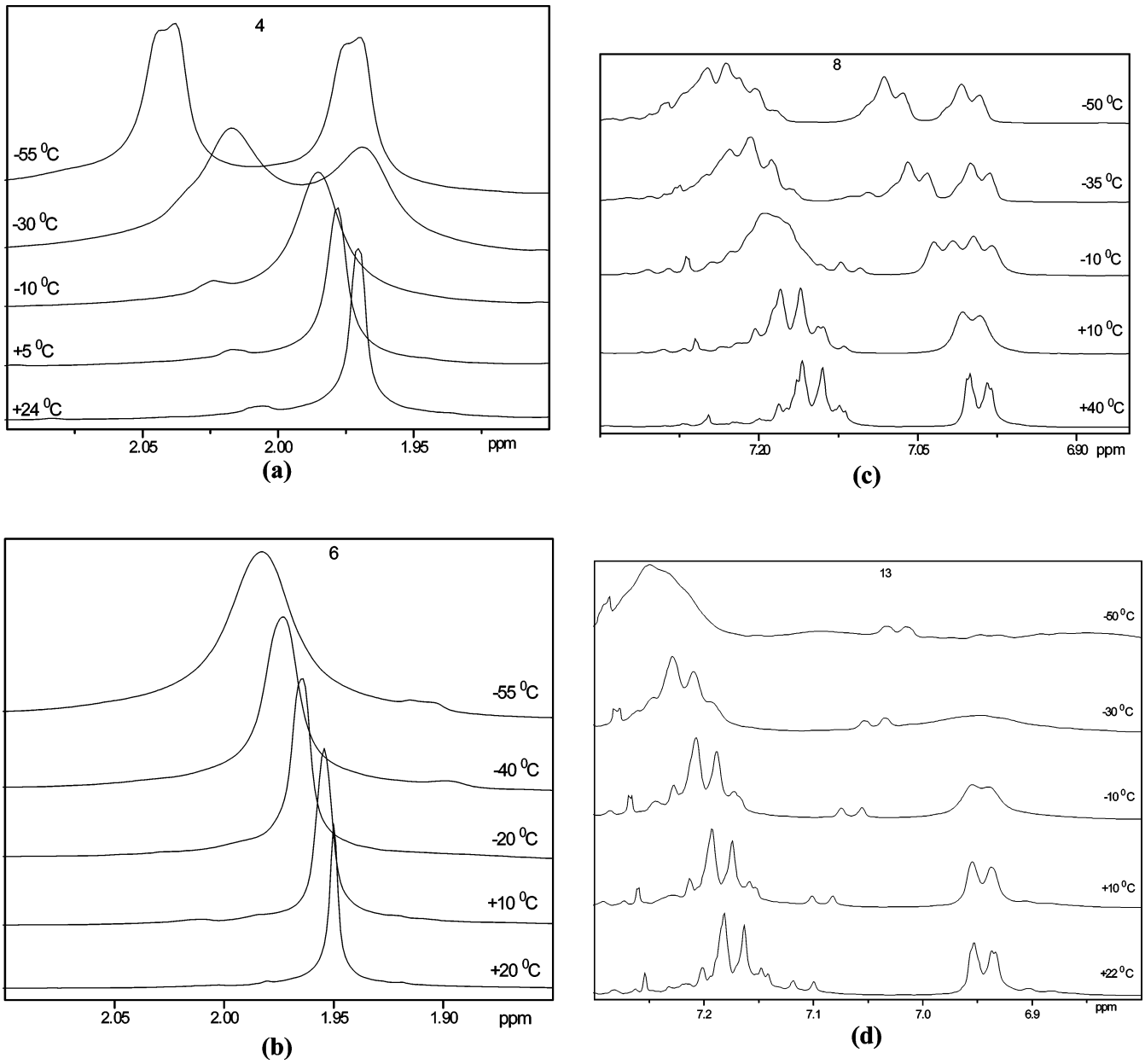

Figure 2. Variable-temperature ^{1}H NMR spectra of the dioxime (methyl/phenyl) signal for (a) **4**, (b) **6**, (c) **8**, and (d) **13**.

Although no signal for CH_2 is observed in **2** at room temperature, two very broad peaks start appearing at 10 °C and finally at −50 °C two peaks appear at 2.26 and 3.21 ppm ($\Delta\delta$ = 380 Hz). Each peak is a doublet because of the coupling between the two geminal hydrogens. Similarly the dmgH methyl appears as a singlet at 1.96 ppm at room temperature and broadens at −10 °C, and finally two peaks of equal intensity appear at 1.92 and 2.05 ppm at −50 °C ($\Delta\delta$ = 52 Hz); **3**−**6** behave similarly, but $\Delta\delta$ values vary depending upon the substituent X. For example $\Delta\delta$ values for CH_2 protons at −55 °C in **5** and **6** are 380 and 236 Hz and the dmgH methyl protons in **6** do not split even at −55 °C (Figure 2c).

