20 The co-ordination chemistry of macrocyclic ligands

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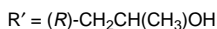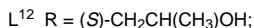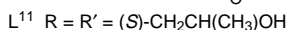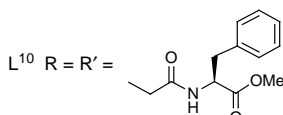
1 Introduction

This report covers the co-ordination chemistry of macrocyclic ligands as described in 1997. The report does not extend to the description of porphyrins and phthalocyanines. Pendant-arm macrocycles are discussed in the section relating to the parent macrocycle, and conjugated or unsaturated ligand systems are referred to in the section relating to the parent saturated system. Of particular note in last year's literature is an increased interest in the co-ordination chemistry of tetradentate ligands and the photochemistry and electrochemistry of supramolecular systems.

2 Tridentate macrocycles

Nitrogen donor ligands
The complex $[Cu^{II}Cl_2(L^1)]$ cleaves double and single stranded RNA hairpin structures at pH 7.2 and 37 °C.[1] Hydrolysis occurs at phosphodiester bonds and does not involve interaction with specific nucleotide bases. Both single and double stranded regions were cleaved with most activity noted in the loop regions. A density functional study of the energetics of oxygen binding and isomerism in dinuclear complexes of L^1 has been reported.[2] Nine isostructural complexes of general formula $[(L^2)M^{II}(\mu\text{-}X)_3M^{II}(L^2)]$ $[BPh_4]$ (M = Mn, Fe, Co, Ni or Zn; X = Cl or Br) ha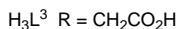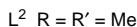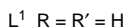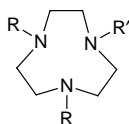ve been characterised by X-ray crystallography.[3] The metal centres in the Mn, Co and Ni complexes are ferromagnetically coupled ($J_{MnMn} = -11.6$; $J_{CoCo} = -13.1$; $J_{NiNi} = -10.5 \text{ cm}^{-1}$) whilst the Fe complex is antiferromagnetically coupled ($J_{FeFe} = +5.8 \text{ cm}^{-1}$). The exchange mechanisms were investigated by variable-temperature magnetic susceptibility measurements and by magnetic and zero-field Mössbauer spectroscopy. A series of six linear trinuclear oximato-bridged complexes of the general formula $[(L^2)Mn^{III}\{\mu\text{-}(nox)_3M^{II}\}Mn^{III}(L^2)]^{2+}$ and $[(L^2)Mn^{IV}\{\mu\text{-}(nox)_3M^{II}\}Mn^{IV}(L^2)]^{4+}$ (M = Mn, Cu or Zn) have been prepared and shown to be quasi-isostructural.[4] All six complexes show two reversible and two quasi-reversible one-electron processes. Most interestingly, in the Mn_3 species the central ion is redox inactive but there is unequivocal evidence for the coupling of the terminal metal centres. High oxidation state rhenium chemistry with L^2 has been investigated by X-ray crystallography and electrochemistry.[5] In acidic media $[Re^{VII}O_3(L^2)]^+$ showed two quasi-reversible reductions with reversibility increasing with pH.

L^1 R = R′ = H

L^2 R = R′ = Me

H$_3$L^3 R = CH$_2$CO$_2$H

L^4 R = R′ = (structure with N–NH)

L^5 R = R′ = (structure with N, N)

H$_3$L^6 R = R′ = (phenol with Me, Me)

H$_3$L^7 R = R′ = (phenol with Bu^t, Bu^t)

H$_3$L^8 R = R′ = (phenol with Et, Bu^t, OMe)

HL^9 R = Pr^i; R′ = (phenol with Et, Bu^t, Bu^t)

L^{10} R = R′ = (phenylalanine methyl ester amide structure)

L^{11} R = R′ = (S)-CH$_2$CH(CH$_3$)OH

L^{12} R = (S)-CH$_2$CH(CH$_3$)OH;

R′ = (R)-CH$_2$CH(CH$_3$)OH
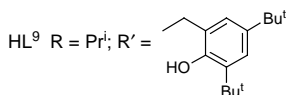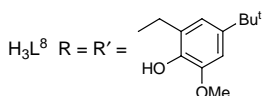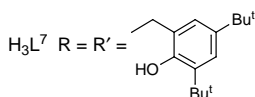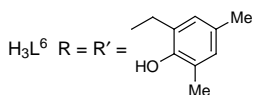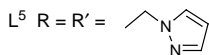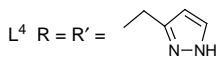
A re-examination of the solid-state structure of '[Ni^{III}(L^3)]' was recently undertaken and energy-dispersive spectroscopy on an original sample of material indicated that the crystal did not contain Ni^{III} but Co^{III}.[6] The Fe^{II}–Fe^{III} complexes of the novel pendant-arm triazacyclononane ligands L^4 and L^5 have been structurally character-ised as the high-spin (Fe^{II} centre) mixed-valence complexes [Fe^{II}(L^4)][Fe^{III}Cl$_4$]Cl and [Fe^{II}(L^5)][Fe^{III}Cl$_4$]Cl.[7] The diamagnetic complex [Fe^{II}(L^4)][ClO$_4$]$_2$ was also ob-tained which indicates that ligand-field strength in Fe^{II} complexes of L^4 is close to the high-spin–low-spin crossover point. The synthesis and electrochemistry of vanadium- and cobalt-(III) complexes of ligands H$_3$L$^{6–8}$ and HL^9 have been described.[8] Com-plexes such as [V^{IV}(L^6)][PF$_6$] show reversible metal-centred one-electron oxidations, whereas complexes such as [Co^{III}(L^7)] show three reversible one-electron oxidations. These latter oxidised species were shown by EPR and electronic spectroscopy to contain ligand-centred phenoxyl radicals. The complexes [Co^{III}(acac)(L^9)]$^+$ and [Co^{III}(L′)(L^9)]$^+$ (H$_2$L′ = 1,2,3,4-tetrachlorocatechol) can be reversibly oxidised to the phenoxyl radical species [Co^{III}(acac)(L^9)]$^{•2+}$, [Co^{III}(L′)(L^9)]$^{•+}$ and [Co^{III}(L′)-(L^9)]$^{2•2+}$. The last two species are (phenolato)(semiquinonato)cobalt(III) and (phenoxyl)(semiquinonato)cobalt(III) respectively. Macrocycles H$_3$L$^{6–9}$ also form stable octahedral complexes with Ga^{III}, Sc^{III}, Fe^{III}, Mn^{III} or Mn^{IV}.[9] Again many of these complexes show three reversible ligand-centred one-electron oxidations giving prod-ucts in which one, two or three phenoxyl radical ligands are present. A novel pendant-arm [9]aneN$_3$ derivative (L^{10}), prepared from the methyl ester of phenylalanine, forms complexes of general formula [M^{II}(L^{10})][M^{II}Cl$_4$] (M = Cu or Zn).[10] These materials were prepared with a view to the synthesis of metal-templated peptide triple-helix formation. The ligands L^{11} and L^{12} display strong selectivity for Mg^{II} over Ca^{II} ions in

solution as demonstrated by ^{13}C NMR spectroscopy;[11] L^{12} bound both Mg^{II} and Ca^{II} whilst ligand L^{11} bound only Mg^{II} with a selectivity of $K_{MgL^{11}}/K_{CaL^{11}} = 590$. A molecular mechanics study of this remarkable selectivity was also presented.

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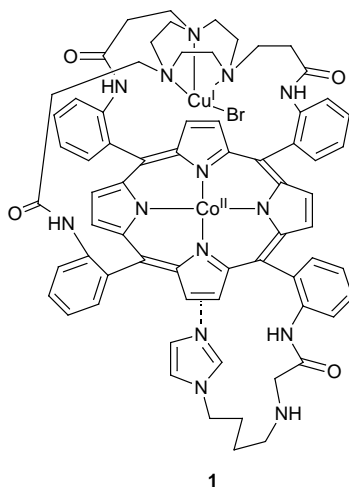
A triazacyclononane unit has been used as one component of a functional cytochrome c oxidase model.[12] Complex **1** consists of a tetraphenylporphyrin cobalt(II) group to which a triazacyclononyl copper(I) bromide moiety is bound *via* amide linkages. Redox experiments demonstrated that the complex irreversibly bound one mole equivalent of molecular oxygen to form a very stable (as demonstrated by mass spectrometry and TLC) bridged peroxo species. The co-ordinated oxygen could be reduced by four equivalents of cobaltocene, whilst electrochemical measurements at physiological pH indicated complete dioxygen reduction in a four-electron process. Triazacyclononane groups bearing pendant alcohol donors have been immobilised on a silica (MCM-41) support (**2**).[13] Subsequent treatment of this material with MnSO$_4$ yields, in combination with H$_2$O$_2$, an effective epoxidation catalyst.

2
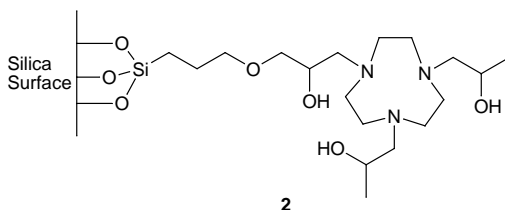
The novel ligand L^{13} was prepared by malonic acid condensation using pyridine building blocks and 1,3,5-tris(bromomethyl)benzene.[14] Bicyclic L^{13} shows exceptionally strong Ag^I binding and unusually high (for a pyridine-based ligand) selectivity over both Cu^I and Cu^{II}. Three new xylene-derived bis(triazacyclononane) ligands have been prepared and their Cu^{II} chemistry investigated.[15] Upon reaction of L^{14} with CuI, and subsequent aerial oxidation the binuclear hydroxo-bridged complex [Cu$_2$(μ-OH)$_2$(L^{14})][BPh$_4$]$_2$ was isolated. The five-co-ordinate copper centres display pseudo-
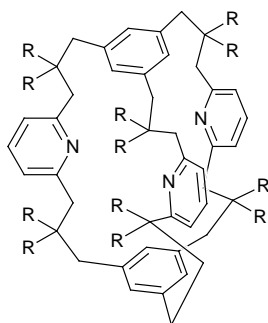
L¹³ R = CO₂Et
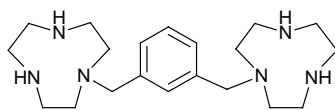
L¹⁴

square-pyramidal geometry. Magnetic susceptibility studies in the range 1.8–300 K showed weak antiferromagnetic coupling ($J = -159 \pm 8\,\text{cm}^{-1}$) between the Cu^{II} centres. The Cu^{II} chemistry of the potentially ditopic ligands L^{15-17} has been investigated.[16] Compound L^{15} exclusively forms mononuclear complexes $[Cu^{II}(L^{15})]^{2+}$ in dilute aqueous solution whilst L^{16} and L^{17} form partially protonated mononuclear complexes or dinuclear complexes. These complexes may be present as oligomers or dimers in aqueous solution. Reaction of Cu^{I} salts with L^{18} and subsequent treatment with O_2 at $-80\,°C$ yields the oxo-bridged dimer $[Cu_2(\mu\text{-O})_2(L^{18})]^{2+}$.[17] It is of note that the presence of the ethylene bridge between the two rings prevents formation of a
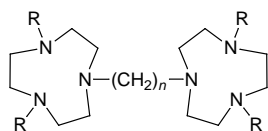
L¹⁵ n = 2; R = H
L¹⁶ n = 5; R = H
L¹⁷ n = 6; R = H
L¹⁸ n = 2; R = Prⁱ
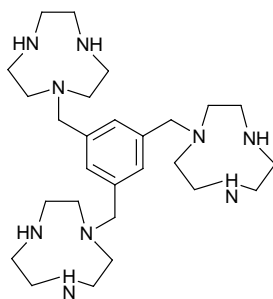
L¹⁹
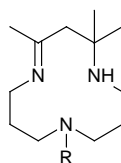
L²⁰ R = H
L²¹ R = Me

peroxo species in contrast to the related bis(tacn-Prⁱ₃) species. The interesting tritopic ligand L^{19} reacts with Cu^{II} salts to yield a trinuclear complex in which all the Cu^{II} sites are identical.[18] Reaction of $[Cu^{II}_3(H_2O)_6(L^{19})][ClO_4]_6\cdot6H_2O$ with a phosphate source yields $\{[Cu^{II}_3(\mu\text{-OH})(\mu_3\text{-HPO}_4)(H_2O)(L^{19})][PF_6]_3\cdot6H_2O\}_n$ which has an infinite lattice structure; the trinuclear Cu^{II} centre bears strong similarities to the trinuclear Cu sites in laccase and ascorbate oxidase. The EPR and magnetic properties of these complexes were also described. The hydroxy-bridged complexes $[\{Ni^{II}(\mu\text{-}$

OH)}$_2$L][ClO$_4$]$_2$ (L = L^{20} or L^{21}) react with β-ketoimines to yield mononuclear five-co-ordinate complexes of general formula [Ni^{II}{C$_6$H$_5$COCHC(NR)CH$_3$}L][ClO$_4$] (R = C$_6$H$_5$, *p*-C$_6$H$_4$CH$_3$, *p*-C$_6$H$_4$OCH$_3$, *o*-C$_6$H$_4$CH$_3$ or *o*-C$_6$H$_4$OCH$_3$).[19] The complexes were characterised by X-ray crystallography and by paramagnetic ^{1}H NMR spectroscopy.

