DALTON

Structure of the copper(II) complex of the reinforced ligand *N*,*N′*-bis(*trans*-2-hydroxycyclohexyl)-*trans*-cyclohexane-1,2-diamine and the metal-ion-size-based selectivity produced by cyclohexanediyl bridges *

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The compound *N*,*N′*-bis(2-hydroxycyclohexyl)-*trans*-cyclohexane-1,2-diamine (L^1) and its complex with Cu^{II} have been prepared. The structure of $[CuL^1][ClO_4]_2$ **1** was determined. The Cu has a distorted octahedral co-ordination, with the four donor atoms provided by L^1 giving Cu−N 1.985(7) and Cu−O 1.947(6) Å. The oxygens from two perchlorates lie on the axial positions with Cu−O 2.749 Å. The perchlorates are involved in a hydrogen bonding network holding layers of $[CuL^1]^{2+}$ cations together with bonds to the hydrogens of the co-ordinated hydroxyls of the cyclohexanediyl groups and the NH hydrogens. Alternating layers of $[CuL^1]^{2+}$ cations have the L^1 ligand as the *SRS* and *RSR* enantiomers. Difficulty in obtaining a sufficiently large data set for L^1 meant that *R* for this structure was not less than 0.13. The structure is thus not reported in any detail, but is sufficient to indicate the conformation of the ligand, which is used as the basis of a molecular mechanics generation of the structure. Both the copper(II) complex of L^1 and L^1 itself have only the *RSR* and *SRS* diastereomeric pair present in the structures, supporting the idea that syntheses involving reaction of cyclohexene oxide with polyamines result in considerable diastereoselectivity. The structure of **1** shows steric crowding, with van der Waals repulsion between hydrogens on adjacent cyclohexyl groups of the L^1 ligand. This crowding becomes more severe as the metal ion becomes larger, which is related to the strong preference the ligand shows for smaller metal ions. This latter effect is indicated by the formation constants (log K_1) of L^1: Cu^{II}, 11.50; Ni^{II}, 6.84; Zn^{II}, 4.77; Cd^{II}, 4.08; Pb^{II}, 4.80; in 0.1 mol dm^{-3} $NaNO_3$ at 25 °C. The effect of cyclohexanediyl bridges on the stability of complexes formed by L^1 is discussed in relation to the stability of complexes of similar ligands that have simple ethylene bridges between their donor atoms.

We have over the last several years attempted to uncover structural features in ligand architecture that can be used with a fair degree of reliability to alter ligand selectivity in a desired direction. Control of ligand selectivity for metal ions is of particular interest in biomedical applications, and in areas such as ligands for clean-up of radioactive waste and the environment.[1] Architectural features that have been identified as useful are chelate ring size[2] (smaller chelate rings favour larger metal ions) and the presence of neutral oxygen donors,[3] which favours larger metal ions. The replacement of ethylene bridges between donor atoms with cyclohexanediyl bridges has been found[4] to shift selectivity in favour of smaller metal ions. (By selectivity in this paper is meant the difference in the formation constant, log K_1, for the metal ions of interest.) More recently, the facile synthesis of a variety of polyamines substituted with cyclohexene oxide has been reported in a preliminary communication,[5a] and complexes of azamacrocycles with *N*-2-hydroxycyclohexyl substituents have been studied.[5b] The synthesis of these compounds involved simply treating polyamines or azamacrocycles with cyclohexene oxide in absolute ethanol, which gives crystalline products that show highly selective addition of cyclohexene oxide, both with respect to the numbers of such groups added as well as the diastereoselectivity of the products. For example, en (ethane-1,2-diamine) reacts even with large excesses of cyclohexene oxide to give only the *meso* form of the *N*,*N′*-disubstituted product in 80% yield.

