Metal-ion Complexation in Aqueous Solutions of 1-Thia-4,7-diazacyclononane-, 1-Thia-4,8-diazacyclodecane- and 2,5-Diazahexane-*N,N'*-diacetic acid

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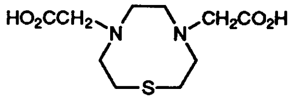
The stability constants of the macrocyclic 1-thia-4,7-diazacyclononane- and 1-thia-4,8-diazacyclodecane-*N,N'*-diacetic acid (H_2L^1 and H_2L^2) and of the open-chain 2,5-diazahexane-*N,N'*-diacetic acid (H_2L^3) with $\mathrm{Mg^{II}}$, $\mathrm{Ca^{II}}$, $\mathrm{Sr^{II}}$, $\mathrm{Ba^{II}}$, $\mathrm{Mn^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$, $\mathrm{Cu^{II}}$, $\mathrm{Zn^{II}}$, $\mathrm{Cd^{II}}$, $\mathrm{Pb^{II}}$ and $\mathrm{La^{III}}$ have been determined in aqueous solution (25 °C, 0.1 mol dm^{-3} KNO_3) by pH potentiometry, and in some cases in combination with visible absorption spectrophotometry. The complexation enthalpies with $\mathrm{Cu^{II}}$ have been determined by adiabatic calorimetry. The electronic absorption spectra of the complexes of $\mathrm{Cu^{II}}$ and $\mathrm{Ni^{II}}$ were also recorded. All metal-ion complexes with H_2L^1 are stronger than with H_2L^3, even for the harder metal ions. The presence of the thioether donor particularly enhances covalent bonding with $\mathrm{Cu^{II}}$ as indicated by a higher heat of complexation, a more favourable entropy change and a stronger ligand-field strength. The change in stability of the complexes upon replacing H_2L^1 with a five-membered chelate ring between the metal ion and the two tertiary nitrogens, by H_2L^2 having a six-membered one, is dependent on the metal-ion size. The larger metal ions are destabilised relative to the small metal ions: the metal ion size-based selectivity for this pair of ligands is controlled by the chelate-ring size. Binding of $\mathrm{Cu^{II}}$ by H_2L^2 is sterically much more efficient than by H_2L^1 and is evidenced by a higher heat of complexation and a stronger ligand field.

There is an extensive amount of data concerning metal-ion complexation in solution by polyaminocarboxylate complexones,[1] and the interest, particularly in macrocyclic *N*-acetate-substituted macrocyclic polyamines, is still growing.[2-14] As metal-ion sequestering agents, they combine covalent bonding to most metal ions through their amino groups with ionic bonding through the sterically very efficient carboxylate groups.[15] They also show remarkable metal-ion selectivities as a result of steric constraints imposed by the degree of flexibility of the macrocyclic framework, in combination with the ability of the metal ion to adapt to the co-ordination geometry of the ligand.[15] For instance, 1,4,7,10-tetraazacyclododecane-*N,N',N'',N'''*-tetraacetic acid (H_4dota) provides a potential octadentate co-ordination which is found to be very effective in binding the hard calcium ion, whereas the sexadentate 1,4,7-triazacyclononane-*N,N',N''*-triacetic acid (H_3tanota) with a smaller and more rigid cyclic framework, is better suited for binding the small $\mathrm{Ni^{II}}$.[15]

1,4,7-Triazacyclononane ([9]aneN_3), the parent amine of H_3tanota, together with [9]aneN_2O and [9]aneN_2S forms a group of cyclic amines with a fairly rigid ring structure fitting best around small metal ions.[16,17] The co-ordination chemistry in solution of H_3tanota has already been the subject of several investigations.[5,8,10,18] The metal-ion complexation properties of 1-oxa-4,7-diazacyclononane-*N,N'*-diacetic acid, the *N*-acetate derivative of [9]aneN_2O, were recently investigated by da Silva and co-workers,[11] and it was found that the cyclic ligand formed slightly more stable complexes than did the linear ethylenediamine-*N,N'*-diacetic acid (H_2edda), except for those of $\mathrm{Ni^{II}}$ and $\mathrm{Cu^{II}}$ which were less stable than those with H_2edda.

