A Reversible Intramolecular Hydrogen-bonding Interaction involving Second-sphere Co-ordination of a Water Ligand

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The crystal structure of $[Cu\{HB(pypz)_3\}(H_2O)][PF_6]$ $\{HB(pypz)_3$ = hydrotris[3-(2-pyridyl)pyrazol-1-yl]borate$\}$ has been determined and reveals a square-pyramidal Cu^{II} centre co-ordinated by two of the three bidentate arms of the ligand and an axial water molecule, while the third, pendant, bidentate ligand arm is involved in a 'chelating' hydrogen-bonding interaction with one of the protons of the axial water molecule; this interaction is not maintained in solution.

Stabilisation of co-ordinated ligands by second-co-ordination-sphere binding interactions is an essential part of substrate-specific host–guest interactions at metalloenzyme active sites. Hydrogen-bonding stabilisation of co-ordinated substrates is quite common: some well-known examples are the hydrogen-bonding interactions between (*i*) water co-ordinated to Zn^{II} at the active site of carboxypeptidase A, and the carboxylate moiety of an adjacent glutamate residue; (*ii*) the terminal hydroperoxide ligand co-ordinated to one of the Fe^{III} centres in oxyhemerythrin, and the adjacent oxo bridge which links the two Fe^{III} centres; (*iii*) the terminal hydroperoxide attached to the Fe^{III} centre of peroxidase, and the imidazolyl moiety of an adjacent histidine residue.[1] Such interactions not only encourage co-ordination of the substrate but can also stabilise the transition states that occur when the catalytic cycle is underway.

Preparing simple model systems which show this behaviour is difficult. The subtle combinations of steric and electronic effects which combine to give metalloenzymes their unique properties are necessarily dependent on the presence of a highly sophisticated ligand whose influences on the metal co-ordination environment extend considerably beyond the primary co-ordination sphere. However, recently a few examples have been reported. In $[Mn^{III}\{HB(dippz)_3\}(Hdippz)(O_2)]$ (Hdippz = 3,5-diisopropylpyrazole) the side-on peroxo ligand is stabilised by hydrogen-bonding to the monodentate pyrazole ligand Hdippz,[2] and in $[Cu^{II}(tppa)(O_2)]^+$ (tppa = tris[{6-(pivaloylamino)pyridin-2-yl}methyl]amine) the side-bound superoxido ligand is stabilised by (*i*) encapsulation within a tris(pivaloyl) cavity, and (*ii*) hydrogen bonding to the NH protons.[3] Attachment of the weakly-co-ordinating anion BF_4^- axially to a Cu^{II} centre was facilitated by an additional hydrogen-bonding interaction between one of the fluorine atoms and a remote amino group pendant from a 2-cyanoguanidine ligand.[4] We describe herein an unusual example of intramolecular second-sphere co-ordination in which the pendant arm of a potentially hexadentate ligand is hydrogen bonded to a water molecule which is itself axially co-ordinated to a Cu^{II} centre, and show that the interaction is removed in solution. The water molecule is therefore a conventional first-sphere ligand, and the pendant group which co-ordinates in turn to the water is the second-sphere ligand.

The podand ligand hydrotris[3-(2-pyridyl)pyrazol-1-yl]-borate $\{[HB(pypz)_3]^-\}$ has a hexadentate cavity which is of an appropriate size to bind lanthanides[5,6] and actinides,[6,7] but with smaller first-row transition-metal dications such as Mn^{II} and Zn^{II} it forms tetrameric complexes $[M_4\{HB(pypz)_3\}_4]^{4+}$ due to the size mismatch between the large cavity and the small metal ions.[8] Reaction of $K[HB(pypz)_3]$ with copper(II) acetate hydrate (1:1 stoichiometry) in methanol afforded a turquoise solution, from which a solid precipitated on addition of NH_4PF_6. Elemental analysis of the recrystallised material indicated the stoichiometry $[Cu\{HB(pypz)_3\}(H_2O)][PF_6]$. Significantly FAB and electrospray mass spectra only showed a peak at m/z = 507 due to $[Cu\{HB(pypz)_3\}]^+$, and gave no evidence for formation of higher nuclearity oligomers: in contrast, electrospray mass spectra of the complexes with Mn^{II} and Zn^{II} showed strong peaks due to the tetrameric molecular ions.[8]

