Syntheses and structures of a range of metal complexes with the ligand *cis*,*cis*-1,3,5-(*E*,*E*)-tris(phenylpropenylideneamino)cyclohexane

Bryan Greener, Simon P. Foxon and Paul H. Walton*

Department of Chemistry, University of York, Heslington, York, UK YO10 5DD.

Received (in Cambridge, UK) 15th January 2000, Accepted 28th February 2000
Published on the Web 12th April 2000

The ligand *cis*,*cis*-1,3,5-(*E*,*E*)-tris(phenylpropenylideneamino)cyclohexane (Ph-protach) was coordinated with a range of metal salts. The products were characterised by IR and ^{1}H NMR spectroscopies and FAB + MS. In addition, the complexes $[Cu(Ph\text{-}protach)(\eta^2\text{-}SO_4)][Cu(Ph\text{-}protach)(\eta^1\text{-}SO_4)(CH_3OH)]$, $[Ni(Ph\text{-}protach)(Cl)]BPh_4$, $[Zn(Ph\text{-}protach)(Cl)]BPh_4$ and $[Cd(Ph\text{-}protach)(NO_3)(CH_3OH)]BPh_4$ were structurally analysed by single crystal X-ray diffraction. Each complex exhibits an N_3 face-capping coordination geometry around the metal ion and a stereochemically-rigid hydrophobic cavity around the metal ion's remaining coordination site(s).

Introduction

Many ligand systems, especially those used in the biomimicry of metalloenzymes, are based on N_3 ligands which enforce a face-capping coordination geometry at the metal centre, for example triazacyclononanes[1] (tacn) and tris(pyrazolyl)borates[2] (Tpb). A ligand system which also enforces an N_3 face-capping coordination geometry at the metal and which is attracting increased attention is that based on *cis*,*cis*-1,3,5-triaminocyclohexane (tach).[3–6] tach can coordinate with several first row transition metals giving stable metal complexes with an adamantane-type structure.[7] tach can be easily derivatised to give a wide range of Schiff base ligands.[8] The high stability of tach–metal complexes and the structural versatility in tach-based Schiff base ligands has led to renewed interest in the ligand and its derivatives,[9–13] particularly as ligands in bioinorganic complexes.[9,11,13,14] Our work has concentrated on the triarylpropenylideneamino derivative (Ar-protach ligands). Systems of the protach type, shown in Fig. 1, are attractive because, upon coordination to a metal, a face-capping N_3 coordination geometry is enforced on one face of the metal and the remaining coordination sites are surrounded by a stereochemically-rigid hydrophobic cavity. This cavity is large enough to encapsulate other small ligands.[15] Thus the ligand system has the potential to provide a basis for the modelling of the primary and secondary coordination environments of metals in some metalloenzymes (*e.g.* carbonic anhydrase).[16] Moreover, such systems have also shown potency in catalysing organic reactions.[17] We have prepared a wide range of *cis*-tach derivatives, and to demonstrate the coordinative versatility of the protach ligand system, we report here the synthesis and characterisation of a variety of novel complexes of the derivative *cis*,*cis*-1,3,5-(*E*,*E*)-tris(phenylpropenylideneamino)cyclohexane (Ph-protach).

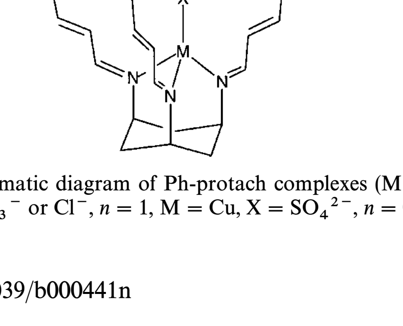

Fig. 1 Schematic diagram of Ph-protach complexes (M = Zn, Ni or Cd, X = NO_3^- or Cl^-, $n = 1$, M = Cu, X = SO_4^{2-}, $n = 0$).

Experimental

Materials

Chemicals were used as received from Aldrich Chemical Company Ltd and Fisons Ltd. Melting points were obtained using a standard Gallenkamp apparatus. NMR spectra were obtained on a JEOL EX270 MHz spectrometer. The spectra were referenced against residual solvent proton peaks. IR spectra were obtained using a Perkin-Elmer 1720 Infra-Red Fourier Transform Spectrophotometer (KBr disks pressed under 6.0 tonnes pressure). Mass spectra were acquired on a Fisons Instruments Autospec using a 0–650 °C temperature range. Analyses were performed by Butterworth Laboratories Ltd, Middlesex, England.

