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# Reactivity studies of aryl cobaloximes with molecular oxygen and electrophiles

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ABSTRACT

The reactivity of aryl cobaloximes, $ArCo(dmgH)_2Py$ [Ar = Phenyl, 1-naphthyl, 2-naphthyl, 4-$NMe_2C_6H_4$, 2-thienyl] with molecular oxygen and electrophiles ($Br_2$ and 2,4-dinitrobenzenesulfenyl chloride) has been investigated. All these complexes do not show any affinity toward molecular oxygen and the reaction with electrophiles either leads to ring substitution and/or the Co–C bond cleavage. The molecular structures of two new aryl cobaloximes and two ring substituted organometallic products have been determined crystallographically. The C–H···O intermolecular hydrogen bonding interactions in the crystal packing lead to different superstructural motifs.



## 1. Introduction

In recent years, the description, spectroscopic data, structure–property relationship and their correlation to the Co–C bonds in organocobaloximes have been most emphasized [1–9]. In an ongoing effort to understand the Co–C stability/reactivity we have published a number of organocobaloximes with different dioximes like gH, dmgH, chgH, dpgH, dmestgH, dSPhgH [1–4,10–13]. The study has shown that the cis influence (effect of dioxime on the Co–C bond) plays an important role. We have recently studied the effect of dioxime and the aryl ring size on the Co–C bond in aryl cobaloximes by spectral and structural studies [14].

The inherently weak Co–C bond in the alkyl/benzyl cobaloximes undergoes homolytic cleavage with visible light, similar to the activation of vitamin $B_{12}$ by apoenzyme [15–18] and the insertion of molecular oxygen into the Co–C bond has extensively been used to test the reactivity of these compounds [19–26]. The benzyl- and (heteroaromatic methyl) cobaloximes have also been shown to be susceptible toward electrophiles and undergo either Co–C bond cleavage and/or ring substitution [27–36], but no such studies have been done on the aryl cobaloximes.

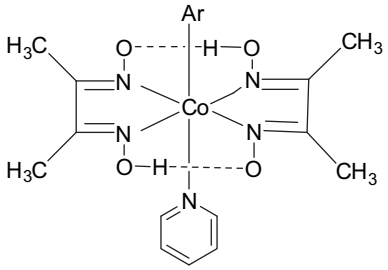
Despite the large number of crystal structures of cobaloximes and their related compounds, very little information is known on the weak interactions in the crystal packing [5,6,9,13,37].

The aim of the present work, therefore, is to study the reactivity of aryl cobaloximes (a) with molecular oxygen under visible light (b) with $Br_2$ and 2,4-dinitrobenzenesulfenyl chloride under electrophilic conditions and (c) to study the crystal packing in these complexes to look for supramolecular structures.

## 2. Result and discussion

### 2.1. Syntheses and characterization of $ArCo(dmgH)_2Py$ (**1**–**5**, Chart 1)

Synthesis and characterization of aryl cobaloximes **1**–**3** have been reported recently from our laboratory and two new complexes **4** and **5** have been synthesized and purified by the published procedure for **1**–**3** [14]. The complexes **4** and **5** are air-stable, yellow crystalline solids, soluble in $CH_2Cl_2$, $CHCl_3$ and sparingly soluble in




Ar = Phenyl, 1-naphthyl, 2-naphthyl, 4-$NMe_2C_6H_4$, 2-thienyl (**1-5**)

**Chart 1.** Aryl cobaloximes [$ArCo(dmgH)_2Py$].

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**Table 1**
Crystal data and structure refinement details for compounds **4**, **5**, **12** and **13**.

| Parameters | **4** | **5** | **12** | **13** |
|---|---|---|---|---|
| Empirical formula | $C_{21}H_{29}CoN_6O_4$ | $C_{18}H_{26}Cl_2CoN_5O_4S$ | $C_{31}H_{45}CoN_8O_{11}S$ | $C_{23}H_{24}CoN_7O_8S_2$ |
| Formula weight | 488.43 | 538.33 | 796.74 | 649.54 |
| Diffractometer | Bruker Apex CCD | Bruker Apex CCD | Bruker Apex CCD | Bruker Apex CCD |
| Temp (K) | 100(2) | 100(2) | 100(2) | 100(2) |
| Crystal system | Triclinic | Monoclinic | Monoclinic | Triclinic |
| Space group | *P*−1 | *C*2/c | $P2_1$/c | *P*−1 |
| *Unit cell dimension* | | | | |
| *a* (Å) | 9.752(3) | 11.928(2) | 8.108(5) | 9.191(5) |
| *b* (Å) | 14.216(4) | 13.229(3) | 30.005(5) | 12.650(5) |
| *c* (Å) | 16.738(5) | 14.869(3) | 14.826(5) | 13.385(5) |
| $\alpha$ (°) | 88.161(5) | 90.000 | 90.000(5) | 69.863(5) |
| $\beta$ (°) | 88.796(5) | 107.31(3) | 91.764(5) | 82.251(5) |
| $\gamma$ (°) | 72.323(5) | 90.000 | 90.000(5) | 78.345(5) |
| *V* (Å$^3$) | 2209.6(10) | 2240.0(8) | 3605(3) | 1427.4(11) |
| *Z* | 4 | 4 | 4 | 2 |
| $\rho$ (calc), g/cm$^3$ | 1.468 | 1.596 | 1.468 | 1.507 |
| $\mu$ (Mo-$K\alpha$) (mm$^{-1}$) | 0.818 | 1.134 | 0.604 | 0.806 |
| *F* (000) | 1024 | 1112 | 1672 | 664 |
| Crystal size (mm$^3$) | 0.26 × 0.20 × 0.18 | 0.43 × 0.32 × 0.23 | 0.30 × 0.26 × 0.22 | 0.27 × 0.23 × 0.21 |
| Index ranges | $-11 \le h \le 10$ | $-15 \le h \le 10$ | $-9 \le h \le 8$ | $-12 \le h \le 12$ |
| | $-15 \le k \le 17$ | $-16 \le k \le 17$ | $-35 \le k \le 35$ | $-21 \le k \le 13$ |
| | $-20 \le l \le 20$ | $-19 \le l \le 19$ | $-15 \le l \le 17$ | $-19 \le l \le 20$ |
| No. of rflns collected | 11,904 | 7040 | 18,262 | 9263 |
| No. of indep rflns | 8061 | 2725 | 6300 | 6662 |
| GOOF on $F^2$ | 1.054 | 1.095 | 1.053 | 1.148 |
| Final *R* indices ($I > 2\sigma(I)$) | $R1 = 0.0495$ | $R1 = 0.0618$ | $R1 = 0.0695$ | $R1 = 0.0593$ |
| | w$R2 = 0.1249$ | w$R2 = 0.1566$ | w$R2 = 0.1773$ | w$R2 = 0.1430$ |
| *R* indices (all data) | $R1 = 0.0619$ | $R1 = 0.0796$ | $R1 = 0.0867$ | $R1 = 0.0831$ |
| | w$R2 = 0.1387$ | w$R2 = 0.1937$ | w$R2 = 0.1917$ | w$R2 = 0.1943$ |
| Data/restraints/param | 8061/0/587 | 2725/1/156 | 6300/0/477 | 6662/0/379 |

