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Protonation State of the Equatorial Ligands and Dynamics of the OH···O Units in a Cobaloxime Biomimetic

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The protonation state of the dimethylglyoxime ligands in the B_{12} coenzyme biomimetic [Co(CCl═CHCl)$(dmgH)_2$(py)]·$CHCl_3$ was investigated by using first-principles molecular dynamics. Our simulations at 173 and 300 K reveal that one of the oxime protons remains bonded to a nitroxyl group, while the proton of the second NO···H–ON unit is essentially shared with similar probability between the two oxygen atoms. This reconciles the results of the experimental determination (Jones, P. G.; Yang, L.; Steinborn, D. *Acta Cryst.* **1996**, *C52*, 2399), showing all N–O distances as equivalent, with the commonly accepted rule that the protonation state of the dimethylglyoxime ligands can be identified by the different N–O distances. Further aspects of the dynamics of the OH···O units, in relation to the occurrence of weak CH···O intermolecular interactions, are analyzed.

1. Introduction

Organocobaloximes have been widely studied as models for the vitamin B_{12} coenzyme.[1] Most of them have the formula $Co(dmgH)_2(L)R$ where dmgH is the monoanion of dimethylglyoxime, L is an axial base, and R is an organoligand (Figure 1). A large number of cobaloximes with different R and L ligands have been reported,[2] with R being CH_3, CCl═CHCl, Cl, or H_2O, among others. The axial base (L) is often a nitrogen-coordinated molecule such as pyridine or imidazole. The simplicity of these molecules allows several properties such as the reactivity of Co−C bonds and the influence of the axial base on the binding energy of the organoligand to be investigated in detail.[3]

The two equatorial dimethylglyoxime ligands are commonly present as monoanionic (dmgH) and the corresponding configuration is denoted as $(dmgH)_2$. Nevertheless, a dmg/$dmgH_2$ configuration, in which both protons are attached to one of the two dimethylglyoxime ligands ($dmgH_2$), while the other ligand remains deprotonated (dmg), is occasionally found[2] (see Chart 1). This has been attributed to the involvement of additional interactions such as strong hydrogen bonds[4] or localized $\pi-\pi$ interactions between the equatorial ligand and phenyl groups of the axial ligand.[5]

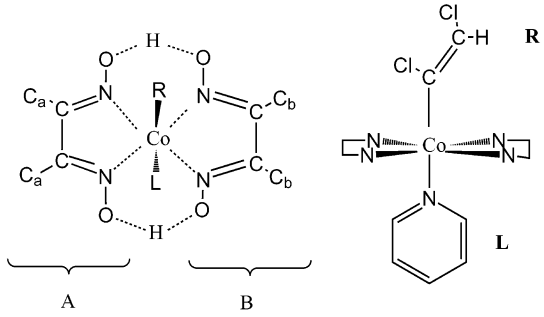

Figure 1. Molecule of Co(CCl═CHCl)$(dmgH)_2$(py) and labeling of the equatorial and axial ligands.

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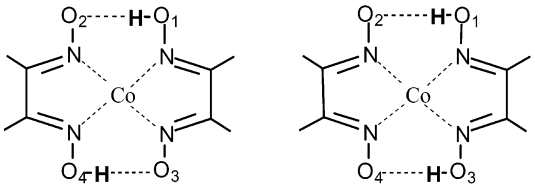
Chart 1



1a $(dmgH)_2$ **1b** $dmg/dmgH_2$

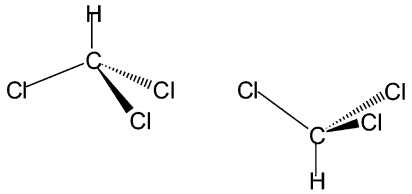
From an experimental point of view, the protonation state of the dimethylglyoxime ligands (dmg, dmgH, or $dmgH_2$) can be identified by a slight lengthening of the Co−N and N−O distances in the $dmgH_2$ unit with respect to those of the dmg unit.[2] In a few cases, the position of the hydrogen atoms is known from neutron diffraction measurements.[4b] However, as the changes in the N−O distances are very small and the positions of the hydrogen atoms are generally not available, the assignment from the structural data alone is often not possible. For instance, for the recently reported organocobaloxime crystal $[Co(CCl{=}CHCl)(dmgH)_2(py)]\cdot CHCl_3$, the protonation state of the dimethylglyoxime ligands could not be elucidated from the experimental determination of the structure.[6] Yet the exact determination of the protonation state of the dimethylglyoxime ligands is necessary to understand the chemistry of this B_{12} biomimetic. To the best of our knowledge, this problem has not yet been addressed with theoretical methods.

