Hydrogen Bonding

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Dispersion-Driven Hydrogen Bonding: Predicted Hydrogen Bond between Water and Platinum(II) Identified by Neutron Diffraction**

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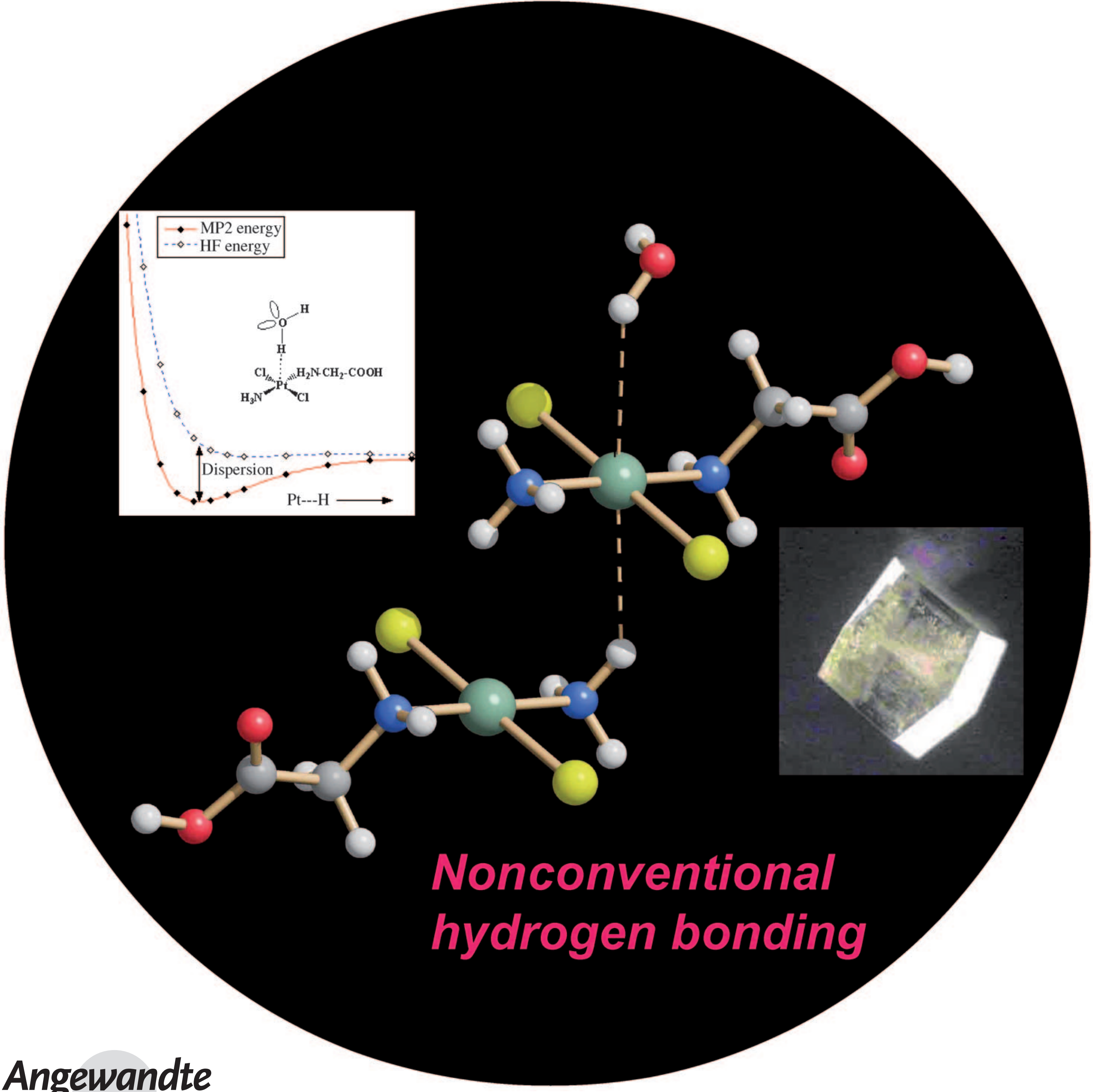

