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Synthesis, characterization, CV, and X-ray structures of aryl cobaloximes

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ABSTRACT

Aryl cobaloximes, $ArCo(dioxime)_2Py$ (**1**–**9**) (Ar = phenyl, 1-naphthyl, 2-naphthyl; dioxime = dmgH, dpgH, gH) have been synthesized and characterized primarily by NMR and elemental analyses and molecular structures of four complexes have also been determined crystallographically. The electronic and steric effects of the aryl ring size and the equatorial dioxime affect the NMR chemical shifts and the X-ray structural parameters. The cyclic voltammetry study shows that the aryl cobaloximes are reduced electrochemically more easily as compared to the corresponding alkyl complexes. These complexes have a robust Co–C bond and are very stable in solution and show no sign of decomposition even on irradiation under oxygen atmosphere – an unusual property of any organocobaloxime.

1. Introduction

Organocobaloximes[1] have extensively been used as structural and functional mimic for vitamin B_{12} [1–4] ever since these were first introduced by Schrauzer four decades ago as model of vitamin B_{12} [5–7]. These represent a unique class of compounds in organometallic and bioinorganic chemistry. Although they do not accurately reproduce all chemical properties of B_{12}, the wealth of available information on their reactivity in comparison with B_{12} derivatives renders cobaloximes as good starting point for understanding the properties of cobalamins [8]. Besides, these have rich coordination chemistry, application in organic synthesis [9–16] and catalysis [17,18], and their stability and redox properties are of particular interest.

Alkyl cobaloximes with dmgH as equatorial dioxime have been studied the most and the examples with other dioximes are rather few and many have recently been reported [19–26]. Surprisingly the examples of aryl cobaloximes, $ArCo(dmgH)_2B$, are limited and there is no report with dioxime other than dmgH [6,27–36]. The literature also lacks information on their general properties like stability in solution, sensitivity toward oxygen, redox behavior and structural studies. With an objective to study all these aspects, we have synthesized and characterized nine aryl cobaloximes, $ArCo(dioxime)_2Py$ (**1**–**9**) [Ar = phenyl, 1-naphthyl, 2-naphthyl; dioxime = gH, dmgH, dpgH] (Chart 1). All the complexes are new except **1**. The complexes **3**, **4**, **6** and **9** have also been structurally characterized by X-ray. Since the steric and electronic nature of the axial and equatorial ligands affect the properties of cobaloximes [37–41], the dioxime and aryl ring size have been varied to study their effect on the structure and on the NMR chemical shifts.

2. Experimental section

2.1. Materials and physical measurements

Cobalt chloride hexahydrate, bromobenzene, and dimethylglyoxime (SD Fine, India), glyoxime (caution! it is highly flammable and explosive when dry; from Alfa Aesar, Lancaster), diphenylglyoxime, 1-bromonaphthalene, 2-bromonaphthalene (all from Aldrich) were used as received without further purifications. Chlorocobaloximes, $ClCo(dioxime)_2Py$ (dioxime = gH, dmgH, dpgH) were prepared according to the literature procedures [6,21,23]. The solvents were purified rigorously by standard procedures prior to their use [42] and THF was dried over sodium/benzophenone.

Cyclic voltammetry measurements were carried out using a BAS Epsilon electrochemical work station with a glassy carbon working electrode, Ag/AgCl reference electrode (3 M KCl) and a platinum-wire counter electrode. All measurements were performed in 0.1 M $^nBu_4NPF_6$ in dichloromethane (dry) at a concentration of 1 mM of each complex. ^1H and ^{13}C spectra were recorded on a JEOL ECX-500

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[1] Cobaloximes have the general formula $RCo(L)_2B$, 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), 1,2-cyclohexanedione dioxime (chgH), diphenylglyoxime (dpgH), dimesitylglyoxime (dmestgH), and dithiophenylglyoxime (dSPhgH).

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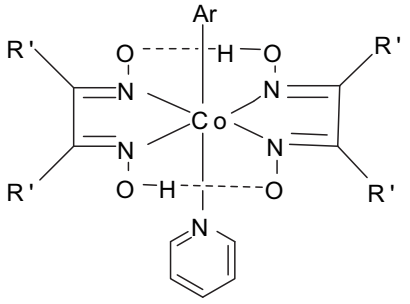

1. PhenylCo(dmgH)$_2$Py
2. 1-naphthylCo(dmgH)$_2$Py
3. 2-naphthylCo(dmgH)$_2$Py
4. PhenylCo(dpgH)$_2$Py
5. 1-naphthylCo(dpgH)$_2$Py
6. 2-naphthylCo(dpgH)$_2$Py
7. PhenylCo(gH)$_2$Py
8. 1-naphthylCo(gH)$_2$Py
9. 2-naphthylCo(gH)$_2$Py

Chart 1. Aryl cobaloximes [ArCo(dioxime)$_2$Py].

FT NMR Spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C) in $CDCl_3$ with TMS as internal standard and the chemical shift values are reported in parts per million. Elemental analyses for C, H and N were performed on CE-440 Elemental Analyzer.

