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The interactions between axial and equatorial ligands in cobaloximes: NMR changes

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Abstract—All three methyl groups in mesitylene become nonequivalent in the ^{1}H NMR spectra of $PhCH_2Co(dmestgH)_2Py$, $PhCH_2(SO_2)Co(dmestgH)_2Py$, and $PhCH_2(O_2)Co(dmestgH)_2Py$, due to weak interactions between the axial benzyl and the equatorial dioxime ligands.

Recent studies have focused on spectral and structural properties of the cobaloximes, $RCo(dmgH)_2Py$, *trans*-bis(dimethylglyoximato)pyridine(organo)cobalt(III) and NMR, in particular, has been used extensively for this purpose.[1–3] In the majority of complexes where R is an alkyl or an inorganic group, the dmgH methyl signal appears as a sharp singlet at around δ 2.0 ppm in the ^{1}H NMR spectra indicating the chemical equivalence of all four methyl groups. A singlet is also expected on the basis of the mean C_{2v} symmetry of the cobaloxime and the fast rotation of the Co–C bond, faster than the NMR time scale. Nonequivalence of dmgH(Me), however, has been observed when either of the axial ligands is chiral.[4]

Schrauzer et al.[5] made an observation in 1981 that benzyl-cobalamin undergoes decomposition faster than the bulky neopentylcobalamin in solution. This decomposition is not solely due to a steric reason; there is an additional force that makes the benzyl–Co bond weaker. Similarly, benzyl cobaloximes behave differently from alkyl cobaloximes.[6] This difference in reactivity must be due to interactions of the benzyl group with the dioxime and such interactions must be lacking in alkyl analogues.

Recently it has been shown that the interaction between an axial group and an equatorial dioxime ligand affects the structure and NMR chemical shifts in cobaloximes, for example, such interactions cause restriction of Co–C and/or C–Ph rotation and seem to be responsible for the nonequivalence of the dmgH(Me) and CH_2 protons in 2-substituted benzyl cobaloximes at sub-zero temperatures.[7] The crystal structures of benzyl cobaloximes show that the benzyl group always lies over one of the dioxime wings and is involved in a π-interaction with the dioxime ring current (see Supplementary data, Figs. S3 and S4). Conclusive evidence of the π-interaction with the dioxime ring current comes from a study of pyrazine bridged dicobaloximes; for example, the pyrazine bridged alkyl complex attains the staggered conformation whereas the benzyl analogue acquires the eclipsed conformation.[8] The same types of interaction between axial and equatorial ligands have been reported by Randaccio et al.[9] in $RCo(DBPh_2)_2L$ and Stynes et al.[10] in $LFe^{II}(DBPh_2)L'$, where this interaction defines the ligand's orientation.

If such weak π-interactions are important, nonequivalence of the dioxime protons will occur irrespective of the nature of the dioxime, and the extent of the nonequivalence will depend on the ring current and puckering of the dioxime. In this Letter, we show that the interactions between the axial and equatorial ligands occur at ambient temperature in dimesitylene complexes and lead to distinct changes in the ^{1}H NMR spectra.

The *ortho*-methyl groups in uncoordinated $dmestgH_2$ (dimesitylglyoxime) are equivalent and appear at δ 2.14 ppm whereas these are nonequivalent in the complexes $ClCo(dmestgH)_2Py$ or $MeCo(dmestgH)_2Py$.[3] This is due to the restricted rotation around the C–C bond

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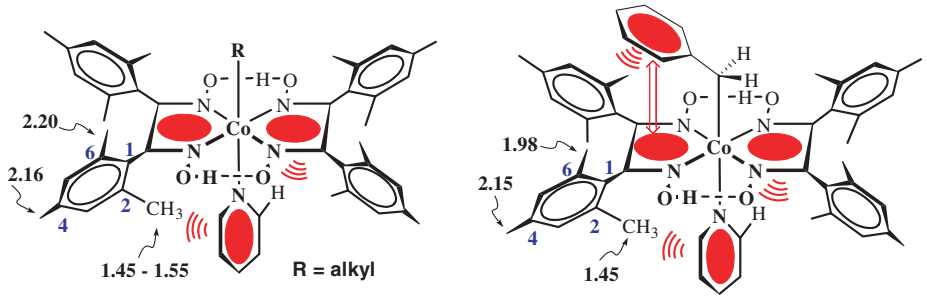