In order further to explore the effect of *N*-acetate substitution on the [9]aneX_3 type of rings, we investigated the metal-ion complexation properties of 1-thia-4,7-diazacyclononane-*N,N'*-diacetic acid (H_2L^1), together with those of 1-thia-4,8-diazacyclodecane-*N,N'*-diacetic acid (H_2L^2), the *N*-acetate derivatives of [9]aneN_2S and [10]aneN_2S respectively. The linear *N,N'*-methyl derivative of H_2edda (H_2L^3) was also included for comparison purposes. The stability constants of their complexes with a series of metal ions of varying size were determined. The thermodynamic functions ΔH° and $T\Delta S^{\circ}$ were also determined for the copper(II) complexes. These data together with the ligand-field parameters for the complexes of $\mathrm{Cu^{II}}$ and $\mathrm{Ni^{II}}$ are used to evaluate the effect of both cyclisation and chelate-ring alternation in H_2L^1 and H_2L^2.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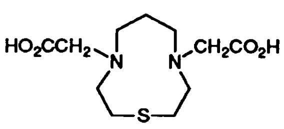
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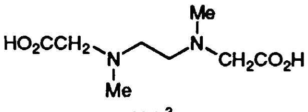
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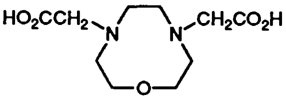
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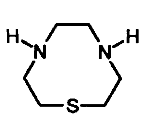
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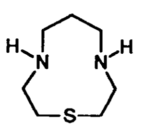
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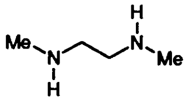
L^7

Experimental

Materials.—The ligands H_2L^1, H_2L^2 and H_2L^3 were synthesised as described,[19,20] L^1 and L^2 were obtained in their $H_3L^+Cl^-$ form, whereas L^3 was in the $H_4L^{2+}2Cl^-$ form. All

Table 1 Summary of the experimental methods and of the conditions for determining the stability constants of H_2L^1, H_2L^2 and H_2L^3 with the series of metal ions Mg^{II},Ca^{II}, Sr^{II}, Ba^{II}, Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, Pb^{II} and La^{III}

	Method			
Ligand	A[a]	B[b]	C[c]	D[d]
H_2L^1	Remaining metal ions	Co^{II}	Cu^{II}	Cu^{II},[e] Ni^{II}[f]
H_2L^2	Remaining metal ions	Ni^{II}, Co^{II}		Cu^{II}[g]
H_3L^3	The series			Cu^{II}[h]

[a] Direct titration pH-metry; metal to ligand ratios 1:1, 1:2 or 1:4 (in case of La^{III}); at least 150 titration points; equilibrium time maximum 30 min, $I = 0.1$ mol dm^{-3}, 25 °C. [b] Out-of-cell pH-metry; 1:1 metal to ligand ratio; 15 solutions; 2 months of storage; $I = 0.1$ mol dm^{-3}, 25 °C. [c] Out-of-cell pH-metry; ligand competition with tren; 1:1:1 metal to H_2L^1 to tren ratio; 15 titration points; fast equilibrium; $I = 0.1$ mol dm^{-3}, 25 °C. [d] Out-of-cell UV/VIS–pH-metry; 1:1 metal to ligand ratio; 15 solutions; 1 month of storage for Ni^{II}, fast equilibrium for Cu^{II}; $I = 1.0$ mol dm^{-3}, 25 °C. [e] $CuHL^1$ species; $0.1 < pH < 1.5$; λ_{max} at 638 nm at pH 1.43; CuL(OH) species, $10.2 < pH < 12.2$, cross-over at 760 nm. [f] NiL^1 species; $1.0 < pH < 1.8$; λ_{max} at 588 nm for the second band. [g] CuL^2 species; $0.1 < pH < 2.1$; λ_{max} at 604 nm. [h] CuL^3 species, $1.2 < pH < 7.7$; λ_{max} at 680 nm.