To contribute to the identification of the protonation state of the dimethylglyoxime ligands, we performed a first-principles molecular dynamics study of the title cobaloxime biomimetic. Our calculations, based on density functional theory (DFT) combined with molecular dynamics (Car−Parrinello approach), allow the evolution of the molecules to be followed a short time interval of time at finite temperature. This makes it possible to grasp the role played by temperature on the dynamics of the bridging OH···O protons in the organocobaloxime crystal $[Co(CCl{=}CHCl)(dmgH)_2(py)]\cdot CHCl_3$. Our results also clarify the problem of the protonation state of dimethylglyoxime ligands in many other cobaloxime B_{12} mimetics and underscore the need to perform dynamical simulations.

2. Computational Details

Our calculations were carried out with the Car−Parrinello molecular dynamics method,[7] which is based on Density Functional Theory (DFT). Previous work has demonstrated the reliability of this method in the description of proton-transfer processes in hydrogen-bonded systems.[8] The Kohn−Sham orbitals are expanded in a plane wave basis set with the kinetic energy cutoff of 70 Ry. Earlier calculations on cobalt-based macrocycles[9] showed that this cutoff is sufficient for achieving a good convergence of energies and structural properties of cobalt complexes. We employ ab initio pseudopotentials, generated within the Troullier−Martins scheme,[10] and the nonlinear core-correction[11] was applied to improve the transferability of the Co pseudopotential. Periodic calculations were done taking into account only the Γ point of the Brillouin zone. Molecular dynamics simulations use a time step of 0.12 fs and the fictitious mass of the electrons was set at 700 au. The deuterium mass was used for hydrogen, which allows a longer simulation step to be used. The total length of the simulations was 5−6 ps for each structure. Further computational details can be found in earlier works on different organometallic systems of biological relevance.[12]

Chart 2



2a **2b**

3. Results and Discussion

3.1. Static Calculations. We started the calculations by optimizing the structure of the isolated $Co(CCl{=}CHCl)(dmgH)_2(py)$ molecule, shown in Figure 1. The initial positions of the hydrogen atoms (not given in the experimental structure) were assumed as in Chart 1a, that is leading to two monoanionic dmgH ligands. The final optimized structure shows that the molecule keeps the $(dmgH)_2$ arrangement. Nevertheless, starting the optimization from the $dmg/dmgH_2$ form (Chart 1b) results in another local minimum that is 2 kcal/mol higher in energy. Therefore, both $(dmgH)_2$ and $dmg/dmgH_2$ arrangements (Chart 1) are stable for an isolated molecule of $Co(CCl{=}CHCl)(dmgH)_2(py)$, but the $(dmgH)_2$ form is energetically the more favored.

While gas-phase calculations are instructive, direct contact with experiment can be achieved only with crystal phase calculations. Experimentally, it is found that $Co(CCl{=}CHCl)(dmgH)_2(py)$ crystallizes in space group $P1$ and a triclinic cell of parameters $a = 8.1522$ Å, $b = 8.8910$ Å, $c = 8.9605$ Å, $\alpha = 82.552°$, $\beta = 89.562°$, and $\gamma = 63.421°$.[6] The C atom of the solvent $CHCl_3$ molecule is disordered over two equally occupied sites on either side of the Cl_3 plane (Chart 2). We considered two different limiting cases in which the solvent molecules are in either position **2a** or **2b**. For consistency, these two crystal structures will also be denoted as **2a** and **2b**.