2.2. Syntheses

2.2.1. General procedure for the preparation of ArCo(dioxime)$_2$Py

In a typical procedure ArMgBr, prepared from ArBr (6.0 mmol) and Mg (6.6 mmol) in 10 mL dry THF, was added drop wise to a magnetically stirred cold slurry of ClCo(dioxime)$_2$Py (1.0 mmol) in 10 mL dry THF under nitrogen. The bluish-green reaction mixture was stirred for 2 h and then heated to reflux for ½ h.

The reaction was quenched with 10 mL of cold 10% aqueous HCl solution. The yellow-orange solid product was filtered. The addition of petroleum ether to the filtrate afforded some more solid product which was combined with the initial crude solid product. In some cases where the solid product did not separate out after the addition of 10% aqueous HCl solution, the addition of petroleum ether resulted in the formation of crude yellow-orange solid product. The crude solid product was washed with ethanol, petroleum ether and water and dried over P_2O_5 by applying vacuum. The crude product was further purified by column chromatography on silica gel. Yield = 65–80%.

2.2.2. Synthesis of phenylCo(dmgH)$_2$Py (**1**)

This complex was prepared following the general procedure using PhMgBr and ClCo(dmgH)$_2$Py and the crude product was purified on a silica gel column using 20% ethyl acetate/chloroform. Yield: 0.351 g (79%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): Py_α = 8.75 (2H, d, J = 4.8 Hz), Py_β = 7.36 (2H, t, J = 7.0 Hz), Py_γ = 7.75 (1H, t, J = 7.6 Hz), 7.38 (2H, d, J = 6.7 Hz), 6.95–6.89 (3H, m), dmgH(Me) = 2.03 (12H, s), O–H···O = 18.45 (s). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 150.34 (C=N, C_q), 150.15 (Py_α), 137.74 (Py_γ), 125.31 (Py_β), 134.85, 126.59, 123.70, 12.24. Anal. Calcd for $C_{19}H_{24}CoN_5O_4$: C, 51.24; H, 5.43; N, 15.73. Found: C, 51.42; H, 5.41; N, 15.52.

2.2.3. Synthesis of 1-naphthylCo(dmgH)$_2$Py (**2**)

This complex was prepared following the above procedure for **1** except that 1-naphthylMgBr was used in place of PhMgBr. Yield: 0.352 g (71%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): Py_α = 8.81 (2H, d, J = 4.8 Hz), Py_β = 7.40 (2H, t, J = 9.9 Hz), Py_γ = 7.74 (1H, t, J = 7.6 Hz), 8.77 (1H, d, J = 9.1 Hz), 7.78 (1H, d, J = 6.7 Hz), 7.59 (1H, d, J = 6.7 Hz), 7.38–7.30 (3H, m), 7.08 (1H, t, J = 7.6 Hz), dmgH(Me) = 1.99 (12H, s), O–H···O = 18.27 (s). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 151.82 (C=N, C_q), 149.90 (Py_α), 137.75 (Py_γ), 125.37 (Py_β), 134.29, 129.08, 128.29, 125.55, 124.22, 123.92, 123.48, 12.24. Anal. Calcd for $C_{23}H_{26}CoN_5O_4$: C, 55.76; H, 5.29; N, 14.14. Found: C, 55.57; H, 5.23; N, 14.07.

2.2.4. Synthesis of 2-naphthylCo(dmgH)$_2$Py (**3**)

This complex was prepared following the above procedure for **1** except that 2-naphthylMgBr was used in place of PhMgBr. Yield: 0.371 g (75%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): Py_α = 8.79 (2H, d, J = 4.9 Hz), Py_β = 7.37 (2H, t, J = 6.7 Hz), Py_γ = 7.76 (1H, t, J = 7.4 Hz), 7.79 (1H, s), 7.71 (1H, d, J = 7.9 Hz), 7.67 (1H, d, J = 7.9 Hz), 7.62–7.60 (1H, m), 7.41 (1H, d, J = 8.5), 7.32–7.25 (2H, m), dmgH(Me) = 2.00 (12H, s), O–H···O = 18.57 (s). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 150.54 (C=N, C_q), 150.35 (Py_α), 137.88 (Py_γ), 125.46 (Py_β), 133.39, 133.25, 132.90, 131.44, 127.46, 127.16, 124.83, 124.54, 123.98, 12.33. Anal. Calcd for $C_{23}H_{26}CoN_5O_4$: C, 55.76; H, 5.29; N, 14.14. Found: C, 55.83; H, 5.27; N, 14.21.

2.2.5. Synthesis of phenylCo(dpgH)$_2$Py (**4**)

This complex was prepared following the general procedure using PhMgBr and ClCo(dpgH)$_2$Py and the crude product was purified on a silica gel column using dichloromethane. Yield: 0.556 g (80%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): Py_α = 9.08 (2H, d, J = 4.8 Hz), Py_β = 7.49 (2H, t, J = 7.0 Hz), Py_γ = 7.88 (1H, t, J = 7.6 Hz), 7.65 (2H, d, J = 7.3 Hz), 7.21–7.14 (12H, m), 7.05 (2H, t, J = 7.3 Hz), 6.98 (1H, t, J = 7.1 Hz), 6.93 (8H, d, J = 6.7 Hz), O–H···O = 18.88 (s). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 151.19(C=N, C_q), 150.42 (Py_α), 138.35 (Py_γ), 125.81 (Py_β), 134.55, 129.85, 129.59, 129.16, 127.89, 127.28, 124.13. Anal. Calcd for $C_{39}H_{32}CoN_5O_4$: C, 67.53; H, 4.65; N, 10.10. Found: C, 67.38; H, 4.59; N, 10.21.