Nonconventional hydrogen bonding

Hydrogen bonding is generally considered to be an interaction between the dipole of a polarized X−H bond (X = electronegative atom) and a region of high electron density, such as a lone pair of electrons, a π molecular orbital, or a σ-bonding pair.[1–3] Recently, several authors reported that filled d orbitals of square-planar d^8 metal ions can also act as hydrogen-bond acceptors.[4–8] In particular, a number of square-planar Pt^{II} compounds provide structural evidence for N−H⋯Pt, O−H⋯Pt, and C−H⋯Pt hydrogen bonds.[7–9] In most cases the hydrogen bonding is either intramolecular or/and involves an anionic platinum center. Two structurally characterized neutral complexes showing an intermolecular X−H⋯Pt interaction (X = N or C) have indicated, however, that even intermolecular H bonding not aided by ionic forces is energetically feasible.[10,11] A ubiquitous and excellent hydrogen-bond donor is water, and the question arises whether in aqueous solutions of square-planar d^8 metal complexes, axial water molecules could form hydrogen bonds to the metal atom. We have previously reported Møller–Plesset second-order perturbation theory (MP2) calculations predicting that neutral Pt^{II} complexes, when interacting with an H_2O molecule in an axial position, prefer its "H-ahead" orientation, corresponding to an O−H⋯Pt hydrogen bond.[12] Such "inverse hydration"[13] of d^8 complexes could represent an impediment for ligand exchange with water (aquation) where the water molecule attacks the metal center along the *z* axis with its oxygen atom. Here we present the experimental proof for the "inverse hydration" of an uncharged Pt^{II} complex. Using single-crystal low-temperature (20 K) neutron diffraction, we have re-determined the structure of *trans*-$[PtCl_2(NH_3)(N\text{-glycine})]\cdot H_2O$ ($\mathbf{1}\cdot H_2O$), for which a previous X-ray diffraction study indicated that the O atom of the water molecule occupies an axial position 3.52 Å away from the Pt atom.[14] Neutron diffraction[15] allowed the accurate localization of H atoms and showed that the water molecule is indeed involved in a hydrogen bond to platinum. Although water-to-metal hydrogen bonding has been suggested to exist previously,[16] this is the first unambiguous structural evidence for nonconventional hydrogen bonding between a water molecule and a metal center.

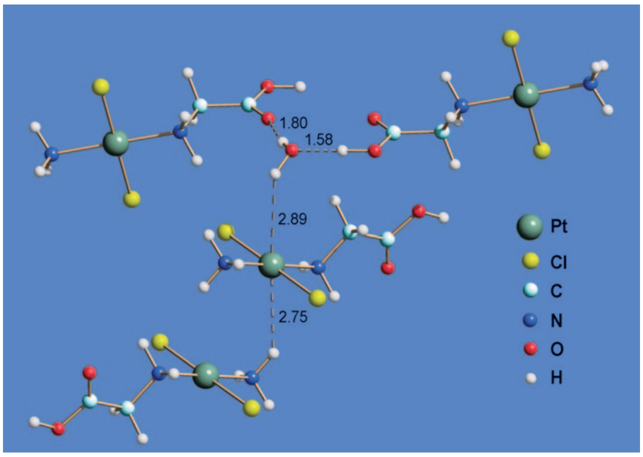

Figure 1. Section of the crystal structure of $\mathbf{1}\cdot H_2O$ determined by neutron diffraction. The nonclassical hydrogen bonds involving the platinum center and the classical hydrogen bonds formed by the H_2O molecule (distances in Å) are shown as dashed lines.