The dpgH complexes **7**−**13** show behavior similar to that in **1**−**6**, but the coalescence temperature is higher in the former, except **11**. Two sets of peaks are observed at room temperature for the dpgH phenyl protons. The *ortho* protons appear as a doublet at 6.96 ppm, and the remaining protons appear as a multiplet. The *ortho* protons coalesce at 0 °C, and two doublets of equal intensity appear below this temperature. The *ortho* protons of one dpgH in each cobaloxime unit give a doublet by vicinal coupling, and the other dpgH unit gives the other doublet. At the limiting temperature, 28 Hz separates the two doublets.

Surprisingly, CH_2 protons in **8** appear as two peaks at 3.10 and 3.84 ppm at room temperature and $\Delta\delta$ is 220 Hz at −50 °C. In **13** no splitting of the CH_2 peak is observed even at −50 °C (Figure 1d) and the coalescence temperature for the dpgH protons is −50 °C. The spectra of CH_2 and dioxime methyl/phenyl protons at different temperature are given in Figures 1 and 2.

A few general observations are made: (a) the $\Delta\delta$ value in the dpgH complexes is always lower than the corresponding dmgH complexes (Table 5); (b) the coalescence temperature of CH_2 is always higher than the dioxime methyl/phenyl protons; (c) the electron-donating substituents OMe or C_2H_5 lower the coalescence temperature of CH_2 and dmgH protons.

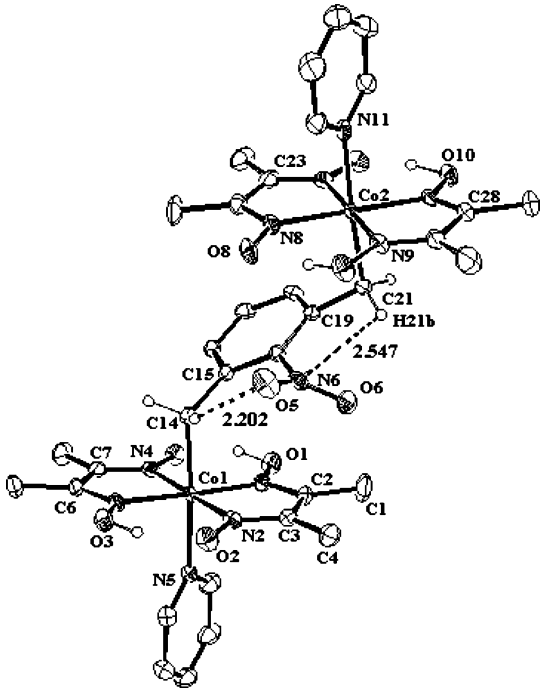

Figure 3. Crystal structure of 2-NO_2-1,3-C_6H_3-[CH_2Co(dmgH)$_2$Py]$_2$ (**5**) with selected numbering scheme. Solvent molecule and hydrogen atoms are omitted for clarity.

Table 6. Selected Bond Lengths and Angles and Structural Data for 5

Co−Co (Å)	7.871
bending between two cobaloxime planes (deg)	13.0
twist angle between two cobaloxime planes (deg)	19.24(2)

	Co1	Co2
Co−C (Å)	2.035(4)	2.057(4)
Co−N_{ax} (Å)	2.054(3)	2.041(3)
C−Co−N_{ax} (deg)	176.47(13)	175.91(14)
Co1−C−C(Ph) (deg)	118.3(2)	115.7(3)
d (Å)	+0.029(9)	−0.0063(8)
α (deg) (dihedral angle)	2.99	8.81
O5···H14B (Å)	2.202(9)	
N6···H21B (Å)		2.547(8)

The molecule attains a near static structure at −55 °C and ^{1}H NMR data show that the nonequivalence of CH_2 as well as dioxime protons arises due to the substituent X. Can one see the interaction of X with CH_2 and the dioxime protons in the solid state? (See the Supporting Information.) The X-ray structure should clarify this question.

X-ray Crystallographic Studies: Description of Structure 5. The X-ray analysis of these crystals showed the composition as 2-NO_2-1,3-C_6H_3-[CH_2Co(dmgH)$_2$Py]$_2$·C_2H_5OH. The "Diamond" diagram of the molecular structure for **5** along with the selected numbering scheme is shown in Figure 3. Selected bond lengths and bond angles are given in Table 6. This is the first crystal structure of any organo-bridged dicobaloxime. The structure matches exactly with the previously proposed tentative structure of 1,3-xylylene-bridged dicobaloxime. Two distinct cobaloxime units are axially bridged together with *meta*-xylylene to form the dicobaloxime unit, and the distance between the two cobalt atoms is 7.871 Å. The nitro group is located at the 2-position. The geometry around each cobalt atom is distorted octahedral with four nitrogen atoms of the dioxime (dmgH) in the equatorial plane.