2.2.6. Synthesis of 1-naphthylCo(dpgH)$_2$Py (**5**)

This complex was prepared following the above procedure adopted for **4** except that 1-naphthylMgBr was used in place of PhMgBr. Yield: 0.566 g (76%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): Py_α = 9.14 (2H, d, J = 4.9 Hz), Py_β = 7.51 (2H, t, J = 7.0 Hz), Py_γ = 7.88 (1H, t, J = 7.6 Hz), 9.04 (1H, d, J = 9.1 Hz), 7.93 (1H, d, J = 7.9 Hz), 7.84–7.83 (1H, m), 7.70 (1H, d, J = 6.7 Hz), 7.54 (1H, t, J = 7.3), 7.48–7.41 (2H, m), 7.19–7.15 (4H, m), 7.12–7.09 (8H, m), 6.82 (8H, d, J = 7.3), O–H···O = 18.77 (s). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 153.33 (C=N, C_q), 150.07 (Py_α), 139.99 (Py_γ), 125.90 (Py_β), 138.27, 134.72, 134.08, 129.84, 129.54, 129.19, 128.82, 128.44, 128.04, 127.96, 127.86, 125.83, 124.51, 124.05, 124.00. Anal. Calcd for $C_{43}H_{34}CoN_5O_4$: C, 69.45; H, 4.61; N, 9.42. Found: C, 69.16; H, 4.54; N, 9.31.

2.2.7. Synthesis of 2-naphthylCo(dpgH)$_2$Py (**6**)

This complex was prepared following the above procedure adopted for **4** except that 2-naphthylMgBr was used in place of PhMgBr. Yield: 0.571 g (77%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): Py_α = 9.13 (2H, d, J = 4.9 Hz), Py_β = 7.53 (2H, t, J = 7.0 Hz), Py_γ = 7.91 (1H, t, J = 8.5 Hz), 8.09 (1H, s), 7.80–7.75 (2H, m), 7.55 (1H, s), 7.36–7.33 (3H, m), 7.20–7.17 (4H, m), 7.14–7.12 (8H, m), 6.90 (8H, d, J = 6.7 Hz), O–H···O = 19.00 (s). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 152.06 (C=N, C_q), 150.46 (Py_α), 138.42 (Py_γ), 125.87 (Py_β), 133.52, 132.98, 132.94, 131.79, 129.78, 129.59, 129.19, 128.05, 127.88, 127.72, 127.19, 125.60, 124.54, 124.13. Anal. Calcd for $C_{43}H_{34}CoN_5O_4$: C, 69.45; H, 4.61; N, 9.42. Found: C, 69.36; H, 4.58; N, 9.42.

2.2.8. Synthesis of phenylCo(gH)$_2$Py (**7**)

This complex was prepared following the above general procedure using PhMgBr and ClCo(gH)$_2$Py and crude product was purified on a silica gel column using 30% ethyl acetate/chloroform mixture. Yield: 0.316 g (71%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): Py_α = 8.75 (2H, d, J = 4.9 Hz), Py_β = 7.42 (2H, t, J = 7.0 Hz), Py_γ = 7.82

(1H, t, $J = 7.6$ Hz), 7.39 (2H, d, $J = 6.7$ Hz), 7.33 (4H, s), 7.00–6.96 (3H, m), O–H···O = 17.85 (s). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 149.95 (Py_α), 139.13 (C=N, C_q), 138.37 (Py_γ), 125.75 (Py_β), 134.37, 127.29, 124.67. Anal. Calcd for $C_{15}H_{16}CoN_5O_4$: C, 46.28; H, 4.14; N, 17.99. Found: C, 46.35; H, 4.03; N, 17.83.

2.2.9. Synthesis of 1-naphthylCo(gH)$_2$Py (**8**)

This complex was prepared following the above procedure used for **7** except that 1-naphthylMgBr was used in place of PhMgBr. Yield: 0.362 g (73%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): $Py_\alpha = 8.84$ (2H, d, $J = 5.5$ Hz), $Py_\gamma = 7.82$ (1H, t, $J = 7.6$ Hz), 8.68 (1H, d, $J = 8.5$ Hz), 7.75 (1H, d, $J = 8.0$ Hz), 7.63 (1H, d, $J = 8.0$ Hz), 7.45 (4H, q, $J = 7.3$ Hz, 2Hs of Py_β and 2Hs of 1-naphthyl), 7.37 (1H, s), 7.34 (4H, s), 7.11 (1H, t, $J = 7.6$ Hz), O–H···O = 17.49 (s). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 149.57 (Py_α), 140.51 (C=N, C_q), 138.33 (Py_γ), 125.82 (Py_β), 139.61, 134.55, 133.74, 128.61, 127.94, 127.85, 126.43, 124.62, 124.21, 123.72. Anal. Calcd for $C_{19}H_{18}CoN_5O_4$: C, 51.95; H, 4.13; N, 15.94. Found: C, 51.73; H, 4.08; N, 15.67.