other reagents were of reagent grade. Distilled and deionised water (Milli-Q quality, conductance < 0.05 μS cm^{-1}) was used throughout for all solutions. Carbonate-free (< 0.5%) potassium hydroxide solutions (*ca.* 0.250 mol dm^{-3}) were prepared from Titrisol ampoules (Merck) and were standardised by titration with potassium hydrogenphthalate (Janssen Chimica). Stock solutions of nitric acid were prepared and standardised with the KOH solutions. These titrations were also used to check the carbonate content of the KOH titrant solution using the Gran method.[21] Metal-ion stock solutions were prepared from metal nitrates (Merck) and were standardised by titration with ethylenediaminetetraacetate (edta),[22] using appropriate conditions and electrodes (Radiometer copper, cadmium or lead solid-state electrodes or mercury electrode). All final solutions for the potentiometric and calorimetric titrations and for the electronic spectral measurements were made up to an ionic strength of 0.1 mol dm^{-3} (occasionally 1.0 mol dm^{-3}) with potassium nitrate (Merck).

Potentiometric Measurements.—The potentiometric measurements were carried out at 25 ± 0.05 °C with the equipment and general procedure previously described.[23,24] The glass electrode was calibrated as a hydrogen-ion concentration probe. In the case of slow complexation reactions, out-of-cell titrations were needed. The solutions, each corresponding to a single titration point, were stored in sealed vials at 25 °C before measuring the pH. Attainment of equilibrium was checked by measuring periodically the pH and the electronic spectrum of a duplicate test solution corresponding to *ca.* 50% of complex formation. In the case of strong complexation, a combination of pH-metry and visible electronic spectrophotometry was used in an acid medium to follow the formation of the complex. All measurements were performed in duplicate. A summary of the experimental methods and of the conditions for determining the stability constants of H_2L^1, H_2L^2 and H_2L^3 with the series of metal ions is given in Table 1. The stability constants of Cu^{II} with the open-chain ligand H_2L^3 were determined both at 0.1 and 1.0 mol dm^{-3} ionic strength. The difference obtained (0.26 ± 0.04 log units) was then applied to the copper(II) complexes with H_2L^1 and H_2L^2 in order to obtain the stability constant values at both ionic strengths. The stability constant for the complex of Cu^{II} with H_2L^1 was determined by a ligand-competition method using tris(2-aminoethyl)amine (tren) as the competing ligand. Protonation and copper(II) complexation data for tren were taken from the literature.[1]

Calorimetric Measurements.—The calorimetric measurements were carried out with a Tronac model 1250 isoperibol calorimeter as described.[20,23] In a typical calorimetric run, a solution (25.00 cm^3) containing the ligand (*ca.* 0.16 mmol) in its neutralised form was titrated with a copper(II) nitrate titrant solution (*ca.* 0.06 mol dm^{-3}). Dilution experiments were also done and the exact concentration of the components in each solution was determined by separate potentiometric titrations.

Spectrophotometric Measurements.—The electronic absorption spectra were recorded at 25 °C on a Hewlett-Packard 8451 A diode-array spectrophotometer in the wavelength region between 190 and 820 nm. A Cary 14 spectrophotometer was used for the nickel(II) complexes in the region between 800 and 1300 nm. Aqueous solutions of metal ion (Cu^{II} or Ni^{II}) and ligand in 0.1 mol dm^{-3} KNO_3 were prepared with a c_L/c_M ratio of *ca.* 1.10:1. A calculated volume of a standardised KOH solution was then added to obtain the pH required for complete complexation. The solutions of the nickel(II) complexes were stored in sealed vials and their spectra recorded periodically until no further change was observed.