Syntheses of ligand and metal complexes

The Schiff base ligand *cis*,*cis*-1,3,5-(*E*,*E*)-tris(phenylpropenylideneamino)cyclohexane (Ph-protach) was prepared as described previously,[17] and was reacted with a range of metal salts. Discrete cationic complexes were precipitated on the addition of sodium tetraphenylborate to alcoholic solutions containing Ph-protach and the metal salt. The syntheses of the chloride, bromide, iodide, nitrate, acetate, sulfate and perchlorate salts of Cu(II), Co(II), Ni(II), Zn(II) and Cd(II) were attempted (sulfate salts were not coordinated in the presence of $NaBPh_4$). Of these, the complexes $[Zn(Ph\text{-}protach)(SO_4)]$, $[Ni(Ph\text{-}protach)(CH_3CO_2)]BPh_4$, $[Co(Ph\text{-}protach)(ClO_4)]BPh_4$, $[Co(Ph\text{-}protach)(NO_3)]BPh_4$, $[Co(Ph\text{-}protach)(Cl)]BPh_4$, $[Co(Ph\text{-}protach)(Br)]BPh_4$ and $[Co(Ph\text{-}protach)(I)]BPh_4$ have been examined previously,[14,16,17] the remainder, which could be isolated as discrete complexes, are described here. The complexes demonstrate the range of metal ion–anion combinations that Ph-protach will accommodate.

$[Cu(Ph\text{-}protach)(\eta^2\text{-}SO_4)][Cu(Ph\text{-}protach)(\eta^1\text{-}SO_4)(CH_3OH)]$, 1. Ph-protach (0.05 g, 0.11 mmol) was dissolved in methanol (5 ml). To this, a solution of copper(II) sulfate pentahydrate (0.03 g, 0.11 mmol) in methanol (3 ml) was added dropwise. A colour change from pale blue to emerald green

DOI: 10.1039/b000441n

Table 1 Single crystal X-ray crystallographic data for **1** · 2CH$_3$OH, **2**, **3** · 3CH$_2$Cl$_2$ and **4** · CH$_3$OH

	1 · 2CH$_3$OH	**2**	**3** · 3CH$_2$Cl$_2$	**4** · CH$_3$OH
Chemical formula	$C_{34.5}H_{39}CuN_3O_{5.5}S$	$C_{57}H_{53}BClN_3Ni$	$C_{60}H_{59}BCl_7N_3Zn$	$C_{59}H_{6i}BCdN_4O_5$
Formula weight	679.29	884.99	1146.43	1029.33
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
μ(Mo-Kα)/mm^{-1}	0.764	0.496	0.775	0.459
$R1$, $wR2$ [$(I) > 2\sigma(I)$]	0.0493, 0.1206	0.0504, 0.1328	0.0733, 0.1853	0.0323, 0.0806
$R1$, $wR2$ (all data)	0.1042, 0.1485	0.1229, 0.1934	0.1414, 0.2276	0.0533, 0.0965
a/Å	14.056(5)	15.579(3)	15.222(10)	15.642(3)
b/Å	17.494(3)	16.549(3)	19.097(9)	17.746(4)
c/Å	14.397(4)	19.916(2)	10.784(10)	10.348(3)
α/°	90	90	99.61(6)	99.861(19)
β/°	109.49(2)	109.335(10)	103.87(7)	105.154(17)
γ/°	90	90	76.73(4)	76.486(15)
V/Å^3	3337.3(15)	4845.1(13)	2941(4)	2677.1(10)
T/K	293(2)	293(2)	293(2)	296(2)
Z	4	4	2	2
Reflections collected	6114	7496	9459	9800
Independent reflections	5644	6868	9028	9427
R_{int} for equivalent reflections	0.0663	0.0627	0.0403	0.0161

occurred immediately. Emerald green crystals formed overnight and were filtered off and dried in a desiccator (0.06 g, 0.09 mmol, 82%). Mp 276.0–276.5 °C. IR (KBr disk) cm^{-1}: 3412(s), 3060(w), 2923(w), 1631(s), 1607(m), 1593(m), 1449(m), 1217(s), 1174(s), 1134(s), 964(s), 750(s), 691(s), 651(s). Elemental analysis for [Cu(Ph-protach)(η^2-SO$_4$)][Cu(Ph-protach)(η^1-SO$_4$)(CH$_3$OH)], $C_{67}H_{70}N_6Cu_2S_2O_9$: found (calculated); C 61.50 (62.15), H 5.30 (5.45), N 6.50 (6.50%).