2.2.10. Synthesis of 2-naphthylCo(gH)$_2$Py (**9**)

This complex was prepared following the above procedure used for **7** except that 2-naphthylMgBr was used in place of PhMgBr. Yield: 0.323 g (65%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): $Py_\alpha = 8.79$ (2H, d, $J = 4.8$ Hz), $Py_\beta = 7.51$ (2H, t, $J = 7.6$ Hz), $Py_\gamma = 7.94$ (1H, t, $J = 8.5$ Hz), 8.16 (1H, s), 7.88 (1H, d, $J = 7.9$ Hz), 7.00 (2H, t, $J = 7.0$ Hz), 7.48–7.44 (3H, m), 7.33 (4H, s). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 150.10 (Py_α), 139.39 (C=N, C_q), 138.49 (Py_γ), 125.93 (Py_β), 133.82, 132.75, 128.61, 128.31, 127.77, 127.36, 126.45, 126.20, 126.11, 125.82, 125.72, 125.08. Anal. Calcd for $C_{19}H_{18}CoN_5O_4$: C, 51.95; H, 4.13; N, 15.94. Found: C, 52.09; H, 4.03; N, 15.71.

2.3. X-ray crystal structure determination and refinements

Single crystals suitable for X-ray crystallographic analyses were obtained by the slow evaporation of solvent from the solution of complexes **3**, **4**, **6** and **9** ($CHCl_3/CH_3OH$ or CH_2Cl_2/CH_3OH). Single crystal X-ray data were collected using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on "Bruker SMART APEX CCD diffractometer" at 293 K for **3** and 100 K for others. The linear absorption coefficients, scattering factors for the atoms and the anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* [43]. The program SMART [44] was used for collecting frames of data, indexing reflections, and determining lattice parameters. The data integration and reduction were processed with SAINT [44] software. An empirical absorption correction was applied to the collected reflections with SADABS [45] using XPREP [46]. All the structures were solved by the direct method using the program SHELXS-97 [47] except **9** (solved by using the program DIRDIF-2008) [48] and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97 [47] program package. All non-hydrogen atoms were refined with anisotropic displacement parameters in all the structure. The hydrogen atom positions or thermal parameters were not refined but were included in the structure factor calculations. The axial pyridine and phenyl ligands in complex **4** were found to be orientationally disordered and the occupancies were fixed at 50/50 percentage for axial atoms (N5/C29) attached to the cobalt atom. The naphthalene ring in complex **9** was found to be disordered and was modeled satisfactorily. The pertinent crystal data and refinement parameters for compounds **3**, **4**, **6** and **9** are compiled in Table 1.

3. Results and discussion

3.1. Syntheses of the aryl cobaloximes

Organocobaloximes, in general, can be prepared from Co(I) [6,20,22–26,49–55], Co(II) [56–61] or Co(III) [6,27–30] reagents. The most common method used is the reaction of Co(I), super nucleophile, with a variety of substrates via nucleophilic substitution on alkyl, acyl, vinyl, acetylenic halides. However, this method works only with the activated aryl halides (arene ring with electron withdrawing groups) and gives poor yield of aryl cobaloxime [30,31,36,62]. Since several organocobalt complexes with tetradentate ligands like Salen, BAE have been prepared by the reaction of cobalt(II) complexes with organic hydrazines in the presence of molecular oxygen [63], Brown et al., while using this method got disappointing yields in the synthesis of aryl cobaloximes [30]. The latter have traditionally been prepared in high yield by the reaction of aryl magnesium halides with Co(III) complex, $ClCo(dmgH)_2B$ [6,27–30]. We have used this method in the present study. The method, unlike the alkylation of Co(I), though requires an inconvenient reverse addition of organomagnesium salt due to the extremely poor solubility of chlorocobaloxime in ethereal solution, but gives good yield of the product (65–80%).

3.1.1. Solubility and stability

The dmgH and dpgH complexes are soluble in common organic solvents (CH_2Cl_2, $CHCl_3$) but sparingly soluble in acetone, methanol, acetonitrile while the gH complexes are sparingly soluble in all these solvents. Complexes (**1**–**9**) are air and moisture-stable solids and do not show any signs of decomposition in solution over a period of 24 h under diffused light and in refluxing $CHCl_3/CH_3OH$ (1:2) mixture for 5 h in air. Also, these complexes do not show any affinity toward molecular oxygen even under irradiation in dichloromethane.

3.2. ^{1}H and ^{13}C NMR spectral studies

^{1}H and ^{13}C NMR data for all the complexes are summarized in Experimental section. The poor solubility of gH complexes (**7**–**9**) in common organic solvents hampered the spectroscopic study of these complexes. The ^{1}H NMR spectra of these complexes are easily assigned on the basis of the chemical shifts. The signals are assigned according to their relative intensities and are consistent with the related alkyl and benzyl cobaloximes with dmgH, dpgH and gH. ^{13}C resonance for Py_α, Py_β, Py_γ and C=N are observed and assigned on the basis of chemical shifts. ^{13}C Py_α and C=N are very difficult to assign in certain cases as they have almost identical chemical shift. In such cases the assignment is confirmed by DEPT spectra.