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Table 1. Optimized Structural Parameters for the Stable Isomers of the Organocobaloxime Crystal Co(CCl=CHCl)(dmgH)$_2$(py) Discussed in the Text[a]

	2a	**2b**		
distance[b]	(dmgH)$_2$	(dmgH)$_2$	dmg/dmgH$_2$	X-ray[6]
Co−R	1.95	1.95	1.94	1.96
Co−L	2.00	2.00	2.01	2.03
O···O	2.48/2.50	2.48/2.50	2.49	2.49
H···O	1.40/1.42	1.37/1.43	1.39/1.41	
O−H	1.10	1.11/1.08	1.11/1.09	
Co−N (A)	1.87/1.89	1.87/1.89	1.89	1.89
Co−N (B)	1.88/1.89	1.88/1.89	1.87	1.89
N−O (A)	1.32/1.36	1.32/1.36	1.35	1.34
N−O (B)	1.32/1.36	1.32/1.36	1.32	1.34
N−C (A)	1.31	1.31	1.31	1.29
N−C (B)	1.31	1.31	1.32	1.30
C−C (A)	1.45	1.45	1.46	1.46
C−C (B)	1.45	1.45	1.45	1.47
C−Ca	1.49	1.49	1.49	1.49
C−Cb	1.49	1.49	1.49	1.48

[a] Distances are given in angstroms and angles in degrees. Structural parameters are defined in Figure 1. When two different values for the same distance were found, both results are given, except when they differ by less than 0.01 Å. In this case the average value is given. [b] R = CCl=CHCl; L = pyridine.

The structure of the [Co(CCl=CHCl)(dmgH)$_2$(py)]·CHCl$_3$ crystal was optimized by keeping the cell parameters fixed. Surprisingly, we found that the asymmetric dmg/dmgH$_2$ arrangement is not a stable minimum for crystal form **2a**. Instead, both arrangements are stable in crystal form **2b** and, moreover, they are practically isoenergetic (their energy difference is less than 0.3 kcal/mol).

The optimized structures of all crystal forms, along with the dimethylglyoxime arrangements found in each case, are summarized in Table 1. To begin with, it is interesting to see which structural parameters (other than the position of the hydrogen atoms) are distinctive of the dimethylglyoxime protonation state. Table 1 shows that the Co−R, Co−L, N−C, and C−C distances are about the same in all cases. The Co−N distances are also very similar, differing by only 0.01−0.02 Å depending upon the type of nitrogen they involve (the Co−N distances associated with an unprotonated N−O are 0.01 Å shorter than those associated with a protonated N−O). On the other hand, the asymmetry of the N−O distances is a good signature of the dimethylglyoxime protonation state. For instance, the N−O distances of (dmgH)$_2$ are the same in both ligands [N−O (A) = N−O (B)]. However, they are different in the case of dmg/dmgH$_2$ [N−O(A) = 1.35 Å, N−O(B) = 1.32 Å]. In particular, the dianionic ligand (dmg) has shorter N−O distances than the neutral one (dmgH$_2$). Our calculations thus show that the N−O distances cannot be all equivalent. Either they differ within the same dimethylglyoxime ligand (1.32/1.36 Å for dmgH) or they differ among different ligands (1.32 Å for the dianionic dmg and 1.36 Å for neutral dmgH$_2$). This is in agreement with neutron diffraction data on related B$_{12}$ mimetics, which show the same behavior of the N−O distances.[4a] However, in the case of the B$_{12}$ mimetic, which is of interest here, the experimental N−O distances are remarkably equivalent.

The results of our calculations provide a simple explanation for this. As both forms (**2a** and **2b**) appear in the crystal structure with equal probability, the degree of ionicity of the dimethylglyoxime should be obtained by averaging over both possible situations, (dmgH$_2$) and dmg/dmgH$_2$, with the former present in a larger amount. In fact, the experimental N−O distances (1.34 Å) fall between the two situations, (dmgH$_2$) and dmg/dmgH$_2$, as evidenced in Table 1. This explains the absence of a clear signature of the protonation state of the dimethylglyoxime ligands in the experimental structure, since both (dmgH$_2$) and dmg/dmgH$_2$ forms are present simultaneously. Other structural parameters (Table 1) that do not depend on the dimethylglyoxime protonation state show a very good agreement with experiment.