[Ni(Ph-protach)(Cl)]BPh$_4$, 2. A solution of nickel(II) chloride hydrate (0.03 g, 0.21 mmol) and sodium tetraphenylborate (0.07 g, 0.21 mmol) in methanol (3 ml) was added to a solution of Ph-protach (0.10 g, 0.21 mmol) in methanol (5 ml). The combined solution was allowed to stand at room temperature for one month, after which time the product formed as red crystals. The crystals were filtered off, washed with methanol and dried in a desiccator (0.11 g, 0.12 mmol, 57%). Mp 222–222.5 °C. IR (KBr disk) cm^{-1}: 3050(w), 3025(w), 3000(w), 2950(w), 1635(s), 1600(m), 1595(s), 1460(w), 1440(w), 1420(w), 1400(w), 1250(w), 1185(s), 1130(m), 1010(w), 750(s), 745(s), 680(s), 675(s), 605(s), 550(w), 505(m). MS FAB (+ve ion): $m/z = 564$ (M$^+$). Elemental analysis for [Ni(Ph-protach)(Cl)] BPh$_4$, $C_{57}H_{53}N_3NiBCl$: found (calculated); C 77.05 (77.35), H 6.05 (6.05), N 4.95 (4.75%).

[Zn(Ph-protach)(Cl)]BPh$_4$, 3. To a stirred solution of Ph-protach (0.20 g, 0.4 mmol) and zinc(II) chloride hydrate (0.05 g, 0.4 mmol) in methanol (50 ml) a solution of sodium tetraphenylborate (0.14 g, 0.4 mmol) in methanol (10 ml) was added dropwise. The resulting white precipitate was filtered off under vacuum, washed with methanol (50 ml) and dried in a desiccator (0.32 g, 0.36 mmol, 90%). Mp 236–237 °C. ^{1}H NMR (CD$_2$Cl$_2$, 270 MHz): [Zn(Ph-protach)(Cl)]$^+$ resonances δ 86.0 (d, 3H, $J = 9.7$ Hz, –N=C*H*–), 7.98 (dd, 3H, $J = 15.8$ Hz, $J' = 9.7$ Hz, =CH–C*H*=CH–), 7.75 (m, 6H, Ar–*H*), 7.58 (m, 9H, Ar–*H*), 7.32 (d, $J = 15.0$ Hz, 3H, Ar–C*H*=), 4.12 (m, 3H, –CR$_2$*H*–), 2.55 (d, 3H, $J = 15.3$ Hz, –C*H*(H)–), 2.09 (d, 3H, $J = 15.0$ Hz, –CH(*H*)–); tetraphenylborate resonances 7.50 (m, 8H, Ar–*H*), 7.17 (t, 8H, $J = 7.3$ Hz, Ar–*H*), 7.00 (t, 4H, $J = 7.3$ Hz, Ar–*H*). IR (KBr disk) cm^{-1}: 3050(w), 3025(w), 3000(w), 2950(w), 1635(s), 1600(m), 1595(s), 1460(w), 1440(w), 1420(w), 1400(w), 1250(w), 1185(s), 1130(m), 1000(w), 950(w), 750(s), 745(s), 680(s), 675(s), 605(s), 550(w), 505(m). MS FAB (+ve ion): $m/z = 570$ (M$^+$). Elemental analysis for [Zn(Ph-protach)(Cl)]BPh$_4$, $C_{57}H_{53}N_3ZnBCl$: found (calculated); C 76.45 (76.80), H 5.90 (6.00), N 4.80 (4.70%).

