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Why Nickel(II) Binds CO Best in Trigonal Bipyramidal and Square Pyramidal Geometries and Possible Consequences for CO Dehydrogenase

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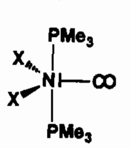
Although Ni(0) forms a very large number of carbonyl complexes, examples involving nickel(II) are extremely rare. As a "hard" metal, Ni(II) does not readily engage in back-donation, so π-acceptor complexes of any type are rare. Recently it has become likely[1] that the Ni present in certain enzymes can act as a binding site for soft ligands, such as H_2 in hydrogenases and CO in CO dehydrogenases (CODH). There are two Ni-containing clusters in *Clostridium thermoaceticum* CODH, cluster C, responsible for CO oxidation and cluster A, associated with acetyl CoA synthesis.[2] There is good evidence[3a] that CO binds to Fe, not Ni, in cluster A, but the binding site in cluster C has not been identified. The Ni-containing CODH from *Rhodospirillum rubrum* has only CO oxidation activity, and the fully oxidized form,[3b] where Ni(II) may be present, reacts with CO. Although there is as yet no crystal structure for any Ni enzyme, an EXAFS study suggests that the coordination sphere around the relevant Ni center in CODH is sulfur rich.[4] We have searched the literature for examples of Ni(II) carbonyl complexes to try to understand how the normally weak π-donor metal, Ni(II), can bind CO. In this paper we look at the geometrical and electronic factors that favor CO binding in an attempt to understand the known examples and see if any general conclusions can be drawn about the probable Ni geometry if Ni binds CO in the enzyme.

Results and Discussion

A search of the Cambridge Crystallographic Database shows a particularly interesting series of Ni(II) carbonyl complexes, made by Dartiguenave et al.,[5] is stable enough for crystal structures to have been obtained. In the absence of more relevant structurally characterized models, we have studied the complexes of type **1**, where L is PMe_3 and X is Cl or I, which are formed via eq 1.Even



1

$$\mathrm{NiX_2(PMe_3)_2 + CO \rightleftharpoons NiX_2(PMe_3)_2(CO)} \qquad (1)$$

though the nonbiological P, Cl ligand set differs from the N-(O-), S-donor set currently suggested for the relevant Ni in CODH from EXAFS study,[4] chloride and thiolate sulfur are both significant π-donors. The theoretical study is greatly helped by the existence of a crystal structure, and this is why we have not attempted to change the ligand set to a more biologically relevant one. The complexes are relatively stable in solution under CO but lose CO to give $[NiX_2(PMe_3)_2]$ under the influence of an inert gas flow which removes the dissociated CO. The CO stretching frequencies of 2015 cm^{-1} (X = I) and 2005 cm^{-1} (X = Cl) are lowered relative to free CO (2149 cm^{-1}) and the Ni–CO distances are short (1.728(23) Å [X = I], 1.730(2) Å [X = Cl]), suggesting that back-donation is significant. ν(CO) of the CO-bound form of CODH is 1995 cm^{-1},[6] close to the values in $[Ni(CO)X_2(PMe_3)_2]$.

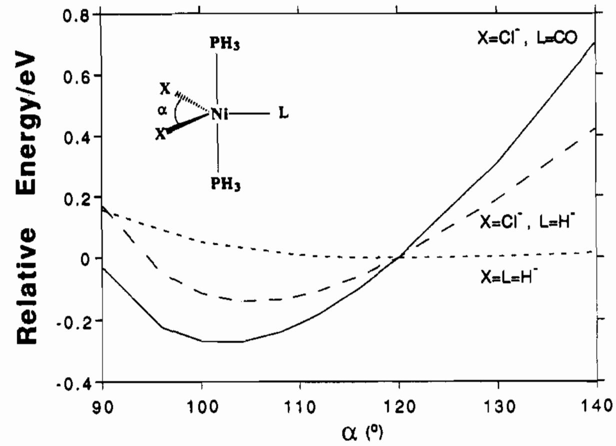


Figure 1. Relative energies of the $[NiX_2(PH_3)_2L]$ system with different X–Ni–X angles.