Schwarzenbach *et al.*[6] reported the complexing properties of *trans*-H_4cdta many years ago. Compared to the simpler analogue H_4edta, the presence of a cyclohexanediyl bridge caused increases in log K_1 of up to 5 log units, which are metal-ion size related.[4] The more rigid cyclohexanediyl bridge might be said to *reinforce* the ligand, and make it more *preorganised*. Reinforcement of bridges between donor atoms of ligands by groups that make them more rigid than do simple ethylene bridges has been accomplished in a variety of ways, including the introduction of a second bridge spanning the two donor atoms.[7,8] Preorganisation[9] is an important concept in ligand design. The more preorganised a ligand is the more nearly are the donor atoms in it constrained to be arranged spatially as required for complexing the metal ion. In this paper we report the synthesis of *N*,*N′*-bis(2-hydroxycyclohexyl)-*trans*-cyclohexane-1,2-diamine (L^1), its structure and the complex $[CuL^1][ClO_4]_2$, and the formation constants of L^1 with Cu^{II}, Ni^{II}, Zn^{II}, Cd^{II} and Pb^{II}. The latter set of metal ions provides a large range of sizes, as shown by the ionic radii, that range from[10] 0.57 to 1.18 Å. The compound L^1 has its four donor atoms, two nitrogens and two oxygens, connected by three cyclohexanediyl bridges. It thus represents the complete replacement of all ethylene bridges by cyclohexanediyl bridges, and as such should show high levels of preorganisation, as well as interesting selectivity properties.

Experimental

Syntheses

***N*,*N′*-Bis(2-hydroxycyclohexyl)-*trans*-cyclohexane-1,2-diamine (L^1).** *trans*-1,2-Diaminocyclohexane (Merck; 1.0 g, 0.008 76 mol) was dissolved in anhydrous ethanol (60 cm^3). Cyclohexene oxide (3.5 g, 0.035 mol) was added dropwise with stirring. The solution was refluxed for 12 h with a $CaCl_2$ drying tube attached to the condenser. Removal of the solvent under reduced pressure gave a colourless viscous oil, which gave an off-white solid on drying under reduced pressure. This was dissolved in acetone (20 cm^3). After standing in a refrigerator for 12 h, the white crystalline solid that had precipitated was fil-

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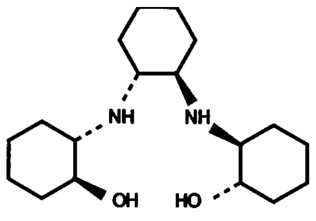
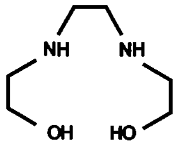
* *Non-SI unit employed*: cal = 4.184 J.


L^1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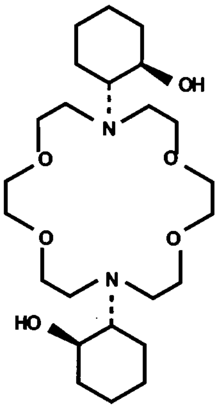
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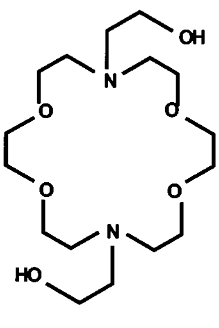
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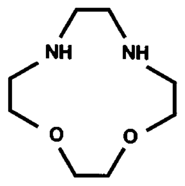
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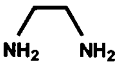
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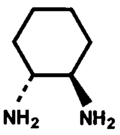
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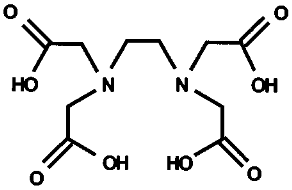
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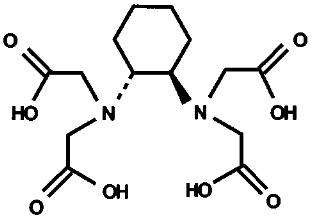
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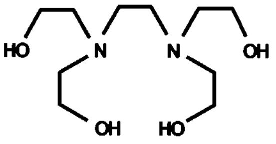
theen

tered off. Mass collected 1.9 g, 73% yield (Found: C, 69.6; H, 11.4; N, 9.0. Calc. for $C_{18}H_{34}N_2O_2$: C, 69.65; H, 11.05; N, 9.0%).