L^{22} R = CH$_2$—

L^{23} R = CH$_2$—

L^{24} R = CH$_2$—

L^{25} R = H
L^{26} R = Me
L^{27} R = Et
L^{28} R = (CH$_2$)$_3$OMe
L^{29} R = (CH$_2$)$_2$OEt

L^{30} R = (CH$_2$)$_3$NH$_2$
L^{31} R = (CH$_2$)$_3$SMe
L^{32} R = (CH$_2$)$_3$PPh$_2$
L^{33} R = CH$_2$Ph
L^{34} R = Pr^i

L^{35}
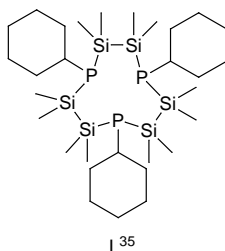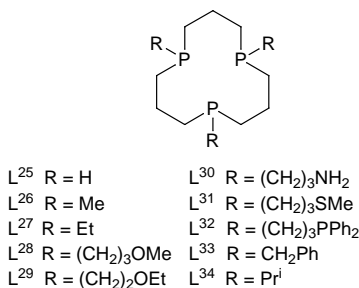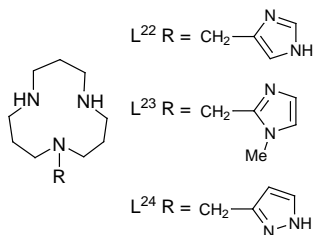
Three new imidazole- and pyrazole-substituted [12]aneN$_3$ ligands have been prepared (L$^{22-24}$).[20] Their basicity constants and co-ordination chemistry with first-row transition metals were examined. The crystal structures of the complexes [{Fe^{II}Cl(L^{24})}$_2$][BPh$_4$]$_2$ and [{Ni^{II}Cl(L^{24})}$_2$][BF$_4$]$_2$ revealed chloro-bridged dimeric structures with approximately octahedral geometry at the metal centres.

Phosphorus-donor ligands

The Cr and Mo tricarbonyl complexes of the tri-secondary phosphine ligand L^{25} have been used to prepare a wide range of tri-tertiary macrocycles L$^{26-34}$ by deprotonation and subsequent alkylation or by radical-catalysed hydrophosphination of appropriate alkenes.[21] These routes should prove useful in preparing a range of pendant-arm phospha macrocycles with a number of additional donor groups. The Fe^{II}, Ru^{II} and Rh^{III} complexes of L^{34} have been investigated.[22] The structure of [Rh^{III}Cl$_3$(L^{34})] has the macrocycle in its typical face-capping mode with the three chloride ligands occupying *cis* sites. In an interesting template synthesis the sequential treatment of *fac*-[Mo(CO)$_3$(PH$_2$Cy)$_3$] with Bu^{n}Li, [ClSiMe$_2$]$_2$ and Bu^{t}Li yields the complex [Mo(CO)$_3$(L^{35})].[23] The ligand could be removed from the template by addition of other strongly chelating ligands, but could not be isolated in a pure form.

Sulfur and mixed-donor ligands

The synthesis and catalytic properties of the trithiacyclononane (L^{36}) complex
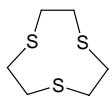
L^{36}
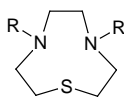
L^{37} R = H
L^{38} R = Me

[Rh^I(PPh$_3$)$_2$(L^{36})][PF$_6$] have been described.[24] This complex readily undergoes a number of ligand substitution reactions and catalyses the demercuration of bis(alkynl) mercurials. Mononuclear and dinuclear Fe^{II} and Fe^{III} complexes of the 1-thia-4,7-diazacyclononanes L^{37} and L^{38} have been prepared.[25] Iron(III) chloride reacts with L^{37} (or L^{38}) to yield complexes [Fe^{III}(L^{37,38})]Cl$_3$, which upon subsequent treatment with sodium acetate and NH$_4$PF$_6$ yields the dinuclear complexes [Fe^{III}$_2$(μ-O)(μ-O$_2$CMe)$_2$(L^{37,38})$_2$][PF$_6$]$_2$. The complex [Fe^{II}$_2$(OH)(μ-O$_2$CMe)$_2$(L^{38})$_2$][ClO$_4$] was prepared anaerobically by treatment of L^{38} with a methanolic solution of Fe^{II}[ClO$_4$]$_2$. Studies of the temperature-dependent magnetic susceptibility showed that all these dinuclear complexes were antiferromagnetically coupled ($J = -125$ cm^{-1}, Fe^{III}$_2$ complexes; $J = -7.4$ cm^{-1}, Fe^{II} complexes). 1-Thia-4,7-diazacyclononane has also been used in the synthesis of a range of sandwich and half-sandwich complexes which were crystallographically characterised.[26] They include [V^{IV}OCl$_2$(L^{37})], [Fe^{II}(L^{37})$_2$][ClO$_4$]$_2$, [Zn^{II}(L^{37})$_2$][PF$_6$]$_2$, [Ru^{II}(cym)(L^{37})][BPh$_4$]Cl$_2$·MeCN, [Rh^{III}Cl$_3$(L^{37})] ·H$_2$O, [Re^{VII}O$_3$(L^{37})][Re^{VII}O$_4$] and [Tl^I(L^{37})][ClO$_4$]. Cobalt(II), Cu^I and Pd^{II} complexes of the oxathia crown L^{39} have been prepared and structurally characterised.[27] In the solid state the complex [Pd^{II}Cl$_2$(L^{39})] shows a long apical interaction [2.968(3) Å] with the ring oxa function. The Cu^I complexes included both mononuclear [Cu^I(L^{39})$_2$]$^+$ and dinuclear [{Cu^{I}Br(L^{39})}$_2$] species. The cation [Co^{II}(L^{39})$_2$]$^{2+}$ has the typical sandwich structure of bis([9]aneX$_3$) (X = donor atom) complexes, with distorted octahedral geometry; it is low spin over a wide temperature range. The Mo-templated synthesis of L^{40} yields the complex [Mo(CO)$_3$(L^{40})] which upon reaction with bromine yields the seven-co-ordinate complex [MoBr$_2$(CO)$_2$(L^{40})].[28]
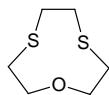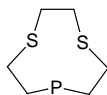
L^{39} L^{40}

3   Tetradentate macrocycles

Nitrogen-donor ligands

The aquation of *cis*-[Co^{III}Cl$_2$(L^{41})]$^+$ in dilute HNO$_3$ has the largest reported rate constant of a *cis*-dichloro complex of a saturated macrocycle.[29] The activation parameters indicated that the rate-determining step was the deprotonation of the substrate. In a recent NMR study the equilibration of *syn* and *anti* isomers of [Co^{III}(S-Ala − H)(L^{42})]$^{2+}$ occurs by two simultaneous mechanisms.[30] The major mechanism

is a base-catalysed one-ended process in which the co-ordinated amino acid partially dissociates to become monodentate. The minor mechanism involves the deprotonation of the amino acid (at the α-carbon) to yield a planar intermediate, effectively an epimerisation process.

L[41] R = R' = H
L[42] R = H; R' = Me

L[43]
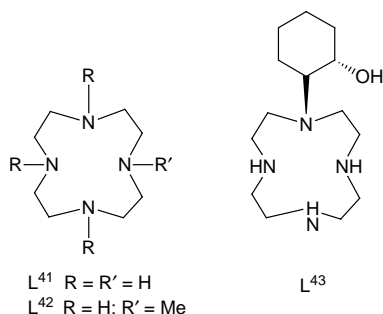
The rate constants of Ca^{II} complex formation for a range of cyclic (tetradentate) and acyclic pendant-arm carboxylate cyclen (L^{41}) derivatives have been determined.[31] In all cases lower rate constants were observed for the macrocyclic ligands compared to those of the acyclic ligands. Plutonium(IV)-selective ligands, including pendant derivatives of cyclen (L^{41}), have been reviewed.[32]

The cyclen-derived ligand L^{43} bears a single pendant arm.[33] Interestingly *cis*-cyclohexene oxide reacts only once (even when used in large excess) with [12]aneN$_4$. The Cu^{II} complex $[Cu(L^{43})][ClO_4]_2$ has five-co-ordinate copper with the Cu^{II}–alcohol distance being somewhat compressed (2.130 Å) from the usual value (≈ 2.25 Å) due to steric congestion between the bulky cyclohexyl group and the macrocyclic ring.

H_2L^{44} R = H; R' = CH_2CO_2H

H_2L^{45} R = CH_2CH_2OH;
        R' = CH_2CO_2H

H_2L^{46} R = (*S*)-$CH_2CH(Me)OH$;
        R' = CH_2CO_2H

H_4L^{47} R = $CH_2P(O)(OEt)OH$;
        R' = CH_2CO_2H

H_4L^{48} R = R' = CH_2CO_2H

L^{49} R = R' = CH_2-N (pyrazolyl)

L^{50} R = H; R' = CH_2-N (pyrazolyl)

L^{51} R = R' =

L^{52} R = R' =

L^{53} R = R' = CH_2CH_2SMe
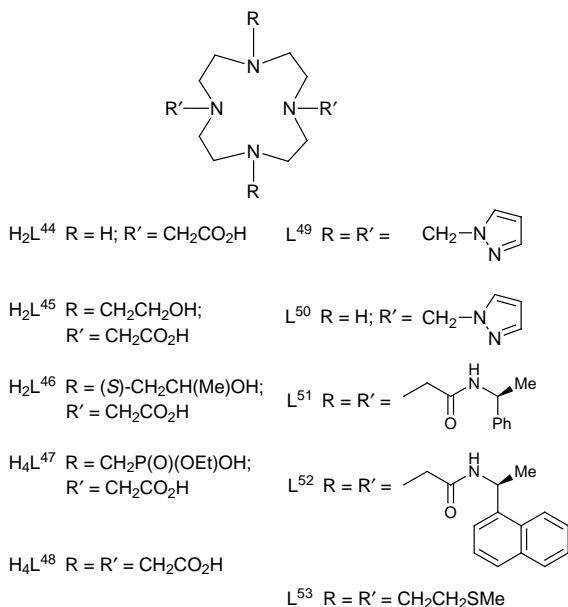
A range of new ligands ($H_2L^{45,46}$ and H_4L^{47}) based upon the bis (pendant arm) ligand H_2L^{44} (H_2doda) has been prepared.[34] Extensive investigation of their Mg^{II}, Ca^{II} and Ln^{III} complexes was undertaken by a range of techniques including potentiometry, NMR spectroscopy and proton relaxivity measurements. The Ni^{II} and Zn^{II} co-ordination chemistry and the protonation constants of H_2L^{44} have been investigated.[35] The crystal structure of the complex $[Ni^{II}(L^{44})]\cdot0.5HClO_4\cdot1.5H_2O$ showed a pseudo-octahedral metal centre with the carboxylate donors occupying *cis* sites. The protonation constants of the ligand indicated that the secondary amine groups were protonated first, then the carboxylates and finally the tertiary amine sites. Carbon-13 NMR spectroscopy of the Zn complex indicates a C_2 symmetric structure similar to that observed for the Ni^{II} species. A range of tetrasubstituted cyclen and cyclam complexes bearing two- and three-carbon pendant carboxylate groups have been examined crystallographically and in a molecular modelling study.[36] The single-crystal structure of the novel dota (H_4L^{48}) complex $Na[La^{III}(L^{48})La^{III}(HL^{48})]\cdot10H_2O$ shows that each metal centre is nine-co-ordinate with eight donors derived from the ligand and one from a bridging carboxylate group.[37] Group 12 metal complexes of the potentially octadentate ligands L^{49} and L^{50} have been reported.[38] The crystal structure of $[Cd^{II}(L^{49})][BPh_4]_2$ indicated an eight-co-ordinate structure. Reaction of L^{50} with Zn^{II} and Hg^{II} salts yields the complexes $[M^{II}L][X]_2$ ($M = Zn^{II}$, $X = ClO_4^-$; $M = Hg^{II}$, $X = PF_6^-$) in which the ligand has lost two pendant groups from *trans* ring positions.

NMR spectroscopic studies show that the Eu^{III} and Tb^{III} complexes of L^{51} are structurally rigid in solution.[39] The Tb^{III} complex is highly luminescent with indirect (phenyl chromophore, $\lambda = 254$ nm) or direct ($\lambda = 380$ nm) irradiation; the latter yielded an intensely circularly polarised emission. The Eu^{III} complex of the analogous naphthyl ligand L^{52} displays strong exciton coupling between adjacent aromatic chromophores.[40] The crystal structure of $[Na(L^{52})][CF_3CO_2]$ revealed a twisted antiprismatic co-ordination geometry in which adjacent naphthyl substituents are orthogonal, important in explaining the exciton coupling in this complex. The Eu^{III} complex of L^{52} also possessed a well defined metal-centred circularly polarised emission. The pendant thioether ligand L^{53} forms an exceptionally stable Ag^I complex ($\log K = 19.63$).[41] It is interesting to note that in the solid state the metal centre is six-co-ordinate being bonded to four nitrogen and two sulfur ligators, with the remaining sulfur donors unco-ordinated.