A few other Ni(II) carbonyl complexes are known,[7] such as $[NiI_2(CO)(fdma)]$[7a] (fdma = 1,1′-(dimethylarsino)ferrocene) and the TBP $[Ni(SiCl_3)_2(CO)_3]$,[7b] where the equatorial CO groups can be displaced by benzene to give $[Ni(SiCl_3)_2(\eta^6\text{-}C_6H_6)]$. A number of cyclopentadienylnickel(II) carbonyl complexes are also known which can also be considered as five-coordinate if Cp is regarded as a tridentate ligand.[7c,d] These complexes have ligands which are even further removed from the biologically relevant ones, and so we have not studied them in detail.

We were interested to find out what special features of **1** allow the formation of a relatively stable series of carbonyls in this case. A striking feature of the structure of $[NiCl_2(PMe_3)_2(CO)]$ (**1**) is that the bond angles in the equatorial plane depart significantly from the ideal angle of 120° normally adopted by a d^8 trigonal bipyramidal (TBP) species. The X–Ni–X angle in **1** is only 107.30(2)°, and the X–Ni–CO angles are 126.33(1)°.

In order to look at the effect of closing the X–Ni–X angle in $[NiX_2(PH_3)_2L]$ on the ability of the metal to back-bond to L (=CO) we have carried out an extended Hückel (EH) study[8a–c] on this system with X = H or Cl and L = H or CO. Figure 1 shows the energy of the system as a function of the X–Ni–X angle. Although the energy profile is relatively flat for X = H

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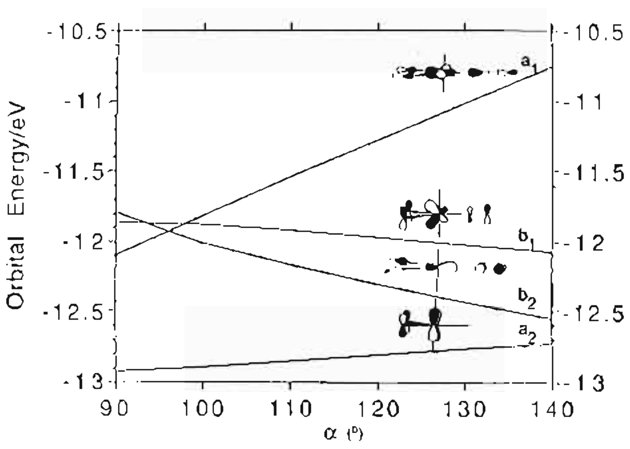
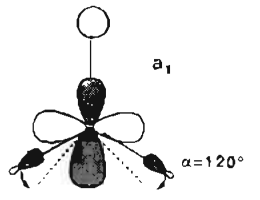


Figure 2. Walsh diagram for $[NiX_2(PH_3)_2L]$.

due to the opposing effects[8d] of the x^2-y^2 and xy orbitals, the optimum X–Ni–X angle (α) is indeed 120°, as expected for a d^8 trigonal bipyramid with three identical ligands in the equatorial plane. Replacing the X groups by Cl leads to a more marked minimum and a decrease in the optimum X–Ni–X angle to 105°. Replacing the H with CO as the L ligand leads to an even sharper minimum and a further angular decrease to 103°, close to the experimental angle of 107° for **1**.

The origin of the preferred geometry of **1** is illustrated in the Walsh diagram (Figure 2). The higher-lying a_1 orbital is significantly stabilized on closing the Cl–Ni–Cl angle because of decreasing interaction with the σ-lone pair on Cl (**2**).[8d] The other b_1 and b_2 orbitals behave in the opposite way because of increasing overlap with the π out-of-plane lone pairs on Cl for b_1 (**3**) and with the σ-lone pair in the case of b_2 (**4**).