[Cd(Ph-protach)(NO$_3$)(CH$_3$OH)]BPh$_4$, 4. Ph-protach (0.10 g, 0.26 mmol) was dissolved in methanol (10 ml). To this solution, a solution of cadmium(II) nitrate tetrahydrate (0.48 g, 1.56 mmol) and sodium tetraphenylborate (0.53 g, 1.56 mmol) in methanol (10 ml) was added dropwise. The solution was shaken and allowed to stand overnight in a sealed container. The product precipitated as colourless needles which were filtered off and dried in a desiccator (0.19 g, 0.19 mmol, 73%). Mp 151.0–151.5 °C. ^{1}H NMR (CD$_3$OD, 270 MHz): [CdPh-protach)(NO$_3$)]$^+$ resonances δ 8.33 (d, 3H, $J = 9.5$ Hz, –N=C*H*–), 8.20–7.40 (m, 21H, Ar–*H*; =CH–C*H*=CH–; Ar–C*H*=), 4.12 (m, 3H, –CR$_2$*H*–), 2.55 (d, 3H, $J = 15.3$ Hz, –C*H*(H)–), 2.09 (d, 3H, $J = 15.0$ Hz, –CH(*H*)–); tetraphenylborate resonances 7.38 (m, 8H, Ar–*H*), 6.85 (t, 8H, $J = 7.1$ Hz, Ar–*H*), 6.71 (t, 4H, $J = 7.1$ Hz, Ar–*H*). IR (KBr disk) cm^{-1}: 3479(m), 3053(m), 1626(s), 1607(s), 1593(s), 1479(m), 1450(m), 1424(m), 1266(m), 746(s), 706(s). MS FAB (+ve ion): $m/z = 647$ (M$^+$). Elemental analysis for [Cd(Ph-protach)(NO$_3$)(CH$_3$OH)]BPh$_4$, $C_{58}H_{57}N_4CdBO_4$: found (calculated); C 70.20 (69.85), H 5.60 (5.75), N 5.70 (5.60%).

Other complexes. [Co(Ph-protach)(CH$_3$CO$_2$)(CH$_3$OH)]-BPh$_4$, [Zn(Ph-protach)(NO$_3$)]BPh$_4$, [Zn(Ph-protach) (CH$_3$CO$_2$)]BPh$_4$, [Zn(Ph-protach)(Br)] BPh$_4$, [Cd(Ph-protach) (Cl)(CH$_3$OH)]BPh$_4$ and [Cd(Ph-protach)(Br)]BPh$_4$ · 2CH$_3$OH were prepared in a similar manner and all gave satisfactory elemental analyses.

X-Ray crystallography

To obtain crystals of sufficient quality for X-ray diffraction studies, the compounds isolated from the syntheses were redissolved in a suitable solvent. Crystals of **1** · 2CH$_3$OH and **4** · CH$_3$OH were grown by allowing methanolic solutions to evaporate slowly over a period of a few days and crystals of **2** and **3** · CH$_2$Cl$_2$ were grown from slow evaporation of a dichloromethane/methanol solution.

Structure solution and refinement details. Structures were solved by Patterson methods with SAPI91, expanded using DIRDIF and refined by full-matrix least-squares on F^2 with SHELXL93.[18] Restraints were applied during the refinement of **3** and **4**. In the refinement of **3**, the dichloromethane molecules were restrained to have the same geometry using the SADI command in SHELXL93. In the refinement of **4**, the O(4)–H(4) distance was constrained to equal 0.82(0.03) Å with the DFIX command in SHELXL93. The bonds C(59A)–O(5A) and C(59B)–O5(B) were restrained to be of equal length within 0.03 e.s.d. using SADI. C(59A) and C(59B) were restrained to have the same anisotropic displacement parameters with the EADP command in SHELXL93. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using a rigid model.

A summary of crystallographic data, experimental details and refinement results for **1**–**4** is given in Table 1. Selected bond distances and angles for **1**–**4** are presented in Fig. 2–5 respectively.

CCDC reference number 440/172. See http://www.rsc.org/suppdata/nj/b0/b000441n/ for crystallographic files in .cif format.

Results and discussion

The complexes $[Cu(Ph\text{-}protach)(\eta^2\text{-}SO_4)][Cu(Ph\text{-}protach)(\eta^1\text{-}SO_4)(CH_3OH)]$, **1**; $[Ni(Ph\text{-}protach)(Cl)]BPh_4$, **2**; $[Zn(Ph\text{-}protach)(Cl)]BPh_4$, **3** and $[Cd(Ph\text{-}protach)(NO_3)(CH_3OH)]BPh_4$, **4** can all be prepared in good yield by addition of Ph-protach to the appropriate metal salt (complex **1**) followed by metathesis of one of the anions with BPh_4^- (complexes **2**–**4**). The preparation method is quite general,[14] and can be used to isolate cationic complexes of Ph-protach (complexes **2**–**4**). The remarkable observation that only one of the two anions is metathesised by the BPh_4^- indicates that, in solution, there is one anion directly coordinated to the metal with another non-coordinated; this observation correlates with the observed crystal structures. It is probable that the steric demands of the Ph-protach ligand destabilises coordination of two anions to the metal centre. The cadmium complex, **4**, is the first example of a Ph-protach complex with a 'heavier' metal, and one of few examples of a tach-based ligand coordinated to a non first-row transition metal or Zn(II). Such an observation shows that tach-based ligands are able to coordinate to 'larger' sized metal ions. As yet we have been unsuccessful in isolating tach-based complexes of 'very large' metal ions; actinides and third row transition metals.