The kinetics of the reaction of the Fe^{II} complex of cyclam (L^{54}) with hydrogen
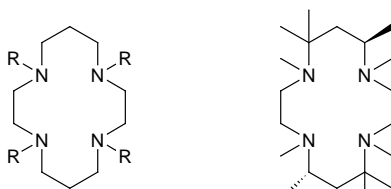
L^{54} R = H
L^{55} R = Me
L^{56} R = $CH_2CH_2OCH_2R_F$
         R_F = perfluoroalkyl
L^{57} R = $CH_2CH(CH_3)OH$
L^{58} R = CH_2PPh_2

L^{59}

peroxide in acetonitrile solution revealed[42] that two oxidation processes occur, with both the metal centre and the ligand being oxidised. An electrochemical study of the kinetics of conversion of the *trans*-I to the *trans*-III isomer of $[Ni^{II}(L^{54})][ClO_4]_2$ indicated that the isomerisation reaction is largely independent of pH and that the half-life of the transient intermediate *trans*-I-$[Ni^{III}(L^{54})]^{3+}$ was ≈ 400 ms.[43] Interestingly this half-life is approximately 10^9 times shorter than that of the corresponding *trans*-I-$[Ni^{II}(L^{54})]^{2+}$ species. The structure and magnetic properties of *catena*-$[Ni^{II}(\mu$-$Cr^{VI}O_4$-$O,O')(L^{54})]$ have been described.[44] The structure consists of one-dimensional chains of $[Ni^{II}(L^{54})]^{2+}$ bridged by $Cr^{VI}O_4^{2-}$ which co-ordinate to axial $Ni^{II}(L^{54})$ positions. The temperature-dependent magnetic susceptibility indicated that adjacent metal centres were ferromagnetically coupled *via* the chromate bridges. The photochemical properties of Cu^{II} macrocyclic complexes including $[Cu^{II}(L^{54})]^{2+}$ may be modified by the addition of polyelectrolytes; steady-state photolysis of solutions containing polycarboxylates [*e.g.* sodium poly(acrylate)] yielded the corresponding Cu^{I} species.[45] The polyelectrolyte serves as a sacrificial electron donor and prevents the degradation of Cu^{I} complexes by hydrolysis and macrocycle cleavage. The visible light photolysis of a range of $Ru^{II}L^{54}$ complexes of the general formula *trans*-$[Ru^{II}L'(L^{54})]X_2$ (L' = pyridine, 4-methylpyridine, *etc.*; X = Cl$^-$ or BF$_4^-$), and the quantum yields of the photoaquation reaction, have been examined.[46] It was proposed that the photoaquation of chloride ligands was hindered by hydrogen bonding to the amine hydrogen atoms. The nature of the excited state involved was also discussed.

The cations $[Cu^{II}(en)_2]^{2+}$ and $[Cu^{II}(L^{54})]^{2+}$ as their perchlorate salts have been incorporated into montmorillonite clay and the properties of the intercalated complexes studied by XANES and EXAFS.[47] The intercalation of the complexes was confirmed by X-ray powder diffraction, whilst the EXAFS experiments indicated that complex ions were located at the centres of siloxane rings, with silicate layers acting as counter anions. The spectroscopy and bonding within these intercalated materials was discussed. The $[NH_3Bu^n]^+$ cations in butylammonium uranyl phosphate were displaced using metal cation complexes including $[M^{II}(L^{54})]^{2+}$.[48] X-Ray powder diffraction indicated that the uranyl phosphate structure remained intact and that the intercalated complexes adoted their typical square-planar geometry.

The relative energies of the conformations of the $[Ni^{II}(L^{54})]^{2+}$ system has been studied by density functional theory.[49] This study, which is the first of its kind, confirmed that earlier calculations (MM-2) were correct; the *trans*-III isomer has the lowest energy and the *trans*-I isomer has a comparable energy.

Tetramethylcyclam (L^{55}) has been used to determine the anion binding properties of copper polyamine complexes.[50] The general result was that N-methylation of N donors increased the Lewis acidity of the metal centre. The crystal structures of two isomeric forms of $[Cu^{II}(L^{55})(tcnq)_2][tcnq]$ have been determined.[51] Both structures consist of parallel chains of $[Cu^{II}(L^{55})]^{2+}$ units linked by dimeric $[(tcnq)_2]^{2-}$ counter ions. The remaining tcnq molecule plays a lattice packing role. The kinetics of the oxidation of sulfite anions by $[Ru^{IV}O_2(L^{55})]^{2+}$ have been studied and the sulfur-containing products analysed by ion chromatography.[52] The sulfur-containing product is SO_4^{2-} and the rate constant was more than two orders of magnitude greater than the prediction from Marcus theory. This implied an inner-sphere reaction mechanism in contrast to much other Ru–oxo redox chemistry. Given that no $S_2O_6^{2-}$ was detected, the complex $[O=Ru^{VI}=O-SO_3]$ was proposed as a possible reaction inter-

mediate. Tetra-N-substituted cyclam derivatives with highly fluorinated pendant groups have been prepared (L^{56}) and their transition-metal complexes used in fluorous biphasic oxidation catalysis.[53]

The synthesis and Ni^{II}, Cu^{II} and Zn^{II} co-ordination chemistry of a pendant-arm derivative of L^{57} has been reported.[54] The kinetics of Cu^{II} complex formation and acid-promoted dissociation were studied by stopped-flow techniques which indicated that complex formation occurred more slowly than with the parent ligand (L^{54}).

A range of high-spin paramagnetic Co^{II} and Ni^{II} complexes of L^{58} has been pre-pared.[55] Both $[Co^{II}Cl(L^{58})][ClO_4]$ and $[Ni^{II}Cl(L^{58})][ClO_4]$ are five-co-ordinate and square pyramidal with four macrocyclic N donors and an apical chloride ligand; the pendant phosphines remain unco-ordinated. Trivalent Ni^{III} complexes have been generated electrochemically in solution by the controlled oxidation of the parent complexes $[Ni^{II}(L^{55})]^{2+}$ and $[Ni^{II}(L^{59})]^{2+}$.[56] The half-lives are 6.7 and 23.5 min for $[Ni^{III}(L^{55})]^{3+}$ and $[Ni^{III}(L^{59})]^{3+}$ respectively. It is worth nothing that $[Ni^{III}(L^{59})]^{3+}$ could oxidise I^-, N_3^- and SCN^- whilst $[Ni^{III}(L^{55})]^{3+}$ could only oxidise I^-.


L^{60} L^{61}
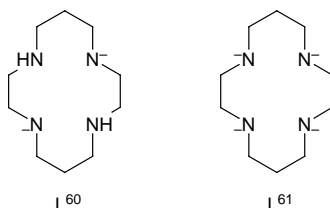
Reaction of L^{54} with two or four equivalents of Bu^nLi yields the bis- or tetra-amido ligands L^{60} and L^{61}.[57] The structure of $[Li_2(L^{60})]$ indicated that each lithium ion was four-co-ordinate with the co-ordination sphere consisting of a thf molecule, an amino donor and two amido donors. The complex $[ZrCl_2(L^{60})]$ was also structurally charac-terised, with the macrocycle in a folded conformation and chloride ligands occupying *cis* sites.

The crystal structures of five isomeric Cu^{II} complexes (with N-based stereochemis-try) of the cyclam type ligands L^{62} and L^{63} have been determined.[58] Reaction of the ligands with $CuCl_2$ in alkaline methanol yielded a complex mixture of isomers which were separated by cation-exchange chromatography. The protonation constants of the pendant amine groups are sensitive to the relative stereochemistry of the amine groups and the secondary amine group of the macrocycle, with a *cis* hydrogen-bonding interaction reducing the pK_a value of the pendant amine group in question. The Au^{III} templated synthesis of the *cis*-dinitro ligand L^{64} has been achieved in good yield from the condensation of $[Au^{III}(en)_2]^{3+}$, nitroethane and formaldehyde.[59] This procedure also generates the Au^{III} complex of the open chain ligand L^{65}. Both complexes contain Au^{III} in a square-planar geometry and, due to the high acidity of the Au^{III} centre, the ligands are mono-deprotonated. The crystal structures of the Co^{III} complexes $[Co^{III}(L^{66})]^{3+}$ and $[Co^{III}(L^{62})]^{3+}$ show significant variations in the metal–ligand bond lengths; the $Co^{II/III}$ self exchange rates varied by as much as two orders of magnitude depending on the *cis* or *trans* disposition of the pendant amine donors.[60] The complex $[Zn^{II}Cl(L^{67})][ClO_4]$ has been prepared and structurally char-acterised.[61] The chloride ligand occupies the apical site of a five-co-ordinate metal
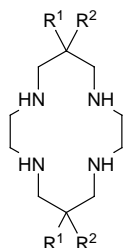
L62 R¹ = NH₂; R² = Me (*trans*)
L63 R¹ = Me; R² = NH₂ (*cis*)
L64 R¹ Me; R² = NO₂
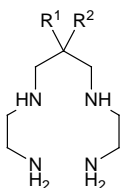
L65
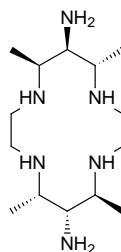
L66
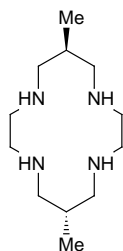
L67
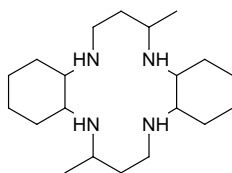
L68
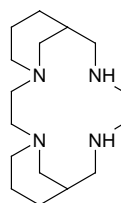
L69

centre with distorted square-pyramidal geometry. The related complex $[Zn^{II}(H_2O)_2(L^{68})]Cl_2$ has a six-co-ordinate Zn^{II} centre with tetragonally distorted octahedral geometry; the co-ordinated water molecules occupy *trans* positions.[62] The isomerisation of (R,R,S,S)-$[Ni^{II}(L^{69})][ClO_4]_2$ to (R,S,R,S)-$[Ni^{II}(L^{69})][ClO_4]_2$ has been described; the latter complex has a weaker ligand field and more positive electrochemical reduction and oxidation potentials.[63] The isomer (R,S,R,S)-$[Ni^{II}(L^{69})][ClO_4]_2$ isomerises back to the (R,R,S,S) form in aqueous solutions containing acetonitrile at 50 °C. The crystal structure of the (R,S,R,S) isomer indicated square-planar Ni^{II} with a large tetrahedral distortion. A possible mechanism for the isomerisation was discussed.

The Ni^{II} complex of the 2,2′-bipyridine functionalised cyclam derivative L^{70} binds 0.5 mol equivalent of Cu^{II} ions in aqueous solution to yield the trinuclear complex $[Cu^{II}(H_2O)\{(Ni^{II}(L^{70})\}_2]^{6+}$.[64] The co-ordinated water molecule at the Cu^{II} site is readily displaced by anions to yield complexes of general formula $[Cu^{II}(X)\{(Ni^{II}(L^{70})\}_2]^{5+}$ (X = NCO^-, N_3^-, NO_3^- or Cl^-), which upon electrochemi-
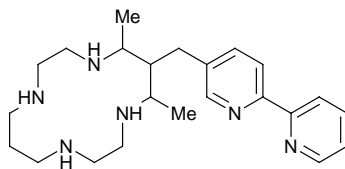
L70

cal oxidation to the corresponding Ni^{III} species underwent anion displacement from Cu^{II} to Ni^{III}. A water molecule completes the co-ordination sphere of Ni^{III}. This process is reversible and hence the position of the anion in the complex can be electrochemically controlled.
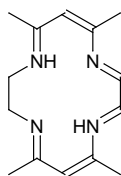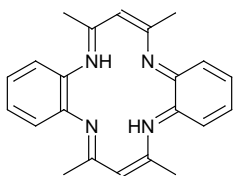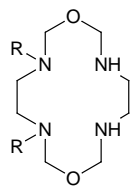
H_2L^{71} H_2L^{72} H_2L^{73} R = CH$_2$CO$_2$H
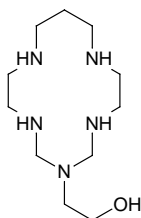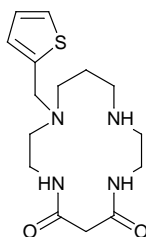
L^{74} L^{75} L^{76}
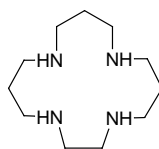
Both [Zr^{IV}(OBu^t)$_2$(L^{71})] and [Hf^{IV}(NMe$_2$)$_2$(L^{71})] have pseudo-octahedral geometry with the alkoxo or amido ligands in *cis* positions.[65] A comparison of the bonding in these complexes with that of the related species [MX$_2$(L^{71})] (X = Cl or CH$_2$Ph) concluded that those ligands which did not participate in π-bonding favoured trigonal-prismatic geometry, and those ligands with filled π-orbitals adopted octahedral geometry.

The reaction of two mole equivalents of Li[NHC$_6$H$_3$R$_2$-2,6] (R = Me or Pr^i) with [Zr^{IV}Cl$_2$(L^{72})] yields the bis(amido) complexes [Zr^{IV}(NHC$_6$H$_3$R-2,6)$_2$(L^{72})].[66] In addition, the complexes [Zr^{IV}(NHR)$_2$(L^{72})] (R = C$_6$H$_3$Me$_2$-2,6, C$_6$H$_3$Pr$^i_2$-2,6, Ph or Bu^t) were also obtained by the addition of H$_2$L^{72} to the bis(alkyl) compounds [Zr^{IV}(CH$_2$SiMe$_3$)$_2$(L^{72})]. In the same account the unsymmetric dinuclear complexes [(L^{72})Zr(μ-NR)$_2$Zr(NHR)$_2$] (R = C$_6$H$_3$Me$_2$-2,6 or Bu^t) were prepared by the reaction of H$_2$L^{72} with [(py)(NHR)$_2$Zr^{IV}(μ-NR)$_2$Zr^{IV}(NHR)$_2$(py)] (R = C$_6$H$_3$Me$_2$-2,6) or [(NHR)$_2$Zr^{IV}(μ-NR)$_2$Zr^{IV}(NHR)$_2$] (R = Bu^t) respectively.