Figure 1 shows the environment of the Pt^{II} ion in the crystal of $\mathbf{1}\cdot H_2O$. It can be seen that Pt is involved in two nonclassical intermolecular hydrogen bonds, one with the NH_3 ligand of a second complex and one with a water molecule. The two hydrogen bonds are nearly collinear, as can be judged from the value of the H⋯Pt⋯H angle of approximately 167°. In addition to the O−H⋯Pt interaction, the water molecule also acts as a donor center for a classical hydrogen bond to a glycine ligand, and as an acceptor in another hydrogen-bonding interaction with a different symmetry-related glycine molecule. The H⋯Pt separations in N−H⋯Pt and O−H⋯Pt of 2.748(3) and 2.885(3) Å, respectively, are at the upper limit of the range 2.1–2.8 Å for such bonding interactions,[17,18] and comparable to the distance of 2.79(1) Å found for the only reported case of intermolecular N−H⋯Pt hydrogen bonding to an uncharged platinum complex.[10] The N−H⋯Pt and O−H⋯Pt angles are 137.0(2)° and 136.5(7)°, respectively, while the O−H⋯O angles associated with the two classical hydrogen bonds involving the water molecule are 169.2(7)° and 179.6(5)°, respectively. Thus it seems that both the H_2O molecule and the ammine ligand orient themselves in a way to allow for a pseudo-octahedral coordination to the Pt center.

In aqueous solutions of square-planar d^8 complexes, the metal center is expected to be approached by water molecules from both sides of the coordination plane. The solid-state structure (Figure 1) suggests that in neutral (and more so in anionic) Pt^{II} complexes two axial water molecules can approach the metal atom simultaneously with the "inverse" orientation, in other words, not with the negatively charged O atom but with one H atom, forming nonclassical hydrogen bonds with Pt. For both hydrogen bonds, Pt is the acceptor atom, and the interesting question arises to what extent the two hydrogen bonds would weaken each other. We have used

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MP2 ab initio calculations to determine the energy associated with **1** having hydrogen-bonding interactions with one and two axial water molecules, respectively (see the Supporting Information). Figure 2 shows the interaction energies at the Hartree–Fock (HF) and at the MP2 levels evaluated as the difference between the total energy of the two (three) interacting species and the sum of the total energies of the individual molecules, corrected for the basis set superposition error (BSSE). The interaction with one water molecule oriented with one of its lone pairs of electrons towards Pt is also shown. Comparison of the hydrogen-bonding interactions with one (Figure 2a) and two (Figure 2c) water molecules shows that the O···Pt separation at the energy minimum (≈ 3.4 Å) is virtually identical in both cases, and the interaction energy for two H_2O molecules (-7.3 kcal mol^{-1}) is only 0.5 kcal mol^{-1} less than twice that for one H_2O molecule (-3.9 kcal mol^{-1}). These results indicate that the mutual weakening of the two hydrogen bonds is very small. The approach of a water molecule with the lone pair of electrons oriented toward Pt is repulsive, except for a very shallow energy minimum at $d \approx 4$ Å seen at both the HF and MP2 levels.

Figure 2a,c shows that two water molecules are likely to donate nonclassical hydrogen bonds to the Pt^{II} center of an uncharged platinum complex simultaneously, without significant mutual weakening of the hydrogen bonds. The environment of the platinum center in **1**·H_2O (Figure 1) can therefore be used as a model for the hydration of neutral (and anionic) Pt^{II} complexes, if one replaces the H-bond-donating NH_3 molecule with H_2O.

The "inverse hydration" (i.e., coordination of water molecules to the central ion with the "H-ahead" orientation) could conceivably slow down the aquation (replacement of anionic ligands by water molecules) of neutral and especially anionic acido complexes, since the hydrogen bond stabilizes the axial water molecule in an orientation unfavorable for nucleophilic attack. In this context, it is interesting to recall the puzzling finding by Martin[19] that the aquation rates for mixed chlorido–ammine–aqua complexes of Pt^{II} are not appreciably dependent on the complex charge. For instance, the first and second aquation rate constants for the antitumor drug *cis*-[$PtCl_2(NH_3)_2$] (cisplatin) are nearly identical[20,21] even though the positive charge of the chlorido–aqua complex (formed after the first aquation) would be expected to strongly impede the departure of the second chlorido ligand. Although the substitution mechanism is associative, the scissile Pt−Cl bond is considerably elongated in the transition state.[22] Aquation rates for analogous palladium(II) diamine complexes do not show any appreciable charge effect either.[23] Based on our present results and previous calculations,[12,24–26] we dare to speculate that this surprising absence of a charge effect could be at least partly ascribed to "inverse hydration", whose inhibitory effect on the aquation should decrease with increasing charge, and could therefore counterbalance the effect of charge separation. The relatively slow aquation of cisplatin, which is the rate-determining step for its pharmacologically relevant reaction with DNA,[27] could be therefore related to the "inverse hydration".