The crystal and molecular structures of **1**–**4** (Table 1) all show the same coordination mode of the Ph-protach ligand. In all cases the ligand coordinates in the expected face-capping fashion with the phenylpropenylidene groups surrounding the metal ion's remaining coordination sites. In complexes **2**–**4** the BPh_4^- anion lies 'outside' the cavity created by the phenylpropenylidene groups and is non-coordinating to the metal ions.

The crystal structure of $\mathbf{1}\cdot CH_3OH$, Fig. 2, was best modelled by incorporating the two different coordination geometries of the sulfate anion, shown in the figure, and refining the occupancy of each component against a free variable during the least-squares refinement. The structure can be represented as $[Cu(Ph\text{-}protach)(\eta^2\text{-}SO_4)]_{0.5}[Cu(Ph\text{-}protach)(\eta^1\text{-}SO_4)(CH_3OH)]_{0.5}$, each unit is shown independently in Fig. 2. The first structure (Fig. 2a) lacks a coordinated methanol molecule but has an aniso-bidentate sulfate anion coordinated to the metal.[14] The second structure (Fig. 2b) contains a methanol molecule and a monodentate sulfate coordinated to the copper ion. In both cases, the metal coordination geometry is distorted square pyramidal with N(1) in the apical position: Cu–N(1) 2.175(3), Cu–N(2) 1.994(4), Cu–N(3) 2.001(3) Å. Unusually, Cu–N=C angles vary widely from 124.4(3)° for N(2) to 132.8(3)° for N(1). Aniso-bidentate sulfate structure; Cu–O(4) 1.976(4), Cu–O(2) 1.998(5) Å, Cu–O(2)–S(1) 99.0(3)° and Cu–O(4)–S(1) 109.9(2)°; monodentate sulfate structure Cu–O(4) 1.976(4), Cu–O(8) 2.138(6) Å and Cu–O(4)–S(1) 109.9(2)°. The two geometries demonstrate the flexibility that Ph-protach allows in the metal coordination geometry, and show the effect of solvent coordination on the coordination mode of sulfate. The cavity produced by Ph-protach plays an important role in preventing complex dimerisation through a potentially bridging sulfate anion, thus the binding modes of sulfate to a single metal ion can be studied. Both the flexibility in coordination mode and the inhibition of the formation of bridged dimetal complexes are useful properties for model complexes which aim to mimic the active sites of metalloenzymes.