The novel bis (pendant arm) ligand H$_2$L^{73} was prepared *via* a template method by the reaction of [Co^{III}(*N,N*′-edda)(en)]$^+$ with formaldehyde under basic conditions.[67] The crystal structure of [Co^{III}(L^{73})]$^+$ indicated that the pendant carboxylates occupy *trans* positions about an octahedral Co^{III} centre. The template synthesis of L^{74} has been achieved by the reaction of 232-tet, ethanolamine and formaldehyde in the presence of a Ni^{II} salt.[68] The complex [Ni^{II}(L^{74})][ClO$_4$]$_2$ has a four-co-ordinate metal centre with the pendant arm N donor and the hydroxyl group unco-ordinated. The crystal structure of the complex [Ni^{II}(SCN)$_2$(L^{74})] has also been determined.[69] The

novel dioxoxcyclam ligand H_2L^{75} has been prepared and its Cu^{II} co-ordination chemistry reported.[70] In the solid-state structure of the Cu^{II} complex of L^{75} the metal ion is four-co-ordinate with the pendant thiophene group remaining unco-ordinated. Electrochemical studies indicated that the presence of the thiophene moiety facilitated the formation of a Cu^{III} species. The co-ordination chemistry of Cr^{III}, Mn^{III}, Fe^{III}, Ni^{II}, Zn^{II} and Rh^{III} with $[15]aneN_4(L^{76})$ has been described.[71]

L^{77} $m = 2; n = 2$
L^{78} $m = 3; n = 2$
L^{79} $m = 2; n = 3$
L^{80} $m = 3; n = 3$
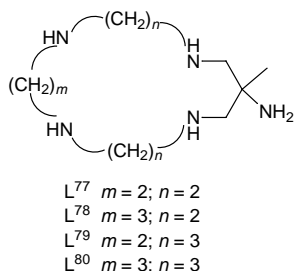
Ligands L^{77-80} have been used to examine the outer-sphere redox reactions between the complexes $[Co^{III}(H_2O)(L^{77-80})]^{3+}/[Co^{III}(HO)(L^{77-80})]^{2+}$ and $[Fe(CN)_6]^{4-}$ in a kinetic study in which the effect of ring size, pressure and temperature was measured.[72] The outer-sphere complex formation constants did not vary with ligand type but the electron transfer rate for $[Co^{III}(H_2O)(L^{77-80})]^{3+}$ increased on increasing ring size.

The first structurally characterised example of an eight-co-ordinate Co^{II} complex
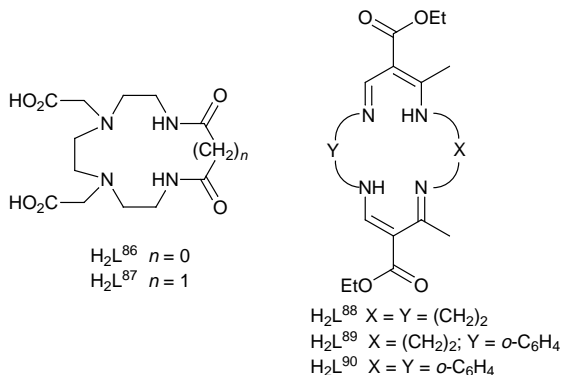

L^{81}

H_2L^{82} R = R' = CH_2CO_2H; $m = n = 0$
H_2L^{83} R = CH_2CO_2H, R' = Me; $m = n = 1$
H_2L^{84} R = R' = CH_2CO_2H; $m = 0, n = 1$
H_2L^{85} R = R' = CH_2CO_2H; $m = n = 1$
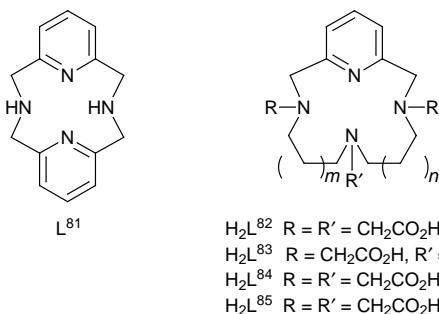
which contains purely five-membered chelate rings has been described.[73] The geometry of the metal centre in the cation $[Co^{II}(L^{81})_2]^{2+}$ is that of a distorted dodecahedron. The measurement of protonation and an extensive range of complex formation constants indicate that the heptadentate ligand L^{82} forms less stable complexes than dota but is also two orders of magnitude less basic.[74] This latter factor may prove useful in biomedical application of L^{82}. In a subsequent paper the related ligand L^{83} was treated in a similar manner and found to form an exceptionally stable complex with Cu^{II} (log $K_{Cu^{II}L83} = 21.61$), which was surprisingly more stable than the analogous Fe^{III} complex (log $K_{Fe^{III}L83} = 20.64$).[75] The protonation and lanthanide ion complex formation of ligands L^{82}, L^{84} and L^{85} have also been described.[76] The co-ordination of histamine and imidazole to Cu^{II}, Zn^{II} and Cd^{II} complexes of H_2L^{86} and H_2L^{87} has been examined using ^1H NMR spectroscopy.[77] Histamine and imidazole displace

water from $[M(H_2O)(L^{86,87})]$ with the formation constants of the Zn^{II} and Cd^{II} complexes being of the same order of magnitude. The electronic and EPR spectra

H$_2$L^{86} $n = 0$
H$_2$L^{87} $n = 1$

H$_2$L^{88} X = Y = (CH$_2$)$_2$
H$_2$L^{89} X = (CH$_2$)$_2$; Y = o-C$_6$H$_4$
H$_2$L^{90} X = Y = o-C$_6$H$_4$

of a range of Fe^{III} complexes of unsaturated tetraazacycles such as H$_2$L$^{88–90}$ have been investigated as a function of axial ligand type.[78] Complexes with H$_2$L$^{88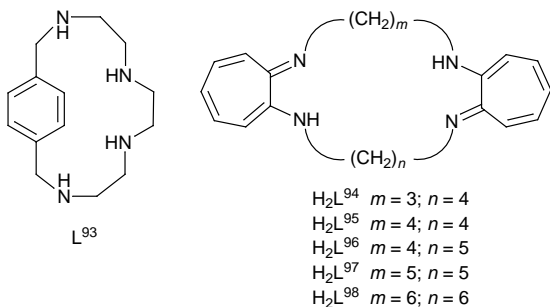}$ formed octahedral low-spin complexes in polar solvents and in the presence of axial co-ligands including pyridines, imidazoles, hydroxide, sulfite, phosphites and phosphines. In the cases which included phosphorus ligands, superhyperfine coupling of the unpaired electron to two phosphorus nuclei was observed. The *cis/trans* bridge isomerism in Co^{II} and Ni^{II} complexes of the cyclidene-type ligands L^{91} and L^{92} has been investigated by NMR spectroscopy and X-ray crystallography.[79] The oxygen binding

L^{91} L^{92}
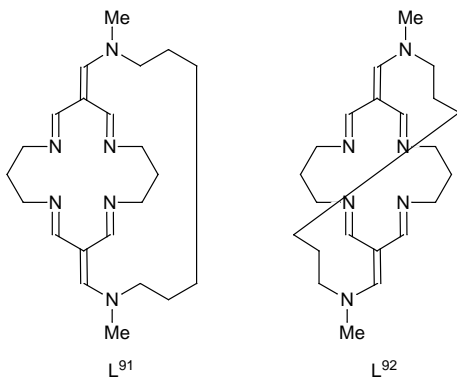
properties of these complexes was also discussed. The Pt^{II} chemistry of the tetraazacyclophane L^{93} has been studied by ^{1}H, ^{13}C and ^{195}Pt NMR spectroscopy as a function of pH.[80] Three different complexes were detected, with the mode of L^{93}–Pt interaction determined by the degree of protonation. At low pH the central two N donors bind in a *cis* manner; at higher pH a benzylic N donor and an adjacent N donor bind whilst the addition of more Pt^{II} results in a dinuclear complex.

H$_2$L^{94} *m* = 3; *n* = 4
H$_2$L^{95} *m* = 4; *n* = 4
H$_2$L^{96} *m* = 4; *n* = 5
H$_2$L^{97} *m* = 5; *n* = 5
H$_2$L^{98} *m* = 6; *n* = 6

L^{93}

Zinc(II) and Cd^{II} complexes of the tropocoronand ligands H$_2$L$^{94–98}$ have been prepared and structurally characterised.[81] The dihedral angle between the five-membered chelate rings varied monotonically as a function of the macrocyclic ring size. With large ring sizes the geometry was approximately tetrahedral and with smaller rings the geometry approached square planar. The four-co-ordinate Co^{III} complexes of H$_2$L^{94} and H$_2$L^{95} have also been described.[82] The co-ordination geometry in [Co^{III}(L^{95})]$^{+}$ is very unusual (for a four-co-ordinate Co^{III} complex) being intermediate between square-planar and tetrahedral. The *trans*-III isomer of the dinuclear Ni^{II} complex of the spiro-cyclam derivative L^{99} has been prepared and its spectroscopic and electrochemical properties reported.[83] The mixed valence Ni^{II}–Ni^{III} species could not be obtained by controlled oxidation of the parent complex but was accessible by the reductive decomposition of the Ni^{III}–Ni^{III} species. The one-pot template synthesis of the dinuclear Cu^{II} complex of the bis(cyclam) ligand HL^{100} was achieved by reaction of Cu(NO$_3$)$_2$, 232-tet, formaldehyde and K$_2$(O$_2$CCHNO$_2$).[84] The structure of the dimeric complex [Cu^{II}$_2$(L^{100})]$_2$[ClO$_4$]$_3$Cl$_3$·6H$_2$O showed the central nitro group to

L^{99}

L^{100}

L^{101}

L^{102}
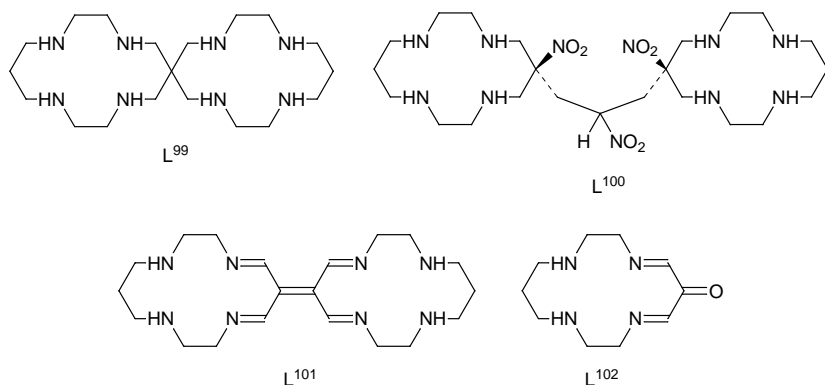
behave as a nitronate ligand by bridging to an adjacent metal centre in the structure. Reaction of the diiron complex [Fe^{II}$_2$(L^{101})]$^{4+}$ with atmospheric oxygen in solution or in the solid-state results in oxidative cleavage of the central olefinic bridge to yield two moles of the mononuclear complex [Fe^{II}(L^{102})]$^{2+}$.[85] The reaction proceeds in high yield and four orders of magnitude more rapidly in dmf than in acetonitrile.
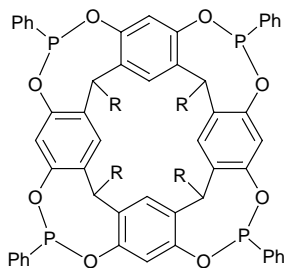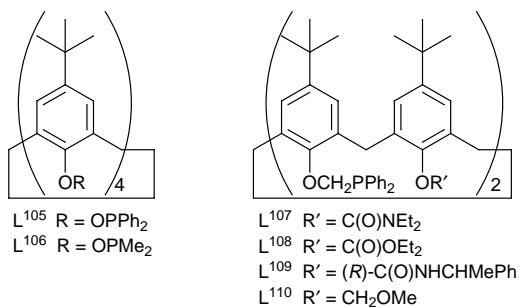
Oxygen-donor ligands

Alkali-metal ions have an effect on the Cr and Mo complex formation of a calix[4]-arene ligand (H_4L^{103}).[86] Reaction of [Mo(NR)(CHCMe$_2$Ph)(O$_3$SCF$_3$)(dme)] (R = C$_6$H$_3$Me$_2$-2,6) in acetonitrile yields the centrosymmetric dimer [{Mo(NR)(L^{103})K$_2$(NCMe)$_3$O}$_2$]. The Mo centre is pseudo-octahedral with two L^{103} derived phenoxide donors and two bridging (to K$^+$) phenoxides. The K$^+$ ions are contained within the calixarene cavity, whilst being stabilised by π interactions of transoid phenoxide rings. Reaction of [Cr(NBu^t)$_2$(OBu^t)$_2$] with H_4L^{103} results in an unusual example of C–H bond activation with the formation of an ether link between two calix[4]arene units. The crystal structure of the La^{III} complex of the partial cone

H$_4$L^{103}

H$_4$L^{104}
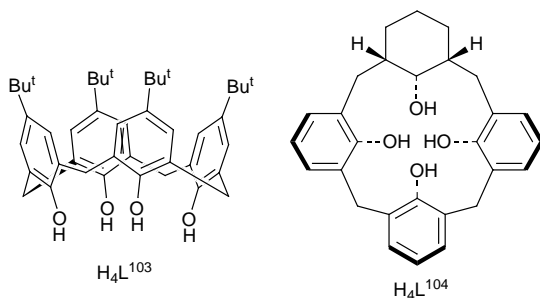
conformer of calix[4]arene ligand L^{103} reveals first- and second-sphere co-ordination towards the metal centre.[87] The metal calixarene interactions involve two amide donors in the first co-ordination sphere and one amide and two ethers in the second which interact *via* a co-ordinated water molecule. The stability constants of a range of *O*-carboxymethyl calixarene ligands with lanthanide and Th^{IV} ions have been investigated.[88] Partially and fully deprotonated mononuclear complexes were observed with the lanthanides and Th^{IV}. The stability constants were found to increase with increasing deprotonation of the ligands; the Th^{IV} complexes were more stable than the analogous Ln^{III} complexes. The synthesis and crystal structure of the Eu^{III} complex of the partially reduced calix[4]arene H_4L^{104} has been described.[89] The centrosymmetric dinuclear complex has the formula [Eu$_2$(dmf)$_4$(HL^{104})$_2$]·4dmf, with L^{104} displaying a similar bonding mode to the parent calix[4]arene itself.