[CuL^1][ClO$_4$]$_2$. The salt $Cu(ClO_4)_2{\cdot}6H_2O$ (Aldrich; 0.6 g, 0.016 mol) was dissolved in deionised water (10 cm^3). To this was added a solution (10 cm^3) of KOH (0.2 g, 0.0322 mol) and the mixture was stirred on an ice-bath for 30 min. The compound L^1 (0.2 g, 0.016 mol) dissolved in water (15 cm^3) was added dropwise with stirring and gentle warming to about 60 °C. A small quantity of $HClO_4$ (12 mol dm^{-3}) was added to redissolve the precipitate that formed. On slow evaporation of the solution on standing purple crystals were deposited, collected and air dried. Mass collected 0.68 g, yield 74% (Found: C, 37.55; H, 5.85; N, 4.75. Calc. for $C_{18}H_{34}Cl_2CuN_2O_{10}$: C, 37.75; H, 6.0; N, 4.9%).

X-Ray crystallography

Crystals of [CuL^1][ClO$_4$]$_2$ **1** and of L^1 were mounted on glass fibres at room temperature. Crystal density was determined by flotation in mixtures of 1,2-dibromoethane and chloroform. Preliminary examination and data collection were performed on a Rigaku AFC5 (oriented graphite monochromator, Mo-Kα radiation, λ 0.710 73 Å) at 293(2) K. Cell parameters were calculated from the least-squares fitting for 25 high-angle reflections ($2 < \theta < 15°$). Omega scans for several intense reflections indicated acceptable crystal quality. For **1** data were collected at θ 11.0 to 20.0°, scan width 0.60 + 0.35 tan θ in ω with a variable scan speed of 0.6 to 5.49° min^{-1}. Weak reflections were rescanned (maximum of two rescans) and the counts for each scan were accumulated. The three standards, collected every 150 reflections, showed no significant trends. Background measurement was by the stationary crystal–stationary counter technique at the beginning and end of each scan for half the total scan time. Lorentz-polarisation corrections were applied. A total of 1150 unique observed reflections were used in further calculations. For L^1 poor crystal quality resulted in difficulty in collecting a sufficiently large data set for adequate solution of the structure, only 471 reflections being obtained. The poor crystal quality resulted in a high R factor of 0.13. However, the structure indicates the conformation adopted, so that this information is used here. In the solution of **1** semiempirical absorption corrections were applied.[11] The structure was solved by direct methods.[12] Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded $R = 0.0563$ at convergence.[13] The structure of **1** is shown in Fig. 1. The crystal data and details of structure refinement for **1** are given in Table 1, selected bond lengths and angles in Table 2.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/549.

Molecular mechanics calculations

The program MM2[14] is available in the CACHE suite of programs, and was used to generate the structure of free L^1 using the crystal coordinates as a trial structure. The structure, showing the hydrogen bonding, is seen in Fig. 2.

Stability constant determination

The protonation constants of L^1 were determined in 0.1 mol dm^{-3} $NaNO_3$ by conventional glass-electrode techniques.[1] The