acetone, $CH_3OH$ and $CH_3CN$. The new aryl cobaloximes (**4** and **5**) have been characterized by elemental analyses, NMR and also by X-ray crystallography.

### 2.2. Molecular structures of *4* and *5*

The pertinent crystal data and refinement parameters for **4** and **5** are given in Table 1 and the selected bond lengths, bond angles and structural parameters are given in Table 2. The molecular structures with selected numbering schemes are shown in Figs. 1 and 2. The geometry around the central cobalt atom is distorted octahedral with four nitrogen atoms of the dioxime in the equatorial plane and pyridine and 4-*N*,*N*-dimethylaminophenyl (4-$NMe_2C_6H_4$) or 2-thienyl are axially coordinated. The crystal structure of **4** contains two molecules in its asymmetric unit and since there is a structure variation, they are numbered as **4**-**A** and **4**-**B** and the crystal data is given separately in Table 2.

The Co(dmgH)$_2$ unit in organocobaloximes undergoes geometrical deformations, due to flexibility, which is roughly represented by the displacement of cobalt out of 4-nitrogen plane (d) [38] and by the butterfly bending angle between two dioxime units ($\alpha$) [38]. The deviations of the cobalt atoms from mean equatorial 4N plane are −0.0191(5), −0.0076(5), −0.0044(4) Å and the butterfly bending angles are −9.04, −4.37, −3.10° in **4**-**A**, **4**-**B** and **5** respectively. The deviation is toward the axial aryl group and the bending of dioxime units is toward base, pyridine. The Co–C bond distances are 1.966(2), 1.972(2), 1.952(4) Å and the Co–$N_{Py}$ bond distances are 2.062(2), 2.058(2), 2.034(2) Å in **4**-**A, 4**-**B** and **5**.

There are some significant differences in structural parameters of **4**-**A** and **4**-**B** and it is believed that these differences arise due to the crystal packing. The packing diagrams of **4**-**A** and **4**-**B** show the presence of intermolecular C–H···O hydrogen bonding leading to the formation of a tetramer structural motif (Figure S1). There are two types of C–H···O hydrogen bonds (C20A–H20F···O2 = 2.686 (2) and C8A-H8A1···O3 = 2.382(2) Å) between **4**-**A** and **4**-**B**.

### 2.3. Reaction of *1*–*5* with $O_2$, $Br_2$ and 2,4-dinitrobenzenesulfenyl chloride

In spite of the fact that the Co–C bond length in aryl cobaloximes is similar to the alkyl and benzyl cobaloximes, these complexes do not show any affinity toward molecular oxygen even under

**Table 2**
Selected bond lengths, bond angles and other relevant structural parameters.

| Parameters | **4** | | **5** | **12** | **13** |
|---|---|---|---|---|---|
| | **4**-**A** | **4**-**B** | | | |
| Co–C (Å) | 1.966(2) | 1.972(2) | 1.952(4) | 1.960(4) | 1.940(4) |
| Co–$N_{py}$ (Å) | 2.062(2) | 2.058(2) | 2.034(2) | 2.050(3) | 2.029(4) |
| C–Co–$N_{py}$ (°) | 179.46(11) | 178.41(11) | 180.00 | 179.29(15) | 178.20(16) |
| $\alpha$ (°) | −9.04 | −4.37 | −3.10 | +2.95 | −4.24 |
| $\tau$ (°) | 81.61(22) | 86.80(25) | 81.08(7) | 86.72(13) | 86.41(85) |
| d (Å) | −0.0191(5) | −0.0076(5) | −0.0044(4) | +0.0135(6) | −0.0105(7) |
| O···O (Å) | 2.458(3) 2.487(3) | 2.468(2) 2.481(2) | 2.496(3) | 2.588(4) 2.459(4) | 2.495(3) 2.487(3) |