The calix[4]arene phosphinite ligands L^{105} and L^{106} have been used to prepare dinuclear platinum–metal complexes.[90] In the complexes [(MCl$_2$)$_2$(L^{105})] (M = Pd^{II} or Pt^{II}) and [{Rh^{I}Cl(CO)}$_2$(L^{105})] the metal centres have square planar geometry with two *cis* phosphinite donors occupying adjacent calixarene lower-rim positions. With L^{105} only mononuclear Ni^{II} complexes could be isolated. The co-ordination chemistry of the diphosphino calixarenes $L^{107–110}$ with platinum group metals has been studied as a means of probing intercavity reactivity.[91]

The tetrakis(phosphonito)calixresorcinarene ligand L^{111} forms chloride-supported tetranuclear Cu^I and Ag^I complexes [M$_4$(μ-Cl)$_4$(L^{111})] (M = Cu^I or Ag^I).[92] These

L^{105} R = OPPh$_2$
L^{106} R = OPMe$_2$

L^{107} R′ = C(O)NEt$_2$
L^{108} R′ = C(O)OEt$_2$
L^{109} R′ = (*R*)-C(O)NHCHMePh
L^{110} R′ = CH$_2$OMe

L^{111} R = (CH$_2$)$_2$Ph

complexes also form the anionic chloride inclusion species $[M_4(\mu\text{-Cl})_4(\mu_4\text{-Cl})(L^{111})]^-$ which selectively bind metal cations by utilising the bridging chloride groups of the parent complex as ligands. Thus the following complexes could be isolated $[\{M_4(\mu\text{-Cl})_4(\mu_4\text{-Cl})(L^{111})\}M']^-$ (M′ = Na, K, Rb or Cs), $[\{M_4(\mu\text{-Cl})_4(\mu_4\text{-Cl})(L^{111})\}_2M']$ (M′ = Zn or Cd) and $[\{M_4(\mu\text{-Cl})_4(\mu_4\text{-Cl})(L^{111})\}_2M']$ (M′ = Hg or Pb). X-Ray crystallography of $[\{Cu^I_4(\mu\text{-Cl})_4(\mu_4\text{-Cl})(L^{111})\}Cs^I_2]$ and $[\{Ag^I_4(\mu\text{-Cl})_4(\mu_4\text{-Cl})(L^{111})\}_2Hg^{II}]$ indicated a sandwich structure with Cs^I or Hg^{II} ions bound between two $[Ag^I_4(\mu\text{-Cl})_4(\mu_4\text{-Cl})(L^{111})]^-$ units.

Phosphorus-donor ligands
The tetraphosphole ligand L^{112} yields an active homogenous catalyst in the Stille coupling reaction.[93] Since the phosphorus donor atoms in L^{112} are part of a phosphole ring the barrier to inversion is very small; L^{112} may be regarded as a single isomer. The structure of $[Pd^{II}Cl_2(L^{112})]$ indicated two transoid P donors bonding to a Pd^{II}Cl$_2$ fragment with the ligand adopting a saddle-shaped conformation. This conformation is thought to favour the formation of Pd^0 species and result in more efficient catalysis. The low yield Pd^{II} and Pt^{II} templated synthesis of the phosphacyclam ligand L^{113} has been described.[94] Crystal structure analyses showed both $[Pd^{II}(L^{113})]^{2+}$ and $[Pt^{II}(L^{113})]^{2+}$ to be square planar with *trans*-III (*R,R,S,S*) conformations of the ligand; owing to the large metal ion radius large distortions of the C–P–C bond angles were noted.

L^{112} L^{113}
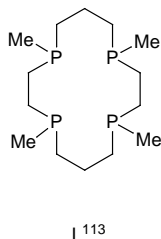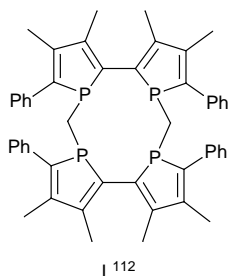
Sulfur- and selenium-donor ligands

Reaction of [{Mo^{II}(μ-Br)Br(CO)$_2$}$_2$] and L^{114} yields seven-co-ordinate complexes of the general formula [MX(CO)$_2$(L^{114})][MX$_3$(CO)$_4$] (M = Mo^{II} or W^{II}, X = Br$^-$ or I$^-$).[95] In the same report the reaction of [MI$_2$(CO)$_2$(NCMe)$_2$] with tetrathia ligands (L$^{115-117}$) yields bimetallic species of general formula [M$_2$I$_4$(CO)$_6$(L$^{115-117}$)] and [WI(CO)$_2$(L$^{115-117}$)][MX$_3$(CO)$_4$]; reaction of [Mo^{III}Cl$_3$(thf)$_3$] yielded polymeric materials with the empirical formula [Mo$_3$Cl$_9$(L$^{115-117}$)$_2$] or the ionic complex [Mo$_2$Cl$_5$(L^{117})$_2$]Cl. It was proposed that these latter materials involved macrocycles bridging between metal centres.

L^{114} L^{115} L^{116} L^{117}

L^{118} L^{119} L^{120} L^{121}
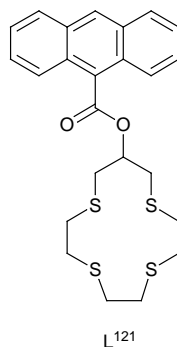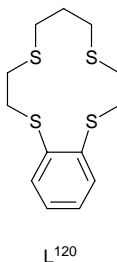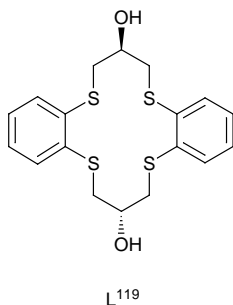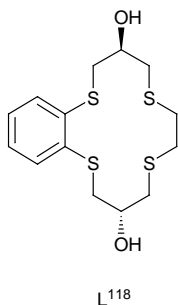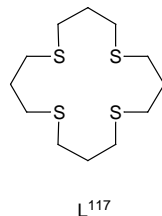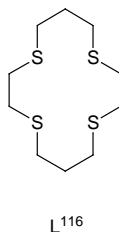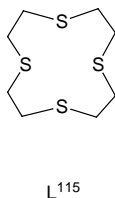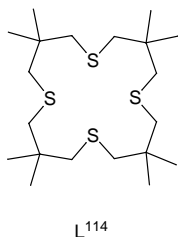
An extensive electrochemical study of Cu complexes of C-substituted [14]aneS$_4$ (L^{116}) derivatives has been reported.[96] The rate and equilibrium constants related to the structural changes that occur during the Cu^{II}–Cu^{I} electron transfer processes were analysed as a function of ligand structure. The crystal structures of the square-planar

Pd^{II} complexes of L[118–120] have been reported.[97] This account also included an interesting ligand synthesis in which ring closure was achieved by reaction of a dithiol with the activated 1,2-dichlorobenzene fragment [Fe^{II}(η^5-C$_5$H$_5$)(η^6-C$_6$H$_4$Cl$_2$-1,2)]$^+$ to yield L[120]. The [14]aneS$_4$ derivative L[121] selectively incorporates Cu^{II} ions in the presence of other first-row transition-metal ions.[98] The presence of Cu^{II} in the ligand cavity is detected by the fluorescence quenching of the pendant anthracenyl group. Biodistribution studies of [105]Rh labelled tetradentate thiamacrocycles in rats have been reported.[99]

EXAFS studies of Cr^{III} complexes of the selena crown L[122] and a range of open chain ligands have been made.[100] These experiments, together with electronic and vibrational spectroscopy, confirm weak metal–ligand interactions, as might be expected from a hard-metal–soft-ligand complex. Reaction of L[122] with [Ru^{III}(dmf)$_6$]Cl$_3$ in boiling EtOH yields *cis*-[Ru^{II}Cl$_2$(L[122])].[101] Analogous dibromo and diiodo complexes were also prepared with the *cis* stereochemistry being verified by ^{77}Se NMR spectroscopy. The *trans* isomers of [Ru^{II}X$_2$(L[122])] (X = Cl or Br) could be prepared by refluxing the corresponding *cis* complexes in nitromethane. Related Os complexes were also prepared. All the complexes have reversible M^{II}–M^{III} couples.

L[122]
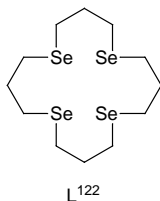
Mixed donor ligands

The heptadentate ligand H$_3$L[123] forms a complex with Gd^{III} of empirical formula [Gd^{III}(H$_2$O)$_5$(L[123])]; the crystal structure contains infinite chains of [Gd^{III}(H$_2$O)(L[123])].[102] Nine-co-ordinate Gd^{III} centres are bound by seven nitrogen and oxygen donors from the ligand with one carboxylate donor bridging to an adjacent centre. The remaining co-ordination site is occupied by a water molecule. An unusual hydrogenolysis of a pendant hydroxyl group of a co-ordinated ligand has been reported.[103] The complex [Co^{III}Cl(L[125])]$^+$ was isolated from the reaction of L[124] with Co^{II} in acid solution in the presence of activated charcoal.

H$_3$L[123]

L[124] R = OH
L[125] R = H
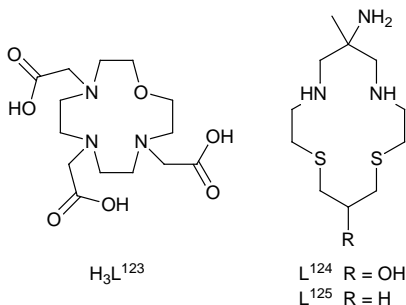
The synthesis of a new P_2S_2 mixed-donor ligand and the resolution of its *cis* (L^{126}) and *trans* (L^{127}) isomers has been described.[104] Only the *trans* isomer reacts with Ni^{II} to yield an isolable product, $[Ni^{II}(NCMe)(L^{127})][ClO_4]_2$. The Ni^{II} centre displays a five-co-ordinate distorted trigonal-bipyramidal geometry in which the axial sites are occupied by phosphorus donors. The synthesis and Co^{II} co-ordination chemistry of the novel mixed-donor ligands L^{128} and L^{129} have been described.[105] In the double salt $[Co^{II}(L^{129})_2][Co^{II}Cl_3(L^{129})]$ the cation $[Co^{II}(L^{129})_2]^{2+}$ is octahedral with the co-ordination sphere made up of two pyridine, two thioether and two phosphine oxide donors. The anion $[Co^{II}Cl_3(L^{129})]^-$ contains four-co-ordinate Co^{II} in a distorted-tetrahedral geometry with three chloride donors and a phosphine oxide completing the co-ordination sphere.
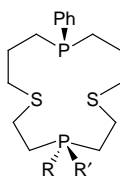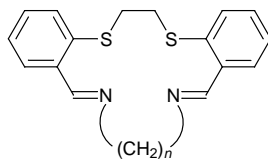

L^{126} R = lone pair ; R′ = Ph (*cis*)   L^{128} R = lone pair   L^{130} n = 3
L^{127} R = Ph ; R′ = lone pair (*trans*)   L^{129} R = O   L^{131} n = 4
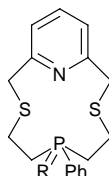
Reaction of the N_2S_2 Schiff-base ligands L^{130} and L^{131} with Cu^{II} salts in MeOH affords two complexes $[Cu^{II}(L^{130})]^{2+}$ and $[Cu^{I}(L^{131})]^+$.[106] In the former complex the Cu^{II} centre has square-planar geometry, whilst in the latter the Cu^{I} ion adopts a flattened tetrahedral geometry. An electrochemical examination of the two complexes indicated a more positive potential for the Cu^{II}–Cu^{I} couple for $[Cu^{I}(L^{131})]^+$ which was interpreted in terms of the more flexible ligand enhancing the formation of Cu^{I}.

Pentadentate macrocycles

The acid-promoted dissociation and formation constants of complexes (Cu^{II} and Pb^{II}) of the bis-carboxylate pendant-arm macrocycles H_2L^{132} and H_2L^{133} have been determined.[107] The complex dissociation reactions were measured in the presence of strong and weak acids and in Cu^{II}/Pb^{II} exchange reactions. The exchange reaction displayed pseudo-first-order kinetics. The 15-crown-5-containing naphthochromene L^{134} binds Pb^{II} ions in the dark, whilst photoirradiation of the complex results in dissociation.[108] The electrochemistry and photophysics of the Ru^{II} complexes of the 15-crown-5-derived ligand L^{135} have been reported, with the two complexes $[Ru^{II}(bipy)_2(L^{135})]^{2+}$ and $[Ru^{II}(L^{135})_3]^{2+}$ binding only one mole of an alkali-metal cation.[109] The Cu^{I} complex of a novel rigid mixed-donor ligand (L^{136}) has been characterised by X-ray crystallography.[110] The metal:crown ratio is 2:1; the $Cu^{I}_4I_4$ cubane units are bridged by L^{136} *via* separate sulfur-donor atoms, with the cavity of the ligand remaining unoccupied.