^{1}H NMR spectral characteristics of aryl cobaloximes are quite different from the reported alkyl and benzyl cobaloximes (Table S1). The key feature is the Py_α resonance which has surprisingly shifted downfield (0.11–0.27 ppm) in dmgH and gH complexes as compared to the free Py_α resonance. This is unusual since Py_α resonance does not shift on coordination to cobalt in alkyl and benzyl cobaloximes (Table S2). The downfield shift is even larger in the dpgH complexes (**4**–**6**) in comparison to the alkyl derivatives. Also, the Py_α resonance varies with the aryl ring size and follows the order 1-naphthyl > 2-naphthyl > phenyl. Since the ring size of 1-naphthyl and 2-naphthyl is similar, the more downfield shift in 1-naphthyl complexes may be due to some electronic reasons. This is in contrast to the alkyl series where it remains almost constant for C1–C5 carbon chain (Table S2). This unexpected high deshielding of Py_α protons can occur due to an increased anisotropy of cobalt on binding with an aryl moiety and/or due to deshielding

Table 1
Crystal data and structure refinement details for compounds **3**, **4**, **6** and **9**.

Parameters	**3**	**4**	**6**	**9**
Empirical formula	$C_{23}H_{26}CoN_5O_4$	$C_{39}H_{32}CoN_5O_4$	$C_{43}H_{34}CoN_5O_4$	$C_{19}H_{18}CoN_5O_4$
Formula weight	495.42	693.63	743.69	439.31
Diffractometer	Bruker Apex CCD	Bruker Apex CCD	Bruker Apex CCD	Bruker Apex CCD
Temp (K)	293(2)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$	$C2/c$
Unit cell dimension				
a (Å)	9.034(1)	15.782(2)	22.371(5)	8.438(1)
b (Å)	16.246(2)	11.123(1)	18.677(5)	20.028(4)
c (Å)	15.531(2)	21.200(3)	20.827(5)	10.557(1)
α (deg)	90.000	90.000	90.000(5)	90.000
β (deg)	105.219(2)	108.020(2)	116.051(5)	98.023(3)
γ (deg)	90.000	90.00	90.000(5)	90.000
V (Å^3)	2199.6(5)	3539.2(8)	7818(3)	1766.8(5)
Z	4	4	8	4
ρ (calc), g/cm^3	1.496	1.302	1.311	1.652
μ (Mo Kα) (mm^{-1})	0.822	0.532	0.491	1.011
F (000)	1032	1440	3200	904
Crystal size (mm^3)	$0.32 \times 0.20 \times 0.16$	$0.31 \times 0.25 \times 0.21$	$0.40 \times 0.35 \times 0.30$	$0.42 \times 0.34 \times 0.21$
Index ranges	$-12 \le h \le 12$	$-20 \le h \le 19$	$-29 \le h \le 20$	$-10 \le h \le 11$
	$-21 \le k \le 13$	$-14 \le k \le 11$	$-20 \le k \le 24$	$-26 \le k \le 16$
	$-19 \le l \le 20$	$-27 \le l \le 28$	$-24 \le l \le 27$	$-14 \le l \le 13$
No. of rflns collected	14,210	22,625	25,323	5715
No. of indep rflns	5435	8752	9707	2173
GOOF on F^2	1.13	1.142	1.099	1.171
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0605$	$R1 = 0.0577$	$R1 = 0.0696$	$R1 = 0.0553$
	$wR2 = 0.1410$	$wR2 = 0.1544$	$wR2 = 0.1726$	$wR2 = 0.1391$
R indices (all data)	$R1 = 0.0997$	$R1 = 0.0832$	$R1 = 0.1154$	$R1 = 0.0840$
	$wR2 = 0.2010$	$wR2 = 0.1861$	$wR2 = 0.2154$	$wR2 = 0.1910$
Data/restraints/param	5435/0/306	8752/0/443	9707/0/518	2173/0/155

by the ring current of dpgH phenyl groups. Py_α shifts upfield in chlorocobaloxime in spite of high cobalt anisotropy. However this should not to be confused because halocobaloximes work differently from organocobaloximes as shown recently by ^{15}N NMR studies [64]. Can the deshielding of Py_α resonance be a result of change in the hybridization as we move from alkyl to aryl? It is difficult to say but the deshielding of Py_α resonance is <0.1 ppm in $CH_2{=}CHCo(dmgH)_2Py$ [65].

The extent of electron density on Co(dioxime)$_2$ can be understood by comparing $\Delta\delta$ ($^{13}C_{C=N}$) [66] values. In general, $\delta^{13}C_{C=N}$ in free dioxime shifts upfield on coordination to cobalt and this upfield shift value [$\Delta\delta$ ($^{13}C_{C=N}$)] is much smaller in aryl cobaloximes as compared to the corresponding alkyl cobaloximes (Table S3). Also, the upfield shift in the alkyl complexes is quite similar within the same series but this is not so in aryl complexes. The [$\Delta\delta$ ($^{13}C_{C=N}$)] value is lower in 1-naphthylcobaloxime as compared to other aryl cobaloximes. This means that the charge density is much lower in 1-naphthyl complexes. This also supports the finding in the ^{1}H Py_α resonance.