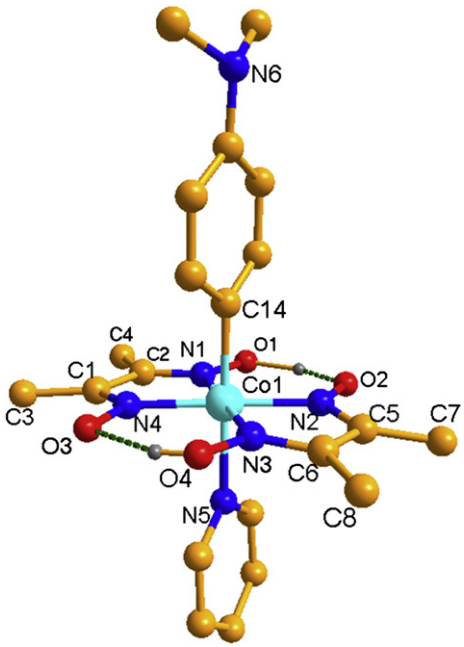



**Fig. 1.** Molecular structure of **4**. All hydrogen atoms have been omitted for clarity (hydrogen atoms involved in the intramolecular hydrogen-bonding interactions are shown).

irradiation for 5 h in $CH_2Cl_2$ and with the result these are very stable in solution. It seems that the ability of $\eta^1$ aryls to have both $\sigma$ donation as well as $\pi$-back bonding through the filled aryl $\pi$-orbitals and empty $\pi^*$ antibonding orbitals provides stability to these complexes.

The reaction with the electrophiles, however, is more encouraging but its reactivity varies drastically with the nature of the electrophile as well as on the aryl ring. The complexes **1**–**4** react with $Br_2$ in $CHCl_3$ under nitrogen atmosphere. The reactions are done with very low concentration of $Br_2$ to avoid the higher order reactions in $Br_2$. The corresponding bromoarenes (**6**–**9**) are the exclusive organic products formed in the reaction and the bromocobaloxime, $BrCo(dmgH)_2Py$ is the inorganic product. These products are formed due to the cleavage of the Co–C bond. On the other hand, 2-thienylcobaloxime (**5**) on reaction with $Br_2$ under identical conditions gives the 5-bromo-substituted organometallic compound (**10**).

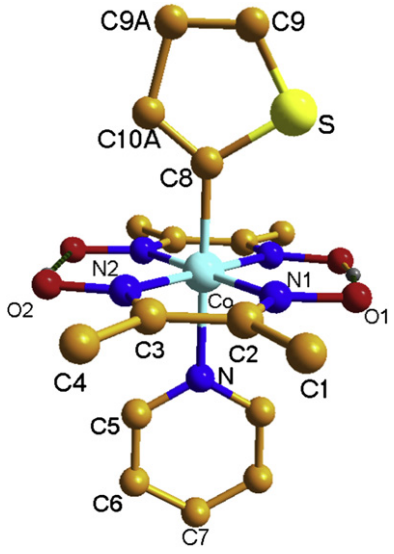



**Fig. 2.** Molecular structure of **5**. All hydrogen atoms and solvent molecule have been omitted for clarity (hydrogen atoms involved in the intramolecular hydrogen-bonding interactions are shown).

Unlike the above, the reaction of **4** with 2,4-dinitrobenzenesulfenyl chloride (RSCl) gives both the organic (**11**) [39] and the ring substituted organometallic products (**12**) in a 43:57 molar ratio[1]. Similarly, the complex **5** exclusively forms 5-substituted organometallic compound (**13**). The latter does not react further with more RSCl but it forms **14** on reaction with $Br_2$ [40]. The complexes **1**–**3** and **10** do not react with RSCl under similar conditions. However, complex **10** afforded unidentifiable mixture of products with $Br_2$. The reaction results are shown in Table 3.

*Blank reaction*: The reaction of 2-bromothiophene with RSCl does not form **14** under identical conditions.

The formation of ring substituted products (**10**, **12** and **13**) is a very significant result as it affords a useful synthetic procedure where an organocobaloxime can be used as a precursor for the formation of a new and modified organocobaloxime. Furthermore, we have also been able to substitute two dis-similar groups on the same thiophene ring which is difficult to obtain from the conventional organic transformation on thiophene.

