Preparations and structures of two cis,cis-1,3,5-triaminocyclohexane-based complexes containing hydrogen-bonded solvent molecules

Leroy Cronin, Bryan Greener, Madeleine H. Moore and Paul H. Walton

Department of Chemistry, University of York, Heslington, York YO1 5DD, UK

Reactions of cis,cis-1,3,5-tri-((E,E)-cinnamylideneaminocyclohexene and the new molecule cis,cis-1,3,5-tri-((E)-3-(2-furyl)prop-2-en-1-ylideneamino)cyclohexane with diazacetonatocin(crypt) hydrate and bis(tetrafluoroborato)cobalt(tetrahydrate) hydrate respectively afforded two novel metal complexes, the crystal structures of which showed chains of hydrogen-bonded solvent molecules within a rigid hydrophobic cavity.

It is well established that, in solution, metal ions can be coordinated by solvent molecules (e.g. H2O, alcohols), where a primary co-ordination sphere is connected via hydrogen bonds to a secondary co-ordination sphere, and so on to further layers. Analogous solution layers are observed within the active sites of metalloproteins (e.g. carbonic anhydrase) often in the form of a small network or chain of hydrogen-bonded water molecules. Usually, these chains are important in the catalytic function of the enzyme. 1 Similar chains are also observed in the solid-state structures of small molecule metal complexes; 2 however, their formation is inconsistent and appears to be by chance.

We present here the synthesis, characterisation and crystal structures of two transition-metal complexes, which were designed specifically to promote the formation of chains of hydrogen-bonded solvent molecules. With such complexes we aim to model more consistently and more accurately the active sites of metalloenzymes that contain chains of hydrogen-bonded solvent molecules.

The ligand design is such that upon complexation to a metal, a face-capping N2 co-ordination geometry is enforced on one active site of metalloproteins (e.g. carbonic anhydrase) often in the form of a small network or chain of hydrogen-bonded water molecules. Usually, these chains are important in the catalytic function of the enzyme. 1 Similar chains are also observed in the solid-state structures of small molecule metal complexes; 2 however, their formation is inconsistent and appears to be by chance.

We present here the synthesis, characterisation and crystal structures of two transition-metal complexes, which were designed specifically to promote the formation of chains of hydrogen-bonded solvent molecules. With such complexes we aim to model more consistently and more accurately the active sites of metalloenzymes that contain chains of hydrogen-bonded solvent molecules.

The ligand design is such that upon complexation to a metal, a face-capping N2 co-ordination geometry is enforced on one active site of metalloproteins (e.g. carbonic anhydrase) often in the form of a small network or chain of hydrogen-bonded water molecules. Usually, these chains are important in the catalytic function of the enzyme. 1 Similar chains are also observed in the solid-state structures of small molecule metal complexes; 2 however, their formation is inconsistent and appears to be by chance.

We present here the synthesis, characterisation and crystal structures of two transition-metal complexes, which were designed specifically to promote the formation of chains of hydrogen-bonded solvent molecules. With such complexes we aim to model more consistently and more accurately the active sites of metalloenzymes that contain chains of hydrogen-bonded solvent molecules.

The ligand design is such that upon complexation to a metal, a face-capping N2 co-ordination geometry is enforced on one active site of metalloproteins (e.g. carbonic anhydrase) often in the form of a small network or chain of hydrogen-bonded water molecules. Usually, these chains are important in the catalytic function of the enzyme. 1 Similar chains are also observed in the solid-state structures of small molecule metal complexes; 2 however, their formation is inconsistent and appears to be by chance.

We present here the synthesis, characterisation and crystal structures of two transition-metal complexes, which were designed specifically to promote the formation of chains of hydrogen-bonded solvent molecules. With such complexes we aim to model more consistently and more accurately the active sites of metalloenzymes that contain chains of hydrogen-bonded solvent molecules.

Reactions of cis,cis-1,3,5-tri-((E,E)-cinnamylideneaminocyclohexene and the new molecule cis,cis-1,3,5-tri-((E)-3-(2-furyl)prop-2-en-1-ylideneamino)cyclohexane with diazacetonatocin(crypt) hydrate and bis(tetrafluoroborato)cobalt(tetrahydrate) hydrate respectively afforded two novel metal complexes, the crystal structures of which showed chains of hydrogen-bonded solvent molecules within a rigid hydrophobic cavity.