Cobalt atoms are displaced (*d*) from the equatorial N4 plane of two dioximes (Co1 = +0.029(9) and Co2 = −0.0063(8)). The opposite sign suggests that Co1 is displaced toward pyridine and Co2 toward the benzyl group. The butterfly bending angles (α) are very different at the two cobalt centers (Co1 = 2.99° and Co2 = 8.81°). The sign of *d* and different values of α suggest that one dioxime unit on Co1 pushes the opposite dioxime unit toward Co2 with the result that one cobalt is displaced toward pyridine and the other toward the benzyl group. [We made similar observations: a negative value of *d* and high α value, in the recently reported mesitylglyoxime cobaloximes. The latter complexes were found to have the maximum *cis* influence among all the reported cobaloximes.[19]] This interaction cannot occur directly between the two dioxime units on Co1 and Co2, as these are too far away (>7.5 Å). This occurs via the axial aromatic ring. The two butterfly bending angles are very different because of this interaction. The two different bond angles Co1−C14−C15 (118.33°) and Co2−C19−C21 (115.67°) support this view. The butterfly bending angle has been related to the stability of the Co−C bond in organocobaloximes,[1a,b,19] and 8.81° is the largest butterfly angle observed so far in any crystal structure of an organocobaloxime. The plane of both the pyridines is almost perpendicular ($\tau \approx 90°$) to the cobaloxime unit. The bridging benzyl group is sandwiched between the two dmgH wings, and the benzene plane is situated with the angles of 34.0° and 24.2° with the cobaloxime planes of Co1 and Co2, respectively. The values point to how crowded or flattened the cobaloximes are. The equatorial planes of the two cobaloxime units are just parallel to each other (angle between the two planes = 13.0°), and also the torsion angle between the two planes is 19.24(2)°.

^{1}H NMR values at low temperature arising due to restricted rotation around the Co−C bond can now be further understood from the crystal structure. One of the methylene protons has a direct interaction with the *ortho* substituent [here the O···H distance is ∼2.20 Å and the N···H distance is ∼2.55 Å], whereas the other one is far away (>3.60 Å) and is not influenced by the *ortho* substitution. The benzene ring is sandwiched between two cobaloxime units and lies above one of the dioxime units. The ring current in benzene influences the chemical shift of the dioxime moiety.

We have found these complexes to be much more unstable in solution as compared to the mononuclear organocobaloximes; for example, one of the Co−C bonds in the *ortho*-xylylene-bridged dicobaloxime cleaved during recrystallization and formed (2-vinyl)benzylcobaloxime.[2] Since the Co−C bond length in dicobaloxime **5** is found to be similar to benzylcobaloximes [Co−C = 2.035(4) and 2.057(4) Å in **5**; 2.112(5) Å in 2-vinyl-C_6H_4-Co(dmgH)$_2$Py, and 2.065(4) Å in $PhCH_2$Co(dmgH)$_2$Py],[2] the question that arises therefore is "can the unstable nature of the Co−C bond be due to the high value of the butterfly bending angle"? A value of 8.81° certainly points toward this direction, but it is difficult to be certain until one has more crystal structures of organobridged dicobaloximes in hand.

(19) Mandal, D.; Gupta, B. D. *Organometallics* **2005**, *24*, 1501.

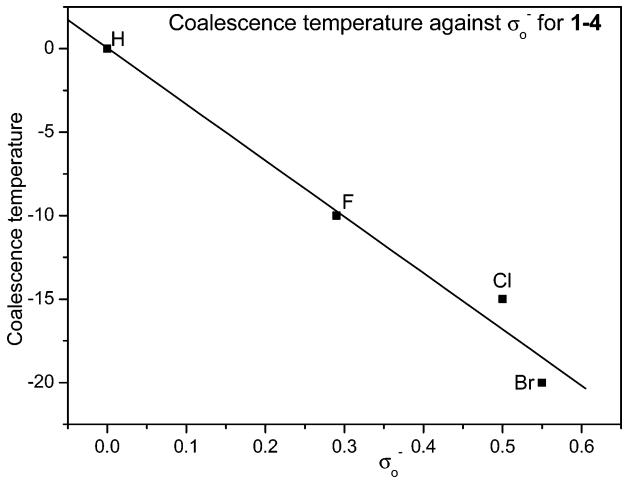

Figure 4. Plot of the coalescence temperature of the CH_3 signal in **1**−**4** against σ_o^-.

