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Co−C Bond Homolysis: Reactivity Difference between Alkyl- and Benzylcobaloximes

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Summary: The Co−C bond is activated toward homolysis due to the interactions between axial and equatorial dioxime ligands. Benzylcobaloxime gives an oxygen-inserted product, whereas the alkyl derivative forms air-stable cobalt(II). The stabilization of the axial R group due to the interaction between axial and equatorial ligands causes the reactivity difference.

Coenzyme B_{12} has long fascinated chemists, and its unique property arises from the different catalytic activities of two different coenzymes. How the Co−C bond is activated toward homolysis or heterolysis is an enduring subject of research.[1,2] Studies on model compounds have continued to complement those on the more complex cobalamin- and B_{12}-based proteins.

Steric factors are known to be important in weakening the Co−C bond, and the Co−C bond length does indeed respond to steric rather than electronic effects in the model compounds, the organocobaloximes $RCo(dmgH)_2B$ (*trans*-bis(dimethylglyoximato)pyridine(organo)cobalt(III)).[2] The bond lengths in structurally characterized complexes vary over a remarkably broad range of 0.2 Å from methyl to adamantyl.[3] Spectroscopic evidence has been presented that even longer bonds occur in more sterically hindered systems which have thus far proved to be too unstable for X-ray structural characterization.[4] Modified cobaloximes have been studied with the aim of modeling more successfully some specific properties of the B_{12} coenzyme, such as reversible homolysis of the Co−C bond when it binds the apoenzyme[5] or the interaction of the corrin side chains with the axial ligands,[6] or avoiding undesired side reactions, such as autoxidation of the metal center, when Co^{II} complexes are studied as oxygen carriers.[7] However, such modifications are limited to a few cases only. Busch et al.[7] have successfully designed various cobalt(II) dioximes as oxygen carriers by electronic as well as steric modifications to stop the autoxidation process. Electronic modification was done by BF_2 bridging, while steric modification was achieved by using bulky dioximes. $Co^{II}(dmestgBF_2)_2$ is the poorest example of an oxygen carrier among various bulky dioximes, as it does not even take up dioxygen (Supporting Information, Scheme S1).

We have recently shown that the dimesitylglyoxime complexes $RCo(dmestgH)_2Py$ (R = alkyl; dmestgH = dimesitylglyoxime) have the maximum cobalt anisotropy and the highest steric cis influence among the commonly studied dioximes.[8] The crystal structures show that both the axial positions are very

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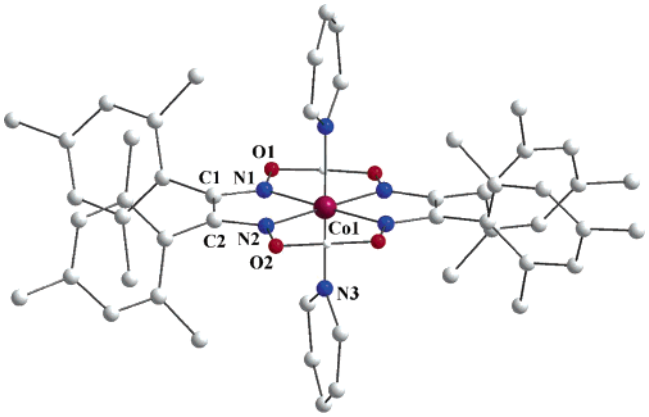

Figure 1. Molecular structure of $Co^{II}(dmetgH)_2(Py)_2$.

much crowded and laterally compressed by the methyl groups of mesityl and, due to this steric crowding, pyridine is puckered (strained) (Supporting Information, Figure S1). The strain is even greater when R = Et, Pr, Bu than it is for the methyl analogue, as observed in ^{1}H NMR; for example, the 2-Me of the mesityl group is shifted upfield in the higher alkyl chain as compared to the case for methyl.[8] It seems that increasing the alkyl chain length increases the bending angle (α) and the 2-Me moves closer to pyridine and becomes affected by its ring current.[9]