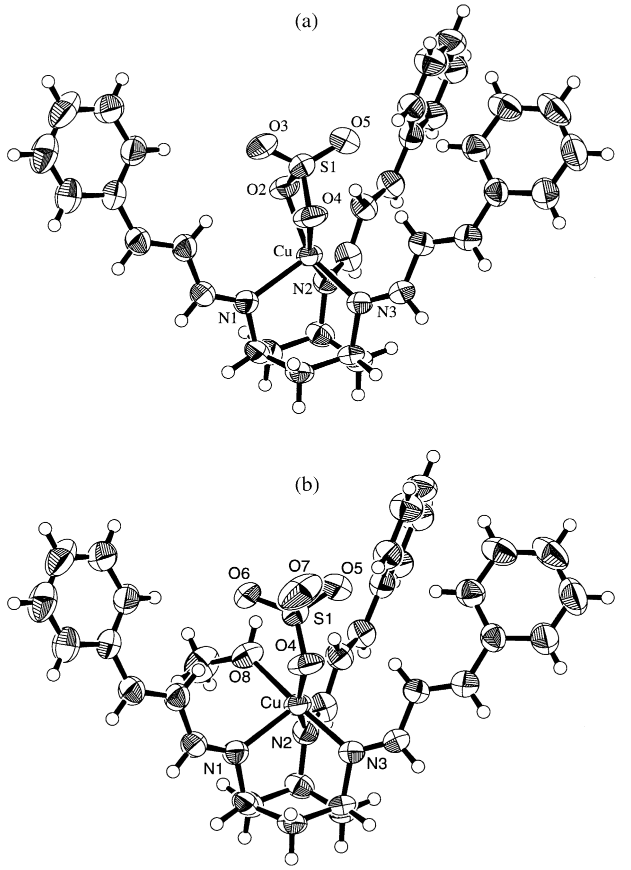

Fig. 2 ORTEP[18] representations (50% probability thermal ellipsoids) of $[Cu(Ph\text{-}protach)(\eta^2\text{-}SO_4)]$ (a) and $[Cu(Ph\text{-}protach)(\eta^1\text{-}SO_4)(CH_3OH)]$ (b). Selected bond lengths (Å) and angles (°): Cu–N(1) 2.175(3), Cu–N(2) 1.994(4), Cu–N(3) 2.001(3), Cu–N(1)–C(7) 132.8(3), Cu–N(2)–C(16) 124.4(3), Cu–N(3)–C(25) 125.8(3); $[Cu(Ph\text{-}protach)(\eta^2\text{-}SO_4)]$ Cu–O(4) 1.976(4), Cu–O(2) 1.998(5); $[Cu(Ph\text{-}protach)(\eta^1\text{-}SO_4)(CH_3OH)]$ Cu–O(4) 1.976(4), Cu–O(8) 2.138(6), Cu–O(4)–S(1) 109.9(2).

In contrast to $\mathbf{1}\cdot CH_3OH$, the coordination geometries exhibited in $[Ni(Ph\text{-}protach)(Cl)BPh_4$, **2** and $[Zn(Ph\text{-}protach)(Cl)]BPh_4\cdot 3CH_2Cl_2 (= \mathbf{3}\cdot 3CH_2Cl_2)$ show a marked lack of flexibility in the metal coordination geometries. The structures of **2** and $\mathbf{3}\cdot 3CH_2Cl_2$ are shown in Figs. 3 and 4 respectively. Both structures show the expected face-capping N_3 coordination geometry and the rigid cavity around the metal ion. The structures demonstrate almost isostructural coordination geometries; both Ni and Zn have C_{3v} coordination symmetries, with the chloride anion in the axial position [Ni(1)–Cl(1) 2.1964(15), Zn(1)–Cl(1) 2.188(2) Å]. Average M–N=C angles show some variation with Ni–N=C 127.3(5) and Zn–N=C 130.5(5)°. The zinc complex structure incorporates three molecules of dichloromethane, with two molecules sandwiched between adjacent phenylpropenylidene groups of the cavity, while the nickel complex does not contain any solvent molecules. We have reported previously the role of the ligand cavity in trapping solvent molecules[14] and complex **3** is a good example of this phenomenon, with the CH_2Cl_2 trapped between the phenylpropenylidene groups. These previous examples in addition to **2** show the ability of the cavity to encapsulate volatile molecules near to the metal centre. It is useful to note that encapsulated water molecules are a common observation in the active sites of several metalloproteins.[19]

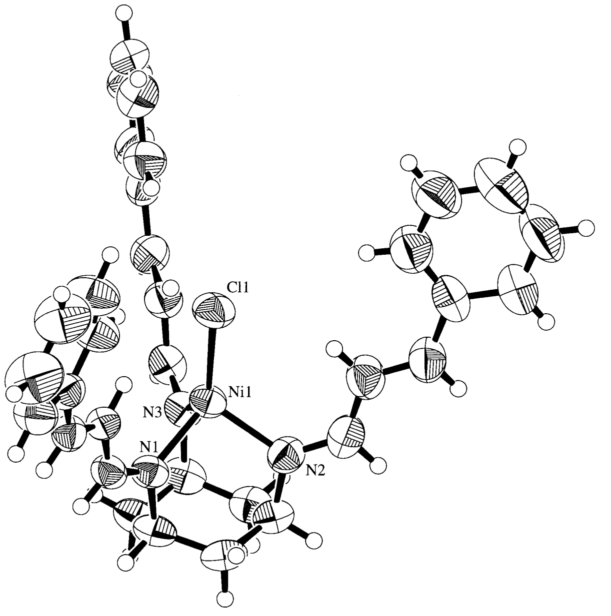

Fig. 3 ORTEP[18] representation (50% probability thermal ellipsoids) of [Ni(Ph-protach)(Cl)]BPh_4 (BPh_4 anion omitted for clarity). Selected bond lengths (Å) and angles (°): Ni(1)–Cl(1) 2.1964(15), Ni(1)–N(1) 1.989(4), Ni(1)–N(2) 1.995(4), Ni(1)–N(3) 1.989(4); N(1)–Ni(1)–Cl(1) 122.66(14), N(2)–Ni(1)–Cl(1) 121.20(15), N(3)–Ni(1)–Cl(1) 124.25(14).