It is well established that, in solution, metal ions can be coordinated by solvent molecules (e.g. H2O, alcohols), where a primary co-ordination sphere is connected via hydrogen bonds to a secondary co-ordination sphere, and so on to further layers. Analogous solution layers are observed within the active sites of metalloproteins (e.g. carbonic anhydrase) often in the form of a small network or chain of hydrogen-bonded water molecules. Usually, these chains are important in the catalytic function of the enzyme. 1 Similar chains are also observed in the solid-state structures of small molecule metal complexes; 2 however, their formation is inconsistent and appears to be by chance.

We present here the synthesis, characterisation and crystal structures of two transition-metal complexes, which were designed specifically to promote the formation of chains of hydrogen-bonded solvent molecules. With such complexes we aim to model more consistently and more accurately the active sites of metalloenzymes that contain chains of hydrogen-bonded solvent molecules.

The ligand design is such that upon complexation to a metal, a face-capping N2 co-ordination geometry is enforced on one active site of metalloproteins (e.g. carbonic anhydrase) often in the form of a small network or chain of hydrogen-bonded water molecules. Usually, these chains are important in the catalytic function of the enzyme. 1 Similar chains are also observed in the solid-state structures of small molecule metal complexes; 2 however, their formation is inconsistent and appears to be by chance.

We present here the synthesis, characterisation and crystal structures of two transition-metal complexes, which were designed specifically to promote the formation of chains of hydrogen-bonded solvent molecules. With such complexes we aim to model more consistently and more accurately the active sites of metalloenzymes that contain chains of hydrogen-bonded solvent molecules.

The ligand design is such that upon complexation to a metal, a face-capping N2 co-ordination geometry is enforced on one active site of metalloproteins (e.g. carbonic anhydrase) often in the form of a small network or chain of hydrogen-bonded water molecules. Usually, these chains are important in the catalytic function of the enzyme. 1 Similar chains are also observed in the solid-state structures of small molecule metal complexes; 2 however, their formation is inconsistent and appears to be by chance.

We present here the synthesis, characterisation and crystal structures of two transition-metal complexes, which were designed specifically to promote the formation of chains of hydrogen-bonded solvent molecules. With such complexes we aim to model more consistently and more accurately the active sites of metalloenzymes that contain chains of hydrogen-bonded solvent molecules.

The ligand design is such that upon complexation to a metal, a face-capping N2 co-ordination geometry is enforced on one active site of metalloproteins (e.g. carbonic anhydrase) often in the form of a small network or chain of hydrogen-bonded water molecules. Usually, these chains are important in the catalytic function of the enzyme. 1 Similar chains are also observed in the solid-state structures of small molecule metal complexes; 2 however, their formation is inconsistent and appears to be by chance.

We present here the synthesis, characterisation and crystal structures of two transition-metal complexes, which were designed specifically to promote the formation of chains of hydrogen-bonded solvent molecules. With such complexes we aim to model more consistently and more accurately the active sites of metalloenzymes that contain chains of hydrogen-bonded solvent molecules.

The ligand design is such that upon complexation to a metal, a face-capping N2 co-ordination geometry is enforced on one active site of metalloproteins (e.g. carbonic anhydrase) often in the form of a small network or chain of hydrogen-bonded water molecules. Usually, these chains are important in the catalytic function of the enzyme. 1 Similar chains are also observed in the solid-state structures of small molecule metal complexes; 2 however, their formation is inconsistent and appears to be by chance.

We present here the synthesis, characterisation and crystal structures of two transition-metal complexes, which were designed specifically to promote the formation of chains of hydrogen-bonded solvent molecules. With such complexes we aim to model more consistently and more accurately the active sites of metalloenzymes that contain chains of hydrogen-bonded solvent molecules.

The ligand design is such that upon complexation to a metal, a face-capping N2 co-ordination geometry is enforced on one active site of metalloproteins (e.g. carbonic anhydrase) often in the form of a small network or chain of hydrogen-bonded water molecules. Usually, these chains are important in the catalytic function of the enzyme. 1 Similar chains are also observed in the solid-state structures of small molecule metal complexes; 2 however, their formation is inconsistent and appears to be by chance.

