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Bonding Forces in Short Hydrogen Bonds. Crystal Structure of $Pd^{II}(dpgH)_2$

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An analysis of the structures of 16 square-planar metal(II)−diglyoxime compounds was undertaken to determine the bonding forces which might alter the O···O distance observed for strong, low-barrier hydrogen bonds. This series of structures includes the X-ray diffraction structure of $Pd^{II}(dpgH)_2$ (dpg = diphenylglyoxime), with data collected at 158 K. This compound crystallizes in the space group *Ibam* with $a = 15.324(2)$ Å, $b = 22.634(3)$ Å, $c = 6.8811(7)$ Å, $V = 2386.6(5)$ Å^3, $Z = 4$, and $R = 4.89\%$ for the 1105 reflections with $|F_o| > 4\sigma(F)$ and 7.91% for all 1490 reflections. The observed Pd−N bond distances are 1.958(6) and 1.959(6) Å. The distance between the two oxygen atoms that participate in the short hydrogen bond is 2.550(10) Å; this distance is the shortest thus far reported for a palladium−diglyoxime compound. The hydrogen atom appears to be nearly centered, with refined O−H distances of 1.32(22) and 1.39(23) Å in the O··H··O system; this interpretation of the hydrogen position is supported by nearly equivalent N−O distances in the strong-hydrogen-bond-containing moiety. Additionally, a search of the Cambridge Structure Database yielded 15 examples of square-planar metal−diglyoxime compounds of Ni(II), Pd(II), or Pt(II). Analysis of bonding forces in this series of compounds indicates that reduction of electron−electron repulsion between the oxygen atoms, either by delocalization of charge or by electron-withdrawing substituent groups, allows a closer approach of the oxygen atoms and a shorter hydrogen bond.

Introduction

Strong hydrogen bonds are an intrinsically interesting bonding system and have been studied for many years by researchers interested in covalent bonding theory.[1−4] Unfortunately, many aspects of hydrogen bonds, particularly what factors cause hydrogen bonds to become shorter, remain poorly understood.[5] Recent implication of strong hydrogen bonds as intermediates in enzymatic catalysis[6−9] gives renewed importance to the search for the chemical forces that allow strong, short hydrogen bonds to exist. A recent review[10] and systematic database studies[5,11,12] underscore the ongoing work in this area.

Palladium(II) diphenylglyoximate ($Pd(dpgH)_2$) is one of a series of metal(II)−diglyoxime compounds that provide an excellent opportunity for a systematic study of short intramolecular hydrogen bonds. Because the steric factors in these compounds should be approximately equal, changes in the intramolecular hydrogen bond can be studied as a function of the electronic effects of the glyoxime substituent groups. The Hammett parameters[13] provide a convenient method of quantifying these electronic effects. Five Pd(II)−diglyoxime structures have been previously reported,[14−18] with various substituents. These compounds are four-coordinate, d^8 compounds with square-planar geometry about the palladium atom. The distances between the oxygen atoms of the O··H··O intramolecular hydrogen bond in these compounds range from 2.583 to 2.749 Å. In addition to the palladium compounds, there are six previously reported Ni(II)−diglyoxime structures[19−24] and four Pt(II)−diglyoxime structures[25−28] that share both the square-planar geometry and the short intramolecular hydrogen bonds. The analysis of these data, along with that provided by the structure of $Pd(dpgH)_2$, should provide new insights into the chemical forces responsible for the variation of hydrogen bond length.