Tetrahedral complexes of Ni(II) with chelating ligands can be prepared by employing sterically hindered ligands or ligands which are capable of forming a restricting cavity around the metal atom. In **2**, the steric restraints of the cavity presumably aid a tetrahedral coordination environment around the metal centre, resulting in the observed four coordinate complex. Despite this apparent preference for four coordinate complexes, the cavity can accommodate six coordinate complexes, as reported previously;[16] there is clearly a balance between electronic and steric effects in determining which metal coordination geometry is observed.

The complex [Cd(Ph-protach)(NO_3)(CH_3OH)]BPh_4·$2CH_3OH$(=**4**·$2CH_3OH$) is shown in Fig. 5. Again, the ligand coordinates in a N_3 face-capping fashion with a cavity surrounding the remaining metal coordination sites. This complex displays a distorted octahedral coordination geometry, with bidentate nitrate [Cd–O distances of 2.341(2) Å and 2.405(2) Å to the coordinated nitrate oxygen atoms] and a methanol molecule [Cd–O 2.396(2) Å] occupying the site left unoccupied by the ligand. A second methanol molecule, positioned in the 'upper' part of the cavity, is hydrogen bonded to the cadmium-bound methanol: O(4)···O(5A) 2.78(12), O(4)···O(5B) 2.71(14) Å; O(4)–H(4)···O(5B) 174(17)° in an analogous fashion to the complex [Zn(Ph-protach)(SO_4)].[14] The difference between the slightly longer M–N bond lengths in **4** and the M–N lengths in **1**–**3** is reflected in the distance between the phenylpropenylidene groups. In **4** the phenylpropenylidene groups are significantly more splayed than in **1**–**3**. In effect the small changes in metal coordinate bond lengths are 'amplified' by the stereochemically rigid phenylpropenylidene groups.

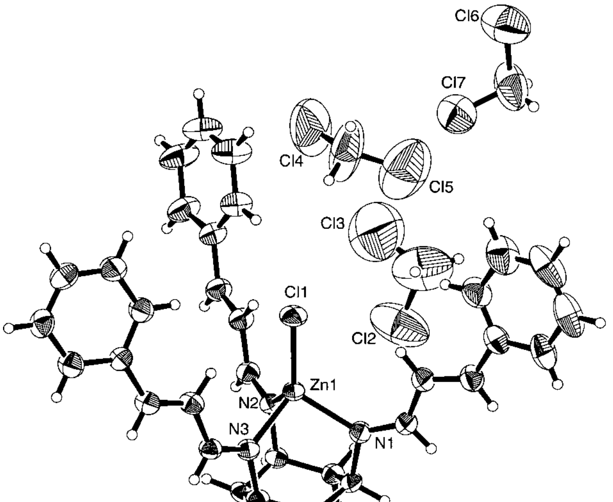

Fig. 4 ORTEP[18] representation (30% probability thermal ellipsoids) of [Zn(Ph-protach)(Cl)]BPh_4·$3CH_2Cl_2$ (BPh_4 anion omitted for clarity). Selected bond lengths (Å) and angles (°): Zn(1)–Cl(1) 2.188(2), Zn(1)–N(1) 2.028(5), Zn(1)–N(2) 2.041(5), Zn(1)–N(3) 2.039(5); N(1)–Zn(1)–Cl(1) 120.20(16), N(2)–Zn(1)–Cl(1) 123.23(15), N(3)–Zn(1)–Cl(1) 121.81(16).

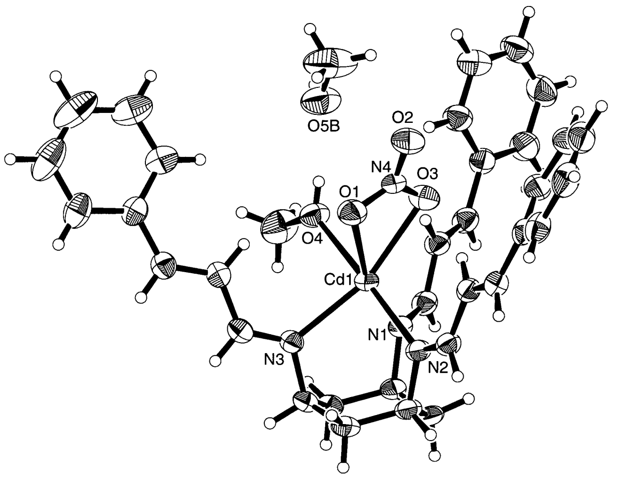

Fig. 5 ORTEP[18] representation (30% probability thermal ellipsoids) of [Cd(Ph-protach)(NO_3)(CH_3OH)]BPh_4·$2CH_3OH$ (BPh_4 anion omitted for clarity). Selected bond lengths (Å) and angles (°): Cd(1)–N(1) 2.273(2), Cd(1)–N(2) 2.351(2), Cd(1)–N(3) 2.265(2), Cd(1)–O(1) 2.341(2), Cd(1)–O(3) 2.405(2), Cd(1)–O(4) 2.396(2), O(4)–O(5B) 2.71(14); O(4)–H(4)···O(5B) 174(17), Cd(1)–N(2)–C(16) 127.5(2), Cd(1)–N(1)–C(7) 126.1(2), Cd(1)–N(3)–C(25) 127.6(2).