### 2.4. Molecular structures of *12* and *13*

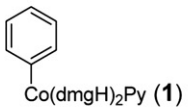
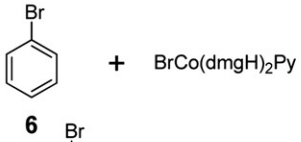
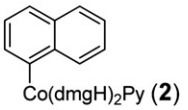
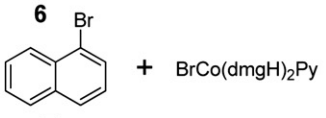
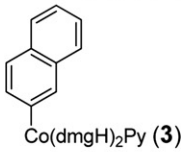
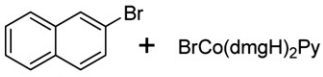
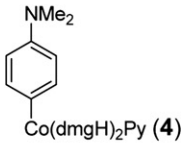
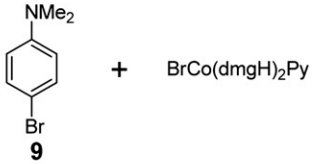
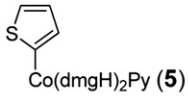
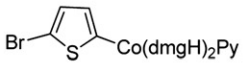
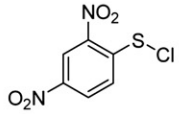
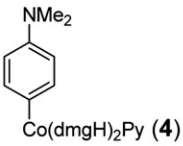
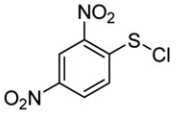
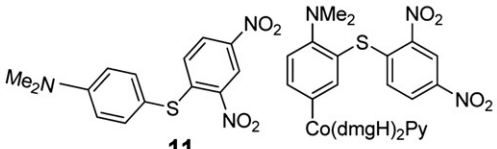
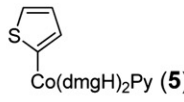
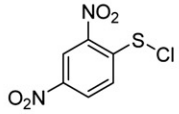
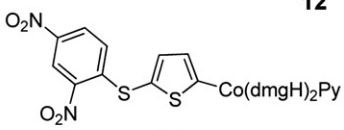
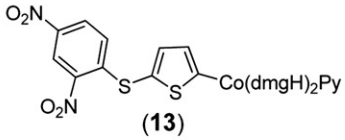
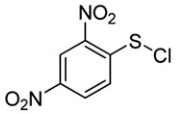
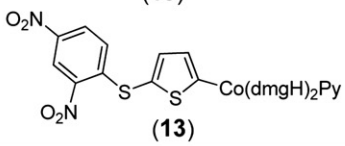
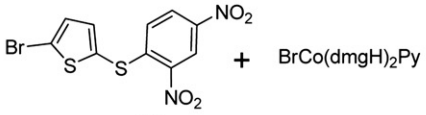
Molecular structures of the complexes **12** and **13** have been determined crystallographically. Details about data collection, refinement, and structure solution are summarized in Table 1 and selected geometrical parameters are given in Table 2. Molecular structures are shown in Figs. 3 and 4. The deviations of the central cobalt atom (d) from the mean equatorial 4N plane are +0.0135(6) and −0.0105(7) Å respectively for **12** and **13**. The butterfly bending angle in **12** is +2.95° while it is −4.24° in **13**. The bending of dioxime units in the former is opposite while in the latter it is similar to their corresponding precursors **4** and **5**, respectively. All other structural parameters in these derivatives do not change much from their corresponding precursors.

These substituted derivatives also show some interesting properties in crystal packing and form different superstructural motifs through intermolecular C–H···O hydrogen bonding. The metric parameters for these weak interactions are given in Table 4. Complex **12** self-assembles via C–H···O interactions resulting two-dimensional supermolecular helices. A left-handed helix is formed along the two-fold screw axis through C10–H10A···O8 [2.511(4) Å] and C11–H11A···O7 [2.548(4) Å] bonds (Fig. 5A and B). Furthermore, this helical structure is connected to another helix and forms a two-dimensional network through three C–H···O interactions [C4–H4B···O1 = 3.079(3), C5–H5B···O3 = 3.047(3) and C20–H20B···O8 = 3.118(4) Å] (Figure S2).

The crystal-packing diagram of compound **13** shows a dimer structural motif involving two C–H···O hydrogen bond interactions [C9–H9···O8 = 2.562(4) Å] shown in Figure S3. Another interesting aspect of crystal packing of **13** is that it shows a two-dimensional lamellar network involving four C–H···O type intermolecular contacts. A one-dimensional double-chain polymeric network is formed due to two C–H···O hydrogen bonds [C8–H8B···O8 = 2.702 (4) and C10–H10···O6 = 2.561(3) Å]. Two such 1-D double chains are connected through two more weak C–H···O hydrogen bonds [C1–H1B···O2 = 2.965(3) and C4–H4C···O2 = 3.620(2) Å] to form a 2-D lamellar network (Figure S4).

[1] Product ratio based on isolated yield (isolation 90%).

**Table 3**
Products of the reactions of $O_2$, $Br_2$ and 2,4-dinitrobenzenesulfenyl chloride with $ArCo(dmgH)_2Py$.

| $ArCo(dmgH)_2Py$ | Reagents | Final products |
|---|---|---|
| $ArCo(dmgH)_2Py$ (**1-5**) | $O_2$ | none |
|  $Co(dmgH)_2Py$ (**1**) | $Br_2$ |  **6** |
|  $Co(dmgH)_2Py$ (**2**) | $Br_2$ |  **7** |
|  $Co(dmgH)_2Py$ (**3**) | $Br_2$ |  **8** |
|  $Co(dmgH)_2Py$ (**4**) | $Br_2$ |  **9** |
|  $Co(dmgH)_2Py$ (**5**) | $Br_2$ |  **10** |
| $ArCo(dmgH)_2Py$ (**1-3**) |  | none |
|  $Co(dmgH)_2Py$ (**4**) |  |  **11** **12** |
|  $Co(dmgH)_2Py$ (**5**) |  |  **13** |
|  (**13**) |  | none |
|  (**13**) | $Br_2$ |  **14** |

## 3. Conclusion

In summary, we have studied the reactivity of aryl cobaloximes with molecular oxygen, $Br_2$ and 2,4-dinitrobenzenesulfenyl chloride. These complexes have no affinity toward molecular oxygen even though the Co–C bond length is similar to the alkyl/benzyl cobaloximes. The reaction with electrophiles leads to the Co–C bond cleavage and/or aryl ring substituted organometallic products depending on the nature of aryl ring. The X-ray structure and crystal packing exhibit some weak interactions to form different types of supramolecular structural motifs.

## 4. Experimental section

### 4.1. Syntheses of aryl cobaloximes (*1*–*5*)

Aryl cobaloximes **1**–**3** have already been reported earlier and the complexes **4** and **5** were synthesized and purified by the published procedure for **1**–**3** [14].