Calculations.—The stability constants were calculated with the computer program SUPERQUAD.[25] The overall complexation enthalpies for the copper(II) complexes were calculated with the program CALO.[20] The necessary data on the protonation constants and the protonation enthalpies of the ligands were determined and reported previously.[20] There was a complication for L^2 (the doubly deprotonated form of H_2L), such that the enthalpy change for its first protonation step could not be determined experimentally in aqueous solution due to the high value for log K_1^H (= 12.9).[20] A minimum value for the enthalpy change for the complexation of Cu^{II} by L^2 was then calculated taking the ΔH° value for the formation of water ($H^+ + OH^- \longrightarrow H_2O$) as the lowest limit for the ΔH° value for the first protonation step of L^2. In all calculations literature values for the dissociation constant and for the dissociation enthalpy of water were used: $pK_w = 13.78$ and $\Delta H^\circ_w = 56.6$ kJ mol^{-1}.[1,23,26] All standard deviations cited represent three times the standard deviations given by the programs.

Results and Discussion

General Observations.—The values for the stability constants of the metal-ion complexes formed with H_2L^1, H_2L^2 and H_2L^3 are given in Table 2. Complex formation of H_2L^1 and H_2L^3 with the alkaline-earth-metal ions and with Mn^{II} and La^{III} only occurs after deprotonation of the carboxylic acid groups. For all other metal ions complexation already starts below pH 4. All metal ions form 1:1 complexes with the three ligands, except for Mg^{II} with H_2L^1 and for the alkaline-earth-metal ions and La^{III} with H_2L^2. In these cases complexation was not detectable before the point where metal-ion hydroxide precipitation was observed. The Irving–William's order of stability is obeyed for the ML complexes with the three ligands.

In addition to the normal ML complexes, the titration curves indicated the formation of hydroxo complexes for Cu^{II}, Zn^{II}, Cd^{II} and Pb^{II} with H_2L^1 and H_2L^3. A protonated complex MHL was found only for Cu^{II} with H_2L^1, whereas H_2L^3 formed a MHL complex with almost all metal ions. The stabilities of the MHL^3 complexes, according to the equilibrium $M + HL^3 \rightleftharpoons MHL^3$, are lower than for the ML complexes with glycine,[1] indicating that in the MHL^3 complex binding occurs through one amino and one carboxylate group, with the remaining amino group being protonated. There is also evidence that H_2L^3 forms a ML_2 complex with Ca^{II} and La^{III}.

Metal Complexes with H_2L^1 *and* H_2L^3.—No exceptional

Table 2 Stability constants of metal-ion complexes of H_2L^1, H_2L^2 and H_2L^3 (25 °C, I = 0.1 mol dm^{-3} KNO_3)

		log K^a		
Metal ion	Species	H_2L^1	H_2L^2	H_2L^3
Mg^{II}	ML	*b*	—	5.36(4)
	MHL			1.3(1)
Ca^{II}	ML	5.01(8)	—	3.91(7)
	MHL			1.6(1)
	ML_2			2.5(1)
Sr^{II}	ML	3.47(8)	—	3.05(1)
Ba^{II}	ML	2.87(8)	—	2.66(1)
Mn^{II}	ML	9.25(1)	8.97(1)	8.48(2)
	MHL			2.36(8)
Co^{II}	ML	13.0(1)	12.0(1)	12.79(1)
Ni^{II}	ML	15.60(2)^c	16.12(2)	15.13(2)
Cu^{II}	ML	19.21(1)	22.19(4)^d	15.73(2)
		18.95(4)^e	21.93(1)^c	15.47(2)^c
	MHL	15.9(2)^c		
	ML(OH)	2.4(2)^c		3.87(3)^c
Zn^{II}	ML	14.03(1)	14.41(2)	12.61(3)
	MHL			4.62(5)
	ML(OH)			2.9(1)
Cd^{II}	ML	12.99(5)	12.95(2)	10.49(1)
	MHL			3.19(5)
	ML(OH)	4.4(1)		2.44(9)
	$M_2L_2(OH)_2$	7.0(1)		
Pb^{II}	ML	12.96	11.13(9)	11.29(2)
	MHL			3.8(6)
	ML(OH)	1.1(1)		2.82(5)
La^{III}	ML	6.02(1)	—	6.60(3)
	MHL			2.24(6)
	ML_2			5.10(6)

