



## Weak interactions between furfuryl and equatorial dioxime ligand in furfuryl(O<sub>2</sub>)Co(dmgh)<sub>2</sub>Py: NMR, X-ray and DFT calculations

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### ARTICLE INFO

#### Article history:

Received 14 October 2009

Received in revised form 16 November 2009

Accepted 17 November 2009

Available online 24 November 2009

#### Keywords:

Dioximes

Furfuryldioximecobaloxime

Structure elucidation

DFT calculations

### ABSTRACT

The crystal and molecular structure of furfuryl(O<sub>2</sub>)Co(dmgh)<sub>2</sub>Py (**1**) has been determined by X-ray diffraction analysis. In the molecular structure of **1**, the furfuryl ring oxygen is pointing inwards and is very close to one of the dmgh (Me) (2.625 Å). It shows unusual C–H...O weak interaction which must be responsible for the observed 1:3 ratio of dmgh methyl protons in NMR spectrum. Also, theoretical calculations using DFT have been performed on **1** for the Co–O and CH<sub>2</sub>–C(furfuryl) bond rotation. Conformational energy diagrams derived from theoretical calculations also indicate that in most stable conformer the furfuryl ring oxygen is very close to one of the dmgh (Me) groups.

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### 1. Introduction

Cobaloximes<sup>1</sup> have extensively been studied and reviewed over the past four decades [1–5]. More than 1500 complexes and >150 crystal structures have been reported and in majority of the examples, dmgh has been used as the equatorial dioxime and the examples with other dioximes are rather few and many have been reported recently [6–13]. Most of the recent studies on cobaloximes have focused on the structure–property relationship [2,13–16]. Cobaloximes are best characterized by NMR and X-ray studies. When R is an alkyl or an inorganic group, the dmgh methyl signal appears as a sharp singlet at around 2.0 ppm in the <sup>1</sup>H NMR spectra of most of the complexes indicating the chemical equivalence of all four methyl groups. However, these methyl groups become non-equivalent and appear as two singlets in the ratio 1:1 when either of the axial ligands is chiral [17,18]. The hindered rotation of the axial Co–C or Co–N bond, caused by the weak, through-space interaction also results in the nonequivalence of the dioxime methyl protons as observed in CF<sub>3</sub>CH<sub>2</sub>Co(dmgh)<sub>2</sub>(2-NH<sub>2</sub>Py) [19], 2-fluorocyclohexylcobaloxime [20], 2-substituted benzyl cobaloximes, 2-naphthylmethylcobaloximes [21,22]. Such weak interactions also lead to structural preferences, for example, the pyrazine bridged alkyl dicobaloximes attain the staggered conformation [23] whereas

the benzyl analogues acquire the eclipsed conformation [24]. The same types of interaction between the axial and equatorial ligands have also been reported by Randaccio et al. in RCo(DBPh<sub>2</sub>)<sub>2</sub>L (DBPh<sub>2</sub> = diphenylboryldimethylglyoximate) [25] and Styne et al. in LFe<sup>II</sup>(DBPh<sub>2</sub>)<sub>2</sub>L [26] where this interaction defines the ligand's orientation. The weak interactions also affect the reactivity and the NMR chemical shifts in cobaloximes. Benzyl cobaloximes in general, behave differently from alkyl cobaloximes [27–29] and this difference in reactivity arises partly due to the interactions of the benzyl group with the dioxime ring current. The chemical shift of dmgh methyl in alkyl cobaloximes is almost constant, while it is upfield shifted in benzyl cobaloxime but still appears as a singlet. The upfield shift occurs due to the C–H...π interaction between the benzyl group and the dmgh methyl (X-ray structures also support this) [22]. The upfield shift is more in 2-naphthylCH<sub>2</sub>cobaloxime [21,22] and the C–H...π interaction is so large in 9-anthracenylCH<sub>2</sub>cobaloxime that it splits the dmgh (Me) into two signals in the ratio 1:1 at room temperature [30]. All three methyl groups of the equatorial mesitylene dioxime in PhCH<sub>2</sub>Co(dmestgh)<sub>2</sub>Py become non-equivalent for a similar reason [31].