#### 4.1.1. 4-N,N-dimethylaminophenylCo(dmgH)$_2$Py (*4*)

Yield: 0.357 g (73%). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$ ppm): $Py_\alpha = 8.74$ (2H, d, $J = 4.72$ Hz), $Py_\beta = 7.34$ (2H, t, $J = 6.86$ Hz), $Py_\gamma = 7.73$ (1H, t,

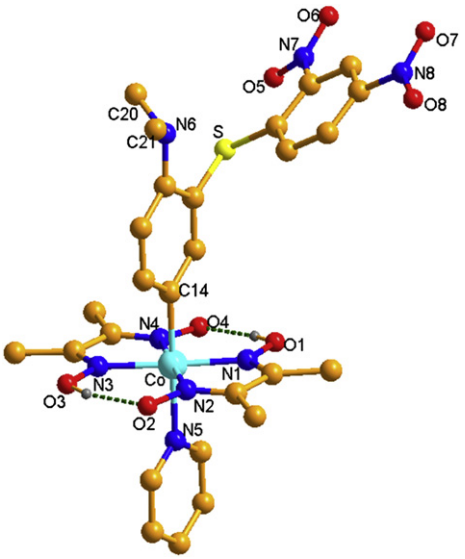



**Fig. 3.** Molecular structure of **12**. All hydrogen atoms have been omitted for clarity (hydrogen atoms involved in the intramolecular hydrogen-bonding interactions are shown).

$J$ = 7.70 Hz), 7.17 (2H, d, $J$ = 9.0 Hz), 6.48 (2H, d, $J$ = 8.56 Hz), dmgH (Me) = 2.03 (12H, s), 2.82 (6H, s), O–H···O = 18.47 (s). $^{13}$C NMR (125 MHz, $CDCl_3$, $\delta$ ppm): 150.19 (C=N, $C_q$), 150.12 ($Py_\alpha$), 147.83, 137.59 ($Py_\gamma$), 134.60, 125.21 ($Py_\beta$), 112.58, 40.87, 12.19. Anal. Calcd for $C_{21}H_{29}CoN_6O_4$: C, 51.64; H, 5.98; N, 17.21. Found: C, 51.48; H, 5.89; N, 17.29.

*4.1.2. 2-ThienylCo(dmgH)$_2$Py (**5**)*

Yield: 0.343 g (76%). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$ ppm): $Py_\alpha$ = 8.68 (2H, d, $J$ = 4.9 Hz), $Py_\beta$ = 7.36 (2H, t, $J$ = 7.0 Hz), $Py_\gamma$ = 7.78 (1H, t, $J$ = 7.6 Hz), dmgH(Me) = 2.11 (12H, s), thienyl protons = 7.15 (1H, d, $J$ = 4.9 Hz), 6.87–6.88 (1H, m), 6.64 (1H, d, $J$ = 3.7 Hz), O–H···O = 18.45 (s). $^{13}$C NMR (125 MHz, $CDCl_3$, $\delta$ ppm): 150.77 (C=N, $C_q$), 150.08 ($Py_\alpha$), 138.10 ($Py_\gamma$), 129.39, 126.73, 126.18, 125.45 ($Py_\beta$), 12.35. Anal. Calcd for $C_{17}H_{22}CoN_5O_4S$: C, 45.23; H, 4.91; N, 15.52. Found: C, 45.01; H, 4.83; N, 15.62.

**Table 4**
Metric parameters of intermolecular C–H···O interactions for **4**, **12** and **13**.

| Bond | Distance (Å) | | | Angle (°) |
|---|---|---|---|---|
| | C–H | C–H···O | C···O | C–H···O |
| Compound **4** | | | | |
| C8A–H8A1···O3 | 0.960(3) | 2.382(2) | 3.115(4) | 132.79(18) |
| C20A–H20F···O2 | 0.959(3) | 2.686(2) | 3.341(4) | 125.92(22) |
| Compound **12** | | | | |
| C4–H4B···O1 | 0.959(4) | 3.079(3) | 4.007(6) | 163.16(29) |
| C5–H5B···O3 | 0.960(4) | 3.047(3) | 3.860(6) | 143.28(29) |
| C20–H20B···O8 | 0.959(6) | 3.118(4) | 4.025(7) | 158.33(36) |
| C10–H10A···O8 | 0.930(4) | 2.511(4) | 3.391(6) | 157.92(30) |
| C11–H11A···O7 | 0.930(4) | 2.548(4) | 3.252(6) | 132.73(29) |
| Compound **13** | | | | |
| C8–H8B···O8 | 0.979(4) | 2.702(4) | 3.243(6) | 115.19(30) |
| C10–H10···O6 | 0.949(5) | 2.561(3) | 3.128(6) | 118.56(30) |
| C9–H9···O8 | 0.950(4) | 2.562(4) | 3.314(6) | 136.26(31) |
| C1–H1B···O2 | 0.980(5) | 2.965(3) | 3.943(6) | 175.76(31) |
| C4–H4C···O2 | 0.980(4) | 3.620(2) | 4.529(5) | 155.41(29) |

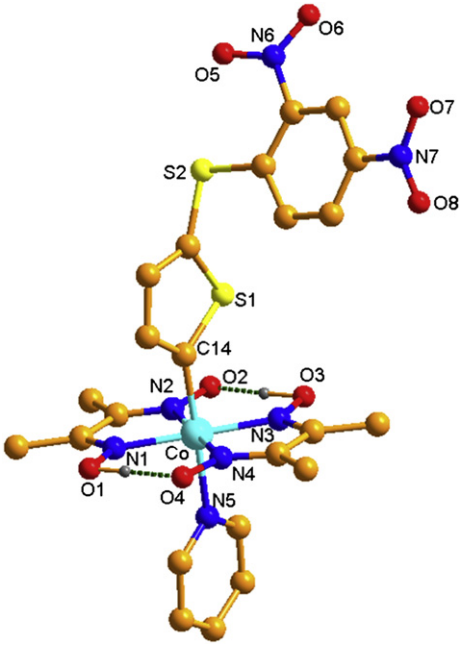



**Fig. 4.** Molecular structure of **13**. All hydrogen atoms have been omitted for clarity (hydrogen atoms involved in the intramolecular hydrogen-bonding interactions are shown).

