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Hydrogen Bonding to Metals

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The Hydrogen Bond, Front and Center**

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The hydrogen bond has for some years been "edging in" toward the geometric center of transition-metal complexes. This largely noncovalent interaction has long been observed at the periphery of transition-metal complexes, and more recently has been studied closer in, where the presence of a metal atom influences the donor or acceptor properties of one of the direct H-bond participants. Even more intimate interactions have been reported in which C–H or N–H bonds, commonly at the peripheries of metal-bound ligands, donate a hydrogen atom to a nominally empty coordination site of a transition metal. Now Kozelka et al.[1] report the preparation of a molecular solid in which a molecule of water acts as a hydrogen-bond donor to an axial coordination site of a square-planar platinum center. There is no room for doubt about the location of all of the atoms involved, including hydrogen: For the first time, the accuracy and fidelity of a high-resolution single-crystal neutron-diffraction analysis has captured water interacting through one of its hydrogen atoms—its electropositive frontside—with a transition metal.

The concept of hydrogen bonding was proposed far from the realm of coordination chemistry. Some time before they were named, hydrogen bonds drew the attention of experimentalists and theorists. In the context of a study on oxyacids, ionization, and solvent polarity, it was noted that "*a free pair of electrons on one water molecule might be able to exert sufficient force on a hydrogen held by a pair of electrons on another water molecule to bind the two molecules together… Such an explanation amounts to saying that the hydrogen nucleus held between 2 octets constitutes a weak 'bond'*."[2]

The involvement of electronegative heteroatoms—N, O—in biological molecules suggested that hydrogen bonding should play an important role in establishing macromolecular conformation. It is not surprising in retrospect that one of the early landmark discoveries in which hydrogen bonding was implicated was the prediction of protein secondary structure on the basis of covalently rigid, conformationally flexible amino acid building blocks held into secondary structures—helices and sheets—by hydrogen bonding. It was here that Pauling et al. placed the hydrogen bond in its biological thermodynamic context: "*The energy of an N–H···O=C hydrogen bond is of the order of 8 kcal mol^{-1}, and such great instability would result from the failure to form these bonds that we may be confident of their presence.*"[3] Just a few years later the essential role of the hydrogen bond in DNA structure became clear.

Decades afterward, and with hundreds of thousands of crystal structures established, the evident structural importance of the "classical" hydrogen bonds, largely involving N and O donors and acceptors, accredited the concept that these interactions could be used in designing molecular solids with specific structural and even physical properties. This "crystal engineering" has its own rubric, based largely on graph sets, which has served as an aid in systematizing the known hydrogen-bonded constructs. Motivated by such developments and by improvements in X-ray diffraction techniques, many researchers today dedicate much effort to characterizing molecular solids with hydrogen-bonded superstructures, supplying the readers of crystal structure journals with detailed descriptions of molecular aggregation patterns mediated by both the classical interactions and the more recent additions to the natural toolkit—hydrogen bonds with C–H donors or π-cloud acceptors.

Apart from the acquisition of vast quantities of new data regarding structures containing hydrogen bonds, there is still an ongoing effort—no less important albeit significantly less extensive—to achieve a new understanding of hydrogen bonding itself. Some of that effort has involved transition metals as possible hydrogen-bond acceptors.[4]

A thermodynamic imperative such as that described by Pauling et al. is not the argument for hydrogen bonding at the center of transition-metal complexes. Nor is it clear that these hydrogen bonds will ever be considered as structure-directing elements for extended supramolecular arrays. The role of such interactions in chemical processes has not yet been as clearly established as the role that the hydrogen bond fulfills in the structures and dynamics of living chemistry. Hydrogen bonds with transition-metal acceptors have been studied, rather, as intriguing extensions—neither mere analogues nor simply further examples—of what is known about the hydrogen-bonding phenomenon itself, about its possible complicity in the mechanisms of reactions at transition-metal centers, and about its place among the several roles that hydrogen plays at the core of transition-metal compounds.

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Within the realm of molecular inorganic chemistry, hydrogen atoms are now known to penetrate the vicinity of transition metals in several ways:[4] as a bound ligand, either neutral H_2 or anionic hydride; as a member of a σ-bond complex, a C−H bond in a side-on contact with the metal; as part of an agostic, three-center, two-electron interaction, in which the transition element is relatively electropositive; and as the donor in a hydrogen bond, a three-center, four-electron interaction that requires an electron-rich transition-metal acceptor. The hydrogen bond to a transition metal appears to exert more of an influence on the electronic structure of the acceptor than is the case for the electronically less flexible acceptors in biological secondary structures. Hydrogen bonds have traditionally been attributed a minor degree of covalency involving the acceptor; this has been used by some as a working definition of the hydrogen bond, as distinct from a simple electrostatic interaction. For transition-metal acceptors (M), a DFT/AIM study of C−H⋯M and N−H⋯M hydrogen bonds[5] (with the DFT results checked against experimental NMR data) concluded that these were closed-shell, electrostatic interactions that developed some covalency at short H⋯M distances. Kozelka et al.,[1] using Hartree–Fock and Møller–Plesset techniques,[5c] find that in their solid the O—H⋯Pt hydrogen bonding involves dispersion—that is, polarization of the electron cloud at the metal, principally the d_{z^2} orbital, by the dipolar donor. The exact nature of the donor dipole could qualify the interaction as either induction or dispersion. They also conclude that covalency does not play a part in this O−H⋯Pt interaction.