We present here the synthesis, characterisation and crystal structures of two transition-metal complexes, which were designed specifically to promote the formation of chains of hydrogen-bonded solvent molecules. With such complexes we aim to model more consistently and more accurately the active sites of metalloenzymes that contain chains of hydrogen-bonded solvent molecules.

The ligand design is such that upon complexation to a metal, a face-capping N2 co-ordination geometry is enforced on one active site of metalloproteins (e.g. carbonic anhydrase) often in the form of a small network or chain of hydrogen-bonded water molecules. Usually, these chains are important in the catalytic function of the enzyme. 1 Similar chains are also observed in the solid-state structures of small molecule metal complexes; 2 however, their formation is inconsistent and appears to be by chance.

We present here the synthesis, characterisation and crystal structures of two transition-metal complexes, which were designed specifically to promote the formation of chains of hydrogen-bonded solvent molecules. With such complexes we aim to model more consistently and more accurately the active sites of metalloenzymes that contain chains of hydrogen-bonded solvent molecules.

The ligand design is such that upon complexation to a metal, a face-capping N2 co-ordination geometry is enforced on one active site of metalloproteins (e.g. carbonic anhydrase) often in the form of a small network or chain of hydrogen-bonded water molecules. Usually, these chains are important in the catalytic function of the enzyme. 1 Similar chains are also observed in the solid-state structures of small molecule metal complexes; 2 however, their formation is inconsistent and appears to be by chance.

We present here the synthesis, characterisation and crystal structures of two transition-metal complexes, which were designed specifically to promote the formation of chains of hydrogen-bonded solvent molecules. With such complexes we aim to model more consistently and more accurately the active sites of metalloenzymes that contain chains of hydrogen-bonded solvent molecules.

The ligand design is such that upon complexation to a metal, a face-capping N2 co-ordination geometry is enforced on one active site of metalloproteins (e.g. carbonic anhydrase) often in the form of a small network or chain of hydrogen-bonded water molecules. Usually, these chains are important in the catalytic function of the enzyme. 1 Similar chains are also observed in the solid-state structures of small molecule metal complexes; 2 however, their formation is inconsistent and appears to be by chance.

We present here the synthesis, characterisation and crystal structures of two transition-metal complexes, which were designed specifically to promote the formation of chains of hydrogen-bonded solvent molecules. With such complexes we aim to model more consistently and more accurately the active sites of metalloenzymes that contain chains of hydrogen-bonded solvent molecules.

The ligand design is such that upon complexation to a metal, a face-capping N2 co-ordination geometry is enforced on one active site of metalloproteins (e.g. carbonic anhydrase) often in the form of a small network or chain of hydrogen-bonded water molecules. Usually, these chains are important in the catalytic function of the enzyme. 1 Similar chains are also observed in the solid-state structures of small molecule metal complexes; 2 however, their formation is inconsistent and appears to be by chance.
I-4MeOH and 2-5MeOH have been determined at room temperature.†

The structure of I-4MeOH (Fig. 1) shows the nickel atom in a near octahedral co-ordination geometry with I co-ordinated in the expected face-capping fashion. The cinnamylidene 'arms' of the ligand form a rigid cavity around the metal's remaining co-ordination sites, which are occupied by a monodentate acetate anion and two methanol molecules. The cavity has an internal diameter of approximately 7 Å and a depth of approximately 6 Å.

The unco-ordinated oxygen of the monodentate acetate can hydrogen bond with a nickel bound methanol O(3)⋯O(2) 2.52(7) Å, O(3)−H(3)⋯O(2) 178(6)°. The hydrogen atom of O(4) (oxygen of the other nickel bound methanol) was located

† All data were collected on a Rigaku AFC6S diffractometer, 298(2) and 294(2) K for 1-4MeOH and 2-5MeOH respectively, ω-2θ scan mode with graphite-monochromatic Mo-Kα radiation. Unit cell indexed by least-squares refinement on diffractometer angles for 20 automatically centred reflections, λ = 0.71069 Å. Solutions by direct methods with SHELXS 86 and expanded using Fourier techniques with DIRDIF. Full-matrix least-squares refinement on F² with SHELXL-93 with all non-hydrogen atoms anisotropic and hydrogens refined using a rigid model. Programs used are given in ref. 4.