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Experimental Section

Synthesis. A 1.98 g sample of diphenylglyoxime (8.25 mmol) was refluxed with 0.72 g of $PdCl_2$ (4.06 mmol) and 0.248 g of NaOH in an ethanol solution for 12 h. The resulting red microcrystals were then purified by recrystallization from acetone. The product of this recrystallization was acidified to pH = 2.0 with HNO_3 in a 50:50 solution of ethanol and water. The product was filtered off and characterized by IR spectroscopy in Nujol (Perkin-Elmer Paragon 1000 FTIR) and by NMR spectroscopy (Varian Gemini, operating at 300 MHz for ^1H; 295 K). A small portion of the product was further refluxed in acetone-d_6 to deuterate the intramolecular hydrogen bond. This product ($Pd(dpgD)_2$) was also characterized by IR spectroscopy. Crystals suitable for X-ray diffraction were grown from slow (~2 months) evaporation of a benzene solution.

Crystallographic Study. An orange crystal of approximate dimensions 0.06 × 0.07 × 0.23 mm was mounted on a glass fiber and transferred to a Siemens P4 rotating-anode diffractometer. The determinations of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out according to standard procedures.[29] Intensity data were collected at 158 K using a $\omega-2\theta$ scan technique with Mo Kα radiation. The raw data were processed with a local version of CARESS,[30] which employs a modified version of the Lehman−Larsen algorithm to obtain intensities and standard deviations from the measured 96-step peak profiles. All 2033 data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was *mmm*.

The crystal belongs to the orthorhombic space group *Ibam* (D_{2h}^{26}; No. 72), with $Z = 4$. This space group was chosen over the noncentrosymmetric space group *Ima*2 by virtue of successful refinement in the centrosymmetric alternative. A total of 2033 data were collected at 158 K in space group *Ibam* and were averaged ($R_{int} = 3.55\%$) to provide 1490 independent and space-group-allowed data.

All crystallographic calculations were performed by using the SHELX 86 and SHELX 93 program sets.[31] The analytical scattering factors for neutral atoms were corrected for both the $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion.[32] The structure was solved by a Patterson map, with the palladium atom occupying the special position 0, 0, 0 (2/*m*, Wyckoff position *c*). All the atoms of the glyoxime backbone were also contained in the mirror plane at $z = 0$. However, those atoms of the phenyl rings (C11, C14, C21, and C24) that should be contained in a true crystallographic mirror plane were found slightly but unmistakably off the plane, a clear indication that the mirror plane at $z = 0$ was actually pseudosymmetric. Due to the lack of lower symmetry alternatives to *Ibam*, it was decided to refine all carbon atoms of the phenyl rings in general positions at half-occupancy, as if there were two disordered positions of the moieties. This led smoothly to convergence, although the *ipso*-carbon atoms of the phenyl rings (C11 and C21) had to be refined isotropically to avoid coalescence with their pseudosymmetric images. All other non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in calculated positions with $d(C-H) = 0.96$ Å,[33] with positional and thermal parameters riding on the adjacent carbon atoms. A total of 143 parameters were refined against all 1490 independent reflections. Refinement converged with $R_{w2} = 13.6\%$ and $R = 7.90\%$ for all data ($R = 4.88\%$ for those 1105 data with $|F_o| > 4\sigma(|F_o|)$). Details of data collection and refinement are provided in Table 1, and selected interatomic distances and angles are collected in Table 2.

Database Search. Crystallographic data were retrieved for the Cambridge Structure Database (CSD)[34] on the basis of a search for structures containing a group 10, 2+ metal ion coordinated to two bidentate glyoxime ligands in square-planar geometry. Any structures where the gyloxime backbone was a part of a ring system (other than the chelate ring) were rejected. Multiple structural determinations of the same compound were analyzed for precision and freedom from close intermolecular contacts; only those structures deemed most reliable were retained. A total of 15 unique structures were identified, 6 for Ni(II), 5 for Pd(II), and 4 for Pt(II). The information from this CSD search is compiled in Table 3.