We now turn to the causes of the occurrence of the dmg/dmgH$_2$ form in the crystal, even though it is clearly the less favorable arrangement in the isolated molecule. Close inspection of the optimized structures shows that each molecule can form either one or two intermolecular interactions of the type C−H···O=N. One of them (the shorter and stronger one) involves the Cl$_3$C−H bond of a solvent molecule, while the other one involves the pyridine C(sp^2)−H bond of a neighboring molecule. The formation of short C−H···O interactions, as a consequence of the close proximity of the C and O atoms, has already been noticed by Jones et al.[6] Figure 2 shows the spatial location of these interactions in the optimized structures of both crystal forms. In the case of form **2a** (Figure 2a), both interactions act on the same OH···O unit. The Cl$_3$C−H···O$_3$=N interaction precludes the protonation of O$_3$, since the interaction is stronger for a nitroxyl oxygen than for the less basic hydroxyl oxygen. The remaining O$_1$−H···O$_2$ unit, not being involved in any short intermolecular interaction, is free to adopt any configuration and, consequently, the molecule adopts the most favorable (dmgH)$_2$ arrangement.

In the case of crystal form **2b**, the two C−H···O interactions act on different OH···O units (Figure 2b). The shortest interaction (Cl$_3$C−H···O$_2$) favors the O$_1$−H···O$_2$ form. However, the situation is less clear-cut for the O$_4$···H···O$_3$ unit. Protonation at O$_4$ (i.e. O$_3$···H−O$_4$) would lead to the more favored (dmgH)$_2$ arrangement, while protonation at O$_3$ (O$_3$−H···O$_4$) would be stabilized through a CH···O$_3$=N interaction with the pyridine ligand of a neighboring molecule. Thus, the molecule can adopt either of the two arrangements, (dmgH$_2$) or dmg/dmgH$_2$, which we found nearly isoenergetic. It is interesting to note that additional calculations in which the CHCl$_3$ solvent molecules were removed from the crystal showed that the molecules return to the (dmgH)$_2$ form. Clearly, it is the CH···O=N interactions that are responsible for the dimethylglyoxime protonation state in the title compound. In this regard, it is worth mentioning that a similar B$_{12}$ mimetic, with ethylene in place of CCl$_2$=CHCl and without solvent molecules, is known to adopt the (dmgH)$_2$ arrangement.[13]

Therefore, we find that while an isolated molecule prefers the (dmgH)$_2$ arrangement, the less favored dmg/dmgH$_2$ form

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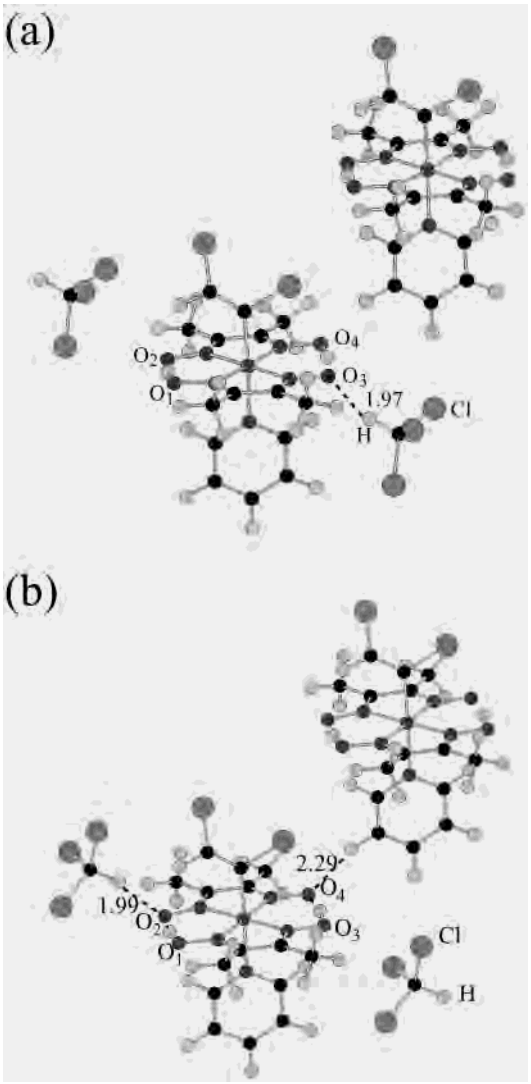

Figure 2. Shortest intermolecular interactions involving the oxime oxygens in the optimized structure of (a) crystal form **2a** and (b) the dmg/dmgH_2 isomer of crystal form **2b**.

can be stabilized in the crystal by the weak C−H···O═N interactions. In other words, subtle changes in the C−H···O═N interactions can determine the protonation state of the dimethylglyoxime ligands. Given the small energy differences among the different structures and the relatively low barrier for the proton transfer in the O···H···O units,[14] it is likely that both ($dmgH_2$) and dmg/$dmgH_2$ forms contribute to the dynamics of the crystal at a given temperature.