While the neutron analysis of *trans*-$[PtCl_2(NH_3)(N\text{-gly})]\cdot H_2O$ by Kozelka et al. is the most definitive aspect of their report, their theoretical calculations are critical in establishing that what they observe in the crystal structure is inherent to the O−H⋯Pt interaction and not an arrangement imposed by the crystalline environment on the atoms involved. Diffraction analyses are conducted using crystalline samples, and diffractionists are aware of the dangers of deriving global conclusions from local features of a single structure. How much of what we see is just the result of having the molecule within a crystal? It was put this way by Hamilton and Ibers:[6]

> "*…we look upon the crystal simply as a device for holding the molecule down so that we can take a good look at it. Any special effects due to the crystalline condition—distortions due to the requirements of intermolecular packing for example—may be looked upon as being undesirable but unavoidable side effects which may partially obscure the information we are really after…*"

The water molecule that donates the hydrogen bond to Pt is also involved in other hydrogen bonds. The Pt complex forms a cyclic dimer through N−H⋯Pt interactions. This second interaction, N−H⋯Pt, may involve the Pt−Cl bond in a way that is not explained. The skeptical observer might ask whether the O−H⋯Pt contact is "just along for the ride". I think not. Calculations of the electronic structure strongly imply that this is a hydrogen bond; and just as the largely covalent metal–ligand bonds have quite different properties from, say, the peptide bond in proteins, this hydrogen bond is not the more rigid, potentially structure-directing hydrogen bond that led Pauling et al. to explain the secondary structures of proteins, and which incites crystal engineers to study analogous concepts in molecular crystals. The interaction reported here possesses the requisite electronic characteristics. It is a three-center, four-electron interaction with a $D(\delta^-)-H(\delta^+)\cdots A(\delta^-)$ charge arrangement. The dispersion effects to which the hydrogen bonding is attributed are directional in nature, in contrast to the attributes that the term "dispersion" usually conjures up. All indications are that the O−H⋯Pt contact in *trans*-$[PtCl_2(NH_3)(N\text{-gly})]\cdot H_2O$ is a stabilizing interaction and satisfies, for example, Steiner's criteria for being termed a hydrogen bond.[7]

Much of the experimental evidence on hydrogen bonds with metal atoms as acceptors is related to the donor side of the interaction: IR frequencies for the D−H bond, which decrease, and NMR chemical shifts for the H atom, which move downfield in a hydrogen bond.[8] The study by Kozelka et al. gives due attention to the acceptor atom M itself. Previous work has explored the effects of hydrogen-bond formation to a metal on the other M−L bonds.[8c] The induced polarization at the metal center seems to be a significant characteristic of this metal–acceptor hydrogen bond.

The association of acceptor changes with hydrogen-bond formation also raises the possibility that existing or future data on transition-metal electronic structure may reveal interactions that could qualify as hydrogen bonds, even without definitive structure analyses. An outsized nephelauxetic effect in a square-planar Co^{II} complex, which was studied many years ago by magnetic and spectroscopic means, was related to the influence of methyl hydrogen atoms in the vicinity of the open fifth and sixth coordination sites.[9a] So strong was the focus at that time on the electronic structure of the transition metal itself that even though the H atoms were imputed in the nephelauxetic effect, a hydrogen bond to the metal was not suggested.

Compounds such as that shown in Figure 1 clearly suggest H⋯M hydrogen bonding.[9b] But in that compound the H-bearing ligand does not have great freedom of motion. In the compound reported by Kozelka et al., the hydrogen-bond donor is unligated water, not an integral part of the Pt-containing molecule. This is as close to a self-standing O−H⋯Pt hydrogen bond as has been analyzed by neutron diffraction. I expect these results to stimulate an expanded

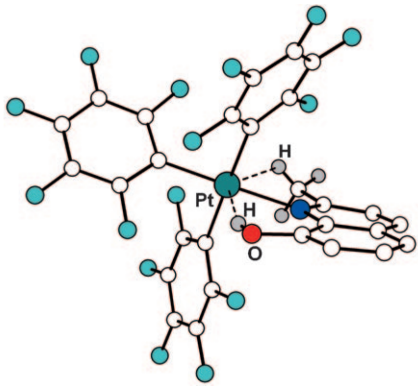

Figure 1. Putative hydrogen-bonding interactions involving a bound ligand in a nominally square-planar Pt^{II} complex; dark blue: N, turquoise: F.[9b]

effort to produce and characterize systems with similar interactions.

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