In 1985, we reported [32,33] a series of heteroaromatic methyl cobaloximes, ArCH<sub>2</sub>Co(dmgh)<sub>2</sub>Py [Ar = thenyl, furyl, picolyl] and their O<sub>2</sub> and SO<sub>2</sub> adducts, ArCH<sub>2</sub>(O<sub>2</sub>)Co(dmgh)<sub>2</sub>Py and ArCH<sub>2</sub>(SO<sub>2</sub>)Co(dmgh)<sub>2</sub>Py, which showed an unusual nonequivalence of the dmgh methyl protons in 1:3 ratio. In the absence of the crystal structure no conclusive explanation could be given then. However, it was attributed to hydrogen bond interaction between the oxime hydrogen and the hetero atom of the axial R group. We have revisited the study. The X-ray structure of **1** and DFT calculations conclusively show that the nonequivalence of dmgh methyl protons

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<sup>1</sup> Cobaloximes have the general formula RCo(L)<sub>2</sub>B, where R is an organic group σ-bonded to cobalt. B is an axial base trans to the organic group, and L is a monoanionic dioxime ligand (e.g. glyoxime (gH), dimethylglyoxime (dmgh), 1,2-cyclohexanedione dioxime (chgH), diphenylglyoxime (dpgH), dimesityl glyoxime (dmestgh), and dithiophenylglyoxime (dSPghH)).

occurs through the weak C–H...O interaction between the dmgH methyl and the hetero atom of the axial furfuryl group.

## 2. Results and discussion

### 2.1. Description of the structure 1

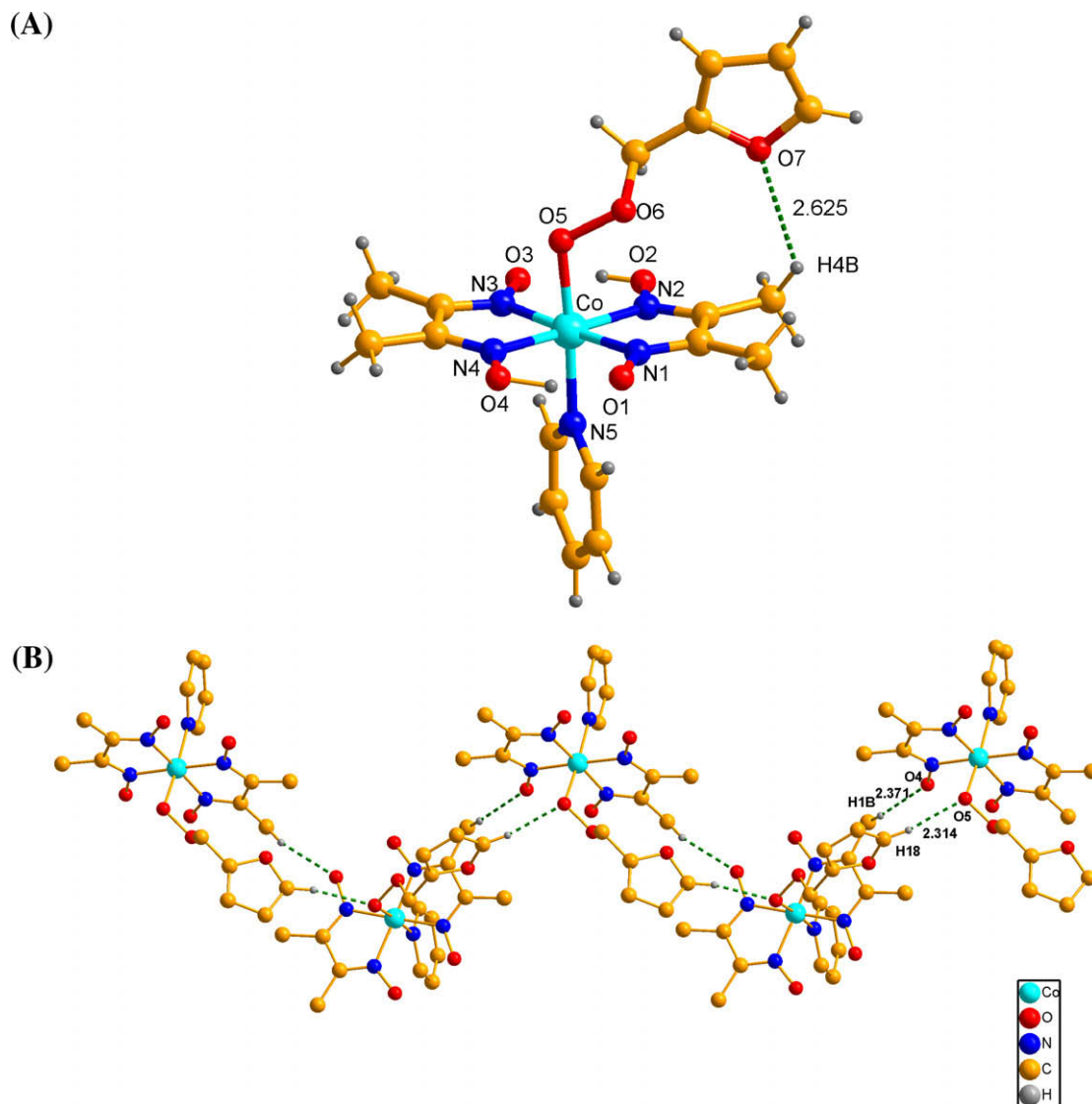
The X-ray data analysis of the crystal shows the composition as furfuryl(O<sub>2</sub>)Co(dmgH)<sub>2</sub>Py with the space group as *Pbca*. The geometry around the central cobalt atom is distorted octahedral with four nitrogen atoms of the dioxime in the equatorial plane and pyridine and O<sub>2</sub>furfuryl are axially coordinated. Its “Diamond” diagram along with the selected numbering scheme is shown in Fig. 1A. The pertinent crystal data and refinement parameters for the structure **1** are given in Table 1 and the selected bond lengths, bond angles, and structural parameters are given in Table 2.