Hexadentate macrocycles

The crystal structure of the complex $[Nd^{III}(NO_3)_3(L^{137})]$ shows the metal centre to be ten-co-ordinate with a distorted bicapped square-antiprismatic geometry.[111] The synthesis of Hg^{II} complexes of the bicyclic ligands L^{138} and L^{139} has been de-

H₂L¹³² *n* = 1
H₂L¹³³ *n* = 2

L¹³⁴

L¹³⁵

L¹³⁶
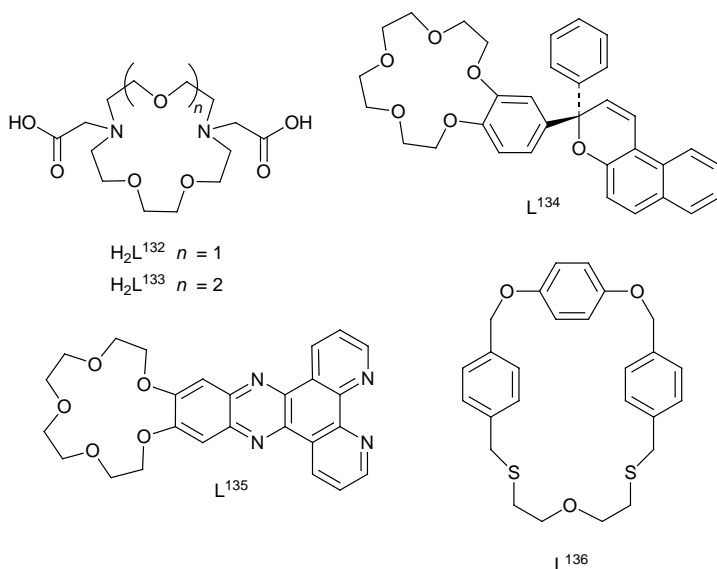
scribed.[112] In a thorough series of kinetic experiments the acid- and chloride-catalysed complex dissociation reactions and a series of formation constants were also investigated. A 1:1 supercomplex of the sepulchrate complex $[Co^{III}(L^{140})]^{3+}$ and calix[6]-arene hexakis(sulfonic acid) $(L^{141})^{6-}$ is formed in solution.[113] The binding constant was determined in NaCl solution as $1600 \, dm^3 \, mol^{-1}$. In the solid state a 2:1 complex, $[Co^{III}(L^{140})]_2[L^{141}]$, was identified. The Co^{III} complex of the novel cage ligand L^{142} undergoes fast electron-transfer reactions, and was examined as a photocatalyst for the generation of hydrogen.[114]

The single-crystal structure of $[La^{III}(NCS)_3(L^{143})]$ indicated a nine-co-ordinate

L¹³⁷

L¹³⁸ R = H
L¹³⁹ R = NH₂

L¹⁴⁰

H₆L¹⁴¹

L¹⁴²

$$L^{143} \quad R = CH_2Ph$$
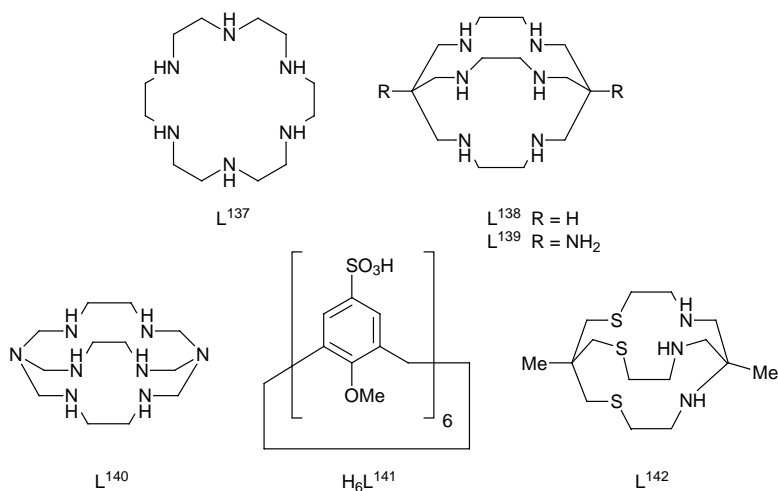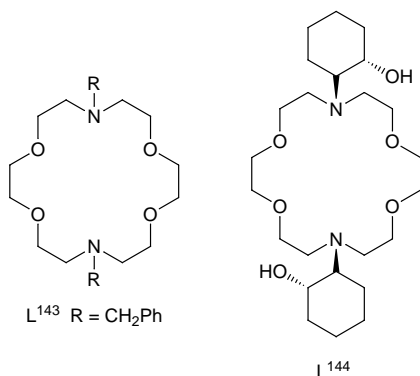
$$L^{144}$$

metal centre with the macrocyclic donor atoms occupying 'equatorial' positions.[115] The complex $[Sr^{II}(H_2O)(L^{144})][NO_3]_2$ crystallises in the chiral space group Cc, with single crystals containing the ligand only as the (R,R) or (S,S) diastereomer.[33] The Sr^{II} ions are nine-co-ordinate with an extensive H-bonding network stabilising the chirality of the entire crystal structure. The bis-anthracenyl diaza-18-crown-6 derivative L^{145} undergoes a reversible photocyclisation to form the cryptand ligand L^{146}.[116] The rates of the forward and reverse reactions are very sensitive to the presence of alkali-metal cations with, for example, Cs^+ retarding both reactions. Ligands with general structure HL^{147} have been used in thermodynamic ion binding studies of univalent ions; complex stability varied in the sequence: $Na^+ < K^+ < Tl^+ \ll Ag^+$.[117] The luminescence of the Eu^{III} complexes of L^{148} and L^{149} is greatly enhanced on binding sodium and potassium ions within the peripheral aza-crown sites.[118] In similar experiments with Tb^{III} no such luminescence enhancement was observed. The enhanced luminescence in the Eu^{III} case arises from the suppression of photoinduced electron transfer from the aza-crown nitrogen to the lumophoric centre.

$$L^{145} \quad \xrightleftharpoons[\text{heat}]{h\nu} \quad L^{146}$$
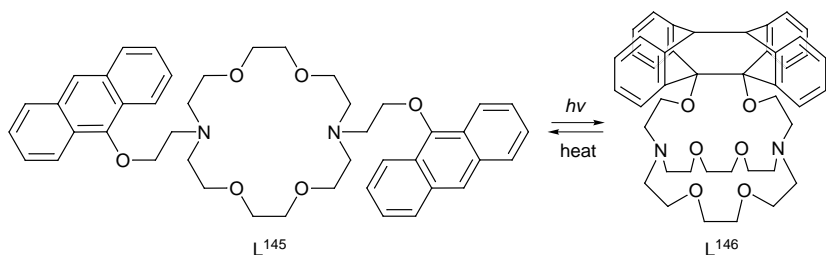
The mono- and di-nuclear Cu^{II} complexes of L^{150} form ternary complexes with ATP.[119] The hydrolysis of ATP to ADP is catalysed by metal-free L^{150} with the presence of Cu^{II} ions inhibiting this process. The dinuclear Co^{II} complex of L^{151} displays a pH-sensitive co-ordination geometry.[120] At pH 4 a complex containing the cation $[Co^{II}_2(H_2O)_2(L^{151})]^{4+}$ was isolated, whilst at pH 6.5 $[Co^{II}_2(\mu\text{-OH})(L^{151})]^{3+}$ was obtained. Both complexes were structurally characterised; the former has trigonal prismatic geometry and the latter a distorted octahedral geometry. The novel pendant-arm phosphonate ligand H_8L^{152} has been prepared.[121] The ^1H NMR spectrum of the
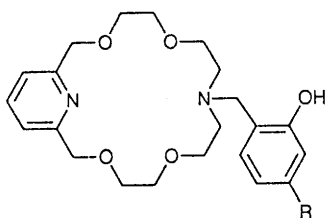
HL[147] R = NO$_2$, CN, Cl, CH$_3$, OCH$_3$
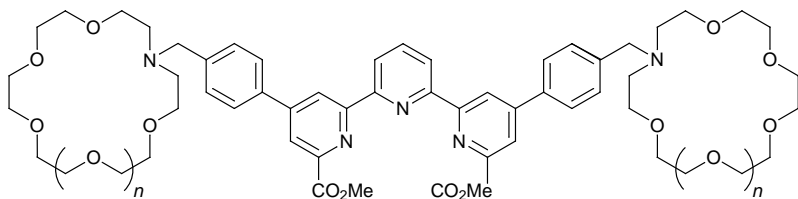
L[148] $n = 0$
L[149] $n = 1$

La^{III} complex indicates that only one of the five possible diastereomers persists in solution. The crystal structure of the La^{III} complex reveals a ten-co-ordinate metal centre in which all six macrocyclic donors and all four pendant arms are co-ordinated.

The triple-decker sandwich complex [(L^{153})Cs(L^{153})Cs(L^{153})]$^{2+}$ has been structurally characterised as the cation in the complex [Cs$_2$(L^{153})$_3$]- [H(cbto)$_2$]$_2$·2Hcbto·2H$_2$O.[122] Each metal centre is 12-co-ordinate with a distorted hexagonal-antiprismatic geometry. The central macrocycle shows significantly longer bonding interactions than those of the terminal rings. The salt [H$_{13}$O$_6$]- [Pt^{IV}Cl$_5$(H$_4$O$_2$)]·2L^{153} has been crystallographically characterised;[123] a cationic [H$_{13}$O$_6$]$^+$ species simultaneously bound by three molecules of L^{153} is indicated. The ligand L^{153} stabilises a hydrogen-bonding lattice in the crystal. The structure of the
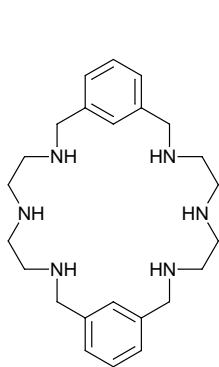
L[150]
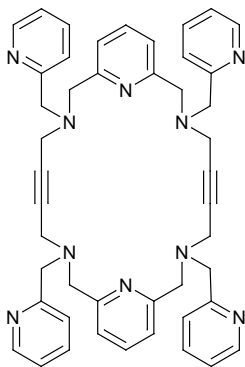
L[151]

H$_8$L[152] R = CH$_2$PO$_3$H$_2$

L^{153} L^{154}
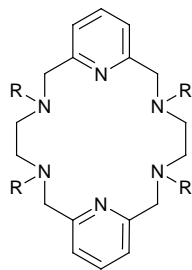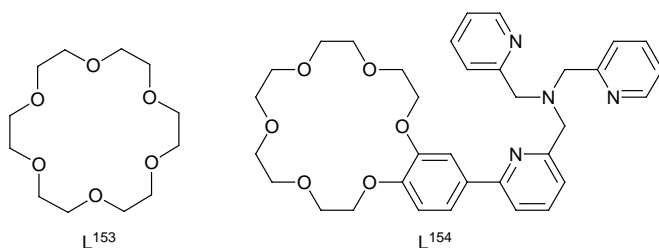
dinuclear Cr^{III} complex $[Cr^{III}_2(\mu\text{-}OH)_2(H_2O)_8][(H_3C)_3C_6H_2SO_3]_4 \cdot L^{153} \cdot 3H_2O$ has been determined.[124] The complex $[Cd^{II}(CN)_2(L^{153})]$ has six crown ether oxygen atoms occupying equatorial positions about a linear NC–Cd–CN unit.[125] Copper complexes of the ditopic ligand L^{154} show small shifts in the Cu$^{I/II}$ couple upon binding a cation or ammonium guest in the crown unit.[126] The greatest shifts were observed for binding K$^+$ and Rb$^+$, *i.e.* when the crown cavity to ionic radius was approximately matched.

H$_3$L^{155} R = Bu^t
H$_3$L^{156} R = Cl
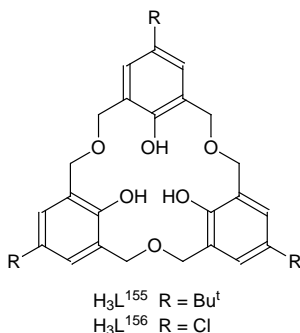
The oxovanadium(v) complex $[V^VO(L^{155})]$ was prepared by the reaction of Li$_3$(L^{155}) with VOCl$_3$.[127] In the solid state a polymeric structure was observed with axial $V^V{=}O \cdots V^V$ interactions between adjacent $[V^VO(L^{155})]$ moieties. The binding constants of H$_3$L^{155} and H$_3$L^{156} towards metal cations vary according to the sequence Na$^+$, Li$^+$, Ca^{2+} < Mg^{2+} < La^{3+} ≪ Y^{3+} < Lu^{3+} ≪ Sc^{3+}.[128]

Schiff-base ligands
The Fe^{II}–Fe^{III} 'mixed' valence Robson's macrocycle complex $[Fe^{II}Fe^{III}(\mu\text{-}OAc)_2(L^{157})]$ $[ClO_4]$ has been shown by Mössbauer spectroscopy to be valence delocalised over a wide temperature range (1.8–364 K).[129] Interestingly the diiron complex of the reduced ligand L^{159} $[Fe^{II}Fe^{III}(OAc)_2(H_2O)(L^{159})][ClO_4] \cdot 2H_2O$ is valence localised, even at ambient temperature. The crystal structure and magnetic properties of the dinuclear complex $[Mn^{II}_2(OAc)_2(L^{158})]$ have been described.[130] The complex is centrosymmetric with the two Mn^{II} centres sharing bridging phenolic and acetate donors. The metal centres are antiferromagnetically coupled ($J = -5 \text{ cm}^{-1}$); the complex catalyses the decomposition of hydrogen peroxide in dmf. A range of heterobinuclear complexes has been prepared using the related ligand H$_2$L^{160}.[131] These materials were obtained in
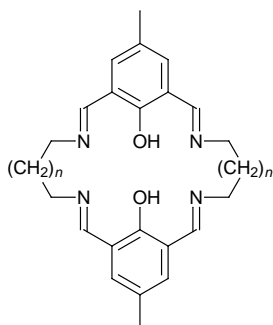
H$_2$L^{157} $n = 1$
H$_2$L^{158} $n = 2$
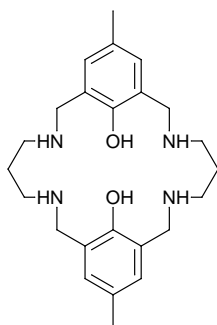
H$_2$L^{159}
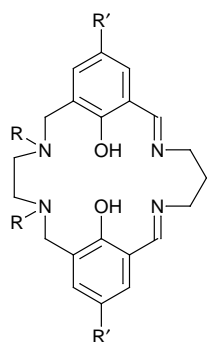
H$_2$L^{160} R = Me ; R′ = Br

H$_2$L^{162}

H$_2$L^{161} R =   ; R′ = Me
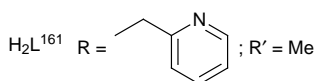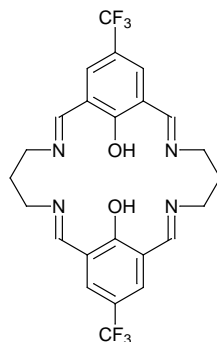
migratory transmetallation reactions of the parent complex $[Pb^{II}Cu^{II}(L^{160})]^{2+}$ to yield $[M^{II}Cu^{II}(L^{160})]^{2+}$ (M = Mn, Co, Ni, Cu or Zn). The pendant-arm Robson-type ligand H$_2$L^{161} forms a range of heterobinuclear complexes including $[Fe^{II}(L^{161})V^{IV}O]^{2+}$ and $[Fe^{II}(\mu\text{-Cl})V^{III}Cl(L^{161})]^{+}$.[132] The latter complex is unusual in that one of the phenoxide groups is not bridging, being bonded exclusively to the V^{III} centre, a very rare observation for compartmental systems. Electrochemical studies showed that the redox potential was strongly influenced by the presence of another metal within the ligand cavity.