Figure 1. $RCo(dmestgH)_2Py$ and $PhCH_2Co(dmestgH)_2Py$.

between the oximinic and phenyl carbons. The methyl group at the 2-position is closer to the axial pyridine ring (C–H $\cdots$ π 2.840 Å) and is highly shielded by its ring current and appears at δ 1.51 ppm (see Fig. 1). This has been confirmed by the ^{1}H NMR of $ClCo(dmestgH)_2$(morpholine) where morpholine lacks the ring current. The crystal structure of $MeCo(dmestgH)_2Py$ shows that both axial positions are very crowded and laterally compressed by the methyl groups of the mesitylene and due to this steric crowding, the pyridine is puckered (strained).[3] Also, the strain is greater when R = Et, Pr or Bu than in the methyl analogue, as observed by ^{1}H NMR; for example, the 2-Me of the mesityl group is shifted upfield in the presence of the higher alkyl chain as compared to methyl.[3] It seems that on increasing the alkyl chain length the bending angle (α) increases and the 2-Me moves closer to the pyridine and is affected by its ring current.

The 6-Me resonance appears at δ 2.20 ppm in $alkylCo(dmestgH)_2Py$. This is significantly shielded (δ 1.98 ppm) in $C_6H_5CH_2Co(dmestgH)_2Py$ and the shielding is much larger in the 2-naphthyl analogue (δ 1.83 ppm). The interaction between the axial benzyl (or naphthyl) and the equatorial dioxime ligand caused this distinct change in the NMR spectrum. The benzyl or naphthyl ring must have the proper orientation to demonstrate this interaction. To see how important this requirement is we studied the ^{1}H NMR spectra of $C_6H_5CH_2O_2Co(dmestgH)_2Py$ and $C_6H_5CH_2SO_2Co(dmestgH)_2Py$ complexes since the expected orientation of the benzyl group varies significantly in these types of compounds.[11–13]

The 6-Me resonance appears slightly downfield, at δ 2.04 ppm, in $C_6H_5CH_2O_2Co(dmestgH)_2Py$ as compared to $C_6H_5CH_2Co(dmestgH)_2Py$.[14] A similar difference in chemical shift was also observed in $C_6H_5CH_2Co(dmgH)_2Py$ and its dioxy product.[6f] The difference in chemical shift may arise because of two factors: (a) the change in cobalt anisotropy[3,15] of $[Co(dioxime)]^+$ due to the peroxo group and (b) the shielding interaction between the axial benzyl and the dioxime ring current. The cobalt anisotropy is higher in the dioxy complex compared to the parent complex whereas the shielding is similar in both the complexes [compare the crystal structure of $C_6H_5CH_2Co(dmgH)_2Py$[16] and $cumyl(O_2)Co(dmgH)_2Py$;[11] both have a similar orientation of the benzyl group which lies over dmgH(Me)] (see Supplementary data, Figs. S3 and S4). The downfield shift in the dioxy complex is due to the higher cobalt anisotropy and the slight reduction in the shielding effect of the benzyl group. However, the change in chemical shift due to cobalt anisotropy is rather small [compare the chemical shift of H3 and H5 of the mesityl group in the benzyl and its dioxy product; these are too far away to be affected by the benzyl ring current].