3.3. X-ray crystallographic studies

Molecular structures of the complexes **3**, **4**, **6** and **9** have been determined crystallographically. Selected bond lengths and bond angles are given in Table 2 and the molecular structures with selected numbering schemes are shown in Figs. 1–4. It can be seen from Figs. 1–4 that all complexes are similar in structure and their molecules have distorted octahedral geometry around the central cobalt atom with four nitrogen atoms of the dioximes (gH, dmgH, dpgH) in the equatorial plane and, pyridine and phenyl (or 2-naphthyl) are axially coordinated.

Co(dioxime)$_2$ unit may undergo geometrical deformations, which is roughly represented by the displacement of the cobalt atom from mean equatorial N_4 plane (d) and by the butterfly bending angle between the two dioxime units (α). Positive values of α and d indicates bending toward R and displacement toward base and vice versa. The deviations of the cobalt atoms from mean equatorial N_4 plane are 0.0239(6), −0.0260(3), 0.0339(6) and 0.0181(6) Å in the compounds **3**, **4**, **6** and **9** respectively. The butterfly bending angle in **3** is 4.40°, while it is −7.67°, 5.05°, and 0.18° in **4**, **6** and **9** respectively.

Only two crystal structures of aryl cobaloximes, 4-pyridylCo(dmgH)$_2$Bu$_3$P [35] and 4-substituted phenylCo(dmgH)$_2$Py [36], are known. The Co–C and Co–N_{py} distances in **3** [1.970(3) and 2.055(3) Å] are comparable to values in 4-substituted phenylCo(dmgH)$_2$Py.

The data in Table 2 shows that the expansion of ring size lengthens the Co–C and Co–N_{py} bond lengths and also induces change in d and α value from negative to positive in dpgH complexes (compare **4** and **6**). Keeping the same axial ligand, the change in equatorial moiety also leads to change in Co–C bond lengths and it follows the order dpgH > gH > dmgH complex (compare **3**, **6** and **9**). In contrast, the Co–C bond length does not change in the alkyl series, MeCo(dioxime)$_2$Py (Table S4).

The pyridine ring is almost parallel to the C–C bonds; the dpgH complexes (**4** and **6**) have the lowest twist angle (torsion angle, τ)

Table 2
Selected bond lengths and bond angles.

Parameters	**3**	**4**	**6**	**9**
Co–C (Å)	1.970(3)	2.023(3)	2.057(4)	2.014(3)
Co–N_{py} (Å)	2.055(3)	2.025(3)	2.066(3)	2.044(5)
C–Co–N_{py} (deg)	178.07(15)	179.19(10)	179.0(12)	176.4(2)
α (deg)	4.40	−7.67	5.05	0.18
τ (deg)[a]	84.47(25)	78.63(12)	72.03(20)	88.81(9)
d (Å)	0.0239(6)	−0.0260(3)	0.0339(6)	0.0181(6)
O···O (Å)	2.478(4)	2.477(2)	2.459(3)	2.496(4)
	2.477(4)	2.465(3)	2.458(3)	

[a] MeCo(dmgH)$_2$Py = 89.7° and for MeCo(dpgH)$_2$Py = 89.8°.

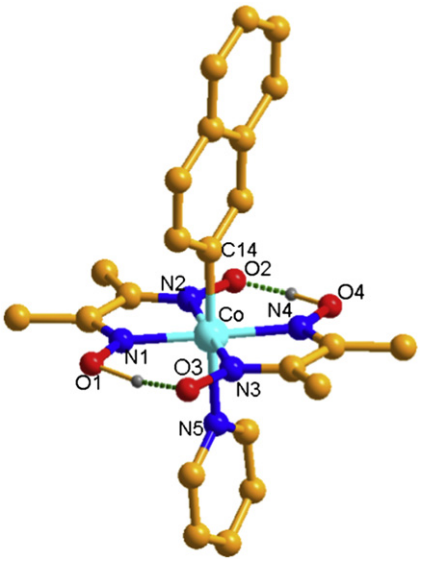

Fig. 1. Molecular structure of **3**. All hydrogen atoms have been omitted for clarity (hydrogen atoms involved in the intramolecular hydrogen-bonding interactions are shown).

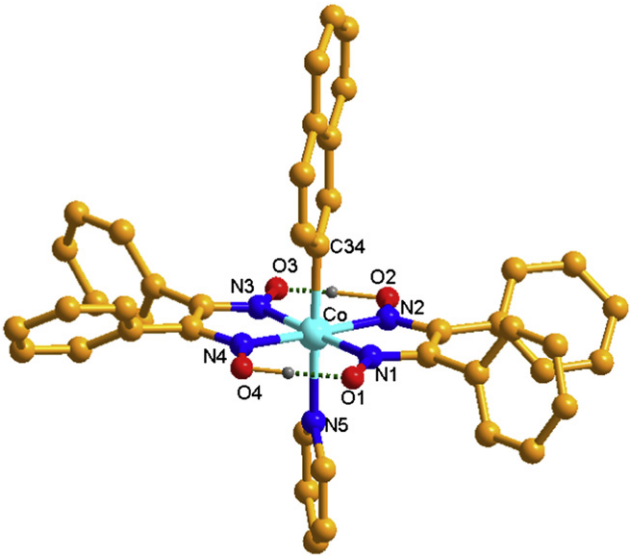

Fig. 3. Molecular structure of **6**. All hydrogen atoms have been omitted for clarity (hydrogen atoms involved in the intramolecular hydrogen-bonding interactions are shown).