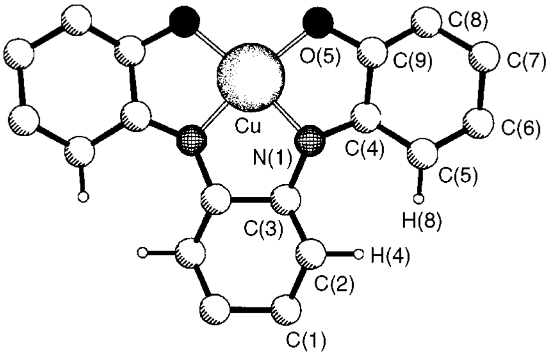

Fig. 1 Structure of the copper(II) complex of L^1, showing the numbering scheme, and the hydrogens H(4) and H(8), which clash sterically on co-ordination of L^1

pH values of the solutions were recorded using a Radiometer PHM 84 pH meter, and GK2402B glass electrode. The high levels of preorganisation of free L^1 meant that complex-formation reactions were slow. Therefore, an out-of-cell technique[15] was employed where sets of solutions with varying concentrations of metal ion, L^1, and acid were prepared in 0.1 mol dm^{-3} NaNO$_3$ and allowed to equilibrate in a water-bath at 25 °C. The equilibria involved were monitored by recording the UV/VIS spectra, and also the pH, of the solutions. For the Cu^{2+}–L^1 solutions a set of low-pH spectra were obtained with a peak maximum for the complex at 651 nm, which was present between pH 2 and 5. Between pH 5 and 11 a new peak with a maximum at 608 nm formed, with an isosbestic point at 650 nm. The variation of the spectra as a function of pH was fitted using the simplex program NLFIT, which gave the formation constants shown in Table 3. The Ni^{2+}–L^1 system also had two sets of clearly differentiated equilibria. At low pH a blue complex with peaks at 370 and 604 nm was formed. At higher pH values a red complex, which colour is suggestive of square-planar Ni$^{\rm II}$, formed with a single intense peak at 491 nm in the electronic spectrum. Since the complexes of L^1 with Pb$^{\rm II}$, Cd$^{\rm II}$ and Zn$^{\rm II}$ do not absorb significantly above 200 nm their formation constants were determined by competition reactions with Ni$^{\rm II}$. Again an out-of-cell technique was used, and the effect of varying concentrations of the metal ions of interest on the spectrum of [NiL^1]$^{2+}$ was used to calculate log K_1. The program NLFIT was used to fit log K_1 values for Pb$^{\rm II}$, Cd$^{\rm II}$ and Zn$^{\rm II}$ to the depression of the bands due to the [NiL^1]$^{2+}$ ion as a function of the concentration of these metal ions.

Results and Discussion

The structure of the complex cation of [CuL^1]$^{2+}$ is shown in Fig. 1. The crystal contains a single enantiomeric pair. For the (*R*,*R*)-*trans*-1,2-diaminocyclohexane moiety of the complex the two *trans*-2-hydroxycyclohexyl substituents have *S*,*S* chirality, while for the (*S*,*S*)-*trans*-diaminocyclohexane moiety the opposite chirality occurs for the 2-hydroxycyclohexyl substituents. These will be referred to as the *SRS* and *RSR* enantiomers respectively. The crystal contains alternating layers of *RSR* and *SRS* enantiomers. The Cu$^{\rm II}$ is co-ordinated to the two nitrogens and two oxygens of the ligand, as well as two oxygens [O(2)] from perchlorates at a distance of 2.749 Å, so that it can be viewed as having a rather distorted octahedral geometry. The perchlorates are held to the [CuL^1]$^{2+}$ cation not only by the long weak bonds to Cu, but also by hydrogen bonds from O(1) on the perchlorate to N(1), with an N···O separation of 2.98 Å. The oxygen atoms O(2) of the perchlorates not only form long bonds to the Cu$^{\rm II}$ of one [CuL^1]$^{2+}$ cation, but hydrogen bond to a hydrogen of an alcoholic oxygen [O(5)] in the next layer of complex cations, with an O(2)···O(5) separation of 2.797 Å. The geometry around Cu$^{\rm II}$ generated by the four donor atoms of L^1 is slightly distorted towards tetrahedral, with the *trans* O–Cu–N angles having values of 165.4° instead of the 180° expected for a regular square plane. An important feature of the structure of [CuL^1]$^{2+}$ shown up by the present study is the potential for steric crowding caused by the presence of three adjacent cyclohexanediyl bridges. The separation of the pairs of hydrogens H(4) from H(8), and H(4′) from H(8′), is only some 2.0 Å (Fig. 1), which is inside the shortest estimates[16] for the sum of the van der Waals radii of two hydrogens of 2.4 Å. This will lead to some steric strain on complex formation for Cu$^{\rm II}$, which should become large as the metal-ion size increases. This is an important aspect of cyclohexylene bridges, and is responsible for the preference for small metal ions induced on replacing an ethylene bridge with a cyclohexenyl bridge. The larger the metal ion the more the substituents at C on adjacent bridges of the ligand are pressed up against each other, and the more serious is the steric strain. This is demonstrated in the MM calculations on L^1 complexes reported below.