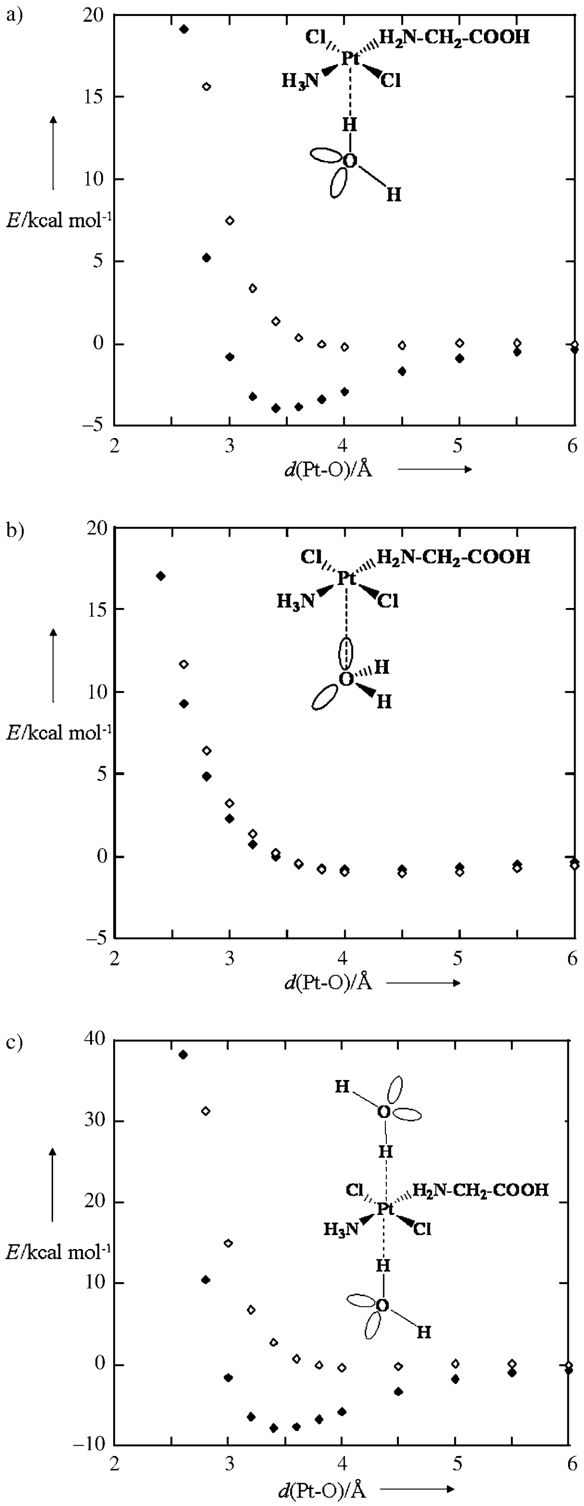

Figure 2. Plots of calculated Hartree–Fock (open diamonds) and MP2 (filled diamonds) interaction energies for **1** interacting with one or two H_2O molecules. a) One H_2O molecule in "H-ahead" orientation; b) one H_2O molecule in "lone-pair-ahead" orientation; c) two H_2O molecules interrelated by an inversion center at the Pt nucleus in "H-ahead" orientation.