The crystal structure[†] of the cation of $[Cu\{HB(pypz)_3\}(H_2O)][PF_6]\cdot0.5Et_2O$ is given in Fig. 1. The Cu^{II} ion is in an approximate square-pyramidal geometry—consistent with the stereoelectronic requirements of the Jahn–Teller effect—co-ordinated by two of the bidentate arms of the ligand as the basal plane and a water ligand in the axial position. The Cu^{II} ion lies 0.32 Å out of the mean plane of the four N-donor atoms towards the axial H_2O. The third bidentate arm of $[HB(pypz)_3]^-$, however, hydrogen bonds with the water ligand, specifically with H(1B), to which it 'chelates' *via* both N-donor atoms. The hydrogen atoms of the water ligand were directly located in the crystal structure. The presence of an interaction between H(1B) and these two nitrogen atoms is also confirmed by (*i*) the *cisoid* arrangement of the two heterocyclic rings in the pendant arm, which would otherwise be expected to be mutually *trans* [assignment of N(12)/C(14) and N(21)/C(23) is unequivocal] and (*ii*) the N···O distances [N(12)···O(1) 3.085, N(21)···O(1), 2.846 Å] which are indicative of weak but

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[†] Crystal data for $[Cu\{HB(pypz)_3\}(H_2O)][PF_6]\cdot0.5Et_2O$: $C_{26}H_{26}BCuF_6N_9O_{1.5}P$, M = 707.9, green needles, crystal size 0.75 × 0.20 × 0.10 mm, triclinic, space group $P\bar{1}$, a = 8.138(3), b = 13.365(5), c = 15.729(4) Å, α = 66.10(2), β = 77.01(2), γ = 79.76(1)°, U = 1516.8(9) Å^3, Z = 2, D_c = 1.550 g cm^{-3}, $F(000)$ = 720, μ(Mo-Kα) = 8.5 cm^{-1}. 4124 Unique data with $2\theta \leqslant 46.5°$ were collected at 293 K using a Siemens SMART diffractometer (Mo-Kα radiation, graphite monochromator, λ = 0.710 73 Å). The structure was solved by conventional heavy-atom methods (SHELXTL) and refined on all F^2 data using SHELXL 93.[9] All non-hydrogen atoms were refined with anisotropic thermal parameters; the C–H hydrogen atoms were included in calculated positions with isotropic thermal parameters; H(1A) and H(1B) (attached to the water ligand) were directly located in the crystal structure from a refinement using only low angle data ($2\theta \leqslant 30°$), and their positions were then fixed for subsequent refinement with all data. Refinement converged at R_1 [selected data with $F > 4\sigma(F)$] = 0.071; wR_2 (all data) = 0.180. The asymmetric unit contains one molecule of the complex and half of a diethyl ether molecule which is located astride an inversion centre. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