The dinuclear complex $[Cu_2^{II}(L^{162})][tcnq]_3$ has been prepared by the reaction of $[Cu_2^{II}(L^{162})][ClO_4]_2$ and Li(tcnq) in the presence of an additional mole equivalent of tcnq.[133] The CF$_3$ group was incorporated to yield more reducible Cu^{II} centres and permit the synthesis of charge-transfer complexes. The structure of crystals of $[Cu^{II}_2(L^{162})][tcnq]_3$ doped with $[Cu^{II}_2(L^{162})][ClO_4]_2$ has each metal centre six-co-ordinate, with the equatorial positions occupied by the macrocycle. The axial donors are derived from the nitrile groups of a bridging tcnq unit with the additional tcnq

molecules occupying stacking positions above and below the bridging group. Hence the structure consists of one-dimensional chains of $[Cu^{II}{}_2(L^{162})(tcnq)]$ with two additional tcnq units stabilising the lattice. The overall stoichiometry is explained by the bulky trifluoromethyl groups creating lattice space that is consequently occupied by an additional π-stacking interaction within the interchain spaces.

L^{163} L^{164}

L^{165}
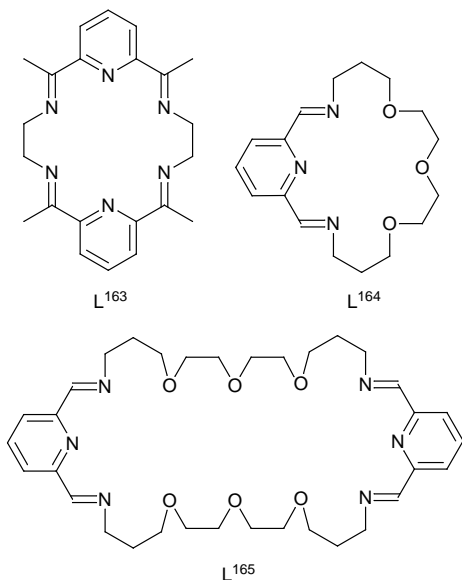
The La^{III} complex of L^{163} is an effective catalyst for the hydrolysis of water-soluble phosphate esters.[134] Rate enhancement of up to three orders of magnitude was achieved, with a metal-bound hydroxide group being the possible catalytic intermediate. The interaction of La^{III}, Eu^{III} and Y^{III} complexes of L^{163} with a range of β-diketones and sodium β-diketonates has been studied in solution by luminescence spectroscopy.[135] The complex $[Eu^{III}(OAc)\{(C_6H_5CO)_2CH\}(L^{163})]\cdot CH_3CO_2\cdot 6H_2O$ was crystallographically characterised; the metal centre is ten-co-ordinate, with the co-ordination sphere consisting of all six macrocyclic *N*-donor atoms, a chelating acetate and a bidentate β-diketonate. Two interesting template syntheses of the novel ligands L^{164} and L^{165} have been reported.[136] The former is obtained when Cu^{II} is used as a template in the condensation of 2,6-diformylpyridine and 1,13-diamino-4,7,10-trioxatridecane; L^{165} is obtained in an analogous reaction with Ni^{II}.

Macrocycles of higher denticity

The heptaaza terpy-derived ligand L^{166} forms a $1:1$ Ag^I complex, $[Ag^I(H_2O)_2(L^{166})]$ $[PF_6]$.[137] Cyclic voltammetry shows a reversible one-electron oxidation, attributed to the formation of a ligand-based radical cation. This result was confirmed by EPR and IR spectroscopies.

L^{166}

L^{167}

L^{168}

L^{169} R = CH$_2$OMe
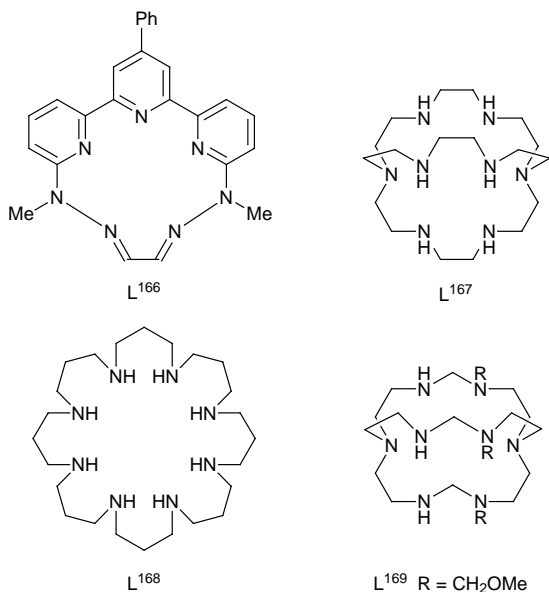
The octadentate cryptand L^{167} forms stable complexes with a range of first-row transition-metal ions (Mn^{II}, Co^{II}, Co^{III}, Ni^{II} or Zn^{II}).[138] In addition, the relative stability of the divalent complexes compared to that of the related sepulchrates has been discussed. In some cases, where the ionic radius was small (Co^{III}, Ni^{II} or Zn^{II}), stable protonated complexes could be isolated. The metal centre in [Mn^{II}(L^{167})][ClO$_4$]$_2$ has approximate octahedral geometry with the six ligand secondary amines forming the co-ordination sphere. Octaaza L^{167} forms mononuclear complexes [M(L^{167})]$^{2+}$ (M = Ni^{II}, Cu^{II} or Zn^{II}) which upon acidification in aqueous solution predominantly yield the protonated complexes [M(HL^{167})]$^{3+}$ and [M(H$_2$L^{167})]$^{4+}$.[139] The structure of [Ni^{II}(HL^{167})]$^{3+}$ indicates that the metal centre occupies one end of the cavity with the proton bound to a vacant secondary amine site at the opposite end. pH-Sensitive switching of electron transfer between [Fe^{III}(CN)$_6$]$^{3-}$ and I$^-$ has been studied in the supercomplex [{Fe^{III}(CN)$_6$}$^{3-}$-(HL^{168})$^{8+}$]$^{5+}$.[140] In acidic media thermal and photo-induced electron transfer was observed with the macrocycle thermodynamically enhancing the thermal process (*via* an anodic shift in the Fe$^{II/III}$ couple upon binding with [H$_8$L^{168}]$^{8+}$) and kinetically enhancing the photoinduced reaction (*via* ion-pair formation). The Co^{II} complex of the cryptand ligand L^{169} has been prepared by a template condensation of Co^{II}, tren and formaldehyde.[141] The crystal structure of the complex [Co^{II}(L^{169})][BF$_4$]$_2$ indicated that the metal centre is five-co-ordinate with trigonal-bipyramidal geometry. Optimised syntheses for the pendant-arm octaaza macrocycles H$_8$L^{170} and H$_8$L^{171} have been published.[142] These ligands form highly water-soluble dinuclear complexes with Y^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Yb^{III} or Lu^{III}, whilst only mononuclear La^{III} complexes could be isolated.

The synthesis of the bis(calix[4]arene) (a 'calix[4]tube') L^{172} has been described.[143] In experiments with alkali-metal cations in solution, K$^+$ was fully incorporated into

R = CH$_2$CO$_2$H

H$_8$L^{170} $n = 0$
H$_8$L^{171} $n = 1$
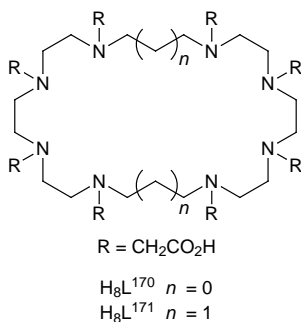
L^{172} within one hour whilst Li$^+$, Na$^+$, Rb$^+$ or Cs$^+$ were only weakly bound after several days. Thus L^{172} is a rare example of an almost completely selective ionophore. The novel, potentially octadentate, ligand L^{173} has been prepared by the template reaction of a Ni^{II} salt, tren and formaldehyde.[144] The structure of [Ni^{II}(L^{173})]$^{2+}$ indicated a tetragonally distorted six-co-ordinate metal.

Mononuclear and phosphate-bridged dinuclear Cu^{II} complexes and a range of protonation studies of the 26-membered macrocycle (L^{174}) have been described.[145] Equilibrium constants were also obtained and compared to those of the related [24]aneN$_6$O$_2$ system. The Ni^{II}, Cu^{II} and Zn^{II} complexes of cryptand L^{175} have been synthesised.[146] All are mononuclear, with general formula [M(L^{175})][ClO$_4$]$_2$. The structure of [Ni^{II}(H$_2$O)(NCMe)(L^{175})][ClO$_4$]$_2$·H$_2$O·2MeCN indicates that the metal is octahedral, being co-ordinated by the 'tren' component of the ligand, with water and acetonitrile molecules completing the co-ordination sphere. The co-ordinated water molecule was found to hydrogen bond to an ether group and the opposing bridgehead nitrogen atom. The crystal structure of the free ligand was also described. The picrate salt of [Co^{II}(NCS)(L^{175})] has a five-co-ordinate trigonal bipyramidal metal centre with four N donors derived from the tren end of the cryptand and an SCN$^-$ ligand occupying the axial site.[147] This complex is an olefin oxidation catalyst.

L^{172}

L^{173}
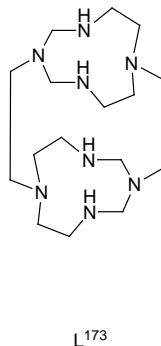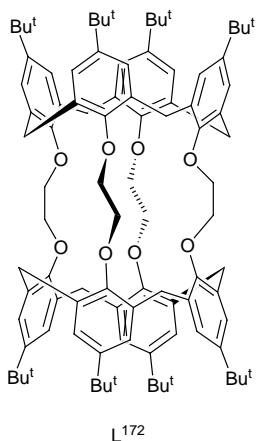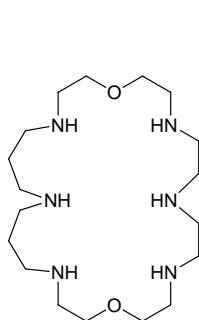
L^{174}
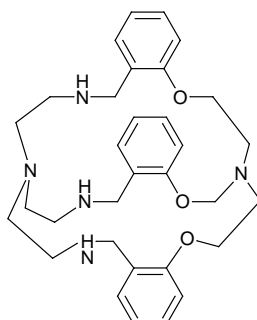
L^{175}

The stability constants of the binuclear Zn^{II} complex of the decadentate large ring ligand L^{176} have been determined.[148] This complex was also used in a kinetic study of phosphate ester hydrolysis; a mechanism which involves a mononuclear Zn^{II} complex is most likely. The structural and spectroscopic properties of binuclear complexes of the new large ring cyclophane ligand H$_4$L^{177} have been investigated.[149] The free ligand displayed fluorescence at 290 nm (210 nm irradiation) the intensity of which was increased upon binding Zn^{II} ions but decreased with the incorporation of Ni^{II} or Cu^{II}. The intensity of a ligand based π–π* transition was increased by an order of magnitude upon co-ordination of Cu^{II} ions, which was thought to arise from the central benzene rings being brought into close proximity upon complex formation. A series of novel mixed-donor large-ring selena-crown ethers (L$^{178-180}$) has been prepared and their co-ordination chemistry with HgI$_2$ examined.[150] All three ligands bind two mole equivalents of HgI$_2$ to form dinuclear complexes of general formula [(HgI$_2$)$_2$(L$^{178-180}$)]. The crystal-structure analysis of [(HgI$_2$)$_2$(L$^{178-180}$)] indicated that only the Se donors of the macrocycle co-ordinated to the approximately tetrahedral Hg^{II} centres, with iodide donors occupying the remaining two co-ordination sites at each metal centre.