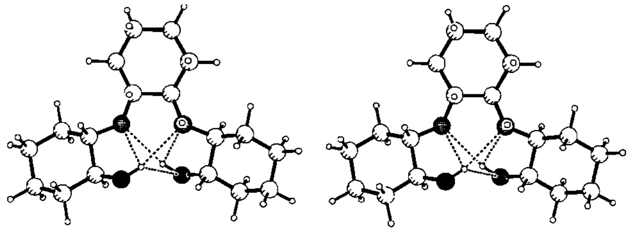

Fig. 2 Stereoview of L^1 showing the internal hydrogen bonding, with structures generated using the MM2 program.[14] The trial structure for the MM2 generation of L^1 was taken from the crystallographic study mentioned in the text, which was sufficient only to indicate the conformation of L^1. The MM2 structure differs little from that found in the crystal structure

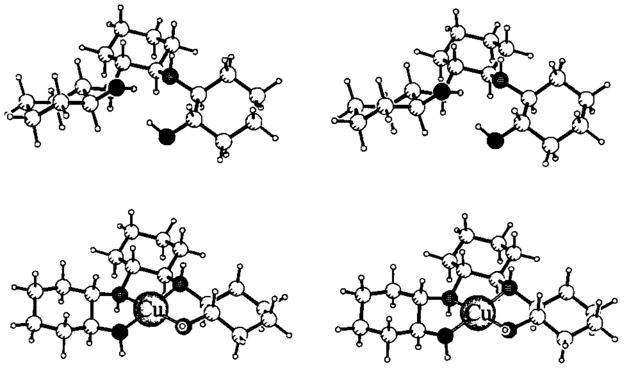

Fig. 3 Comparison of the structures of free L^1 and the complex [CuL^1]$^{2+}$, showing the change in orientation of the 2-hydroxycyclohexyl groups that occurs on co-ordination

The structure of L^1 is shown in Fig. 2. Unlike the copper(II) complex of L^1, the 2-hydroxycyclohexyl groups are rotated around to maximise hydrogen bonding within the cavity, and minimise the H···H repulsions which become not inconsiderable on co-ordination to Cu$^{\rm II}$ or other metal ions. In Fig. 2 the L^1 molecule is shown in stereoview, indicating the internal hydrogen bonding that stabilises the conformer observed. The structure in Fig. 2 was derived from the coordinates of the crystallographic study, but was energy minimised using MM2[14] to give better bond lengths and angles. An interesting question is the extent to which the free L^1 is preorganised for co-ordinating to metal ions. The hydrogen-bonding structure seen in Fig. 2 should act to hold it in a fairly rigid conformation. However, as seen in Fig. 3, the 2-hydroxycyclohexyl groups in free L^1 are in a quite different orientation to that found for the copper(II) complex. One can estimate the effect of conformational changes required to form the complex by the method of Hay *et al.*[17] The strain energy of free L^1 can be calculated, in this case using MM2. So as not to skew the results, the hydrogen-bonding part of the strain energy was omitted from the calculation. The internal hydrogen bonding present in some

Table 1 Crystal data and structure refinement* for $[CuL^1][ClO_4]_2$ **1** and L^1