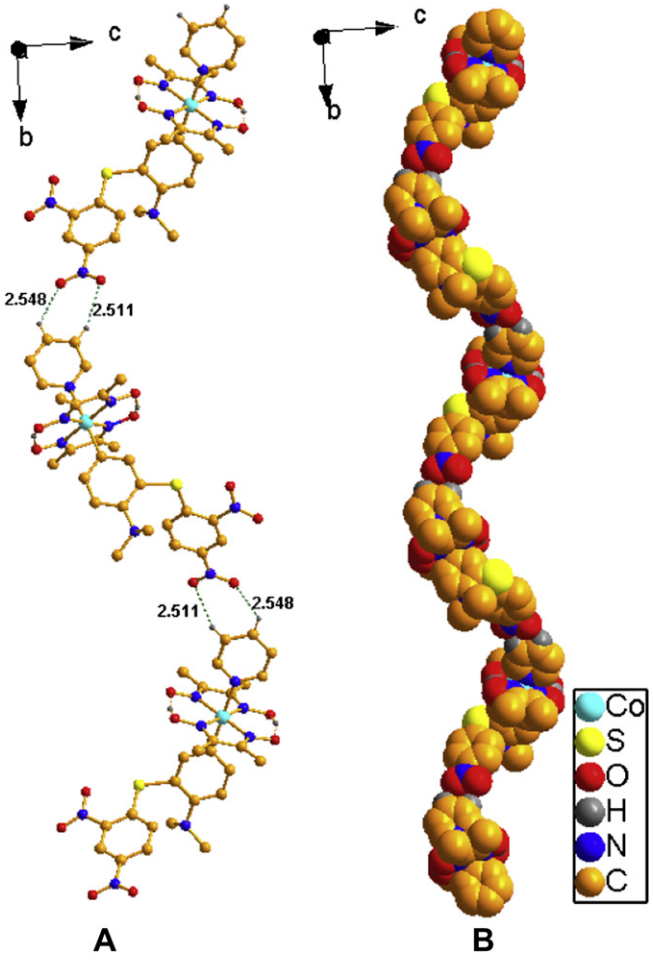



**Fig. 5.** (A) 1-D helical assembly resulting from C–H···O interactions in **12**. (B) Space-filling view of the left-handed helix of **12**. All of the hydrogen atoms, except those involved in hydrogen bonding, have been omitted for clarity.

### 4.2. Reaction of aryl cobaloximes with $Br_2$: general procedure

A solution of $Br_2$ (0.2 mmol in 10 mL dry $CHCl_3$) was added drop wise to a solution of organocobaloxime (0.2 mmol in 25 mL dry $CHCl_3$) in dark at 0 °C under nitrogen atmosphere. On completion of reaction, the solvent was evaporated under vacuum and the resulting solid was washed with ether (3 × 5 mL). The ethereal washings were evaporated to obtain organic product. The solid inorganic part was further purified by column chromatography on silica gel. The complexes **1**–**4** on reaction with bromine formed the corresponding bromoarenes (**6**–**9**). These were characterized by $^1$H NMR and mass spectrometry. However, complex **5** led to the formation of 5-bromo-2-thienylCo(dmgH)$_2$Py (**10**).

#### 4.2.1. 5-Bromo-2-thienylCo(dmgH)$_2$Py (*10*)

Yield: 0.056 g (53%). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$ ppm): $Py_\alpha$ = 8.62 (2H, d, $J$ = 6.1 Hz), $Py_\beta$ = 7.35 (2H, t, $J$ = 6.4 Hz), $Py_\gamma$ = 7.76 (1H, t, $J$ = 7.6 Hz), dmgH(Me) = 2.12 (12H, s), thienyl protons = 6.72 (1H, d, $J$ = 3.7 Hz), 6.36 (1H, d, $J$ = 3.7 Hz), O–H···O = 18.35 (s). $^{13}$C NMR (125 MHz, $CDCl_3$, $\delta$ ppm): 151.02 (C=N, $C_q$), 150.06 ($Py_\alpha$), 138.22 ($Py_\gamma$), 130.70, 129.49, 125.51 ($Py_\beta$), 109.36, 12.42. Anal. Calcd for $C_{17}H_{21}BrCoN_5O_4S$: C, 38.50; H, 3.99; N, 13.21. Found: C, 38.66; H, 3.89; N, 13.09.

### 4.3. Reaction of aryl cobaloximes with 2,4-dinitrobenzenesulfenyl chloride: general procedure

A solution of 2,4-dinitrobenzenesulfenyl chloride (0.2 mmol in 4 mL dry $CH_2Cl_2$) was added drop wise to a solution of aryl cobaloxime (0.2 mmol in 10 mL dry $CH_2Cl_2$) in dark at 0 °C under nitrogen atmosphere. The reaction was stirred at 0 °C for 1 h and then slowly brought to room temperature and stirred further for 3 h. After completion of reaction, the solvent was evaporated under vacuum to obtain crude products which were purified by column chromatography on silica gel. Complexes **1**–**3** did not react with 2,4-dinitrobenzenesulfenyl chloride. However, complex **4** formed **11** and **12** and the complex **5** afforded **13**.