Crystal data: 1-4MeOH: C₁₃H₁₉BN₂NiO₆, M = 1036.80, monoclinic, space group P2₁/n (no. 14), a = 21.401(13), b = 12.493(4), c = 23.697(1) Å, β = 112.904°, U = 5836(5) Å³, Z = 4, Dₐ = 1.17(1) g cm⁻³, Dcal = 1.18 g cm⁻³, F(000) = 2208. Pale green block, crystal dimensions 0.7 × 0.7 × 0.4 mm. A crystal of 1-4MeOH was mounted in a sealed Lindemann tube with methanol-glycerol. μ(Mo-Kα) = 3.84 cm⁻¹, ω scan width = 1.21 + 0.30 tan θ, ω scan speed 4° min⁻¹; 8480 reflections measured (5.02 < 2θ < 45.04°) (h, k, l, +/−). 7632 unique [absorption correction (max., min. transmission factors = 1.00, 0.881)]. The weighting scheme was w = |F²|/(σ(F²) + (0.0865F²)¹/² + 6.02P), P = |max(I, 0) + 2F²|³ gave satisfactory agreement analysis. Final R₁, wR₁ values on all data were 0.118, 0.360 and R₁, wR₁ values on |F > 2σ(F)| data were 0.054, 0.140, goodness of fit on F² = 1.066. The unco-ordinated oxygen of the monodentate acetate is disordered unequally over two positions [O(2) and O(22)] with O(2) being 77% occupied. In both positions the oxygen can hydrogen bond with a nickel

Crystal data: 2-5MeOH: C₁₃H₁₉BN₂CoN₂O₆, M = 1395.26, monoclinic, space group P2₁/n (no. 14), a = 19.220(18), b = 15.417(8), c = 27.713(18) Å, β = 103.796°, U = 7975(10) Å³, Z = 4, Dₐ = 1.15(1) g cm⁻³, Dcal = 1.16 g cm⁻³, F(000) = 2972. Blood red blocks, crystal dimensions 0.7 × 0.6 × 0.4 mm. A crystal of 2-5MeOH was mounted in a sealed Lindemann tube with methanol-glycerol. μ(Mo-Kα) = 2.74 cm⁻¹, ω scan width = 0.84 + 0.30 tan θ, ω scan speed 4° min⁻¹; 15 383 reflections measured (5.02 < 2θ < 50.00°) (h, k, l, +/−) gave satisfactory (max., min. transmission factors = 1.00, 0.791). The weighting scheme was w = |F²|/(σ(F²) + (0.0805F²)¹/² + 5P), P = |max(I, 0) + 2F²|³ gave satisfactory agreement analysis. Final R₁, wR₁ values on all data were 0.217, 0.203 and R₁, wR₁ values on |F > 2σ(F)| data were 0.068, 0.145; goodness of fit on F² = 1.002. The hydrogen atoms of O(4), O(5) and O(6) (the oxygen atoms of the co-ordinated methanol molecules) were located in a Fourier-difference map.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, J. Chem. Soc., Dalton Trans., 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186:178.

![Scheme 3 Synthesis of complex 2](image)

![Fig. 1 ORTEP diagram (30% probability thermal ellipsoids)](image)
of approximately 6 Å. Of the three co-ordinated methanols, two are involved in hydrogen bonding with other methanol molecules. The oxygen, O(4), of a co-ordinated methanol is hydrogen bonded to the oxygen, O(11), of a free methanol, O(4)···O(11) 2.64(6) Å, O(4)−H(80)···O(11) 170(6)°. The oxygen, O(5) of another co-ordinated methanol is hydrogen bonded to the oxygen, O(10) of a free methanol, O(5)···O(10) 2.54(6) Å and O(5)−H(81)···O(10) 174(6)° which is, in turn, hydrogen bonded to the oxygen, O(9), of another free methanol, with O(10)···O(9) 2.69(4) Å, O(9)−H(9)···O(10) 160(10)°. The cavity encapsulates six methanol molecules in total (including the three co-ordinated methanol molecules), with five participating in two hydrogen-bonded solvent chains. Two tetraphenylborate anions and two further methanol molecules complete the structure.

The complexes 1 and 2 demonstrate that a rigid, protective cavity surrounding metal co-ordination sites creates an environment that promotes the formation of chains of hydrogen-bonded solvent molecules. Future work will investigate the properties of these complexes by studying their reactions with particular attention to processes that require proton transfer.

Acknowledgements

L. C. and B. G. thank the EPSRC for maintenance grants.

References