While studying the dmestgH complexes, we have made an important observation. During crystallization in a dichloromethane−methanol mixture, *n*-BuCo(dmestgH)$_2$Py, decomposed and gave nice orange crystals; the crystal data showed it to be $Co^{II}(dmestgH)_2Py_2$ (Figure 1).[10] Benzyl analogues, on the other hand, are highly unstable in solution. The workup must be carried out rapidly under an argon atmosphere; otherwise, the product is contaminated with the oxygen-inserted product. A solution of 4-CN-$C_6H_4CH_2$Co(dmestgH)$_2$Py kept for crystallization in air gave crystals which on X-ray analysis showed it to be the oxygen-inserted product 4-CN-$C_6H_4CH_2$-(O_2)Co(dmestgH)$_2$Py (Figure 2).[10] A clear reactivity difference between alkyl- and benzylcobaloximes is observed. The results are remarkable, since the alkyl cobaloximes, in general, are air stable and do not readily decompose in solution. Also the decomposition, if any, does not result in air-stable Co^{II}. The question is, how does this reactivity difference arise? Does the weak interaction between the benzyl and the dioxime play any role in the weakening of the Co−C bond?

Schrauzer et al.[11] in 1981 reported that benzylcobalamin undergoes decomposition faster than bulky neopentylcobalamin in solution and that this is not solely due to steric reasons; there is an additional force that makes the benzyl−Co bond weaker. There are many more instances where benzylcobaloximes are shown to behave differently from the alkylcobaloximes: for example, the Co−C bond dissociation energy (BDE) decreases

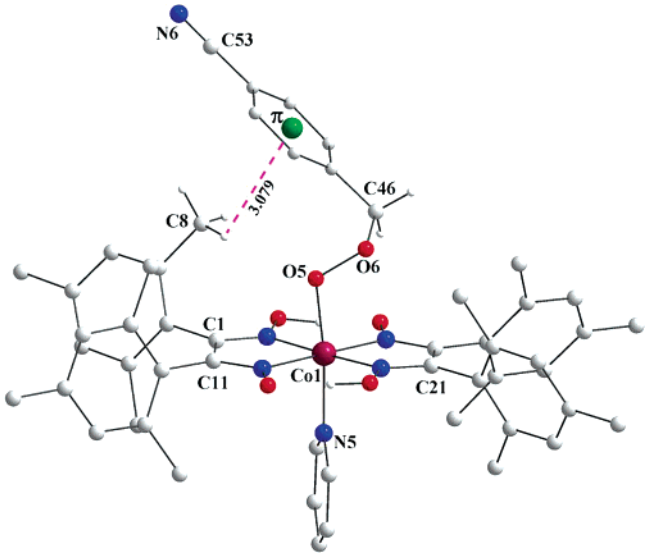

Figure 2. Molecular structure of 4-CN-$C_6H_4CH_2(O_2)$Co-(dmestgH)$_2$Py.

∼17 kJ/mol on going from Me to benzyl;[12] the thermal decomposition shows different product formations in alkyl- and benzylcobaloximes.[13] Oxygen insertion, studied as a reliable process to test the Co−C bond stability/reactivity, is much more facile in benzylcobaloxime than in alkylcobaloxime.[14] Thermolysis of benzyl-[Co] shows an intermolecular reaction between freely diffusing radicals ($PhCH_2^•$ and Co^{II}[macrocycle]$^•$) and has revealed a selective recombination of these radicals (99.999%) over bibenzyl (0.001%) formation.[15] This is attributed to the persistent radical effect; while the benzyl radical can couple in a chain terminating step, the Co^{II} radicals cannot. This leads to buildup of the persistent radicals in solution and steers the reaction to a single pathway in a highly selective fashion (cage mechanism).

Recently, the benzyl group was shown to have a π-interaction with the equatorial dioxime in many crystal structures, and it is oriented over one of the dioxime wings and not over the O−H···O.[16] Also, these interactions cause the nonequivalence of the dioxime protons and the CH_2 protons become diastereotopic in 2-substituted benzylcobaloximes.[16] The π interactions can have a significant effect on the structure; for example, the pyrazine-bridged alkyldicobaloxime has a staggered conformation, whereas the conformation switches over to eclipsed in the benzyl analogue.[17]

In this context the present results showing the reactivity difference between alkyl- and benzylcobaloximes are very important. The tight interaction of the axial ligand with the dioxime moiety activates the Co−C bond homolysis (steric cis influence), and the reaction is accelerated by destabilization of the reactant or electronic stabilization of the Co^{II} homolysis product by the dmestgH ligand.[1]