	1	L^1
Empirical formula	$C_{18}H_{34}Cl_2CuN_2O_{10}$	$C_{18}H_{34}N_2O_2$
M	572.93	310.98
a/Å	14.175(1)	12.072(2)
b/Å	19.249(2)	17.789(4)
c/Å	9.214(1)	10.414(2)
β/°	103.86(1)	122.82(2)
U/Å^3	2440.95(6)	1872.42(2)
D_c, D_m/g cm^{-3}	1.559, 1.543	1.103, 1.092
μ/mm^{-1}	11.75	0.4
F(000)	715	690
Crystal size/mm	0.22 × 0.15 × 0.09	0.43 × 0.39 × 0.28
Crystal colour and habit	Blue plate	Colourless plate
Scan speed/° min^{-1}	0.6–5.49	0.6–2.75
θ Range for data collection/°	11–20	10.43–23.3
Reflections collected	5306	609
Independent reflections	1150	471
Final *R*	0.0563	0.1303

* Details in common: monoclinic, space group *C*2/*c*; *Z* = 4; ω–2θ scans; scan width 0.60 + 0.35 tan θ.

Table 2 Selected bond lengths (Å) and angles (°) in $[CuL^1][ClO_4]_2$ **1**

Cu–N(1)	1.985(7)	Cu–O(5)	1.947(6)
N(1)–Cu–N(1′)	90.1(4)	N(1)–Cu–O(5)	85.9(3)
N(1)–Cu–O(5′)	165.4(4)	O(5)–Cu–O(5′)	101.3(4)
Cu–N(1)–C(3)	106.3(5)	Cu–N(1)–C(4)	102.9(5)
Cu–O(5)–C(9)	111.5(5)		

Table 3 Protonation and formation constants of L^1 with a variety of metal ions, in 0.1 mol dm^{-3} $NaNO_3$ at 25 °C

Lewis acid	Equilibrium	log *K*
H^+	$H^+ + OH^- \rightleftharpoons H_2O$	13.78*
	$L + H^+ \rightleftharpoons HL^+$	9.54(2)
	$HL^+ + H^+ \rightleftharpoons H_2L^{2+}$	4.52(2)
Cu^{2+}	$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	11.50(5)
	$CuL^{2+} + OH^- \rightleftharpoons CuLH_{-1}{}^+$	7.53(5)
	$CuLH_{-1}{}^+ + OH^- \rightleftharpoons CuLH_{-2}$	5.62(5)
Ni^{2+}	$Ni^{2+} + L \rightleftharpoons NiL^{2+}$	6.84(5)
	$NiL^{2+} + OH^- \rightleftharpoons NiLH_{-1}{}^+$	9.81(5)
	$NiLH_{-1}{}^+ + OH^- \rightleftharpoons NiLH_{-2}$	8.96(5)
Zn^{2+}	$Zn^{2+} + L \rightleftharpoons ZnL^{2+}$	4.77(5)
Cd^{2+}	$Cd^{2+} + L \rightleftharpoons CdL^{2+}$	4.08(5)
Pb^{2+}	$Pb^{2+} + L \rightleftharpoons PbL^{2+}$	4.80(5)

* Ref. 16.

Table 4 Formation constants for Cu^{II} complexes of ligands with N_2O_n donor sets

	Ligand					
	en	dheen	L^1	[12]aneN_2O_2	theen	dach
Donor set	N_2	N_2O_2	N_2O_2	N_2O_2	N_2O_4	N_2
log K_1 Cu^{II}	10.5	9.68	11.50	8.66	8.49	10.94

Formation constants from ref. 17; except L^1, this work.