Table 1. Crystallographic Data for $Pd((dpgH)_2$

space group	*Ibam*
a, Å	15.324(2)
b, Å	22.634(3)
c, Å	6.8811(7)
V, Å^3	2386.6(5)
Z	4
T, K	158
2θ limit, deg	$4 < 2\theta < 55$
no. of rflns collcd	2033
no. of indep rflns	1490
no. of rflns with $F > 4.0\sigma(F)$	1105
hydrogen atoms	riding model, riding isotropic *U*
weighting scheme	$w^{-1} = \sigma^2(F_o^2) + 0.0000P^2 + 47.2301P$ where $P = (F_o^2 + 2F_c^2)/3$
no. of params refined	143
R_{w2} (all data, F^2), %	13.6
R indices (all data, *F*), %	7.90
R indices ($F > 4.0\sigma(F)$), %	4.88
data-to-param ratio	10.3:1
$\Delta(\rho)$, e Å^{-3}	+0.87, −0.86

[a] $R_{w2} = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$, $R = \sum||F_o| - |F_c||/\sum|F_o|$.

Table 2. Selected Bond Distances and Angles for $Pd(dpgH)_2$

Bond Distances (Å)			
Pd1−N1	1.958(6)	Pd1−N2	1.959(6)
N1−O1	1.349(9)	N2−O2	1.348(10)
N1−C1	1.299(10)	N2−C2	1.302(12)
O1−H2	1.39(23)	C1−C2	1.467(11)
O2−H2	1.32(22)	C1−C11	1.507(11)
O1···O2	2.550(10)	C2−C21	1.510(12)
Pd1···Pd1A	3.441(1)		
Bond Angles (deg)			
N1−Pd1−N2	79.2(3)	N1−Pd1−N1a	100.8(3)
Pd1−N1−O1	119.5(5)	Pd1−N2−O2	119.6(6)
Pd1−N1−C1	117.3(5)	Pd1−N2−C2	116.9(6)
O1−N1−C1	123.2(7)	O2−N2−C2	123.5(7)
N1−C1−C2	113.1(7)	N2−C2−C1	113.5(7)
N1−C1−C11	122.7(7)	N2−C2−C21	121.8(7)
N2−O2··H2	120(9)	O1··H2··O2	141(9)

Discussion

Spectroscopic Data. The Nujol IR spectrum of $Pd(dpgH)_2$ is characterized by a broad, intense band at 1660 cm^{-1}, two sharp, medium-intensity bands at 1300 and 890 cm^{-1}, a broad, double-peaked, medium-intensity band centered at 1120 cm^{-1}, and two sharp, intense bands at 740 and 690 cm^{-1}. Several of these bands can be assigned unambiguously.[35] The broad band at 1660 cm^{-1} results from the O−H stretch (ν_{OH}). The ν_{OH} modes of strong hydrogen bonds are typically broad, intense bands in this region, and this band disappears in the IR spectrum of $Pd(dpgD)_2$. The double-peaked band centered at 1120 cm^{-1} is generated by the N−O stretches; the nearly equivalent N−O distances observed in $Pd(dpgH)_2$ cause these bands to nearly coalesce.

The ^1H NMR in $CDCl_3$ at room temperature showed only a rough doublet, attributable to the phenyl protons, at 7.3 ppm. This was probably due to exchange between the proton in the intramolecular hydrogen bond and the deuterium from the $CDCl_3$ solvent. The sample was re-examined using CCl_4 as a

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Table 3. Collected Data for Metal(II)−Diglyoxime Compounds