Conclusions

The ligand *cis,cis*-1,3,5-(*E,E*)-tris(phenylpropenylideneamino) cyclohexane (Ph-protach) can coordinate to a range of metal ions, including second row transition metals. Such complexes demonstrate that the ligand coordinates to the metal in a N_3 face-capping geometry, with the phenylpropenylidene groups of the ligand forming a rigid hydrophobic cavity around the metal ion's remaining coordination sites. Other small exogenous ligands coordinated to the metal ion are encapsulated within this cavity. The complexes show that a range of metal coordination geometries can be accommodated by the cavity of Ph-protach, however there appears to be a preference for four coordinate C_{3v} coordination, presumably as a result of the steric constraints of the cavity. Moreover, the complexes show a significant degree of solvent inclusion within the cavity, much like the encapsulation of water molecules in the active sites of metalloproteins. As such, complexes of Ph-protach are potential mimics of metalloenzyme active sites where both primary and secondary coordination environments of the metal are modelled.

Acknowledgements

B.G. and S.P.F. acknowledge the EPSRC for the provision of maintenance grants.

References

1 E. Kimura, *Prog. Inorg. Chem.*, 1994, **41**, 443.

2 R. Alsfasser, S. Trofimenko, A. Looney, G. Parkin and H. Vahrenkamp, *Inorg. Chem.*, 1991, **30**, 4098.

3 F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, 1957, **79**, 1572.

4 F. L. Urbach, J. E. Sarneski, L. J. Turner and D. H. Busch, *Inorg. Chem.*, 1968, **7**, 2169.

5 H. Stetter and J. Bremen, *Chem. Ber.*, 1973, **106**, 2523.

6 E. B. Fleischer, A. E. Gebala and D. R. Swift, *J. Chem. Soc., Chem. Commun.*, 1971, 1280.

7 R. A. D. Wentworth and J. J. Felten, *J. Am. Chem. Soc.*, 1968, **90**, 621.

8 J. E. Bollinger, J. T. Mague and D. M. Roundhill, *Inorg. Chem.*, 1994, **33**, 1241.

9 J. E. Bollinger, J. T. Mague, C. J. O'Connor, W. A. Banks and D. M. Roundhill, *J. Chem. Soc., Dalton Trans.*, 1995, 1677.

10 T. Bowen, R. P. Planalp and M. W. Brechbiel, *Bioorg. Med. Chem. Lett.*, 1996, 807.

11 T. Itoh, H. Hisada, T. Sumiya, M. Hosono, Y. Usui and Y. Fujii, *Chem. Commun.*, 1997, 677.

12 G. Park, F. H. Lu, N. Ye, M. W. Brechbiel, S. V. Torti, F. M. Torti and R. P. Planalp, *J. Biol. Inorg. Chem.*, 1998, 449.

13 X. S. Tan, Y. Fujii, T. Sato, Y. Nakano and M. Yashiro, *Chem. Commun.*, 1999, 881.

14 B. Greener, M. H. Moore and P. H. Walton, *Chem. Commun.*, 1996, 27.

15 C. J. Boxwell and P. H. Walton, *Chem. Commun.*, 1999, 1647.

16 B. Greener, L. Cronin, M. H. Moore and P. H. Walton, *J. Chem. Soc., Dalton Trans.*, 1996, 3337.

17 B. Greener and P. H. Walton, *J. Chem. Soc., Dalton Trans.*, 1997, 3733.

18 C. K. Johnson, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976. P. T. Beurskens, G. Admiraal, G. Beurskens, G. Bosman, W. P. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF program system, Technical report of the crystallography laboratory, University of Nijmegen, The Netherlands, 1992. G. M. Sheldrick, SHELXL93, A Computer Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993. F. Hai-Fu, SAPI91, structure analysis programs with intelligent control, Rigaku Corporation, Tokyo, Japan, 1993.

19 D. N. Silverman and S. Lindskog, *Acc. Chem. Res.*, 1988, **21**, 30.