Ligand Design and Metal-ion Recognition. The Interaction of Copper(II) with a Range of 16- to 19-Membered Macrocycles incorporating Oxygen, Nitrogen and Sulfur Donor Atoms†

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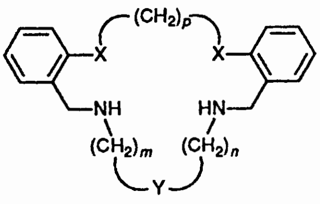
The interaction of copper(II) with a series of quinquedentate macrocycles incorporating nitrogen, oxygen, and/or sulfur donor atoms is reported. These ligands form part of a structural matrix in which a systematic variation in donor atom pattern and ring size is present (and against which structure–function relationships are more clearly seen). Stability constants for the 1:1 copper complexes have been determined in 95% methanol (I = 0.1 mol dm^{-3}, NEt_4ClO_4) at 25 °C. The study demonstrates the extremely large stability differentials [up to 10^{10} for copper(II)] that may be achieved through structural variation within the ligand framework employed for this study. The contribution of the respective donor atom types to overall complex stability was found to follow the expected order of NH(aliphatic) > NH(anilino) > S > O. Based on earlier X-ray studies, the molecular mechanics modelling of two representative examples is also reported.

The use of macrocyclic ligands for selective complex formation is of considerable current interest[1,2] and frequently the motivation for such studies has been to investigate the factors that favour metal-ion selectivity.[3] As part of an overall study of the latter type involving transition and post-transition ions, we have prepared the extended ligand series L^1–L^{24}. In our experience, metal complexation studies across a range of such related ligands (which show a stepwise variation in their properties) provide a useful background upon which further ligand design may be based.

In previous investigations a number of the O_2N_3-donor systems of the present type, incorporating 17- to 19-membered rings, have been demonstrated to exhibit metal-ion recognition behaviour.[4,5] In these studies, ring-size control was used to induce structural dislocations and hence alter the relative thermodynamic stabilities of particular cobalt(II), nickel(II), zinc(II) and cadmium(II) complexes. As an extension of this work, a study of the interaction of the first two of these ions with a much extended series of ligands (including sulfur-containing species) has recently been reported.[6] We now present the results of a comparative investigation of the interaction of copper(II) with the extended ligand series L^1–L^{24}.



	X	Y	*m*	*n*	*p*
L^1	NH	NH	2	2	2
L^2	NH	S	2	2	2
L^3	NH	O	2	2	2
L^4	NH	NH	3	3	3
L^5	O	NH	2	2	1
L^6	O	S	2	2	1
L^7	O	O	2	2	1
L^8	O	NH	2	2	2
L^9	O	S	2	2	2
L^{10}	O	O	2	2	2
L^{11}	O	NH	3	2	2
L^{12}	O	NH	3	3	2
L^{13}	O	NH	4	2	2
L^{14}	O	S	3	3	2
L^{15}	O	NH	2	2	4
L^{16}	O	S	2	2	4
L^{17}	O	O	2	2	4
L^{18}	S	NH	2	2	1
L^{19}	S	S	2	2	1
L^{20}	S	NH	2	2	2
L^{21}	S	S	2	2	2
L^{22}	S	O	2	2	2
L^{23}	S	NH	3	3	2
L^{24}	S	S	2	2	3

Experimental

Physical Measurements.—These were obtained as described previously.[5] Conductance, magnetic moment and spectrophotometric data for a selection of metal complexes isolated during the study are listed in Table 1. The potentiometric (pH titration) log *K* data were processed using local versions of MINIQUAD[7] and SUPERQUAD.[8] All values are the mean of between two and five individual determinations at various metal:ligand ratios. Unless otherwise indicated, log *K* values

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† *Non-SI units employed:* dyn = 10^{-5} N, D ≈ 3.33 × 10^{-30} C m.