Whereas the hydrogen bond has been considered traditionally to be primarily an electrostatic interaction,[28–30] it is now recognized that induction, dispersion, and covalency contribute as well, to extents that vary between different types of hydrogen bonds.[1–3] We report here an interaction which in all features resembles a hydrogen bond but is almost entirely dispersion-driven. It involves a doubly occupied orbital on the acceptor atom (the Pt $5d_{z^2}$ orbital in D_{4h} symmetry) which confers the interaction with the directionality (preference for a linear O−H···Pt arrangement along the normal to the coordination plane) typical for hydrogen bonds; however, its electrostatic interaction with the O−H dipole merely brings the otherwise repulsive electrostatic energy to nearly zero. This can be seen in the Hartree–Fock (HF) interaction curves (Figure 2 a,c) where electrostatic forces, which are the only long-range forces, would show up at Pt−O separations above 4.5 Å. It can be seen that both with one (Figure 2 a) and two (Figure 2 c) H_2O molecules, the HF interaction energy is nearly zero down to $d\approx 3.5$ Å. This indicates that not only electrostatic forces but also covalent forces are negligible. Covalent forces would become manifest as an HF energy minimum at $d\approx 3$–4 Å. The fact that the HF interaction energy is nearly zero down to $d\approx 3.5$ Å and then increases therefore indicates that neither electrostatic nor covalent forces are appreciable in the interaction between **1** and H_2O. The clue to the binding interaction is provided by the MP2 curves (Figure 2 a,c) which show, in contrast to the HF curves, a clear minimum near $d=3.4$ Å. Since MP2 calculations account for dispersion, whereas HF calculations do not, the difference indicates that the binding energy of this nonclassical hydrogen-bonding interaction comes almost exclusively from dispersion. Obviously, Pt^{II} is a particularly polarizable hydrogen-bonding acceptor, and its dispersion interaction with the water hydrogen atom is stronger than that of other acceptors.

In conclusion, we report here the first crystallographic evidence for a hydrogen-bonding-like interaction between a water molecule and a d^8 metal ion, based on neutron diffraction. According to our HF and MP2 calculations, the interaction is almost entirely dispersion-driven and thus represents a limiting case of hydrogen bonding. We speculate that for square-planar d^8 metal complexes of zero or negative charge, such hydrogen bonding with water molecules might affect the solvolysis mechanism and be at the origin of anomalously slow aquation rate constants previously reported for some Pt^{II} complexes.

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[1] T. Steiner, *Angew. Chem.* **2002**, *114*, 50–80; *Angew. Chem. Int. Ed.* **2002**, *41*, 48–76.

[2] P. Hobza, Z. Havlas, *Theor. Chem. Acc.* **2002**, *108*, 325–334.

[3] M. Goswami, E. Arunan, *Phys. Chem. Chem. Phys.* **2009**, *11*, 8974–8983.

[4] A. Albinati, C. Arz, P. S. Pregosin, *Inorg. Chem.* **1987**, *26*, 508–513.

[5] S. G. Kazarian, P. A. Hamley, M. Poliakoff, *J. Am. Chem. Soc.* **1993**, *115*, 9069–9079.

[6] R. H. Crabtree, O. Eisenstein, G. Sini, E. Peris, *J. Organomet. Chem.* **1998**, *567*, 7–11.

[7] A. Martín, *J. Chem. Educ.* **1999**, *76*, 578–583.

[8] L. Brammer, *Dalton Trans.* **2003**, 3145–3157.

[9] A. Albinati, F. Lianza, P. S. Pregosin, B. Müller, *Inorg. Chem.* **1994**, *33*, 2522–2526.

[10] J. M. Casas, L. R. Falvello, J. Forniés, A. Martín, *Inorg. Chem.* **1996**, *35*, 56–62.

[11] G. Bruno, S. Lanza, F. Nicolò, *Acta Crystallogr.* **1990**, *C46*, 765–767.

[12] J. Kozelka, J. Bergès, R. Attias, J. Fraitag, *Angew. Chem.* **2000**, *112*, 204–207; *Angew. Chem. Int. Ed.* **2000**, *39*, 198–201.