[a] K_{ML} = [ML]/[M][L], K_{ML_2} = $[ML_2]$/[ML][L], K_{MHL} = [MHL]/[M][HL]; $K_{ML(OH)}$ = [ML(OH)]/[ML][OH] dm^3 mol^{-1}, $K_{M_2L_2(OH)_2}$ = $[M_2L_2(OH)_2]/[ML]^2[OH]^2$ dm^9 mol^{-3}; charges are omitted. [b] No complex formation detected. [c] At 25 °C, I = 1.0 mol dm^{-3} KNO_3. [d] Estimated value at I = 0.1 mol dm^{-3}. [e] Estimated value at I = 1.0 mol dm^{-3}.

Table 3 Effect on the stability of the ML complexes on passing from L^5 to H_2L^1, from L^6 to H_2L^2 and from L^7 to H_2L^3

	Δ log K_1		
Metal ion	$L^5 \longrightarrow H_2L^{1a}$	$L^6 \longrightarrow H_2L^{2a}$	$L^7 \longrightarrow H_2L^{3b}$
Co^{II}	4.96	4.7	7.76
Ni^{II}	4.51	6.02	8.21
Cu^{II}	6.55	10.34	5.76
Zn^{II}	6.49	7.56	7.59
Cd^{II}	6.17	6.45	5.51
Pb^{II}	6.10	—	—

[a] Calculated with data from Table 2 and from ref. 24. [b] Calculated with data from Table 2 and from refs. 1 and 27.

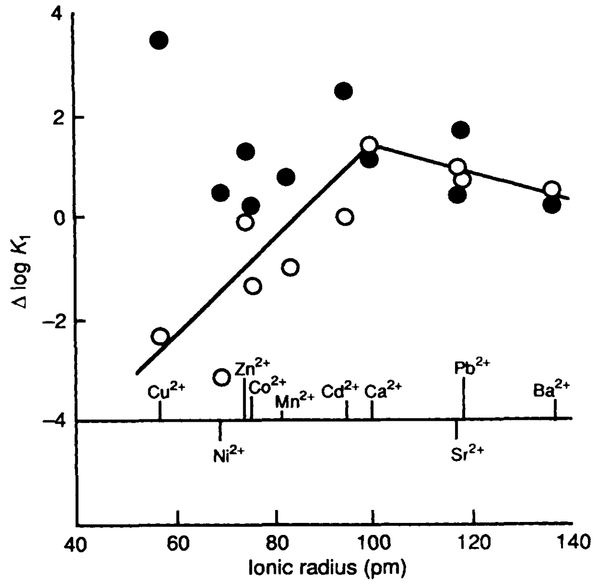

Fig. 1 Change in stability constant (Δ log K_1) for the ML complexes of H_2L^1 (●) and H_2L^4 (○) relative to the ML complexes of H_2L^3 as a function of metal ionic radius. The data for the metal ionic radii for octahedral co-ordination are taken from ref. 28. For Cu^{II} the ionic radius for square-planar co-ordination (57 pm) is used

Table 4 Thermodynamic and electronic spectral data for the copper(II) complexes of H_2L^1, H_2L^2 and H_2L^{3a}