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(10) Crystal data for **Co(dmetgH)$_2$(Py)$_2$** (from DCM and methanol; CCDC 251399): $C_{50}H_{56}CoN_6O_4$, M_r = 863.94; monoclinic; space group *I*2/*a*; *a* = 12.128(2), *b* = 31.999(9), *c* = 12.130(2) Å; β = 98.012(15)°; *V* = 4662(3) Å^3; *Z* = 4; ρ = 1.231 g cm^{-3}; *T* = 293(2) K; reflections measured/unique 3213/3046; final *R* = 0.0621 (R_w = 0.1260); Enraf-Nonius CAD4 Mach2 instrument using θ−2θ scan. Crystal data for **4-CN-$C_6H_4CH_2(O_2)$Co(dmestgH)$_2$Py·C_6H_6·2CH_3CN** (from DCM, acetonitrile and benzene; CCDC 607226): $C_{63}H_{69}CoN_8O_6$, M_r = 1093.19; triclinic; space group *P*1̄; *a* = 14.2170(11), *b* = 14.3381(11), *c* = 16.6229(13) Å; α = 112.3520(10), β = 95.6900(10), γ = 111.5940(10)°; *V* = 2799.0(4) Å^3; *Z* = 2; ρ = 1.297 g cm^{-3}; *T* = 100(2) K; reflections measured/unique 18 867/13 342; final *R* = 0.0748 (R_w = 0.1041); Bruker CCD Detector using φ−ω scan.

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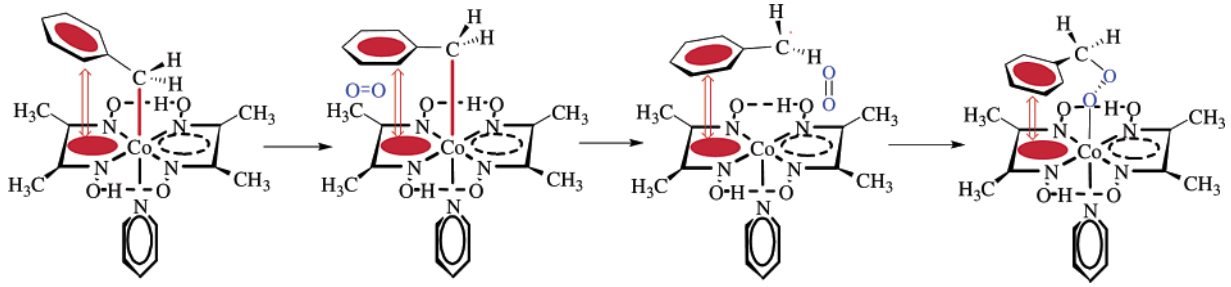
Scheme 1. Plausible Cage Effect Mechanism of Oxygen Insertion Reaction



The formation of Co^{II} as the end product in the alkylcobaloximes points to its stabilization by the macrocyclic ligand. The oxygen-inserted product is formed in the benzylcobaloxime due to the stabilization of Co^{II} by the macrocyclic ligand and the formation of a stable benzyl radical, which remains intact inside the cage by the interaction with the macrocyclic ligand. This leads to buildup of the persistent radicals in solution and steers the reaction in a highly selective manner. The very fact that the dioxy complex is formed indicates that the benzyl group is in the vicinity of the reaction center [$Co^{II}(O_2)$]. This can be seen as a cage effect. However, there is a possibility that the difference in reactivity may partly arise due to the difference in the stability of the benzyl and alkyl radicals.

Structural Aspects. $Co^{II}(dmetgH)_2(Py)_2$. This is the first crystal structure of an air-stable Co^{II}(dioxime) complex. The earlier reported crystal structure of $Co^{II}(dmgH)_2(Py)_2$[18] was found to be very reactive toward molecular oxygen. The crystal structure shows that both of the axial positions are occupied by pyridine. The Co−N_{py} bond distance (2.050(4) Å) in $Co^{II}(dmestgH)_2$ is considerably shorter as compared to that in $Co^{II}(dmgH)_2(Py)_2$ (2.25 Å). We are, at present, unable to provide any explanation for this difference. The formation of the bis(pyridyl) complex, $Co^{II}(Py)_2$, indicates the rupture of the Co−C bond followed by dissociation of base (pyridine). This seems plausible, since pyridine is already in a strained position and is loosely bound to cobalt in $MeCo(dmetgH)_2Py$.[8] This is very much similar to the Co−C bond homolysis in AdoCbl, where it shows a large geometric effect in the most flexible part of the system Co−N_{Im} bond (base-on and base-off).[19]

$Co^{II}(dmestgH)_2(Py)_2$ has also been characterized by EPR, and in the presence of air its solution shows an EPR spectrum similar to that of the $[Co^{II}-O_2]^{\bullet}$ radical and its oxygen binding is reversible (Supporting Information, Figures S2 and S3). The autoxidation is stopped due to the electronic and steric demands of dimesitylglyoxime. The $Co^{II}(dmestgH)_2(Py)_2$ catalyzes the aerial oxidation of PPh_3 to $P(O)Ph_3$.