L^{176}

H$_4$L^{177}

L^{178} $n = 1$
L^{179} $n = 2$
L^{180} $n = 3$
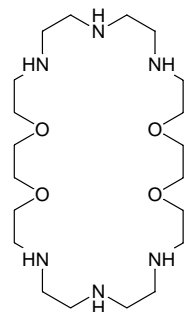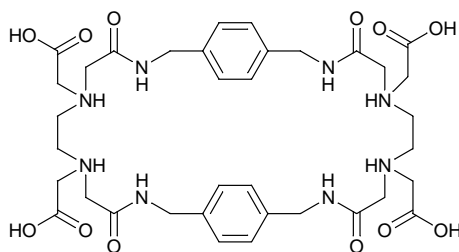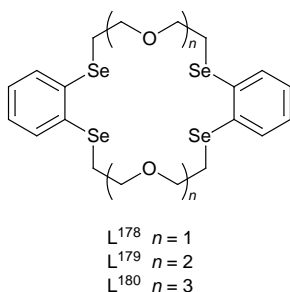
Schiff-base ligands

The Cu co-ordination chemistry of the macrobicyclic Schiff base L^{181} has been examined.[151] Reaction of L^{181} with [Cu^I(NCMe)$_4$][BF$_4$] yielded the homodinuclear complex [Cu$^I_2$(L^{181})][BF$_4$]$_2$; the ligand remains intact with the complex cation displaying C_{3h} symmetry and each copper centre in approximate trigonal-pyramidal geometry. The Cu^I···Cu^I separation was 6.250 Å. In contrast, the reaction of L^{181} with hydrated Cu^{II}[BF$_4$]$_2$ resulted in cleavage of the bicyclic structure (*via* elimination of a diacetylpyridinyl unit) to yield the dinuclear Cu^{II} complex of the bibracchial ligand L^{182}; the Cu^{II} centres adopt approximate trigonal-bipyramidal geometry. Lanthanum(III) and Y^{III} nitrate salts have been used in the template synthesis of the Schiff-base cryptand H$_3$L^{183} by the condensation of 2,6-diformyl-4-methylphenol and tren.[152] The isolated complexes have the general formula [M$^{III}_2$(L^{183})][NO$_3$]$_6$· xH$_2$O·$y$solv. The Dy^{III} complex consisted of mononuclear [Dy^{III}(NO$_3$)(L^{183})]$^{2+}$ cations and [Dy^{III}(NO$_3$)$_5$]$^{2-}$ anions (ten-co-ordinate Dy^{III}). The cation has an eight-co-ordinate Dy^{III} centre with a co-ordination sphere consisting of four nitrogen atoms from the tren component of the ligand, three (protonated) phenolic oxygen groups and a monodentate nitrate ion. Lanthanum(III)-templated synthesis of the large ring Schiff-base ligand H$_2$L^{184} has been described.[153] The crystal structure of the binuclear complex [La$^{III}_2$(OAc)$_4$(L^{184})]·4MeCN·3H$_2$O showed that each La^{III} was contained within the ligand cavity. Each metal ion is 12-co-ordinate with approximate bicapped dodecahedral symmetry. The co-ordination sphere of each ion consists of two chelating acetate groups, two phenolate oxygens and four imine nitrogens. The large ring

L^{181} L^{182}
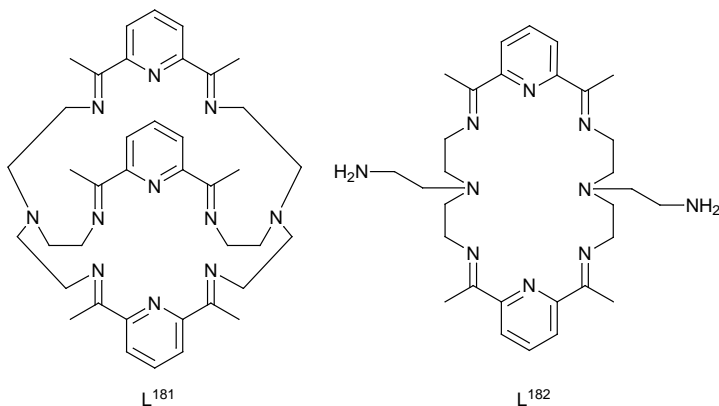
Schiff-base ligand L^{185} forms a dinuclear Cu^I complex upon treatment with $[Cu^I(NCMe)_4][ClO_4]$.[154] The two metal centres have tetrahedral geometry stabilised by a π-stacking interaction of the *m*-substituted benzene rings. The benzenethiol-containing ligand H_2L^{186} forms a 1:2 Zn^{II} complex $[Zn^{II}_2(L^{186})][CF_3SO_3]_2$.[155] Most unusually (for a compartmental ligand) the thiophenolate donors do not bridge the metal centres. The macrocycle adopts a distorted, folded conformation with the two metal centres in distorted tetrahedral geometries, with three nitrogen donors and a unidentate thiophenolate donor.

H_3L^{183}

H_2L^{184}
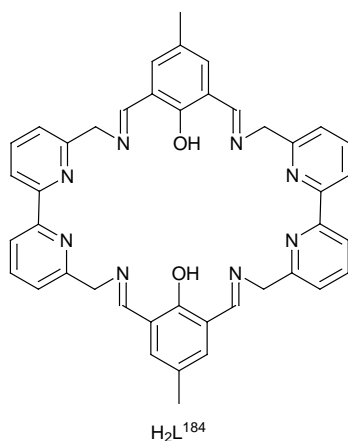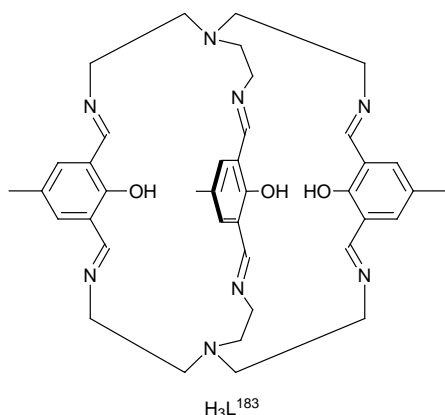
The template synthesis of the tetranuclear Ni^{II} complex $[Ni^{II}_4(OH)(MeCO_2)_3(MeCO_2H)(L^{187})]\cdot MeOH$ has been described.[156] Each metal centre is six-co-ordinate being bonded to benzenethiolate, alkoxy, imino, hydroxy and bridging acetate donors. Thus each Ni^{II} ion is linked to an adjacent metal centre *via* three types of bridging group (an alkoxide, a 1,3-acetate and the central hydroxide).

The symmetrically substituted phthalocyanine complexes $[M(L^{188})]$ ($M = H_2$, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} or Zn^{II}) have been prepared.[157] The complexes proved to be extremely

L^{185}

H_2L^{186}

H_4L^{187}

L^{188} R =
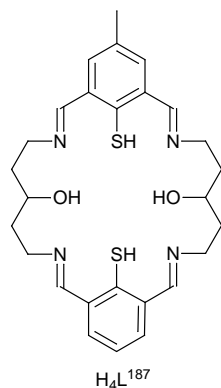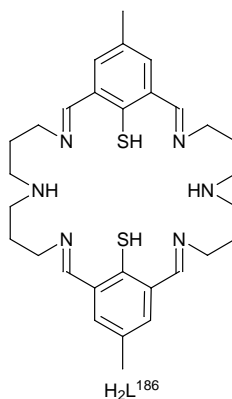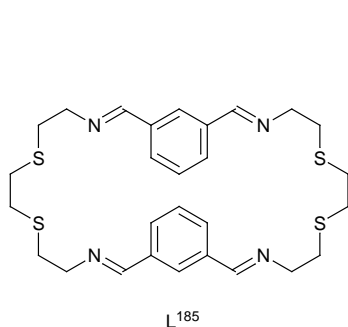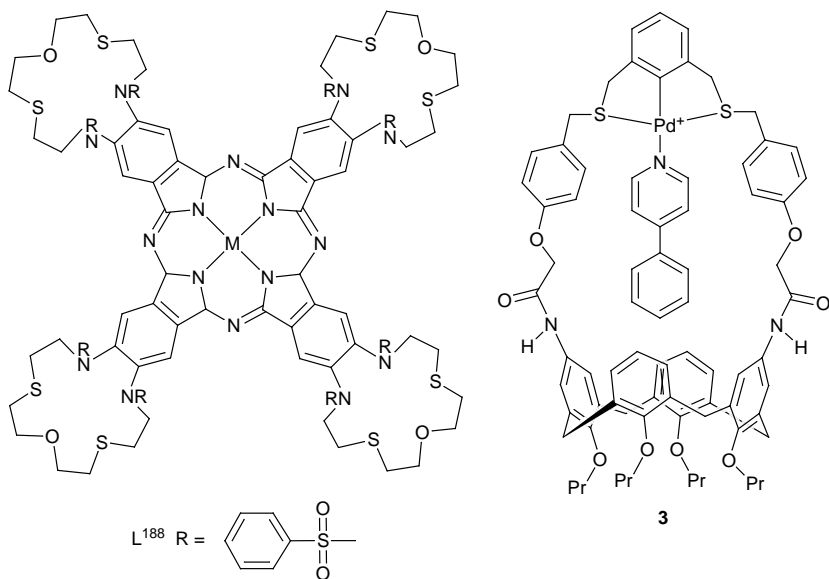
insoluble which hampered further complexation studies. The metalloreceptor **3** has been prepared; the complex displays both first- and second-sphere co-ordination to a molecule of 4-phenylpyridine.[158] This is achieved *via* pyridyl binding to the Pd^{II} centre and inclusion of the phenyl group in the lipophilic cavity of the calix[4]arene component.

The novel 56-membered macrocycle L^{189} has been prepared and a range of complexes, including threaded structures and catenands, characterised.[159] For the mononuclear complex $[ReCl(CO)_3(L^{189})]$ (which has an unco-ordinated phen unit) energy transfer occurred between the unco-ordinated and co-ordinated phen units, with irradiation of the former resulting in emission from the latter. The phen-containing macrocycle L^{190} and rigid linear pyridyl ligands such as L^{191} form multi

L^{189}
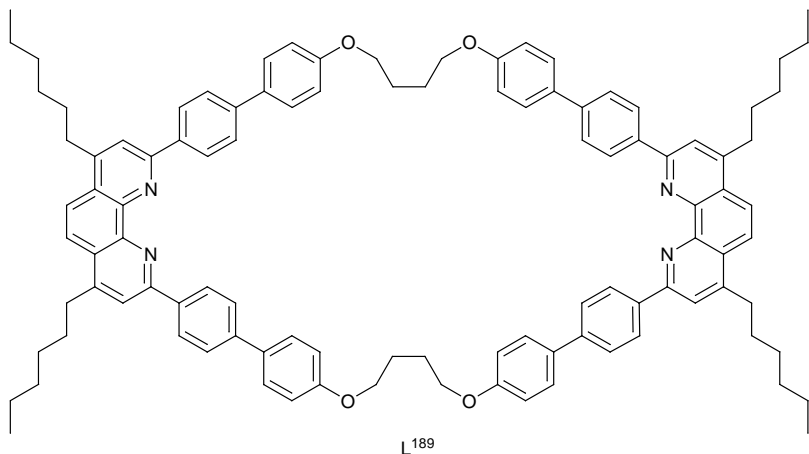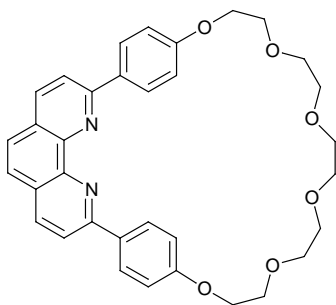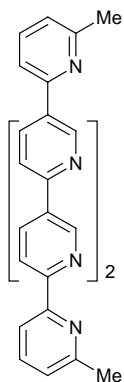
L^{190}

L^{191}

L^{192}

L^{193}

L^{194}

L^{195}
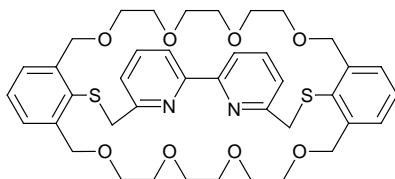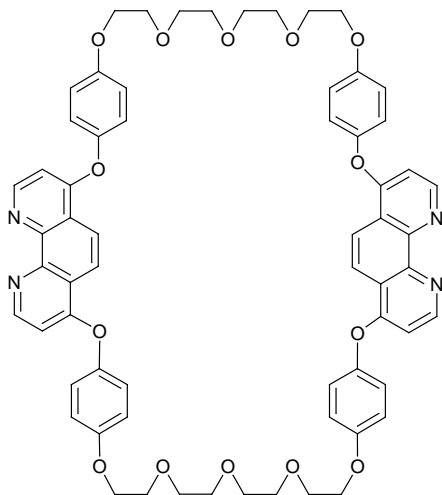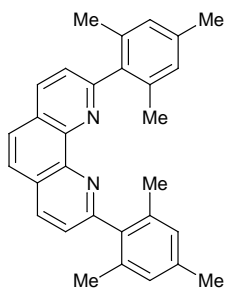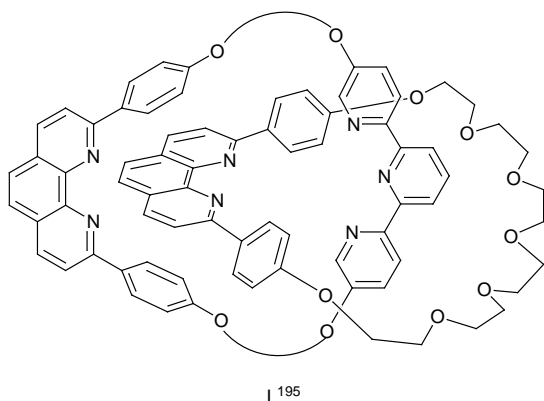
component pseudo-rotaxane complexes of the type $[\{Cu^I(L^{190})\}_3(L^{191})][PF_6]_3$.[160] The structures were confirmed in the solid state by X-ray crystallography and in solution by NMR spectroscopy. The bipyridine-containing macrobicyclic ligand L^{192} shows a very high affinity for Ag^I ions, with good selectivity over dications (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} or Pb^{II}) in liquid-membrane transport experiments.[161]

The combination of a large ring macrocycle L^{193} and the bulky 2,9-phenanthroline ligand L^{194} permits the synthesis of the dinuclear complex $[Cu^I_2(L^{193})(L^{194})_2]^{2+}$.[162] Each metal centre is bound in an exocyclic manner by two different phen fragments which are not susceptible to common ligand exchange processes. The electrochemical rearrangement of the Cu complex of the mixed-donor site catenate ligand L^{195} can be monitored by EPR spectroscopy.[163] One component of the ligand contains phen units, whilst the other contains both phen and terpy moieties. Thus the oxidation of $[Cu^I(L^{195})]^+$ [bis(phen) co-ordination sphere] to $[Cu^{II}(L^{195})]^{2+}$ results in a rearrangement to $[Cu^{II}(L^{195})]^{2+}$ (phen-terpy co-ordination sphere).

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