Co(dioxime)<sub>2</sub> unit may undergo geometrical deformations, which is roughly represented by the displacement of the cobalt atom out of the plane of four nitrogens in the dioxime (*d*) and by the bending angle between the two dioxime units ( $\alpha$ ). Positive value of *d* (0.0383) and  $\alpha$  (7.41) indicates displacement towards L and

bending towards R. The crystal structure of **1** also shows an interesting property. A dimeric structure is formed due to C–H...O nonclassical intermolecular hydrogen bonding. This propagates further as a one dimensional zigzag polymeric sheet (Fig. 1B).

### 2.2. Description of nonequivalence of dmgH methyl protons

The nonequivalence (1:3) in **1** is unusual and is possible only if one of the dmgH (Me) has some interaction either through the aromatic ring (C–H... $\pi$ ) or through the hetero atom (C–H...O) of the axial R group. The X-ray structure of **1** clearly shows that the plane of the furfuryl ring is perpendicular to the dioxime plane and therefore, cannot have any C–H... $\pi$  interaction with the dmgH methyl. However, the furfuryl ring oxygen is pointing inwards and is very close to one of the dmgH (Me) (2.625 Å) and thus must be responsible for the observed nonequivalence. Interestingly, the crystal structures of dioxycobaloximes in the literature are limited. In all structures the C–H... $\pi$  interaction is the prominent feature. Cumyl(O<sub>2</sub>)Co(dmgH)<sub>2</sub>Py (**A**) [34], in spite of having prominent C–H... $\pi$  interaction (3.432 Å) does not show the nonequivalence of dmgH (Me). Also, dmgH (Me) appears as a singlet in tetra-



**Fig. 1.** (A) Molecular structure of furfuryl(O<sub>2</sub>)Co(dmgH)<sub>2</sub>Py (**1**). (B) A zigzag arrangement of molecules of **1** through C–H...O nonclassical intermolecular hydrogen bonding (most of hydrogen atoms are omitted for clarity).