[67] while the gH complex **9** has the highest. Also the twist angle is smaller in the aryl cobaloximes as compared to their methyl derivatives and an increase in ring size decreases the twist angle (compare **4** and **6**). The C–Co–N_{py} bond angles are, however, similar to alkyl complexes (Table S4). In all the complexes, the plane of aryl group is almost perpendicular to the plane of the dioxime ligand as expected and is nearly coplanar with the pyridine plane. This co-planarity is due to the steric interaction between axial groups and the equatorial ligands.

3.3.1. Crystal packing

Crystal packing in complexes **3** and **6** is stabilized by C–H···O type intermolecular hydrogen bonding. However, it is stabilized by C–H···O type intermolecular hydrogen bonding as well as by π···π interactions in **9**. The two C–H···O [C18–H18···O4 = 2.620(3), and C10–H10···O1 = 2.642(3) Å] interactions in **3** lead to linear superstructure (Fig. S1). The crystal-packing diagram of **6** also shows the presence of intermolecular C–H···O [C41–H41···O2 = 2.433(2) Å] hydrogen bonding leading to the formation of a dimer structural motif (Fig. S2). The crystal-packing diagram of **9** shows 2-D lamellar network involving intermolecular C–H···O (C9–H9A···O1 = 2.460(3) Å) interactions as well as π···π interactions. The C–H···O hydrogen bonds are in the same plane constituting a hexagon and π···π stacking occurs between pyridine and one ring of 2-naphthyl group with a distance 4.003 Å between the centroids of stacked rings (Fig. S3).

3.4. Electrochemical study (cyclic voltammetry)

The electrochemical behavior of **1**–**7** has been studied in order to know the effect of the aryl groups as well as the dioxime on the redox potentials of the metal centers. The cyclic voltammograms

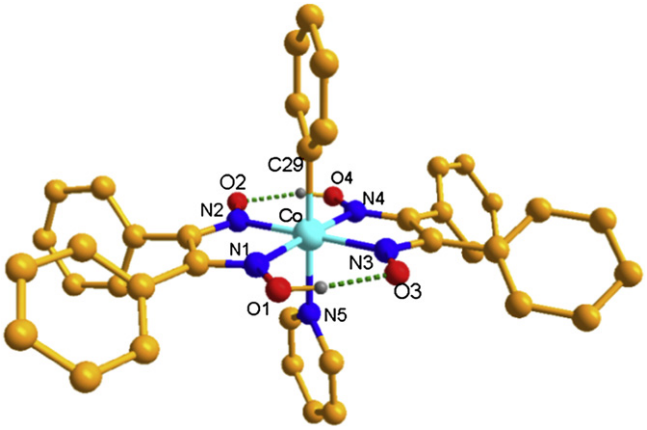

Fig. 2. Molecular structure of **4**. All hydrogen atoms have been omitted for clarity (hydrogen atoms involved in the intramolecular hydrogen-bonding interactions are shown).

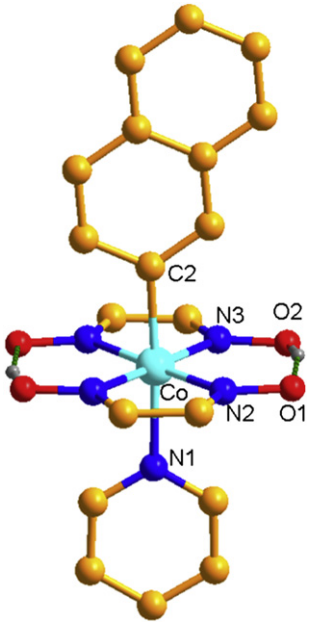

Fig. 4. Molecular structure of **9**. All hydrogen atoms have been omitted for clarity (hydrogen atoms involved in the intramolecular hydrogen-bonding interactions are shown).

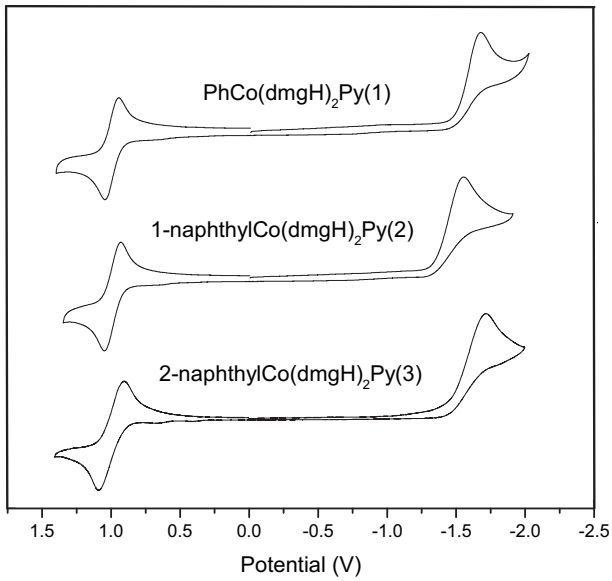

Fig. 5. Cyclic voltammograms for **1**–**3** in CH_2Cl_2 with 0.1 M $^nBu_4NPF_6$ as supporting electrolyte at 0.1 V/s at 25 °C.

are shown in Figs. 5 and 6 and the CV data are given in Table 3. In all cases except **5**, one irreversible reductive response corresponding to Co(III)/Co(II) and one quasi-reversible oxidative response corresponding to Co(IV)/Co(III) process is observed. A comparison of the current heights of two responses strengthens our hypotheses. In present study the Co(III)/Co(II) redox process is considerably cathodically shifted and due to this, the Co(II)/Co(I) response is further cathodically shifted and therefore is not observed even down to −1.8 V.