metal	substituent	R(O···O), Å	Hammett σ_p	sum of N−O bond valences	$\delta(O_{avg})$	$\delta(O_{avg})^2$	ref	CSD refcode
Ni	NH_2	2.532(4)	−0.66	1.87	−0.57	0.319	22	OXONFM
Ni	NH_2 and Me	2.511(6)		1.96	−0.52	0.270	19	DEFJUT
Ni	Me	2.462(na)	−0.17	1.99	−0.51	0.255	21	NIMGLO03
Ni	Me and Et	2.454(5)		2.02	−0.49	0.240	23	NIMGEL01
Ni	H	2.454(6)	0.00	2.04	−0.48	0.230	24	NIGLOX10
Ni	NEt_2	2.437(10)		2.03	−0.49	0.235	20	BOKWED10
Pd	NH_2	2.749(11)	−0.66	1.86	−0.57	0.325	16	BETWEC
Pd	Me	2.623(4)	−0.17	2.07[a]	−0.47[a]	0.216[a]	17	PDMGLO02
Pd	α-furyl	2.583(4)	0.02	1.97	−0.52	0.265	15	CIWDIV10
Pd	H	2.582(12)	0.00	1.97	−0.52	0.265	18	GLOXPD
Pd	$C_{10}H_{20}NO_4$	2.569(6)		1.95	−0.53	0.275	14	VEHXEL
Pd	Ph	2.550(10)	−0.01	2.01	−0.50	0.245	this study	
Pt	NH_2	2.950(12)	−0.66	1.74	−0.63	0.397	27	OXAPTC
Pt	H	2.65(2)	0.00	2.04	−0.48	0.230	28	GLYOPT
Pt	Me	2.641(19)	−0.17	2.01	−0.50	0.245	25	PTMGLO02
Pt	Cl	2.56(5)	0.23	2.22	−0.39	0.152	26	BOHWOK

[a] Values believed to be anomalous.

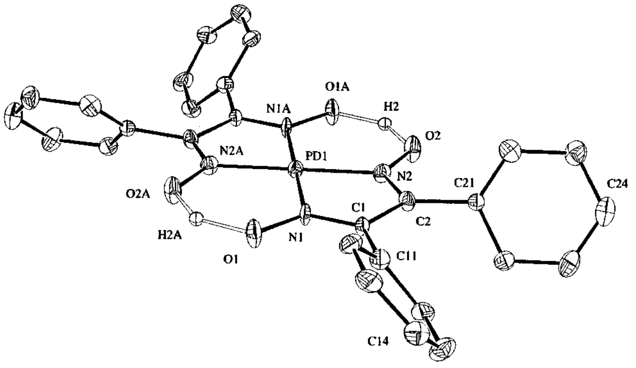

Figure 1. ORTEP diagram of the $Pd(dpgH)_2$ molecule (50% probability ellipsoids).

solvent. This resulted in a rough doublet at 7.3 ppm and a smaller singlet at 12.3 ppm. A singlet above 10 ppm is typical of intermediately strong hydrogen bonds.[7,10] The sensitivity of the solution NMR measurements was limited due to the poor solubility of $Pd(dpgH)_2$ in all standard NMR solvents.

Crystal Structure of $Pd(dpgH)_2$. The crystal consists of discrete molecular units of $Pd(dpgH)_2$ with no unusually close intermolecular contacts; the distance between palladium atoms in adjacent molecules is 3.441(1) Å. A diagram of the $Pd(dpgH)_2$ molecule, with its numbering scheme, is given in Figure 1. The geometry about the palladium atom is square planar, with the two glyoxime moieties providing two nitrogen atoms each for coordination. The palladium atom lies precisely in the plane defined by the four coordinating nitrogen atoms; this plane is the mirror plane at $z = 0$; a 2-fold crystallographic axis relates the two glyoxime moieties. The observed Pd−N distances are 1.958(6) and 1.959(6) Å, and the N−Pd−N angle contained in the chelate ring is 100.8(3)°. These values are similar to previously reported distances and angles for other palladium−diglyoxime compounds.[14−18] The distances in the glyoxime backbone are as follows: O1−N1 = 1.349(9) Å, N1−C1 = 1.299(10) Å, C1−C2 = 1.467(11) Å, C2−N2 = 1.302(12) Å, and N2−O2 = 1.348(10) Å. It can be seen that, for all cases, distances between analogous atoms are insignificantly different. Concerning the short hydrogen bond, the O−H distances were H2−O1 = 1.39(23) Å and H2−O2 = 1.32(22) Å; these O−H distances are clearly equivalent within the large experimental error. The distance O1···O2 is 2.550(10) Å, and the O··H··O angle is 141(9)°. This O··H··O angle is typical of Pd and Pt diglyoxime compounds where the hydrogen position has been determined. All distances and angles involving the phenyl moieties are within accepted values.[36]