**Table 1**  
Crystal data and structure refinement details for **1**.

| 1  |  |
|--|--|
| Empirical formula  | C <sub>18</sub> H <sub>24</sub> CoN <sub>5</sub> O <sub>7</sub>  |
| Formula weight   | 481.35   |
| Diffractometer   | Bruker CCD   |
| T (K)  | 100(2)   |
| Crystal system   | Orthorhombic   |
| Space group  | <i>Pbca</i>  |
| <i>Unit cell dimension</i>                                   |  |
| <i>a</i> (Å)   | 16.0323(15)  |
| <i>b</i> (Å)   | 15.0822(14)  |
| <i>c</i> (Å)   | 17.3907(16)  |
| $\alpha$ (°)   | 90.000   |
| $\beta$ (°)  | 90.000   |
| $\gamma$ (°)   | 90.000   |
| <i>V</i> (Å <sup>3</sup> )                                   | 4205.1(7)  |
| <i>Z</i>   | 8  |
| $\rho$ (calc) (g/cm <sup>3</sup> )                           | 1.521  |
| $\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )                   | 0.867  |
| <i>F</i> (0 0 0)   | 2000   |
| Crystal size (mm <sup>3</sup> )                              | 0.33 × 0.26 × 0.22   |
| Index ranges   | −21 ≤ <i>h</i> ≤ 21, −13 ≤ <i>k</i> ≤ 19,<br>−19 ≤ <i>l</i> ≤ 23 |
| Number of reflections collected                              | 26 636   |
| Number of independent reflections                            | 5222   |
| Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>               | 1.180  |
| Final <i>R</i> indices ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) | <i>R</i> <sub>1</sub> = 0.0915, <i>wR</i> <sub>2</sub> = 0.1746  |
| <i>R</i> indices (all data)                                  | <i>R</i> <sub>1</sub> = 0.1246, <i>wR</i> <sub>2</sub> = 0.1883  |
| Data/restraints/parameters                                   | 5222/0/292   |

**Table 2**  
Selected bond lengths (Å), bond angles (°) and structural data for (**1**) and known dioxy complexes (**A**, **B**, **C**).

| Parameters                          | <b>1</b>   | <b>A</b> <sup>a</sup> | <b>B</b> <sup>b</sup> | <b>C</b> <sup>c</sup> |
|-------------------------------------|------------|-----------------------|-----------------------|-----------------------|
| Co–O <sub>ax</sub>                  | 1.901(3)   | 1.897(7)              | 1.898(2)              | 1.923(3)              |
| Co–N <sub>ax</sub>                  | 1.994(3)   | 1.994(7)              | 2.013(2)              | 2.007(4)              |
| O–O                                 | 1.440(4)   | 1.454(7)              | 1.456(1)              | 1.415(6)              |
| O–C                                 | 1.418(5)   | 1.461(7)              | 1.449(1)              | 1.428(8)              |
| Co–O–O                              | 115.18(22) | 112.41(3)             | 112.84(4)             | 115.27(30)            |
| O–O–C                               | 107.04(30) | 111.15(3)             | 107.15(3)             | 108.20(47)            |
| Co–O–O–C                            | 116.19(29) | −131.57(3)            | −113.94(5)            | 100.06(45)            |
| O–C–C                               | 108.68(38) | 100.77(3)             | 104.92(3)             | 112.21(56)            |
| O–O–C–C                             | 178.18(33) | 172.34(3)             | 164.36(5)             | 63.66(66)             |
| N <sub>py</sub> –Co–O <sub>ax</sub> | 176.44(14) | 175.25(2)             | 176.88(4)             | 177.97(18)            |
| <i>d</i> (Å)                        | 0.0383(5)  | 0.0267(4)             | 0.0290(9)             | 0.011(9)              |
| $\alpha$ (°)                        | 7.41(23)   | 6.91(2)               | 4.78(4)               | 3.17(29)              |
| $\tau$ (°)                          | 64.76(17)  | 88.16(10)             | 85.34(12)             | 79.83(32)             |

<sup>a</sup> C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>2</sub>C(O<sub>2</sub>)Co(dm<sub>g</sub>H)<sub>2</sub>Py [49].<sup>b</sup> 4-Me-C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)CH(O<sub>2</sub>)Co(dm<sub>g</sub>H)<sub>2</sub>Py [51].<sup>c</sup> C<sub>2</sub>H<sub>5</sub>OOC(CH<sub>2</sub>)(CH<sub>3</sub>)CH(O<sub>2</sub>)Co(dm<sub>g</sub>H)<sub>2</sub>Py [52].

hydrofurfurylCo(dm<sub>g</sub>H)<sub>2</sub>Py and its dioxy adduct [35]. A comparison of the molecular structure of **1** with the reported dioxy complexes<sup>2</sup> (**B** and **C**) [36,37] shows many similarities in the structural parameters. However, the crystal structure data in **1** resembles most with structure **B**.

