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

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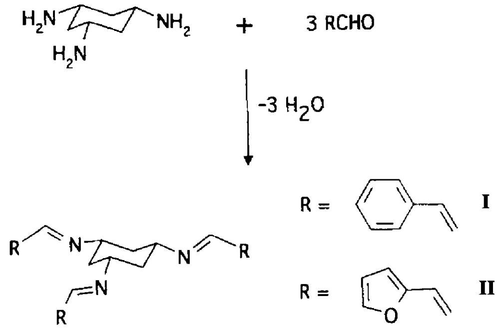
Reactions of *cis,cis*-1,3,5-tri-(*E,E*)-cinnamylideneaminocyclohexane and the new molecule *cis,cis*-1,3,5-tri-(*E,E*)-3-(2-furyl)prop-2-en-1-ylideneaminocyclohexane with diacetatonickel(II) hydrate and bis(tetrafluoroborato)cobalt(II) hydrate respectively afforded two novel metal complexes, the crystal 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 co-ordinated by solvent molecules (*e.g.* H_2O, 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 solvation 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.

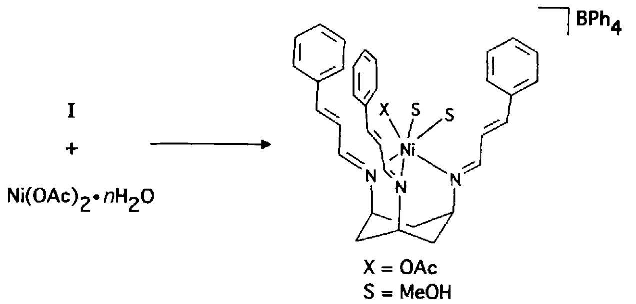
We present here the synthesis, characterisation and crystal structures of two transition-metal complexes, which were designed specifically to promote the formation of chains of hydrogen-bonded solvent molecules. With such complexes we aim to model more consistently and more accurately the active sites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

The ligand design is such that upon complexation to a metal, a face-capping N_3-co-ordination geometry is enforced on one face of the metal atom and the remaining co-ordination sites are surrounded by a rigid, hydrophobic cavity. The cavity is large enough to encapsulate several small solvent molecules.

cis,cis-1,3,5-Tri-(*E,E*)-cinnamylideneaminocyclohexane **I** was prepared from the condensation of *cis,cis*-1,3,5-triaminocyclohexane (tach) and cinnamaldehyde as previously reported.[3] *cis,cis*-1,3,5-Tri-(*E,E*)-3-(2-furyl)prop-2-en-1-ylideneaminocyclohexane **II** is a new molecule, and was synthesised in 77% yield† from the condensation of 3-(2-furyl)acrolein and tach in a similar manner to **I**, see Scheme 1. Addition of **I** to diacetatonickel(II) tetrahydrate in the presence of sodium tetraphenylborate in methanolic solution at room temperature afforded the new complex (acetato-κ*O*) [*cis,cis*-1,3,5-tri-(*Z,E*)-cinnamylideneamino-κ^3*N,N′,N″*-cyclohexane]nickel(II) tetraphenylborate **1** in 68% yield,‡ see Scheme 2. Addition of **II** to bis(tetrafluoroborato)cobalt(II) hexahydrate in the presence of sodium tetraphenylborate in methanolic solution at room temperature afforded the new complex tris(methanol-κ*O*) [*cis,cis*-1,3,5-tri-(*Z,E*)-3-(2-furyl)prop-2-en-1-ylideneamino-κ^3*N,N′,N″*-cyclohexane]cobalt(II) bis(tetraphenylborate) **2** in 64% yield,§ see Scheme 3. The crystal structures of both