Of particular interest in the structural analysis of $Pd(dpgH)_2$ is the strong intramolecular hydrogen bond. As is well-known, the position of the hydrogen nucleus is not found by X-ray diffraction; what is measured is the maximum of the electron density, which may be called the X-ray-determined hydrogen position.[33,37] For O−H moieties involved only in weak hydrogen bonds, the difference between the actual and X-ray-determined hydrogen positions is about 0.2 Å.[3,37] However, in short hydrogen bonds, this situation is somewhat different. The bonding electron density decreases between the hydrogen atom and nearer oxygen atom, while simultaneously increasing between the hydrogen atom and farther oxygen atom. The net result tends toward a diffuse, elongated region of electron density stretching between the two oxygen atoms.[38,39] This arrangement of electron density reduces the difference between the actual and X-ray-determined positions of the hydrogen atom but also results in larger uncertainty in the apparent hydrogen position, in that no distinct maximum of electron density is encountered. The large esd's for the H-O distances (H2··O2 = 1.32(22) Å and H2··O1 = 1.39(23) Å; the isotropic displacement parameter of H2 is 0.169 Å^2) show that this may be the case for the hydrogen atom in the intramolecular hydrogen bond of $Pd(dpgH)_2$. Additionally, the hydrogen atom may have a large actual vibrational amplitude. The energy barrier between the two potential energy wells may be lower than the vibrational energy of the proton at 158 K, so that the proton can move between the two minina, even in the solid state.[40] Either interpretation is consistent with a low-barrier hydrogen bond, where the hydrogen atom is close to equidistant from the two oxygen atoms but not exactly centered. The equivalence of the two N−O distances associated with the hydrogen bond also is indicative of a nearly-centered hydrogen atom.[38,41]

Strong Hydrogen Bonding in Metal(II)−Diglyoxime Compounds. The pertinent structural data for the metal(II)−digly-

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oxime compounds of Ni, Pd, and Pt are collected in Table 3. It should be noted that the standard deviation in the esd's of the observed $R(\mathrm{O}\cdots\mathrm{O})$ distances is 0.018 Å. The Hammett parameter σ_p is an empirically derived value indicating the electronic character of the substituent groups.[13] Positive values for σ_p indicate electron-withdrawing groups, while negative values denote electron-donating character. The bond valence (s, which is analogous to the bond order) of the N−O bonds associated with the intermolecular strong hydrogen bond was calculated by using the following equation:[42]

$$s = \exp[(R_{\mathrm{NO}} - d_{\mathrm{NO}})/0.37]$$

where R_{NO} is the N−O single bond expectation distance, taken as 1.35 Å, and d_{NO} is the observed N−O bond distance. Bond valence is used, rather than raw bond distance, because it gives a clearer indication of the multiple-bond character of the N−O bonds.