#### 4.3.1. 3-(2,4-dinitrobenzenesulfenyl)-4-NMe$_2$C$_6$H$_4$Co(dmgH)$_2$Py (*12*)

Yield: 0.078 g (57%). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$ ppm): 9.07 (1H, d, $J$ = 2.2 Hz) $Py_\alpha$ = 8.65 (2H, d, $J$ = 6.2 Hz), $Py_\gamma$ = 7.75 (1H, t, $J$ = 7.55 Hz), 7.94 (1H, dd, $J$ = 10.3 Hz, 1.4 Hz), 7.42 (1H, dd, $J$ = 8.25 Hz, 2.05 Hz), 7.33–7.36 (3H, m), 6.84 (1H, d, $J$ = 8.95 Hz), 6.77 (1H, d, $J$ = 8.95 Hz), 2.62 (6H, s), dmgH (Me) = 2.04 (12H, s), O–H···O = 18.34 (s). $^{13}$C NMR (125 MHz, $CDCl_3$, $\delta$ ppm): 153.30, 150.53 (C=N, $C_q$), 150.26, 150.21 ($Py_\alpha$), 143.98, 143.58, 143.05, 138.58, 138.07 ($Py_\gamma$), 128.94, 125.89, 125.54 ($Py_\beta$), 121.56, 120.77, 119.09, 45.05, 12.39. Anal. Calcd for $C_{27}H_{31}CoN_8O_8S$: C, 47.23; H, 4.55; N, 16.32. Found: C, 47.31; H, 4.49; N, 16.35.

#### 4.3.2. 5-(2,4-dinitrobenzenesulfenyl)-2-thienylCo(dmgH)$_2$Py (*13*)

Yield: 0.083 g (64%). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$ ppm): $Py_\alpha$ = 8.63 (2H, d, $J$ = 5.2 Hz), $Py_\beta$ = 7.39 (2H, t, $J$ = 6.6 Hz), $Py_\gamma$ = 7.80 (1H, t, $J$ = 7.8 Hz), dmgH(Me) = 2.17 (12H, s), aromatic/thienyl protons = 9.03 (1H, d, $J$ = 2.0 Hz), 8.09 (1H, dd, $J$ = 8.8 Hz, 2.0 Hz), 7.11 (1H, d, $J$ = 3.2 Hz), 7.06 (1H, d, $J$ = 9.2 Hz), 6.74 (1H, d, $J$ = 2.8 Hz), O–H···O = 18.35 (s). $^{13}$C NMR (125 MHz, $CDCl_3$, $\delta$ ppm): 151.18 (C=N, $C_q$), 150.75, 149.99 ($Py_\alpha$), 144.05, 143.38, 138.42, 138.36 ($Py_\gamma$), 132.46, 129.08, 126.60, 125.64 ($Py_\beta$), 124.45, 121.07, 12.48. Anal. Calcd for $C_{23}H_{24}CoN_7O_8S_2$: C, 42.53; H, 3.72; N, 15.09. Found: C, 42.18; H, 3.80; N, 15.14.

### 4.4. 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 **4** ($CHCl_3$/$CH_3OH$), **5** ($CH_2Cl_2$/$CH_3OH$), **12** (EtOH/$CH_3OH$/$CH_2Cl_2$) and **13** ($CHCl_3$/$CH_3OH$). Single-crystal X-ray data were collected using graphite-monochromated Mo-$K\alpha$ radiation ($\lambda$ = 0.71073 Å) on "Bruker SMART APEX CCD diffractometer" at 100 K. The linear absorption coefficients, scattering factors for the atoms and the anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* [41]. The program SMART [42] was used for collecting frames of data, indexing reflections, and determining lattice parameters. The data integration and reduction were processed with SAINT software [42]. An empirical absorption correction was applied to the collected reflections with SADABS [43] using XPREP [44]. All the structures were solved by the direct method using the program SHELXS-97 [45] and were refined on $F^2$ by the full-matrix least-squares technique using the SHELXL-97 [45] 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 thiophene ring in complex **5** was found to be orientationally disordered and was modeled satisfactorily. The 'SQUEEZE' option in PLATON was used to remove disordered solvent molecule from the overall intensity data in complex **13**.

## Acknowledgment

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## Appendix A. Supplementary material

CCDC 762046, 762047, 762048 and 762049 contains 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.

## Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2010.12.008.

## References

[1] G. Dutta, K. Kumar, B.D. Gupta, Organometallics 28 (2009) 3485–3491 and refs cited therein.
[2] D. Mandal, B.D. Gupta, Organometallics 24 (2005) 1501–1510.
[3] M. Bhuyan, M. Laskar, D. Mandal, B.D. Gupta, Organometallics 26 (2007) 3559–3567.
[4] D. Mandal, B.D. Gupta, Organometallics 26 (2007) 658–670.
[5] B.D. Gupta, V. Singh, R. Yamuna, T. Barcley, W. Cordes, Organometallics 22 (2003) 2670–2678.
[6] B.D. Gupta, R. Yamuna, D. Mandal, Organometallics 25 (2006) 706–714.
[7] S.J. Moore, P. Siega, R.J. Lachicotte, L. Randaccio, P.A. Marzilli, L.G. Marzilli, Inorg. Chim. Acta 362 (2009) 993–1002.
[8] R. Dreos, A. Felluga, G. Nardin, L. Randaccio, P. Siega, G. Tauzher, Inorg. Chem. 40 (2001) 5541–5546.
[9] X. Zhang, D. Han, Y. Li, H. Chen, Inorg. Chim. Acta 359 (2006) 1121–1128.
[10] B.D. Gupta, R. Yamuna, V. Singh, U. Tiwari, Organometallics 22 (2003) 226–232.
[11] B.D. Gupta, K. Qanungo, R. Yamuna, A. Pandey, U. Tiwari, V. Vijaikanth, V. Singh, T. Barcley, W. Cordes, J. Organomet. Chem. 608 (2000) 106–114.
[12] B.D. Gupta, V. Singh, K. Qanungo, V. Vijaikanth, R. Yamuna, T. Barclay, W. Cordes, J. Organomet. Chem. 602 (2000) 1–4.
[13] B.D. Gupta, V. Vijaikanth, V. Singh, Organometallics 23 (2004) 2069–2079.
[14] K. Kumar, B.D. Gupta, J. Organomet. Chem. 695 (2010) 2233–2239.
[15] K.L. Brown, Dalton Trans. (2006) 1123–1133.
[16] K.L. Brown, Chem. Rev. 105 (2005) 2075–2149.
[17] J.M. Pratt, B.R.D. Whitera, J. Chem. Soc. A (1971) 252–255.
[18] D.N.R. Rao, M.C.R. Symons, J. Chem. Soc. Faraday Trans. 1 (1984) 423–434.