free L^1 would represent only some of the hydrogen bonding, as all L^1 are capable of hydrogen bonding to the solvent, which would not be taken into account. The Cu^{II} was deleted from the $[CuL^1]^{2+}$ structure obtained crystallographically here, and again the steric energy calculated using MM2, omitting any hydrogen bonding contributions. One finds that the steric energy of free L^1 is 28.1 kcal mol^{-1}, while that of the ligand obtained from the complex by removing the Cu^{II} is 31.2 kcal mol^{-1}. (One should be careful to manage the atom types in MM2 correctly, as mentioned for those interested in repeating these types of calculations.†) This increase in strain energy of 3.1 kcal mol^{-1} on complex formation for L^1, which Hay has termed the reorganisation energy (U_{reorg}), can be compared to a U_{reorg} of 2.5 kcal mol^{-1} for the formation of the copper(II) complex of cyclam (1,4,8,11-tetraazacyclotetradecane). The cyclam ligand is generally regarded as being well preorganised for complexing Cu^{II}, so that this calculation suggests that U_{reorg} for L^1 when complexing Cu^{II} is not large.

Stability of complexes of L^1

The protonation and formation constants for L^1 are shown in Table 3. The protonation constants are somewhat lower than those of dheen,[18] which has pK_1 = 9.24 and pK_2 = 6.26; dheen has only ethylene bridges between the donor atoms of its N_2O_2 donor set, where L^1 has all cyclohexanediyl bridges. This possibly reflects steric hindrance to hydration of the protons on the nitrogens of L^1 by its bulky cyclohexanediyl bridges, or that the internal hydrogen bonding in L^1 would be disrupted by protonation. The lower protonation constants of L^1 as compared to other diamines such as dheen, or en itself, are attractive, since this makes L^1 more effective at lower pH values when complexing metal ions. What is of particular interest in Table 3 is the high value of log K_1 for Cu^{II} with L^1. This is seen for some ligands with N_2O_n donor sets in Table 4. One sees that L^1 forms more stable complexes with Cu^{II} than either dheen, which has sterically non-crowding ethylene bridges, or [12]aneN_2O_2 which is a macrocycle. It also forms complexes with Cu^{II} that are more stable than either the en complex, with no 2-hydroxyethyl groups on it, or the theen complex, which has four 2-hydroxyethyl groups. The high stability of the copper(II) complex of L^1 may be due to what one might term[19] 'hidden inductive effects'. As the alkyl substituents on donor atoms such as nitrogen or oxygen become larger, so the inductive effects become larger. In the gas phase this becomes evident as the orders of proton basicity are,[1] for example, $CH_3NH_2 \ll CH_3CH_2NH_2 \ll (CH_3)_2CHNH_2 \ll (CH_3)_3CNH_2$. In aqueous solution the proton on the nitrogen is no longer bare as in the gas phase, but has an extensive solvation sphere. The result of this is that, due to adverse steric effects, the increasing bulk of the alkyl substituents from methyl through to *tert*-butyl offsets the inductive effects, and there is no increase in protonation constants. The inductive effects are therefore 'hidden', and have given many researchers the impression that the inductive effects of N-alkyl substituents are very weak. When the inductive effects are sufficiently large they may outweigh adverse steric effects. It seems possible here that the inductive effects of the three cyclohexyl groups are large enough to outweigh any adverse steric effects, and lead to complexes with Cu^{II} that are more stable. This happens in other examples where cyclohexyl moieties are present, as in dach itself. Thus, dach forms complexes with Cu^{II} that have log K_1 values that are higher than the en complex, which we suggest would have a contribution from the electron-releasing properties of the cyclohexyl group. Further contributions to the stability of complexes of L^1 and dach would come from the rigidity of the ligand, which preorganises the ligand more strongly than analogues that have simple ethylene bridges.

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† The atom type for the three-co-ordinate sp^3-hybridised nitrogen is type 8 in MM2. When a metal ion co-ordinates to the nitrogen it is now assigned by the program as type 39, a quaternary nitrogen. Types 8 and 39 nitrogens have ideal C–N bond lengths of 1.438 and 1.499 Å respectively in MM2. If one deletes the metal ion from the complex, and then locks the atoms in position so as to calculate the energy of the ligand in its exact structure in the metal complex, a high energy will result. The program changes the N atom type back to type 8, but the C–N bonds are locked in at the long values appropriate for type 39. One should enter the 'Edit internals' function if using the CACHE system, and change the nitrogens back to type 39, so that the ideal C–N bond length is that appropriate to the complex. For oxygen donors this problem does not arise.