Some of the chemical forces responsible for the variation in hydrogen bond strength are identifiable in these series of compounds. Parts a and b of Figure 2 show the effect of the sum of the N−O bond valences and Hammett σ_p, respectively, on $R(\mathrm{O}\cdots\mathrm{O})$ for compounds of each of the three metal centers. Figure 2a shows that increased N−O bond valence correlates with shorter $R(\mathrm{O}\cdots\mathrm{O})$; i.e., greater multiple-bond character near the hydrogen bond leads to a stronger hydrogen bond. This result is in accord with Gilli's concept of resonance-assisted hydrogen bonds.[5,12,41] (It is noted that the data for Pd(dmgH)$_2$ appear to be anomalous, at least inasmuch as the N−O bond orders are concerned. Standard deviations and R^2 for Figures 2a, 3, and 4 were calculated by omitting this data point. We intend to independently determine the structure of Pd(dmgH)$_2$ to verify the N−O bond distances.) The good internal consistency between slopes is an indication of the reproducibility of the observed correlation; the overall standard deviation from linearity for Figure 2a is 0.025 Å; this is only slightly larger than the overall uncertainty (0.018 Å) in the measurement of $R(\mathrm{O}\cdots\mathrm{O})$. Figure 2b shows a similar positive correlation between σ_p and $R(\mathrm{O}\cdots\mathrm{O})$, indicating that electron-withdrawing groups (positive σ_p) tend to shorten the hydrogen bond, while electron-donating groups result in longer $R(\mathrm{O}\cdots\mathrm{O})$. Again, the slopes show good internal consistency, and the overall standard deviation from linearity is 0.026 Å.

Both relationships shown in Figure 2 suggest an underlying physical cause for the observed effects. It is reasonable to expect that as the N−O bond order increases, the charge on the oxygen atom should decrease. Similarly, one might expect that electron-withdrawing substituents, such as chlorine, might decrease the charge on the terminal oxygen atom, and electron-donating substituents, such as $-\mathrm{NH_2}$, ought to increase this charge. Both plots, therefore, suggest that that the reduction of the partial charges on the oxygen atoms will result in a shorter $R(\mathrm{O}\cdots\mathrm{O})$.

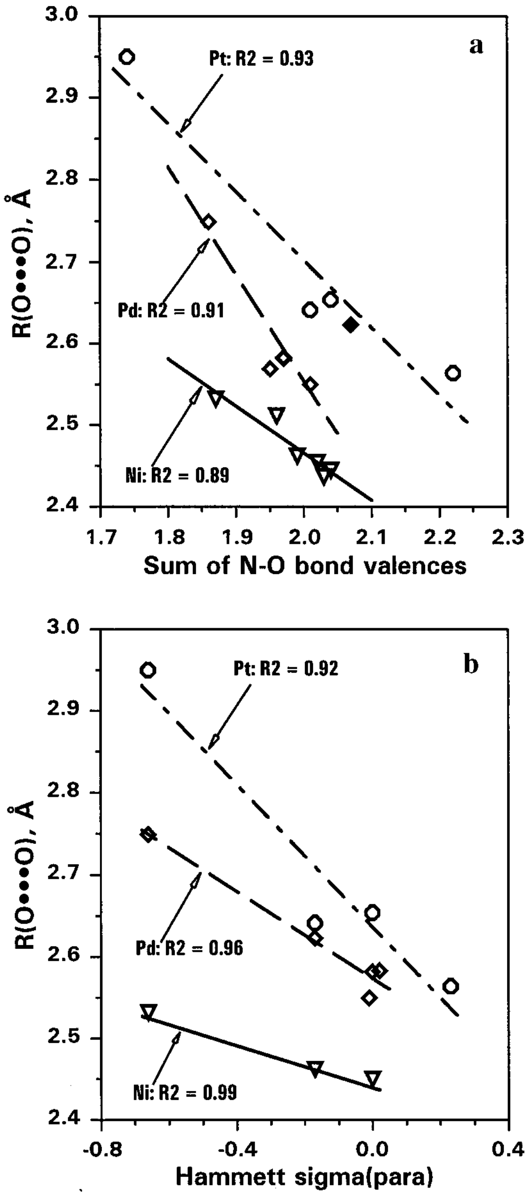

Figure 2. Plots of (a) $R(\mathrm{O}\cdots\mathrm{O})$ vs N−O bond order and (b) Hammett parameter σ_p vs N−O bond order. Nickel diglyoximes = ▽, —; palladium diglyoximes = ◇, – –; platinum diglyoximes = ○, – - –. Note that the filled diamond in Figure 2a is the data point for Pd(dmgH)$_2$ which contains apparently anomalous N−O bond lengths. The point has not been included in the calculation of standard deviations or R^2 for Figure 2a, 3, or 4.