R–O–O–R' dihedral angle is a significant parameter for all the peroxides. Evidently, the same minimization of lone pair–lone pair (LP–LP) interactions that governs the structure of hydrogen peroxide (dihedral angle 112°) is the dominant factor in **1**. The Co–O–O–C dihedral angle gives useful information about the bond pair–lone pair (BP–LP) and LP–LP repulsions around the O–O bond in such

complexes, for example cumyl(O<sub>2</sub>)Co(dm<sub>g</sub>H)<sub>2</sub>Py (**A**), with the tertiary carbon bonded to Co(O<sub>2</sub>), has the highest value of −131.57° whereas it is −113.94 and 100.06° in the *sec*-alkyl(O<sub>2</sub>) complex **B** and **C**, respectively. Higher the angle, higher is the BP–LP interaction. The C–O–O angle also gives similar information; **A** has the highest angle (111.15°) and the maximum BP–LP interaction. The dihedral angle and C–O–O angle in **1** suggest that although Co(O<sub>2</sub>) is bound to a primary carbon, the steric crowding of the dioxime on the furfuryl ring is similar to *sec*-alkyl (**B**). The steric interaction of the [Co(dioxime)<sub>2</sub>] moiety with the axial ligand can also be inferred from the Co–O–O angle; it is higher in **1** as compared to the value in **B**.<sup>3</sup> Is it possible that the higher rate of oxygen insertion reported earlier in furfuryl cobaloxime as compared to the benzyl analogue is due to the variation in the steric *cis* influence [33]? We have recently reported that a small subtle variation in the Co–O–O–C, C–O–O and Co–O–O angles and in the *d* and  $\alpha$  value result in different orientation of the axial R group, for example, the naphthyl ring is almost perpendicular to the dioxime plane in 2-naphthylCH<sub>2</sub>O<sub>2</sub>Co(dm<sub>g</sub>H)<sub>2</sub>Py whereas the benzyl ring is somewhat tilted in the benzyl complex [38].

The O–O, Co–N<sub>py</sub> and Co–O bond distances in **1** are similar to the reported peroxy complexes, the significant difference, however, lies in the very high *d* and  $\alpha$  values as compared to all the reported dioxy complexes (**A**, **B**, and **C**). The large  $\alpha$  may have resulted due to C–H...O interaction. The effect of these interactions on the <sup>1</sup>H NMR chemical shifts has already been discussed above.