Scheme 1 Synthesis of compounds **I** and **II**



Scheme 2 Synthesis of complex **1**·2MeOH

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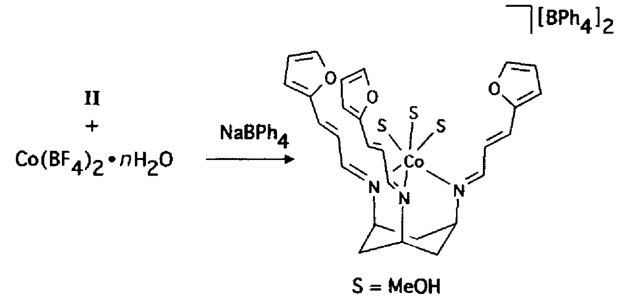
† *cis,cis*-1,3,5-Triaminocyclohexane·trihydrochloride (1.00 g, 4.2 mmol) was dissolved in an aqueous 1.25 mol dm^{-3} NaOH solution (10 cm^3) which was added to a solution of 3-(2-furyl)acrolein (1.54 g, 12.6 mmol) in diethyl ether (25 cm^3). The mixture was stirred at room temperature for 5 h. The precipitate was isolated and dried in air to give **II** as a cream powder (1.42 g, 3.2 mmol, 77%), m.p. 147–148 °C (decomp.) (Found: C, 72.00; H, 6.00; N, 9.25. Calc. for $C_{27}H_{27}N_3O_3\cdot0.5H_2O$: C, 72.00; H, 6.25; N, 9.35%). ^{1}H NMR (CD_3OD, 270 MHz): δ 8.16 (d, 3 H, $^3J_{HH}$ 9.2, N=CH), 7.66 (d, 3 H, $^3J_{HH}$ 1.7, OCH), 7.01 (d, 3 H, $^3J_{HH}$ 16.0, N=CHCH=C*H*), 6.75 (dd, 3 H, $^3J_{HH}$ 16.0, $^3J_{HH}$ 9.2, =NCH=C*H*), 6.68 (d, 3 H, $^3J_{HH}$ 3.4 Hz, CCH), 6.56 [dd, 3 H, $^3J_{HH}$ 3.4, $^3J_{HH}$ 1.7 Hz, CH(C*H*)CH], 4.93 (s, H_2O), 3.52 (m, 3 H, CR_2H) and 1.85 (m, 6 H, CH_2). IR (cm^{-1}, KBr pressed pellet): 3454s, 2928m, 2856m, 1633s, 1622s, 1479m, 1382m, 1290m, 1150m, 1026m, 1012m, 983m, 925m, 884m, 743m, 734m, 595m and 564m. FAB positive ion mass spectrum (nitrobenzyl alcohol matrix): $m/z = 442\ (M + H)^+$.

‡ A solution of diacetatonickel(II) tetrahydrate (0.05 g, 0.21 mmol) and sodium tetraphenylborate (0.07 g, 0.21 mmol) in methanol (3 cm^3) was mixed with a solution of **I** (0.10 g, 0.21 mmol) in methanol (5 cm^3) and stirred for 5 min. Pale green crystals of **1**·4MeOH were obtained by evaporation (0.13 g, 0.14 mmol, 68%), m.p. 217–217.5 °C (Found: C, 77.85; H, 5.95; N, 5.05. Calc. for $C_{59}H_{56}BN_3NiO_2$: C, 78.00; H, 6.20; N, 4.65%). IR (cm^{-1}, KBr pressed pellet): 3852m, 3748m, 3743s, 3674s, 1634s, 1539s, 1265m, 1177m, 996m, 748m, 706s, 688s, 612m, 559m and 515m. FAB positive ion mass spectrum (nitrobenzyl alcohol matrix): $m/z = 588\ (M^+ - BPh_4^-)$. Measured density = 1.17(1) g cm^{-3}.

§ A solution of bis(tetrafluoroborato)cobalt(II) hexahydrate (0.039 g, 0.11 mmol) and sodium tetraphenylborate (0.04 g, 0.11 mmol) in methanol (5 cm^3) was mixed with a solution of **II** (0.05 g, 0.11 mmol) in methanol (5 cm^3) and stirred for 5 min. Addition of water (1 cm^3) and standing for 48 h precipitated blood red crystals of **2**·5MeOH (0.09 g, 0.07 mmol, 64%), m.p. 89–91 °C (decomp.) (Found: C, 75.45; H, 6.15; N, 3.65. Calc. for $C_{78}H_{79}B_2CoN_3O_6$: C, 75.85; H, 6.45; N, 3.40%). IR (cm^{-1}, KBr pressed pellet): 3438m, 3054m, 1625s, 1602s, 1476m, 1425m, 1388m, 1267m, 1118m, 1019m, 735s, 708s and 613m. Measured density = 1.15(1) g cm^{-3}.



Scheme 3 Synthesis of complex **2**

1·4MeOH and **2**·5MeOH have been determined at room temperature.¶

The structure of **1**·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 in a Fourier-difference map in the direction of O(6), which is the oxygen atom of a free methanol molecule within the cavity, with O(4)···O(6) 2.70(7) Å, O(4)–H(5)···O(6) 171(7)°. The O(6) methanol is, in turn, hydrogen bonded to a further free methanol at the 'top' of the cavity, O(6)···O(5) 2.81(7) Å, O(6)–H(6)···O(5) 148(12)°. The cavity holds four methanol molecules in total, with three as part of a hydrogen-bonded chain extending from the metal to the 'top' of the cavity. Large Ni–N=C angles, averaging 129.6(3)°, indicate substantial steric strain between the cinnamylidene groups and the contents of the crowded cavity. A tetraphenylborate anion completes the structure.