While the correlations of N−O bond order and σ_p to $R(\mathrm{O}\cdots\mathrm{O})$ both point to the charge on the oxygen atoms as an important factor in determining hydrogen bond distance, it would naturally be preferable to directly analyze charge versus $R(\mathrm{O}\cdots\mathrm{O})$. We believe this is possible, using the bond valence model (BVM).[4] In the BVM, each oxygen atom should have a total of two units of bond valence as a sum of its contacts to the hydrogen and nitrogen atoms; any value less than 2 can be interpreted as a partial charge on the oxygen atom. The BVM conception of a O··H··O hydrogen bond has the hydrogen atom in the low-energy position in a (usually too large) cavity between the two oxygen atoms. This low-energy position allows the hydrogen atom to have a total of one unit of bond valence in the sum of the two O−H contacts. Using X-ray diffraction, it is impossible to determine the exact value of the individual O−H contacts. However, neutron diffraction evidence from other compounds shows[11,43] that there is very nearly a total of 1 unit of bond valence in the two hydrogen−oxygen contacts in any O··H··O system, regardless of the position of the hydrogen atom or $R(\mathrm{O}\cdots\mathrm{O})$. Therefore, the *average* bond valence of the two oxygen atoms can be calculated as

$$s(\mathrm{O_{avg}}) = (s_{\mathrm{N-O'}} + s_{\mathrm{N-O''}} + 1.00)/2$$

where $s_{\mathrm{N-O'}}$ and $s_{\mathrm{N-O''}}$ are the two nitrogen−oxygen bond valences. The average partial charge ($\delta(\mathrm{O_{avg}})$) on the two

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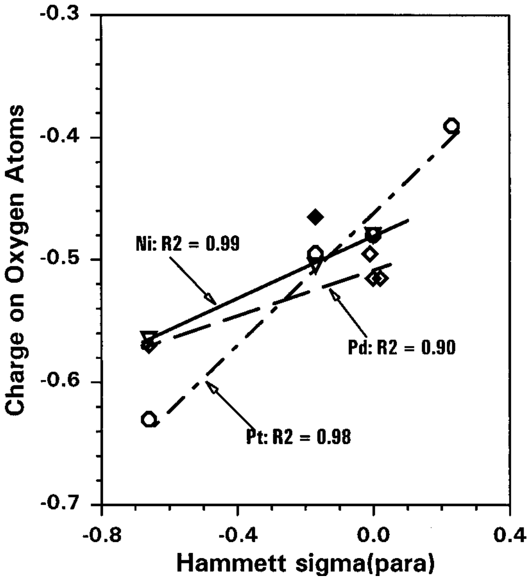

Figure 3. Plot of $\delta(O_{avg})$ vs Hammett parameter σ_p. Nickel diglyoximes = ▽, —; palladium diglyoximes = ◇, – –; platinum diglyoximes = ○, – - –. See Figure 2 for note on Pd(dmgH)2.

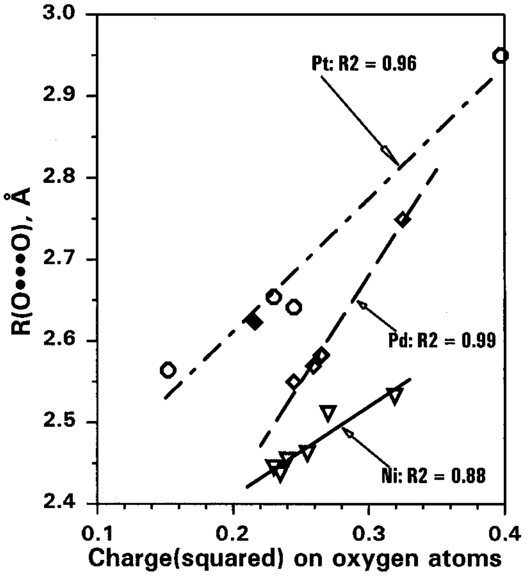

Figure 4. Plot of R(O···O) vs $\delta(O_{avg})^2$. Nickel diglyoximes = ▽, —; palladium diglyoximes = ◇, – –; platinum diglyoximes = ○, – - –. See Figure 2 for note on Pd(dmgH)2.