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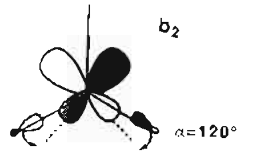

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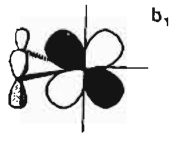

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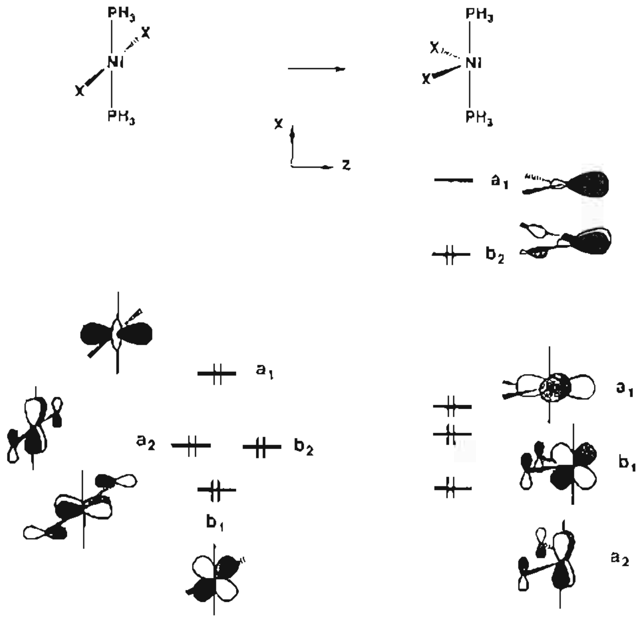
What favors CO binding in this Ni(II) species? To look at this problem, we start with a square planar *trans*-$[NiX_2L_2]$ fragment and study its distortion toward a bent C_{2v} fragment, the symmetry labels of which will be used in the discussion. As shown in diagram **5**, the lower b_1 orbital is fully nonbonding. The a_2 and b_2 orbitals are destabilized in a π manner by the Cl lone pairs. The higher a_1 is weakly antibonding with the four ligands. Upon bending, the X–Ni–X angle decreases from 180°, causing the b_2 orbital to be strongly destabilized and hybridized away from the two X ligands.[9] The a_2 is weakly stabilized and the b_1 destabilized due the change in the overlap with the Cl lone pairs. The most significant change is found in the destabilization of the b_2 orbital. This orbital, which is the HOMO of the fragment, is thus a powerful π-donor to a CO coordinated at the vacant site. Additional back-donation is also provided by the b_1 orbital. We have therefore been able to convert Ni(II), usually a weak π-donor, into a strong π-donor. The monotonic increase in the Ni–CO bond order (as measured by the Mulliken overlap population) as α decreases from 140° to 90° confirms that X–Ni–X bending favors Ni–CO bonding.



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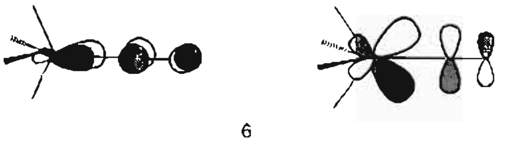
The CO ligand need not necessarily be equatorial. One structurally characterized complex, $[NiI_2(CO)(fdma)]$, although TBP, has CO apical. This is presumably because the chelating diarsine fdma has to occupy one of the equatorial sites. We are not aware of any structure where halide is apical, and we assume that CO is axial because the two I ligands have a strong preference for the equatorial site. The ν(CO) value obtained in this case, 2054 cm^{-1}, shows that the CO is significantly less well bound than in **1**, where it was equatorial. Rossi and Hoffmann[10] have shown that if σ-effects alone are considered, strong σ-donors, such as AsR_3 and CO, tend to avoid the equatorial positions in order not to destabilize the equivalent of the a_1 and b_2 orbitals. However, π-acceptors have a preference for the equatorial site. The resulting structure is therefore a compromise between opposing σ- and π-effects for all the ligands present. The reason that CO can still bind to Ni(II) in this instance is due to the availability of b_1 and a_2 as π-donor orbitals.

The square pyramidal geometry is often very close in energy to that of the TBP. Five-coordinate geometries intermediate between the TBP and square pyramid are also known. In a pure square pyramid, if the CO is apical and the four basal ligands are strongly bent away from the apical site, the metal has two destabilized d_π-orbitals[9] capable of back-bonding into the two empty π^*-orbitals of CO (**6**), so this is also a favorable situation, although one not yet realized experimentally. In other words, the binding of a π-acceptor like CO is encouraged by the formation of pentacoordinated species, either TBP or square pyramidal.