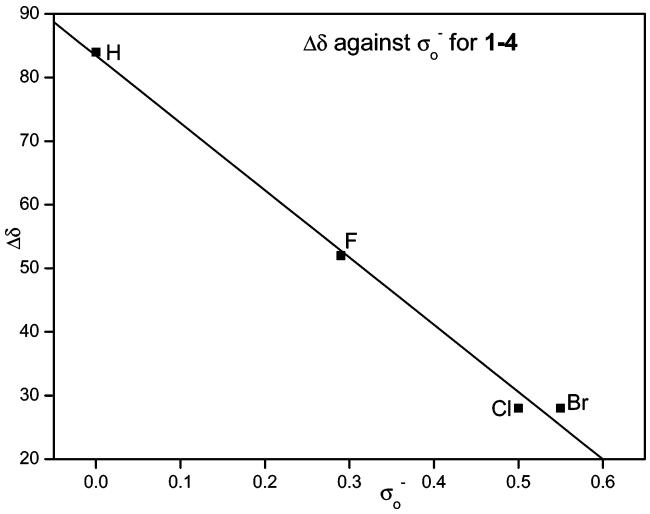

Figure 5. Plot of $\Delta\delta$ of the CH_3 signal in **1**−**4** against σ_o^-.

The variable-temperature ^{1}H NMR details in **1**−**13** clearly show that both electronic as well as steric factors are operating in restricting the Co−C bond rotation.

As the substituent X is *ortho* to the $CH_2Co(L)_2Py$ moiety, the changes observed in CH_2 protons in different complexes include electronic effects, steric effects, and intramolecular secondary interactions of the substituent.[20] The effect of an *ortho* substituent in ^{1}H NMR spectroscopy is well known,[21] and it is, in general, considered as an electronic effect and is independent of the steric effect.[20] As the *ortho* substituent constant (σ_o^-) increases, a decrease in the chemical shift of the observed hydrogen occurs.[21] We have observed no correlation between the coalescence temperature or $\Delta\delta$ value and σ_o^- for CH_2 protons; however, dioxime methyl/phenyl protons correlate well with σ_o^-. For example, σ_o^- correlates well with the coalescence temperature of the dmgH methyl protons (correlation coefficient $R = -0.99$) and with $\Delta\delta$ of dmgH methyl protons ($R = -0.99$) in **1**−**4** (Figures 4 and 5). This suggests that with an increase in σ_o^- both the coalescence temperature and $\Delta\delta$ decrease in **1**−**4**. An opposite trend is observed in the dpgH complexes: here as the σ_o^- increases, the coalescence temperature and $\Delta\delta$ also increase. This means that the dioxime methyl/phenyl protons are influenced predominantly by the electronic factors, whereas the CH_2 protons are affected both by electronic effects and by some other factor.

In general, the trend shows that the electron-donating groups OMe and Et decrease the coalescence temperature. This may happen by lengthening of the Co−C bond or a higher Co−C−C(Ph) bond angle may push the two cobalt centers away. We have not been able to test this speculation, as all efforts to grow a single crystal of **6**, **12**, or **13** have failed.

(20) Charton, M. *Prog. Phys. Org. Chem*. **1971**, *8*, 235.
(21) Tribble, M. T.; Traynham, J. G. In *Advances in Linear Free Energy Relationships*; Chapman N. B., Ed.; J. Plenum Press: New York, 1972; Chapter 4.

The restricted rotation in these dicobaloxime systems raises one more question. Although the general perception is that the Co−C bond rotation is very fast in mononuclear organocobaloximes, is it possible to slow it down at low temperature and see the nonequivalence in the equatorial dmgH protons and in the methylene bound to cobalt? Benzyl $Co(dmgH)_2Py$ does not show nonequivalence even at −55 °C. Studies are underway to check this in substituted benzyl cobaloximes.

Conclusion

2-Substituted *m*-xylylene-bridged dicobaloximes have been synthesized and characterized for the first time. The variable-temperature ^{1}H NMR studies show that the Co−C bond rotation is restricted at subzero temperature and leads to the nonequivalence of the methylene and the dioxime protons. The coalescence temperature of the CH_2 signal and the equatorial dioxime protons depends on the bridging phenyl group. The crystal structure of 2-nitro *m*-xylylene-bridged dicobaloximes shows that the bridging phenyl ring lies above one of the dioxime units and its ring current influences the chemical shift of the dioxime protons. The *ortho* substituent constant (σ_o^-) correlates well with the dioxime protons, whereas no correlation is found with the methylene protons.

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Supporting Information Available: Figure for interaction of X (*ortho* substituent) with CH_2 and dioxime protons and the CIF file for crystal structure **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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