Ligand	Species	$-\Delta H^\circ$/ kJ mol^{-1}	$T\Delta S^\circ$/ kJ mol^{-1}	ν_{d-d}/ cm^{-1}
H_2L^1	CuL^1	46.0	63.6	15 620 (155)^b
	$CuHL^1$			14 920 (120)
H_2L^2	CuL^2	> 55.0^c	< 70.0	16 610 (121)
H_2L^3	CuL^3	32.6	57.2	14 620 (138)

[a] At 25 °C, I = 0.1 mol dm^{-3}; ΔH° ±0.6 kJ mol^{-1}, $T\Delta S^\circ$ ±0.9 kJ mol^{-1}. [b] Molar absorption coefficient in dm^3 mol^{-1} cm^{-1}. [c] Estimated value as the enthalpy change for the first protonation step of L^2 cannot be determined experimentally; ΔH° for the reaction $Cu^{II} + HL^2 \longrightarrow CuL^2 + H^+$ is 0.9 kJ mol^{-1}, to compare with −4.6 kJ mol^{-1} for the corresponding reaction with HL^1.

selectivities arise upon *N*-acetate substitution on L^5 to form H_2L^1 (see Table 3), although the Δ log K_1 values* for the complexes of Ni^{II} and Co^{II} for the relationship (L^5,H_2L^1) turn out to be much lower than for the relationship (L^7,H_2L^3) with the linear counterparts without the S donor (L^7 is *N*,*N*′-dimethylethylenediamine). One can also see from Table 2 that all metal ions form stronger complexes with H_2L^1 than with H_2L^3. This change in stability for the relationship (H_2L^3,H_2L^1), expressed by Δ log K_1, is plotted in Fig. 1 against the metal ionic radius. Except for the high value (3.48 log K units) for Cu^{II}, the Δlog K_1 values for the other metal ions are rather scattered between 0.0 and 2.0, and do not show any particular dependence on the metal-ion size. Actually two effects are operative in the relationship (H_2L^3,H_2L^1): first, there is the linking of the two methyl groups in H_2L^3 into the macrocyclic framework of H_2L^1, and secondly the addition of the soft S donor in H_2L^1. The observation that Δ log K_1 for Ca^{II} is even higher than for Ni^{II} or Co^{II} demonstrates that both hard and borderline metal ions can take advantage of the macrocyclic structure. Only Cu^{II} and Cd^{II} are capable of gaining substantial extra stability from the interaction with the S donor, as they are softer Lewis acids.[29] The increase in complex stability for CuL^1 relative to CuL^3 is due both to an enthalpic and an entropic contribution (see Table 4), and is accompanied by an increase in the ν_{d-d} value from 14 620 to 15 620 cm^{-1}. Thus, despite the S donor being forced to occupy the less-favoured axial site, the ligand-field strength and the Cu–N_{tert} bond overlap in the CuL^1 complex have clearly increased. This would be impossible without the whole ring skeleton being adjusted to a low strained conformation. The ligand-field strength in the $CuHL^1$ complex is appreciably lower than in the normal CuL^1 complex. The loss of one chelate ring in CuL^1 through protonation of a carboxylate group is the most likely explanation.

Only electronic spectral data are available for the nickel(II) complexes (see Table 5). The ν_1 band of NiL^3 features no shoulder at both high and low energy. The mixed-donor nature of L^1 will be responsible for a less-symmetrical ligand field

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* Δ log K_1 for a particular metal ion is the difference between log K_1 for the complex with the second ligand indicated in the relationship between parentheses minus log K_1 for the complex with the first one.

Table 5 Electronic spectral data for the nickel(II) complexes of H_2L^1, H_2L^2 and H_2L^3 [a]

Ligand	Species	ν_1/cm^{-1}	ν_2/cm^{-1}	ν_3/cm^{-1}
H_2L^1	NiL^1	10 400 (43) [b] 12 120 (sh) (18) 8 500 (sh) (9)	17 120(13)	27 030(21)
H_2L^2	NiL^2	10 225 (25) 12 315 (sh) (10) 8 700 (sh) (10)	16 835 (7)	27 320(13)
H_2L^3	NiL^3	9 830 (13)	16 290 (5)	27 030(9)

[a] At 25 °C, $I = 1.0$ mol dm^{-3}. [b] Molar absorption coefficient in dm^3 mol^{-1} cm^{-1}.