3.2. Molecular Dynamics Simulations. To analyze the effect of the temperature on the protonation state of the dimethylglyoxime ligands, we performed a series of classical molecular dynamics simulations on the [Co(CCl═CHCl)-$(dmgH)_2$(py)]·$CHCl_3$ crystal. Previous experience with hydrogen-bonded systems has shown that quantum effects are only of quantitative relevance.[8b] Two simulations were performed for each crystal form (**2a** and **2b**), one at 173 K, which is the temperature at which the crystal structure was determined,[6] and another one at 300 K, since most of the

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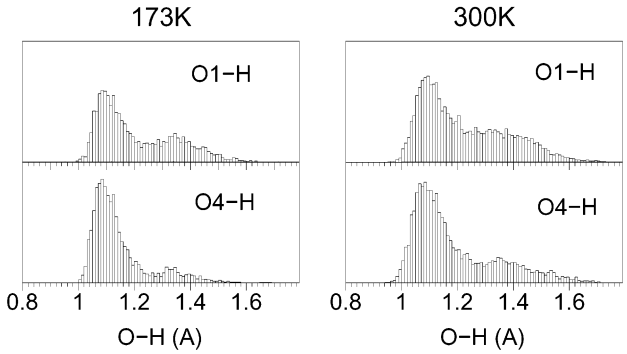

Figure 3. Probability distribution of the O_1−H and O_4−H bond lengths (see atom numbering in Chart 1) in crystal form **2a** of [Co(CCl═CHCl)-$(dmgH)_2$(py)]·$CHCl_3$ at (a) 173 and (b) 300K.

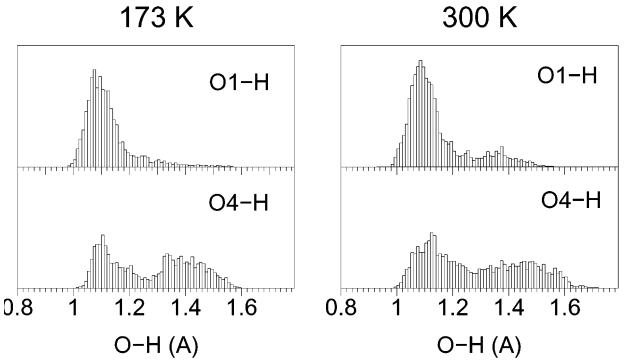

Figure 4. Probability distribution of the O_1−H and O_4−H bonds (see atom numbering in Chart 1) in crystal form **2b** of [Co(CCl═CHCl)$(dmgH)_2$-(py)]·$CHCl_3$ at (a) 173 and (b) 300K.

B_{12} mimetics based on dimethylglyoxime are crystallized at room temperature.[2]

Molecular dynamics simulations at 173 K on crystal form **2a** show that the bridging protons often jump from one dimethylglyoxime ligand to another. This leads to a delocalization of the protons, as is evidenced in the probability distribution of the O−H distances. Figure 3 shows that there is a well-defined maximum at 1.09 Å for both O_1−H and O_4−H distributions, while longer O−H distances have a relatively low population even at 300 K. Analysis of the correlation between both O−H distances shows that the $(dmgH)_2$ arrangement is the dominant one. This picture is consistent with the results of the structural optimizations which showed that the $(dmgH)_2$ form is the only minimum. Another feature that comes out of Figure 3 is that O_1−H is more delocalized into larger distances than O_4−H, at both temperatures. An explanation for this can be found by relating these distances with the intermolecular interactions affecting the oxime oxygens in each case. The short Cl_3C−H···O═N interaction acting on O_3 (Figure 2a) favors the protonation of O_4, which makes the O_3−H···O_4 configurations (i.e. longer H···O_4 bonds) less probable than the O_3···H−O_4 configurations.