Cobalt(II) is a free radical initiator and has several important applications.[7,20] In general, Co^{II} low-spin complexes are highly air sensitive: for example, $Co^{II}(dmgH)_2(Py)_2$ takes up oxygen and is instantly autoxidized to Co^{III}, in contrast to the case for $Co^{II}(dmestgH)_2(Py)_2$. The autoxidation can be stopped by modifying the dioxime moiety, $Co^{II}(dmgBF_2)_2$.[7]

4-CN-$C_6H_4CH_2(O_2)$Co(dmestgH)$_2$Py. In the previously reported molecular structures of (Me/Cl/Br)Co(dmestgH)$_2$Py,[8] *d* is negative, α is very high, and τ deviates greatly from 90°.[21] In contrast, *d* is always postive, α is low, and $\tau \approx 90°$ in cobaloximes with other dioximes (gH, dmgH, dpgH) (Supporting Information, Table S1). Benzyl analogues of dmestgH are even more strained, as they are highly unstable in solution. Interestingly, the strain in the molecule is released after the oxygen insertion, as α (3.17°) is low and *d* (+0.011 Å) becomes similar to those of other cobaloximes.

The crystal structure of 4-CN-$C_6H_4CH_2(O_2)$Co-(dmestgH)$_2$-Py is important, since only three structures of peroxocobaloximes have been reported in the literature.[22] This is the first crystal structure of a peroxo complex with a dioxime other than dmgH that also has the Co(O_2) unit attached to a primary carbon (all of the three structures reported earlier are with dmgH and have Co(O_2) bound to a secondary or tertiary carbon).[22] A comparison of the molecular structure of 4-CN-$C_6H_4CH_2$-(O_2)Co(dmestgH)$_2$Py with that of cumyl(O_2)Co(dmgH)$_2$Py[22a] shows that the Co−N (1.995(3) vs 1.994 Å) and Co−O distances (1.896(2) vs 1.897 Å) are identical. The C−H···π interaction and orientation of Bn−O−O group in these two systems are similar but not identical. Similar orientations of the benzyl group and C−H···π interactions have been observed in the benzylcobaloximes $ArCH_2Co(dmgH)_2Py$ (Supporting Information, Figure S6 and S7). Such interactions should have implications for the mechanism of the oxygen insertion in organocobaloximes. The oxygen insertion rate data for Me, *n*-Bu, and Bn Co(dmestgH)$_2$Py complexes show $k_{obs} = 2.5 \times 10^{-4}$, 4.5×10^{-4}, and 5.0×10^{-2} s^{-1}, respectively. The rates were measured at 0 °C, and the insertion was over within 2 min in the case of benzyl. This suggests that the difference in the rates in the methyl and butyl complexes is due to the difference in the Co−C bond dissociation energies (BDE). In contrast, the differences in the k_{obs} values and in the product formations in the butyl and benzyl complexes suggest that not only are the BDE's different but also the recombination step must have some influence. This reactivity difference is similar to that for the AdoCbl and MeCbl. Moreover, this is an important input, since many mechanisms have been proposed but no conclusive mechanism exists.[14] Since the activation due to the interactions between the equatorial and axial ligands and substrate (O_2) binding are the key factors for the homolysis of the Co−C bond, in view of the stabilization of axial organic radical a plausible mechanism can be written as in Scheme 1.

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(21) *d* is the deviation of the cobalt atom from the mean equatorial N_4 plane; the butterfly bending angle α is the dihedral angle between two dioxime planes, and τ is the torsion angle between two planes, the axial base pyridine and the plane that bisects the dioxime C−C bonds through the cobalt atom. Positive signs for α and *d* indicate bending toward R and displacement toward base and vice versa.

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Supporting Information Available: Text, tables, and figures giving EPR, crystal data comparison, supporting notes and figures, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org. Crystal data are also available from the Cambridge Crystallographic Database as CCDC Nos. 251399 and 607226.

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