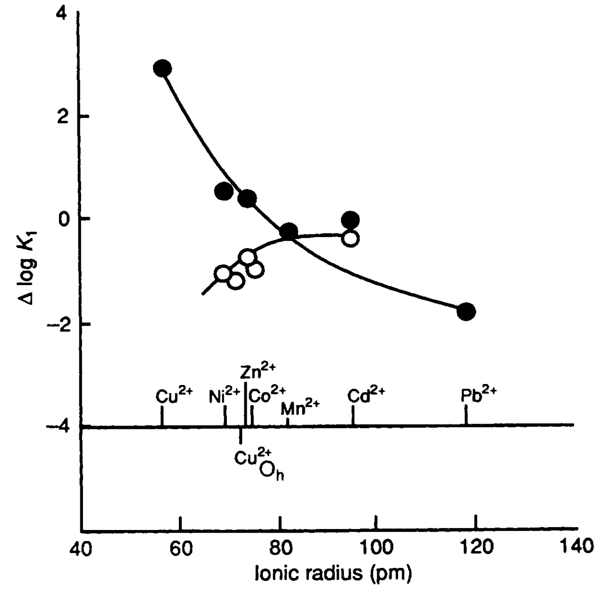

Fig. 2 Change in stability constant (Δ log K_1) for ML complexes in passing from H_2L^1 to H_2L^2 (●) and from L^5 to L^6 (○) as a function of metal ionic radius. The data for the metal ionic radii for octahedral co-ordination are taken from ref. 28. For Cu^{II} the octahedral ionic radius (73 pm) is used for L^5 and L^6, whereas for H_2L^1 and H_2L^2 the square-planar ionic radius (57 pm) is used

around Ni^{II} and hence can account for the more complicated spectrum. Although an octahedral model is not formally correct in such a case,[30] the maximum intensity in the ν_1 band of NiL^1 may still be a reasonable approximation of the ligand-field strength parameter 10 *Dq*, provided that mixing of the $^3A_2 \longrightarrow {}^3T_2$ transition with the spin-forbidden $^3A_2 \longrightarrow {}^1E$ transition can be neglected.[31] This is usually the case if ν_1 (max.) is lower than about 11 000 cm^{-1} or Dq/B smaller than 1.5.[30] It then follows that the ligand-field strength in NiL^1 is about 580 cm^{-1} higher than in NiL^3. Calculating the Racah parameter *B* using $(\nu_2 + \nu_3 - 3\nu_1)/15$[30] gives 922 cm^{-1} for NiL^3 and 863 cm^{-1} for NiL^1, indicating a greater covalency of the metal–ligand bonds in the latter complex.