The ΔE_p for Co(IV)/Co(III) wave is higher than that of a reversible one electron process and increases with increasing scan rate (100–200 mV/s); thus indicating the quasi-reversible nature of the electron transfer. All complexes undergo oxidation to Co(IV) and as

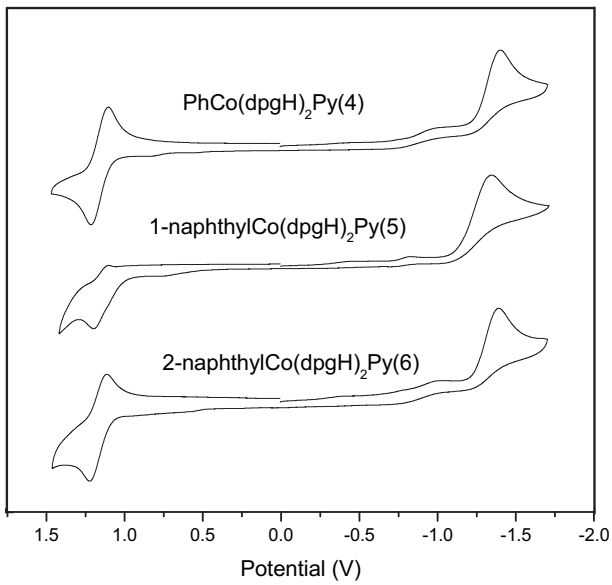

Fig. 6. Cyclic voltammograms for **4**–**6** in CH_2Cl_2 with 0.1 M $^nBu_4NPF_6$ as supporting electrolyte at 0.1 V/s at 25 °C.

Table 3
CV data for **1**–**7** in CH_2Cl_2 and $^nBu_4NPF_6$ at 0.1 V/s at 25 °C.

No.	Co(III)/Co(II)			Co(IV)/Co(III)					
	E_{pc}[a] (V)	E_{pc}[b] (V)	i_{pc} (μA)	$E_{1/2}$[a] (V)	$E_{1/2}$[b] (V)	ΔE_p (mV)	i_{pc} (μA)	i_{pa} (μA)	i_{pa}/i_{pc}
1	−1.66	−2.09	13.89	1.00	0.57	100	13.39	14.13	1.06
2	−1.54	−1.97	8.25	0.99	0.56	120	14.86	16.56	1.11
3	−1.71	−2.14	2.83	0.99	0.56	185	33.07	58.49	1.77
4	−1.39	−1.82	16.47	1.14	0.71	109	16.67	18.15	1.08
5	−1.34	−1.77	41.45	1.18[c] irrev	0.75	–	–	12.24	–
6	−1.39	−1.82	12.69	1.16	0.73	110	5.82	13.02	2.24
7	−1.37	−1.80	11.68	1.24	0.81	122	12.79	32.68	2.56

[a] Vs Ag/AgCl.
[b] Vs Fc/Fc^+ Fc/Fc^+ ($E_{1/2} = 0.4269$ V).
[c] Value refers to E_{pa}.

indicated by value of i_{pa}/i_{pc} which is greater than one, the oxidized products ($ArCo^{IV}(dioxime)_2Py$) are stable.

Complex **5** shows one irreversible oxidative wave corresponding to Co(IV)/Co(III) at 1.18 V and one irreversible reductive wave corresponding to Co(III)/Co(II) at −1.34 V. The reduction potential in the aryl cobaloximes, as expected, is less negative as compared to the alkyl cobaloximes within the same series of dioxime (Table S5). This shows that the aryl cobaloximes are easily reduced and this may simply be due to the lower donor power of the aryl group, as compared to alkyl, which puts less negative charge on the cobalt.

4. Conclusion

In this work we have described synthesis, spectral and structural characterization of a series of aryl cobaloximes containing different aryl groups and equatorial dioximes. Aryl ring size and the nature of dioxime affect the structural parameters and their effect on the Py_α resonance is rather unusual for an organic group of a cobaloxime. These complexes are reduced electrochemically more easily as compared to the corresponding alkyl complexes.

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Appendix. Supplementary material

CCDC 727613, 727614, 727615, and 762045 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jorganchem.2010.06.012.

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[66] $\Delta\delta(^{13}C_{C=N})$ value has been taken instead of $\delta(^{13}C_{C=N})$. This is to avoid the direct effect of substituent on δ(C=N) value. $\Delta\delta(^{13}C_{C=N})$ represents the field effect.
[67] The torsion angle (τ) is the angle between two virtual planes that bisects cobaloxime plane. This shows twist angle of pyridine with respect to the line joining the midpoints of C–C bond of two oxime units.