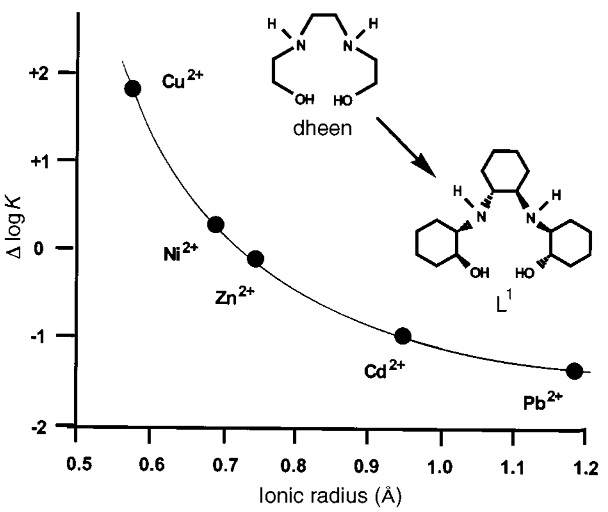

Fig. 4 The change in complex stability, $\Delta\log K$, that occurs on substitution of ethylene bridges in dheen with cyclohexanediyl bridges to give L^1, plotted as a function of ionic radius[10] of the metal ions. The $\Delta\log K$ values are simply $\log K_1$ for the L^1 complex minus $\log K_1$ for the dheen complex. Formation constants for L^1 complexes, this work; for dheen complexes from ref. 18. The figure shows how cyclohexanediyl bridges increase the complex stability of small relative to large metal ions

For metal ions other than Cu^{II} the effect of the cyclohexanediyl bridges is to produce a steady decrease in stability of the L^1 complexes relative to the dheen complexes as the size of the metal ion increases. This is illustrated in Fig. 4, where the change in complex stability in passing from the dheen to the L^1 complex is plotted against the ionic radius of the metal ion. One sees the same type of relationship as was observed[4] for ligand pairs such as *trans*-H_4cdta and edta, or L^2 and L^3, where the substitution of ethylene bridges by cyclohexanediyl bridges shifts the ligand selectivity in the direction of smaller metal ions.

An interesting aspect of the chemistry of L^1 complexes is the acidity of the protons on the co-ordinated 2-hydroxycyclohexyl groups. Thus, the L^1 complex of Cu^{II} has its first deprotonation at pH 6.25, as compared to 7.7 for the Cu^{2+} ion.[17] For Ni^{II} the first proton is lost at pH 8, as compared to pH 10 for the Ni^{2+} ion itself. One might suppose that this increased acidity of the co-ordinated hydroxyl groups relates at least partly to the hydrophobic environment provided by the cyclohexyl groups, which favours a loss of protons that leads to an accompanying drop in overall charge on the complex. The acidity of the co-ordinated hydroxyls for the nickel(II) complex may also be a function of the change from the blue high-spin complex to a red low-spin complex ($\lambda_{max} = 491$ nm) on loss of the protons. The $S = 0$ nickel(II) ion has a much smaller ionic radius (0.45 Å) than the $S = 1$ nickel(II) ion (0.69 Å), so that loss of protons and a change of spin state to the smaller $S = 1$ ion would lead to a reduction in steric crowding between adjacent cyclohexyl groups.

This study has shown some of the interesting co-ordinating properties that are induced in ligands that have cyclohexanediyl bridges. The L^1 ligand is preorganised for co-ordination to small metal ions, and in future papers the co-ordinating properties of further ligands containing cyclohexanediyl bridges will be presented.

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