At this point, it is interesting to compare the relationships (H_2L^3,H_2L^1) and (H_2L^3,H_2L^4) where H_2L^4 has the neutral oxygen donor instead of the sulfur donor. The relationship (H_2L^3,H_2L^4) is also shown in Fig. 1 and features a peak in Δ log K_1 at an ionic radius of about 105 pm corresponding to the size of Ca^{II}. This observation is very well comparable with those found for other pairs of ligands where neutral oxygen donors are added: 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane relative to 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane([18]aneN_2O_4) or oxydiacetate relative to oxalate.[15] As pointed out by Hancock and Martell,[15] adding neutral oxygen donors to existing ligands leads to steric crowding in a complex which becomes larger as the metal ion becomes smaller. The upward Δ log K_1 trend with increasing metal-ion size thus reflects the relief of steric strain in the complex up to a metal ionic radius of 100–110 pm. For that metal-ion size the crowding is believed to be at its lowest level. The downward trend thereafter reflects the decrease in intrinsic M–O donor strength as the charge density on the metal ion further decreases. Thus, ligand H_2L^4 with the hard O donor exhibits a much more pronounced differentiation in its complexation of metal ions in relation to their size than does ligand H_2L^1 with the soft S donor. The greater covalent character of the metal-to-ligand bonding with the small 3d metal ions is partly responsible for their higher Δ log K_1 values in the relationship (H_2L^3,H_2L^1) relative to the relationship (H_2L^3,H_2L^4). In addition, it is very likely that steric crowding in the metal-ion complexes of H_2L^1 with the smaller metal ions is lower than in the corresponding complexes with H_2L^4. Indeed, it has been shown that of the parent cyclic amines [9]aneN_2O and [9]aneN_2S, the latter has a greater preference for smaller metal ions.[16] So, less crowding and more covalent bonding raise the Δ log K_1 values for the small metal ions in the relationship (H_2L^3,H_2L^1). On the other hand the Δ log K_1 values for the larger more ionic metal ions are larger for the relationship with the harder H_2L^4 than with the softer H_2L^1, but both relationships show the same downward trend with increasing metal-ion size and decreasing metal-ion charge density.

Metal Complexes with H_2L^2.—Fig. 3 shows the effect of increasing the chelate-ring size on the stability of the complexes with H_2L^1 as a function of the metal ionic radius. Replacing the five-membered chelate ring between the two nitrogens and the metal ion in the ML^1 complexes by a six-membered one in the ML^2 complexes leads to an increase in complex stability for the small metal ions, whereas there is a decrease for the larger ones. This behaviour is analogous to that found for open-chain ligand pairs such as 3,6-diazaoctane-1,8-diamine and 3,7-diazanonane-1,9-diamine or ethylenediaminetetraacetic acid (H_4edta) and trimethylenediaminetetraacetic acid (H_2tmdta), and for flexible macrocyclic multidentate ligand pairs such as [12]aneN_4 and [14]aneN_4 or H_4dota and H_4teta ([12]aneN_4 = 1,4,7,10-tatraazacyclododecane, [14]aneN_4 = 1,4,8,11-tetraazacyclotetradecane, H_4teta = 1,4,8,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴-tetracetic acid).[15,17] For all these macrocyclic ligand pairs, the metal ion size-based selectivity is controlled by the size of the chelate rings rather than by the macrocyclic ring size.[17] The decreasing Δ log K_1 values with increasing metal-ion size are then a consequence of the larger metal ions fitting better with lower strain in a five- than in a six-membered chelate ring.[15,17,32] This behaviour found for the ligand pair H_2L^1 and H_2L^2 is opposite to that found for the parent diamine pair L^5 and L^6 which shows a metal-ion selectivity controlled by the macrocyclic ring size (see also Fig. 2).[24] For CuL^2 the increase in stability has both an enthalpic and an entropic contribution, and results in an increase in the ligand-field strength of about 1000 cm^{-1}, relative to CuL^1 (see Table 4). The chelate-ring alternation in H_2L^2 apparently allows for an even less-strained and thus more-efficient complexation of Cu^{II} as indicated by the considerable increase in complexation heat. The favourable co-ordination of Cu^{II} by H_2L^2 is, of course, also reflected in the high Δ log K_1 value (10.34 log *K* units) upon *N*-acetate substitution for the relationships (L^6,H_2L^2) in Table 3.

The highest intensity in the ν_1 band for NiL^2 (10 225 cm^{-1}) is somewhat lower than for NiL^1. Also the position of the ν_2 band for NiL^2 is observed at a slightly lower energy than for NiL^1, and the calculated value for *B* (899 cm^{-1}) is intermediate between the values for NiL^1 and NiL^3. In contrast to what is usually observed upon alternation of chelate-ring size (5–6–5 in L^2, 5–5–5 in L^1), the (octahedral) ligand-field strength is higher in NiL^1 than in NiL^2.

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