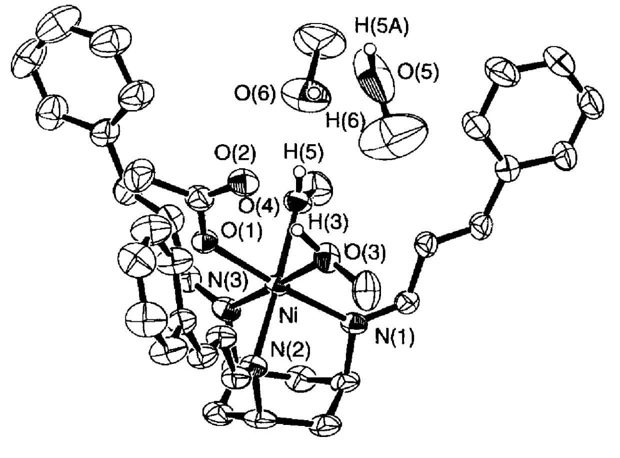


Fig. 1 ORTEP[5] diagram (30% probability thermal ellipsoids) showing the structure of **1**·4MeOH. Only hydroxyl hydrogens are shown, carbons are unshaded, the tetraphenylborate anion is omitted for clarity. Selected bond distances (Å) are as follows: N(1)–Ni 2.106(5), N(2)–Ni 2.105(4), N(3)–Ni 2.117(5), O(1)–Ni 2.076(4), O(3)–Ni 2.084(4), O(4)–Ni 2.148(4)

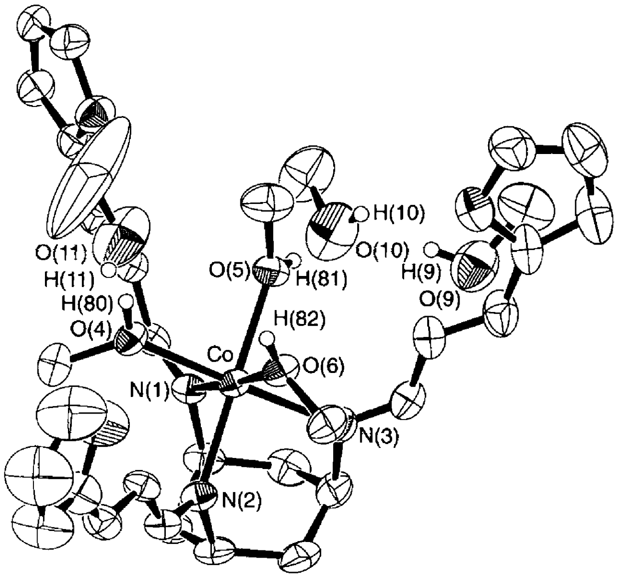


Fig. 2 ORTEP[5] diagram (30% probability thermal ellipsoids) showing the structure of **2**·5MeOH. Only hydroxyl hydrogens are shown, carbons are unshaded, the two tetraphenylborate anions and the two external methanol molecules are omitted for clarity. Selected bond distances (Å) are as follows: N(1)–Co 2.124(4), N(2)–Co 2.130(4), N(3)–Co 2.148(5), O(4)–Co 2.139(4), O(5)–Co 2.129(4), O(6)–Co 2.157(4)

The structure of **2**·5MeOH (Fig. 2) shows the cobalt atom in a near octahedral co-ordination geometry with **II** co-ordinated in a face-capping fashion. The furylpropen-3-ylidene 'arms' of the ligand, with large Co–N=C angles averaging 129.3(4)°, form a rigid cavity around the metal's remaining co-ordination sites which are occupied by three methanol molecules. The cavity has an internal diameter of approximately 8 Å and a depth

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¶ All data were collected on a Rigaku AFC6S diffractometer, 296(2) and 294(2) K for **1**·4MeOH and **2**·5MeOH respectively, ω–2θ scan mode with graphite-monochromated Mo-Kα radiation. Unit cell indexed by least-squares refinement on diffractometer angles for 20 automatically centred reflections, λ = 0.710 69 Å. Solutions by direct methods with SHELXS 86 and expanded using Fourier techniques with DIRDIF. Full-matrix least-squares refinement on F^2 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: $C_{63}H_{72}BN_3NiO_6$, M = 1036.80, monoclinic, space group $P2_1/n$ (no. 14), a = 21.401(13), b = 12.493(4), c = 23.697(11) Å, β = 112.90(4)°, U = 5836(5) Å^3, Z = 4, D_m = 1.17(1) g cm^{-3}, D_c = 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, 0.88)]. The weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0865P)^2 + 6.02P]$, $P = [\max(I_o, 0) + 2F_c^2]/3$ gave satisfactory agreement analysis. Final R_F, wR_1 values on all data were 0.118, 0.360 and R_F, wR_1 values on $[I_o > 2\sigma(I_o)]$ data were 0.054, 0.140; goodness of fit on F^2 = 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 bound methanol.

Crystal data: **2**·5MeOH: $C_{83}H_{99}B_2CoN_3O_{11}$, M = 1395.26, monoclinic, space group $P2_1/n$ (no. 14), a = 19.220(18), b = 15.417(8), c = 27.713(18) Å, β = 103.79(6)°, U = 7975(10) Å^3, Z = 4, D_m = 1.15(1) g cm^{-3}, D_c = 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, $+k$, $+l$), 14 035 unique [absorption correction (max., min. transmission factors = 1.00, 0.79)]. The weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0805P)^2]$, $P = [\max(I_o, 0) + 2F_c^2]/3$ gave satisfactory agreement analysis. Final R_F, wR_1 values on all data were 0.217, 0.203 and R_F, wR_1 values on $[I_o > 2\sigma(I_o)]$ data were 0.068, 0.145; goodness of fit on F^2 = 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.

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

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