oxygen atoms is then simply

$$\delta(O_{avg}) = s(O_{avg}) - 2.00$$

The plot of $\delta(O_{avg})$ versus σ_p is given in Figure 3. This shows that the partial charge of the oxygen atoms, derived in the above manner, displays the expected trend in relation to the electronic properties of the substituent groups, in that electron-donating substituents increase $\delta(O_{avg})$ and electron-donating substituents have the opposite effect. The overall standard deviation from linearity for Figure 3 is 0.0095 atomic charge unit. While the absolute magnitude of these partial charges may be open to examination, the correlation of $\delta(O_{avg})$ with σ_p does appear to validate this technique for comparison of partial charges in similar compounds, such as the metal–diglyoxime compounds.

From Coulomb's law, the repulsive force between the oxygen atoms will be proportional to the product of the two partial charges; this can be approximated by $(\delta(O_{avg}))^2$. The plot of $(\delta(O_{avg}))^2$ versus R(O···O) is given in Figure 4. This figure reveals that decreasing $(\delta(O_{avg}))^2$ strongly correlates with decreased R(O···O); the standard deviation from linearity for this plot is 0.018 Å, showing an improved linear fit over Figure 2a,b. Brown has suggested that, if steric factors are essentially equal, R(O···O) will be a function of the repulsion between the two oxygen atoms.[44,45] As mentioned previously, in the BVM, the hydrogen atom is considered to take the low-energy position between the two oxygen atoms in the O··H··O system. The attractive bonding forces of the two O··H contacts sum to 1 valence unit, and there is no net energetic advantage to short hydrogen bonds over longer hydrogen bonds. Since the attractive forces across the O··H··O system remain essentially constant, R(O···O) is determined primarily by electron–electron repulsion and steric factors. It has been shown previously that steric forces alone can cause considerable shortening of R(O···O).[38] If steric factors are held constant, as in each series of metal–diglyoxime compounds, electron–electron repulsion should largely determine R(O···O). Of course, other factors, such as the O··H··O angle[44] or crystal packing forces, may exert some influence on R(O···O), but the data presented in Figure 4 show that, in the absence of steric variation, electron–electron repulsion between the oxygen atoms will be the *primary* force determining R(O···O). Therefore, the results presented herein are fully in agreement with the BVM conception of the hydrogen bond and help extend it from its original context to discrete molecular systems. These results also provide a physical basis for Gilli's observation of delocalized multiple-bond character in the region of strong hydrogen bonds,[5,12,41] in that delocalization will reduce the charge concentration on the oxygen atoms in the O··H··O system.

Concluding Remarks

It appears clear, from these results and the previous work of Brown and Gilli, that short, low-barrier hydrogen bonds can only form when the acid and base atoms involved in the hydrogen bond are able to approach each other more closely than normal, either forced together sterically or having lower-than-normal partial negative charges on the non-hydrogen atoms. The results of this study indicate that electron-withdrawing substituents produce shorter hydrogen bonds in sterically equivalent compounds and that these shorter hydrogen bonds are the product of reduced electron–electron repulsion between the oxygen atoms of the O··H··O moiety. While the full impact of these conclusions on the present debate concerning low-barrier hydrogen bonds in enzymatic catalysis is unclear,[6–9,46–49] this finding should provide a more informed framework from which to conduct the discussion.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure of Pd(dpgH)2 is available on the Internet only. Access information is given on any current masthead page.

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