The corresponding distance distribution for crystal form **2b** is shown in Figure 4. The O_1−H distribution shows a maximum at 1.1 Å, exactly as in crystal form **2a** (Figure 3), but there is little population for larger distances. Figure 2b shows that in this case the short Cl_3C−H···O═N interaction acts on O_2, favoring the short O_1−H distances. As a

consequence, the O_1-H distribution resembles that of O_4-H in crystal form **2a** (Figure 3). On the other hand, the distribution of O_4-H appears quite different from those analyzed up to now. It has two maxima, localized at 1.1 and 1.4 Å, both with a similar population. This is consistent with the results of the structural optimizations which showed both $(dmgH)_2$ and $dmg/dmgH_2$ arrangements to be isoenergetic. Note that the difference between both situations is in the position of the $O_4\cdots H\cdots O_3$ proton. Therefore, *the bridging proton of the* $O_4\cdots H\cdots O_3$ *unit (Figure 2b) can be considered as equally shared among both oxygen atoms, and described as a low-energy-barrier hydrogen bond.*

These results have important implications for the assignment of a protonation state to the dimethylglyoxime ligands of the B_{12} mimetic $Co(CCl{=}CHCl)(dmgH)_2(py)$. First of all, one of the bridging protons can be associated essentially with one or the other of the oxime oxygens, while a second proton cannot be assigned to merely one oxygen. Together with the structural results, which showed the existence of several minima very close in energy, this explains why it is not possible to identify the protonation state of the dimethylglyoxime ligands unambiguously. Even at 173 K, one of the bridging protons is delocalized among both oxime oxygens. The crystal structure actually reflects the behavior of the system, for it is an average among all possible structural conformations.

4. Conclusions

In this work we have investigated the protonation state of the dimethylglyoxime ligands in the B_{12} coenzyme biomimetic $[Co(CCl{=}CHCl)(dmgH)_2(py)]\cdot CHCl_3$ by means of first-principles molecular dynamics (Car−Parrinello approach). Our calculations show that the N−O distances depend on the protonation state of the dimethylglyoxime ligands, which in this case is largely determined by the orientation of the solvent molecules. Even though the dimethylglyoxime ligands act preferentially as monoanionic, small changes in the weak C−H···O intermolecular interactions between the solvent and the oxime oxygen atoms are enough to change their anionic character. In addition, molecular dynamics simulations at 173 and 300 K show that one of the bridging OH···O protons can be essentially associated to one oxime oxygen, while the proton of the second dimethylglyoxime ligand is essentially shared between the two oxygens. This explains the absence of a clear signature of the protonation state of the dimethylglyoxime ligands in the structural determination.

The results presented here show that small changes in the directionality of weak intermolecular interactions can contribute to the delocalization of the oxime protons. This is at variance with the common assumption that only strong hydrogen bonds can stabilize the $dmg/dmgH_2$ configuration, as happens in $Co(NO_2)_2(dmg)(dmgH_2)$,[15] $Co(NO_2)(H_2O)(dmg)(dmgH_2)$,[4b] or Co(methyl 5-deoxy-β-D-ribofuranos-5-yl)(dmg)($dmgH_2$)(py).[16,17] This aspect should be taken into account in the synthesis of cobaloxime biomimetics with the desired dimethylglyoxime arrangement. Additional calculations in other cobaloxime biomimetics with different ionization states for the dimethylglyoxime ligands are in progress. Preliminary results evidence a very similar dependence of the N−O distances on the protonation state of the dimethylglyoxime ligands with respect to what we found for $[Co(CCl{=}CHCl)(dmgH)_2(py)]\cdot CHCl_3$.[18]

Finally, we have shown that first-principles molecular dynamics can be a useful tool to complement experimental studies of cobaloxime biomimetics.

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(17) $\pi-\pi$ interactions of the R ligand with the dimethylglyoxime have also been invoked as responsible for the $dmg/dmgH_2$ configuration. This aspect, which has no relevance for the compound investigated here, will be addressed in a forthcoming publication.

(18) For instance, in the case of $Co(NO_2)(H_2O)(dmg)(dmgH_2)$ (**4b**) the N−O distances associated with the dianionic ligand (dmg^{2-}) are 0.06 Å shorter than those associated with the neutral ligand ($dmgH_2$). In the case of $Co(py)(H_2O)(dmgH)_2$ (Randaccio, L.; Zangrando, E. *Cryst. Struct. Comm.* **1974**, *3*, 565) the N−O distances corresponding to unprotonated oxygen are 0.04 Å shorter than those for protonated oxygen. Neither of these examples contain solvent molecules in the crystal.