[13] J. Bergès, J. Caillet, J. Langlet, J. Kozelka, *Chem. Phys. Lett.* **2001**, *344*, 573–577.

[14] I. A. Baidina, N. V. Podberezskaya, L. F. Krylova, S. V. Borisov, *J. Struct. Chem.* **1981**, *22*, 463–465.

[15] Crystal data for **1**·H_2O: $C_2H_{10}Cl_2N_2O_3Pt$, $M_r=376.11$, monoclinic, space group $P2_1/c$, $a=14.5469(6)$, $b=5.2811(2)$, $c=11.9056(5)$ Å, $\beta=115.382(3)°$, $V=826.34(6)$ Å, $Z=4$, $\rho_{calcd}=3.023\,g\,cm^{-3}$, $\mu=0.201\,mm^{-1}$. Neutron diffraction data were collected at the ILL reactor, using the D19 diffractometer equipped with the new horizontally curved "banana-shaped" position-sensitive detector, on a crystal of approximately $0.5\,mm^3$, cooled to 20(2) K ($\lambda=0.94614(3)$ Å, Cu(331) monochromated). No significant changes in the crystal mosaic nor splitting of peaks were observed during cooling. The space group $P2_1/c$ was confirmed at 20 K. A total of 13069 Bragg reflections were collected ($2\theta\leq 123.18°$), yielding 4813 unique reflections. The starting structural model was based on the atomic coordinates of the heavy atoms from an X-ray structure determination at 120(2) K (see the Supporting Information for details), while all hydrogen atoms were located from Fourier difference maps. The structure was refined by full matrix least squares on intensities, using anisotropic displacement parameters for all atoms. Final agreement factors were $R_1=0.0932$, $R^2_w=0.2356$ for 3002 observed reflections $[I>2\sigma(I)]$ and 181 refined parameters. CCDC 771462 and 771463 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] D. Braga, F. Grepioni, E. Tedesco, K. Biradha, G. R. Desiraju, *Organometallics* **1997**, *16*, 1846–1856.

[17] J. M. Casas, L. R. Falvello, J. Forniés, A. Martín, *Inorg. Chem.* **1996**, *35*, 6009–6014.

[18] W. Yao, O. Eisenstein, R. H. Crabtree, *Inorg. Chim. Acta* **1997**, *254*, 105–111.

[19] D. S. Martin, Jr., *Inorg. Chim. Acta Rev.* **1967**, *1*, 87–97.

[20] M. S. Davies, S. J. Berners-Price, T. W. Hambley, *Inorg. Chem.* **2000**, *39*, 5603–5613.

[21] J. Vinje, E. Sletten, J. Kozelka, *Chem. Eur. J.* **2005**, *11*, 3863–3871.

[22] Z. Chval, M. Sip, *J. Mol. Struct.* **2000**, *532*, 59–68.

[23] H. Hohmann, R. van Eldik, *Inorg. Chim. Acta* **1990**, *174*, 87–92.

[24] E. C. Beret, J. M. Martínez, R. R. Pappalardo, E. Sánchez Marcos, N. L. Doltsinis, D. Marx, *J. Chem. Theory Comput.* **2008**, *4*, 2108–2121.

[25] E. C. Beret, R. R. Pappalardo, N. L. Doltsinis, D. Marx, E. Sánchez Marcos, *ChemPhysChem* **2008**, *9*, 237–240.

[26] J. Fedoce Lopes, W. R. Rocha, H. F. Dos Santos, W. B. DeAlmeida, *J. Chem. Phys.* **2008**, *128*, 165103.

[27] P. Horacek, J. Drobník, *Biochim. Biophys. Acta Nucleic Acids Protein Synth.* **1971**, *254*, 341–347.

[28] L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, **1948**, chap. IV.

[29] W. H. Baur, *Acta Crystallogr.* **1965**, *19*, 909–916.

[30] A. D. Buckingham, P. W. Fowler, *J. Chem. Phys.* **1983**, *79*, 6426–6428.