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Other Possible Geometries. Since the details of the structure in the enzyme are unknown, a brief comment on other possible geometries for Ni(II) is appropriate. In the case of low-spin Ni(II) species, the 4-coordinate square planar geometry is also known. To our knowledge, no example of CO bonded to Ni(II)

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in a square planar geometry has been characterized. The square planar geometry has been suggested[11] for one series of Ni(II) carbonyls, but no structurally verified example has been found. It is likely that average d-orbital energies in 16e species are at lower energy than in an 18e complex, because fewer ligands are donating to the metal in the 4-coordinate case. Furthermore in the square planar case, the σ-nonbonding $M(d_\pi)$ orbitals (a_2, b_2, b_1) are low in energy. This associated with the relatively poor metal center results in them being inefficient π-donor orbitals.

In the high-spin series, both octahedral and tetrahedral geometries are known. In a d^8 octahedron the M–L σ^* e_g orbitals are singly occupied and significantly weaken the M–L σ-bonds. In addition, the potentially back-bonding d_π orbitals are σ nonbonding and so weakly donating toward one of the π-acceptor ligands in the coordination sphere. In the tetrahedron, the two lower-lying orbitals are also σ nonbonding and the higher-lying ones are not fully doubly occupied. These species are therefore less able to engage in strong back-bonding and seem less likely.

Influence of the Ligand on Metal π-Donor Ability. It therefore appears that the ligand set in **1**, notably the π-donor chloride, makes Ni(II), normally a poorly π-back-bonding ion, into a much better π-base, reminiscent of Ni(0). The same principle applies to the other Ni(II) carbonyls. An even more striking example of the same type is $Ni(SiCl_3)_2(CO)_3$, where the silyl groups are σ- but not π-donors. In this case as many as three CO ligands are able to bind in the equatorial plane; only Ni(0) would be expected to bind three terminal CO groups. As we previously discussed,[12] the SiR_3 group is exceptionally strongly σ-donating and thus is one of the most effective promoters of metal π-donor ability. We therefore consider all of these systems as examples of "hidden" Ni(0) since they are formally Ni(II), but owing to the strongly σ- or π-electron-donating nature of the ligands, they behave like Ni(0), for example, in binding CO. Other biologically relevant electron donor ligands such as thiolate should have a similar effect.

Relation with CODH. CO dehydrogenase from *C. thermoaceticum* contains[3a] three clusters (A, B, and C). Cluster A, containing Ni and Fe, is involved in acetyl CoA synthesis, and cluster C, also containing Ni and Fe, is involved in CO oxidation. Both need to bind CO at some stage of the catalytic cycles, but Fe, not Ni, is believed to be the CO-binding site in cluster A. The binding site in cluster C is unknown. Our work suggests that if CO binding by Ni(II) is important, the most favorable geometries are TBP with CO probably equatorial or square pyramidal with CO axial. The Ni in the CO oxidation site may bind CO during the catalytic cycles but not in any isolable state.

If Ni(I) should prove to be a better description of the Ni in cluster C, the geometric requirements are not so strict, because Ni(I) is intrinsically a better π-back-bonding ion; it therefore might or might not assume a TBP or distorted tetrahedral geometry. Holm[13a] has studied a CODH model compound for the CoA synthesis site that forms a TBP Ni(I) carbonyl with CO axial, and Mascharak[13b] also has a similar complex. The chemistry of the CO oxidation site has been successfully modeled[14] with a dimeric Ni(II) species, which mediates CO oxidation and must therefore bind CO, although no Ni(II) CO complex can be isolated in this case.

Conclusion

We suggest that the binding properties of Ni(II) can be significantly modified by a judicious choice of ligand set and coordination geometry. In particular, the presence of strongly donor ligands enhances the ability of the metal to bind CO. If CO binds to Ni during the catalytic cycles in CODH, some of these principles may help facilitate the CO binding.

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