A further change in conformation of the benzyl group occurs in $C_6H_5CH_2SO_2Co(dioxime)_2Py$.[12] Here the benzyl group lies vertically up and perpendicular to the dioxime plane and is too far away to have any interaction with the 6-Me group. The ^{1}H NMR spectrum of $C_6H_5CH_2SO_2Co(dmestgH)_2Py$ should, therefore, be similar to $XCo(dmestgH)_2Py$. However, the 6-Me is highly deshielded and the signal appears at δ 2.48 ppm. This must be due to its interaction with the SO_2 group that lies close to it (Fig. 2). A similar observation was made earlier in the corresponding gH (glyoximato) and dmgH (dimethylglyoximato) complexes; for example, the gH (or dmgH) protons appear at δ 7.24 (2.00) ppm in $C_6H_5CH_2Co(gH)_2Py$ ($C_6H_5CH_2Co$-

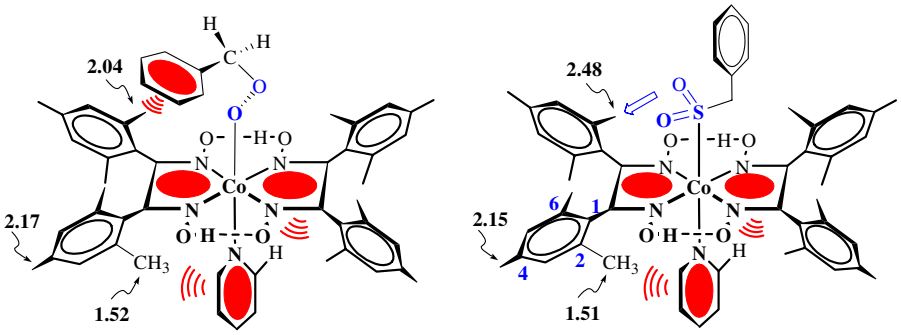

Figure 2. $PhCH_2(O_2)Co(dmestgH)_2Py$ and $PhCH_2(SO_2)Co(dmestgH)_2Py$.

$(dmgH)_2Py$) and at δ 7.55 (2.30) ppm in $C_6H_5CH_2SO_2$-$Co(gH)_2Py$ ($C_6H_5CH_2SO_2Co(dmgH)_2Py$).[12,17] However, unlike dmestgH, the downfield shift here is not due to the close proximity of the SO_2 group with the gH or dmgH(Me) protons. It results mainly from the cobalt anisotropy. The gH or dmgH(Me) protons are close to the $[Co(dioxime)_2]^+$ moiety and are affected much more than the dmestgH(Me) protons. The identical chemical shift of the 2-Me in ethyl, benzyl or naphthyl–$CH_2Co(dmestgH)_2Py$ indicates similar shielding by the pyridine ring current in these complexes. Interestingly, the chemical shift of the 2-Me group is identical in $MeO_2Co(dmestgH)_2Py$, $C_6H_5CH_2O_2Co(dmestgH)_2Py$ and $C_6H_5CH_2SO_2Co(dmestgH)_2Py$ and is justified in view of the above discussion.

All the ^1H NMR chemical shifts can be explained on the basis of 'through space' interactions between the axial and equatorial dioxime ligands. ^{13}C NMR spectra give more conclusive evidence. Since ^{13}C works through bond and not through space, it is expected that ^{13}C chemical shifts for the mesitylene methyl groups should not change much with the changes in the axial organic group since these are more than five bonds away from the axial group. This is what is observed. The ^{13}C NMR chemical shifts of the mesitylene group are almost the same in all the alkyl/benzyl/benzyl–O_2/benzyl–SO_2 complexes.

It is quite significant to see how all three methyl groups in the mesitylene become nonequivalent due to different interactions in the molecule in spite of the fact that the molecule is highly symmetrical. Since such weak π-interactions are important, as the preliminary results show, the nonequivalence will occur irrespective of the nature of the dioxime, and the extent of nonequivalence will depend on the ring current interaction and puckering in the dioxime. A similar effect is observed in the gH complexes also; for example, the gH protons appear upfield (δ 7.24 ppm) in $C_6H_5CH_2Co(gH)_2Py$[12] as compared to $MeCo(gH)_2Py$[18] (δ 7.42 ppm). Further studies on the axial to equatorial ligand interaction in other cobaloxime systems are in progress.

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Supplementary data

^1H NMR Tables, representative spectra and supporting figures are given as Supplementary data, which can be found in the online version, at doi:10.1016/j.tetlet.2007.01.140.

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