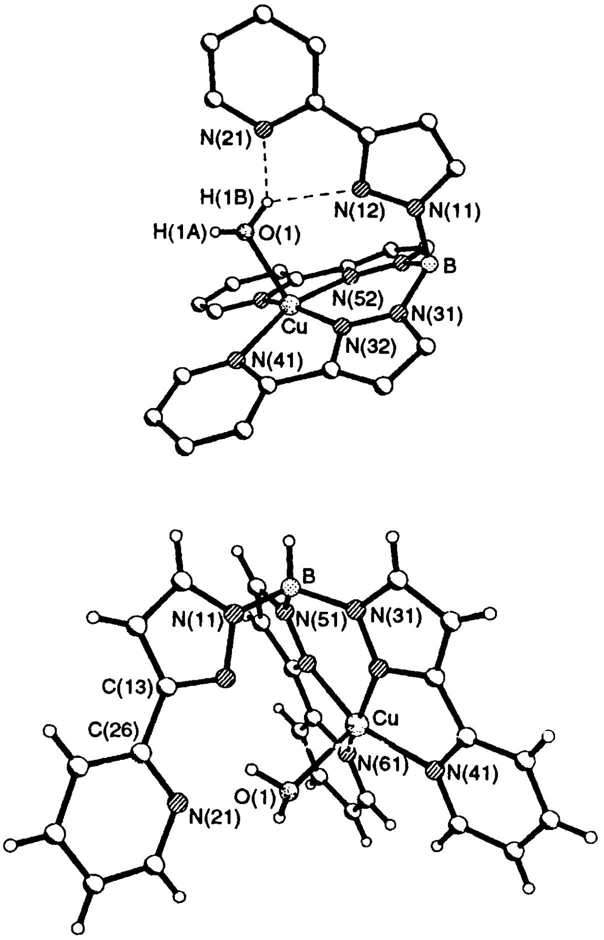

Fig. 1 Two views of the crystal structure of the cationic part of $[Cu\{HB(pypz)_3\}(H_2O)][PF_6]\cdot 0.5Et_2O$. Selected bond lengths (Å) and angles (°): Cu–N(52) 1.946(5), Cu–N(32) 1.949(5), Cu–N(41) 2.079(5), Cu–N(61) 2.084(5), Cu–O(1) 2.152(4); N(52)–Cu–N(32) 87.1(2), N(52)–Cu–N(41) 160.1(2), N(32)–Cu–N(41) 79.5(2), N(52)–Cu–N(61) 79.7(2), N(32)–Cu–N(61) 157.8(2), N(41)–Cu–N(61) 107.8(2), N(52)–Cu–O(1) 102.6(2), N(32)–Cu–O(1) 107.9(2), N(41)–Cu–O(1) 95.5(2), N(61)–Cu–O(1) 92.4(2). For details of the hydrogen bonding between H(1B) and N(12)/N(21), see text

definite O–H ··· N hydrogen bonding.[10] The uncertainty in the O–H(1B) bond length from the crystal structure is large, but if we assume a typical bond length of 0.96 Å then the N(12)–H(1B) and N(21)–H(1B) distances are 2.32 and 2.17 Å respectively, and the N(12)–H(1B)–N(21) bite angle is *ca.* 76°. In the solid state, therefore, co-ordination of the axial water ligand is stabilised by additional second-co-ordination-sphere interactions with the pendant arm of the ligand; the water molecule may be considered to occupy a 'binding pocket' defined by the metal at one end and the pendant ligand arm at the other. Co-ordination of other potentially hydrogen-bonding axial ligands in the same way may be possible and is being investigated.

Comparison of solid-state and solution IR spectra show that this interaction is not maintained in solution. The IR spectrum of a microcrystalline film (prepared by allowing a solution to evaporate on the surface of a KBr disc) (Fig. 2) shows a broad, shallow band at *ca.* 3400 cm^{-1} characteristic of a hydrogen-bonded O–H group. By contrast, in solution (CD_3CN was used to avoid possible problems with the C–H vibrations) two sharp, intense O–H peaks occur at 3628 and 3545 cm^{-1}. These are the symmetric and asymmetric O–H stretching vibrations characteristic of an isolated water ligand *without* hydrogen bonding. In solution, therefore, the pendant arm is released and can no doubt participate in interactions with the polar solvent; in the absence of solvent interactions the pendant arm reverts to its hydrogen-bonding interactions with the apical water ligand. The co-ordination geometry about the Cu^{II} appears however to be maintained in solution; the EPR spectrum (MeCN–thf glass, 77 K) has parameters ($g_{\parallel} = 2.238$; $g_{\perp} = 2.073$; $A_{\parallel} = 587$ MHz) typical of Cu^{II} in an environment based on a tetragonal geometry with little or no tetrahedral distortion.[11] In particular the large value of $A_{\parallel}$ and the relatively low value of $g_{\parallel}$ are nearly identical to those observed in another Cu^{II} complex with a rigorously planar N_4 donor set based on pyrazole ligands.[12]

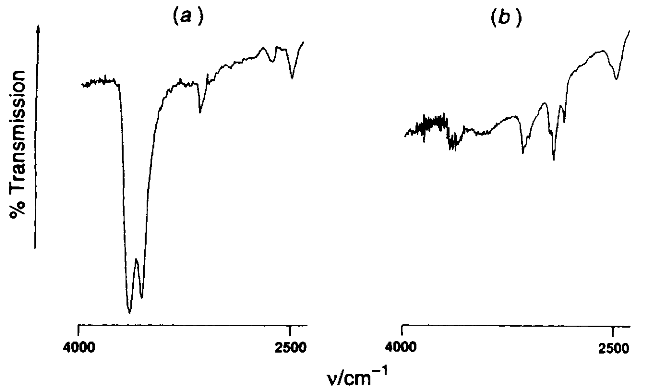

Fig. 2 The IR spectra of $[Cu\{HB(pypz)_3\}(H_2O)][PF_6]$ (*a*) in CD_3CN solution, (*b*) as a solid film

The structure of this mononuclear Cu^{II} complex is in interesting contrast to the tetrameric structures of the Mn^{II} and Zn^{II} complexes, in which the metal ions are in highly distorted 'octahedral' environments. The apical N–B–N angles are all very close to the ideal tetrahedral values, indicating that the ligand is in a strain-free conformation; the cavity size that is ideal for lanthanides and actinides is also ideal for a $\{Cu(H_2O)\}^{2+}$ fragment.

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