### 2.3. Theoretical calculations

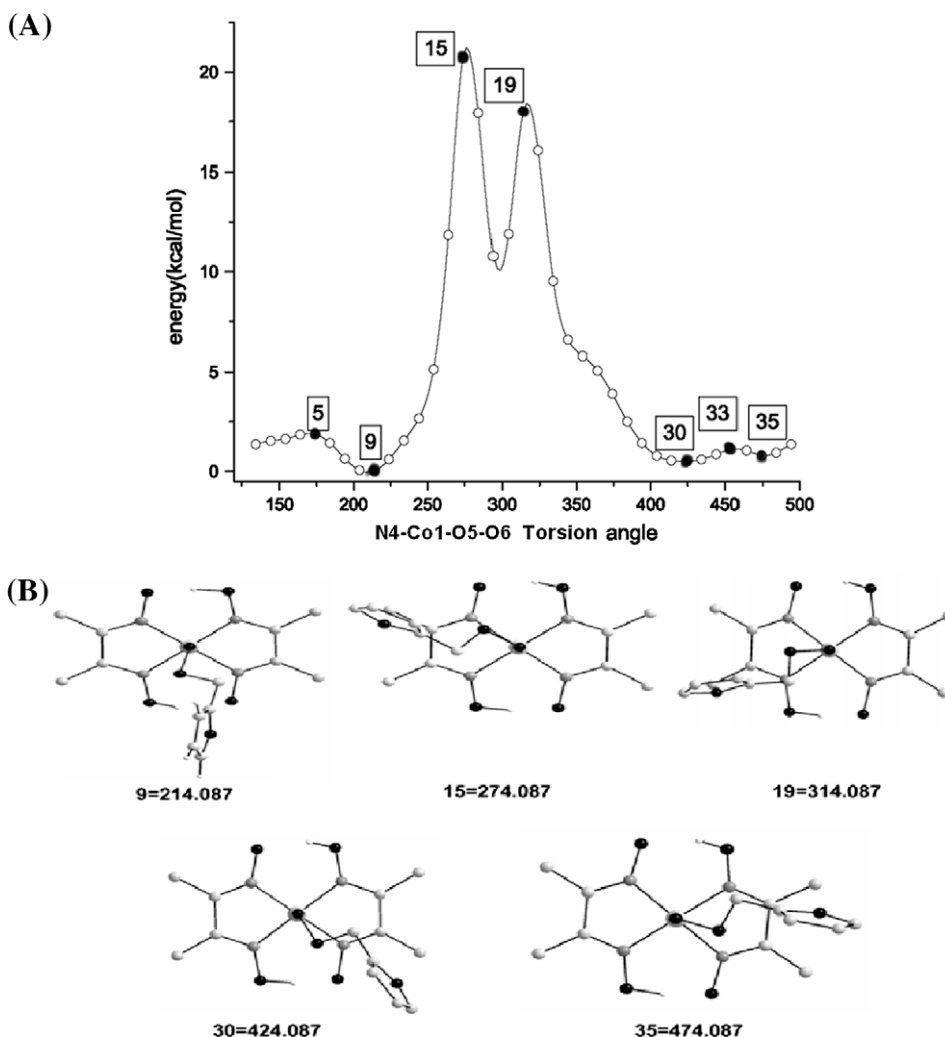
Quantum chemical calculations on the density functional theory (DFT) level of theory have been performed on **1** to get an insight into the hindered rotation of the Co–O and CH<sub>2</sub>–C(furfuryl) bond. The orientation of axial furfurylO<sub>2</sub> ligand with respect to the equatorial (dm<sub>g</sub>H)<sub>2</sub> ligand was measured by means of the torsion angle N4–Co1–O5–O6 (134.09°) and the single point calculation were performed at each point after rotation of the torsion angle by 10°. In doing so the Co–O bond rotation is considered. A conformational energy diagram for the rotation of furfurylO<sub>2</sub> group around the Co–O bond by 360° is shown in Fig. 2A. The diagram shows energy minima at 214.087° (9), 424.087° (30) and at 474.087° (35). The lowest energy conformation (9) has the furfuryl ring over O–H...O bridge which is an uncommon situation and no structure is known where the aryl group lies over the O–H...O group. There are two maxima at 274.087° (15) and at 314.087° (19) but the former is 2.71 kcal/mol higher in energy than latter. These occur due to some repulsive interactions between the furfuryl ring and the dioxime ring current; furfuryl ring lies above one of the dioxime moiety which is quite common in cobaloximes. The rotational conformers are shown in Fig. 2B.

Again the CH<sub>2</sub>–C(furfuryl) bond orientation is defined by the torsion angle O6–C14–C15–O7 (77.76°) and the single point calculations were done at each point after a rotation of the torsion angle by 10°. Conformational energy diagram and calculated structures of rotational conformers for the rotation of furfurylO<sub>2</sub> group around the CH<sub>2</sub>–C(furfuryl) bond by 360° is shown in Fig. 3A and B, respectively.

The diagram shows two maxima at angles 87.336° (2) and 267.345° (20). After (20) a further increase in the torsion angle causes a steep decrease in energy to get the most stable

<sup>2</sup> We have considered only those structures which have dm<sub>g</sub>H as the equatorial ligand, R(O<sub>2</sub>)Co(dm<sub>g</sub>H)<sub>2</sub>B. No structure has been reported in the literature with R as primary carbon.

<sup>3</sup> We have not considered the comparison with the value of 115° in **C** since it lacks the interaction between the axial and the equatorial ligand.



**Fig. 2.** (A) Conformational energy diagram for Co–O bond rotation in **1**. Equilibrium structure and transition states are marked by closed circles. (B) Calculated structures of rotational conformers of **1** due to Co–O bond rotation.

conformation (30). Here, the furfuryl oxygen is very close to one of the dmGH (Me) group as was observed in the X-ray study also.

### 3. Conclusion

The X-ray study as well as DFT level calculations clearly show that an unusual C–H...O interaction occur in furfuryl(O<sub>2</sub>)Co(dmGH)<sub>2</sub>Py complex that leads to 1:3 nonequivalence of the dmGH methyl groups.

### 4. Experimental

Compound **1** was prepared as described before [33].