[19] C. Fontaine, K.N.V. Duong, C. Marienne, A. Gaudemer, C. Giannotti, J. Organomet. Chem. 38 (1972) 167–178.
[20] C. Marienne, C. Giannotti, A. Gaudemer, J. Organomet. Chem. 54 (1973) 281–290.
[21] J. Deniau, A. Gaudemer, J. Organomet. Chem. 191 (1980) C1–C2.
[22] M. Kijima, H. Yamashita, T. Sato, J. Organomet. Chem. 474 (1994) 177–182.
[23] B.D. Gupta, S. Roy, Inorg. Chim. Acta 108 (1985) 261–264.
[24] B.D. Gupta, M. Roy, I. Das, J. Organomet. Chem. 397 (1990) 219–230.
[25] B.D. Gupta, V. Vijaikanth, V. Singh, J. Organomet. Chem. 570 (1998) 1–7.
[26] G. Dutta, M. Laskar, B.D. Gupta, Organometallics 27 (2008) 3338–3345.
[27] F.R. Jensen, V. Madan, D.H. Buchanan, J. Am. Chem. Soc. 93 (1971) 5283–5284.
[28] R.D. Garlatti, G. Tauzher, G. Costa, J. Organomet. Chem. 182 (1979) 409–413.
[29] G.W. Daub, Prog. Inorg. Chem. 22 (1977) 409–423.
[30] S.N. Anderson, D.H. Ballard, M.D. Johnson, J. Chem. Soc. Perkin Trans. 2 (1972) 311–318.
[31] B.D. Gupta, M. Kumar, S. Roy, Inorg. Chem. 28 (1989) 11–18.
[32] B.D. Gupta, S. Roy, Tetrahedron Lett. 25 (1984) 3255–3256.
[33] B.D. Gupta, M. Kumar, Chem. Lett. (1987) 701–704.
[34] B.D. Gupta, M. Kumar, Inorg. Chim. Acta 181 (1991) 73–79.
[35] B.D. Gupta, V. Dixit, J. Organomet. Chem. 533 (1997) 261–264.
[36] B.D. Gupta, V. Dixit, I. Das, J. Organomet. Chem. 572 (1999) 49–58.
[37] X. Zhang, Y. Li, Y. Mei, H. Chen, J. Organomet. Chem. 691 (2006) 659–666.
[38] Positive sign of $\alpha$ and d indicates bending towards R and displacement toward base and vice versa.
[39] 4-(2,4-dinitrobenzenesulfenyl)-*N*, *N*-dimethylaniline (**11**). $^1$H NMR (500 MHz, $CDCl_3$, $\delta$ ppm): 9.07 (1H, d, $J = 2.2$ Hz), 8.10 (1H, dd, $J = 9.04$ Hz, 2.2 Hz), 7.37 (2H, d, $J = 8.8$ Hz), 7.04 (1H, d, $J = 9.04$ Hz), 6.78 (2H, d, $J = 9.04$ Hz), 3.06 (6H, s). $^{13}$C NMR (125 MHz, $CDCl_3$, $\delta$ ppm): 151.07, 137.07, 126.53, 121.39, 113.42, 40.19.
[40] 2-Bromo-5-(2,4-dinitrobenzenesulfenyl)thiophene (**14**). Yield: 57.60%. $^1$H NMR (500 MHz, $CDCl_3$, $\delta$ ppm): 9.10 (1H, d, $J = 2.3$ Hz), 8.28–8.25 (1H, m), 7.26 (1H, d, $J = 4$ Hz), 7.22–7.21 (1H, m), 7.07 (1H, d, $J = 3.45$ Hz). $^{13}$C NMR (125 MHz, $CDCl_3$, $\delta$ ppm): 145.04, 143.98, 139.79, 139.13, 137.94, 132.22, 128.64, 127.81, 125.07, 121.47. Anal. Calcd for $C_{10}H_5BrN_2O_4S_2$: C, 33.25; H, 1.40; N, 7.76. Found: C, 33.37; H, 1.38; N, 7.72.
[41] International Tables for X-ray Crystallography, vol. IV, Kynoch Press, Birmingham, England, 1974.
[42] Smart & SAINT Software Reference manuals, Version 6.45. Bruker Analytical X-ray Systems, Inc., Madison, WI, 2003.
[43] G.M. Sheldrick, SADABS, Software for Empirical Absorption Correction, Ver. 2.05. University of Göttingen, Göttingen, Germany, 2002.
[44] XPREP, 5.1 ed. Siemens Industrial Automation Inc., Madison, WI, 1995.
[45] G.M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement. University of Göttingen, Göttingen, Germany, 2008.