#### 4.1. Crystal structure determination and refinements

An orange colored single crystal of compound **1** suitable for X-ray diffraction was obtained by a slow evaporation of solvent, (hexane/ethylacetate). 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 *Internation-*

*tional Tables for X-ray Crystallography* [39]. The data integration and reduction were processed with SAINT [40] software. An empirical absorption correction was applied to the collected reflections with SADABS [41] using XPREP [42]. The structure was solved by the direct method using SIR-97 [43] and was refined on  $F^2$  by the full-matrix least-squares technique using the SHELXL-97 [44] program package. All non-hydrogen atoms were refined anisotropically in the structure. The hydrogen atoms of the OH group of oxime were located on difference Fourier maps and were constrained to those difference Fourier map positions. The hydrogen atom positions or thermal parameters were not refined but were included in the structure factor calculations.

#### 4.2. Computational methods

The density functional theory (DFT) calculations were performed with the GAUSSIAN 03 suite of programs [45] using Becke's three-parameter hybrid exchange functional [46] and the Lee–Yang–Parr correlation functional (B3LYP) [47,48]. The double- $\zeta$  basis set of Hay and Wadt (LanL2DZ) with an effective core potential (ECP) was used for Co to represent the innermost electrons of the cobalt atom [49–52], and the main group elements were described using the 6-31G(d) basis sets. The calculations were performed in

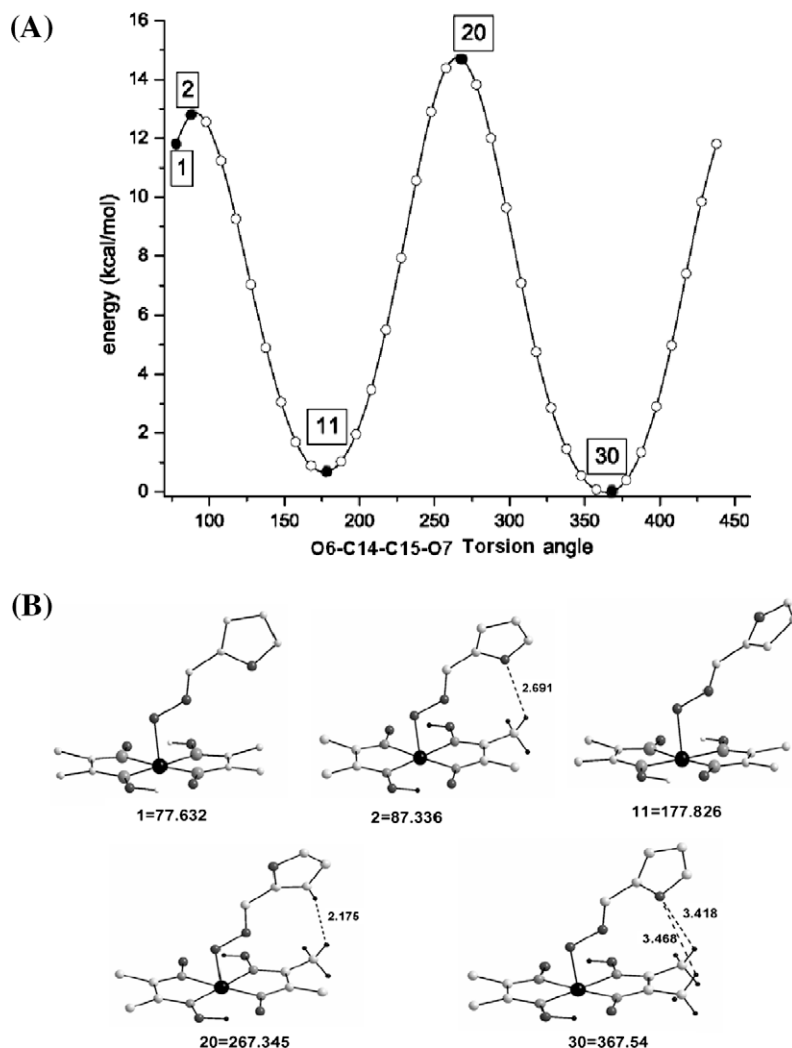


Fig. 3. (A) Conformational energy diagram for C–C bond rotation in **1**. Equilibrium structure and transition states are marked by closed circles. (B). Calculated structures of rotational conformers of **1** due to C–C bond rotation.

the gas phase, and the solvation effects were not considered. Closed single point calculations have been done using the atomic coordinates provided by the X-ray structure of **1**.

### Acknowledgement

We thank DST, New Delhi for funding this project.

### Appendix A. Supplementary material

CCDC 743311 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://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.2009.11.028](https://doi.org/10.1016/j.jorganchem.2009.11.028).

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