Table 1 Physical data for the copper(II) complexes of selected macrocyclic ligands

Complex	Conductance[a]/ S cm^2 mol^{-1}	Magnetic moment μ^b	IR (cm^{-1})[c]			Electronic spectra λ/nm	
			ν(OH)	ν(NH)	Anion (ClO_4)	Solid	Solution[d]
$[Cu(NO_3)L^5]ClO_4 \cdot 0.5H_2O$	99	1.78	3450, 3235	3245, 1070	1120	590	620 (113)
$[Cu(NO_3)L^{15}]ClO_4$	113	1.87		3210	1080	625	630 (182)
$[CuL^{18}][ClO_4][NO_3] \cdot H_2O$	202	1.81	3540, 3630	3210	1090	570, 800	575 (196), 810 (weak)
$[CuL^{20}][ClO_4]_2 \cdot H_2O$	200	1.89	3785, 3602	3110	1080	545, 745	545 (276), 755 (98)
$[CuL^{22}][ClO_4]_2$	162	1.88		3210	1080	595	600 (181)

[a] In methanol (23 °C). [b] At 23 °C. [c] Nujol mull. [d] In methanol. ε/dm^3 mol^{-1} cm^{-1} given in parentheses.

of less than 9 have an estimated error of ±0.1, ranging up to ±0.3 for values above 14.

*Macrocycle and Complex Synthesis.**—The free macrocycles were synthesised by reduction of their corresponding diimine precursors using $NaBH_4$ or $LiAlH_4$.[4,9–11]

$[Cu(NO_3)L^5]ClO_4 \cdot 0.5H_2O$. Copper(II) nitrate trihydrate (0.07 g) in acetonitrile (20 cm^3) and solid lithium perchlorate (0.08 g) were added to a boiling solution of L^5 (0.10 g) in acetonitrile (20 cm^3). The solution was filtered and cooled. On standing, a blue crystalline solid separated; yield 0.07 g (Found: C, 40.7; H, 4.5; N, 9.9. Calc. for $C_{19}H_{25}ClCuN_4O_9 \cdot 0.5H_2O$: C, 40.6; H, 4.7; N, 10.0%). Fast atom bombardment (FAB) mass spectrum: *m/z* 494, $[Cu(NO_3)L^5]^+$.

$[Cu(NO_3)L^{15}]ClO_4$. Copper(II) nitrate trihydrate (0.07 g) in ethanol (10 cm^3) and solid lithium perchlorate (0.09 g) were added to a boiling solution of L^{15} (0.10 g) in ethanol (10 cm^3). The solution was filtered and cooled. On standing, dark blue crystals separated; yield 0.04 g (Found: C, 44.3; H, 5.4; N, 9.3. Calc. for $C_{22}H_{31}ClCuN_4O_9$: C, 44.4; H, 5.3; N, 9.4%). FAB mass spectrum: *m/z* 494, $[Cu(NO_3)L^{15}]^+$.

$[CuL^{18}][ClO_4][NO_3] \cdot H_2O$. In a similar manner to that used for the synthesis of the copper(II) complex of L^{15}, copper(II) nitrate trihydrate (0.08 g) in ethanol (5 cm^3) and solid lithium perchlorate (0.1 g) were added to a boiling solution of L^{18} (0.10 g) in ethanol (25 cm^3) to yield blue-purple crystals; yield 0.06 g (Found: C, 38.2; H, 4.5; N, 9.3. Calc. for $C_{19}H_{25}ClCuN_4O_7S_2 \cdot H_2O$: C, 37.9; H, 4.5; N, 9.3%). FAB mass spectrum: *m/z* 484, $[Cu(NO_3)L^{18}]^+$.

$[CuL^{20}][ClO_4]_2 \cdot H_2O$. In a similar manner to that used for the synthesis of the copper(II) complex of L^{15}, copper(II) nitrate trihydrate (0.1 g) in ethanol (20 cm^3) and solid lithium perchlorate (0.1 g) were added to a boiling solution of L^{20} (0.15 g) in ethanol (25 cm^3) to yield purple crystals; yield 0.10 g (Found: C, 36.6; H, 4.2; N, 6.0. Calc. for $C_{20}H_{27}Cl_2CuN_3O_8S_2 \cdot H_2O$: C, 36.7; H, 4.5; N, 6.4%). FAB mass spectrum: *m/z* 535, $[Cu(ClO_4)L^{20}]^+$. A related procedure starting from copper(II) perchlorate hexahydrate has recently been reported for the synthesis of this complex (in its anhydrous form) for use in an X-ray structure determination.[12]

$[CuL^{22}][ClO_4]_2$. In a similar manner to that used for the synthesis of the copper(II) complex of L^{15}, copper(II) nitrate trihydrate (0.07 g) in methanol (15 cm^3) and solid lithium perchlorate (0.08 g) were added to a boiling solution of L^{22} (0.10 g) in ethanol (25 cm^3) to yield brown-green crystals; yield 0.10 g (Found: C, 37.6; H, 4.1; N, 4.3. Calc. for $C_{20}H_{26}Cl_2CuN_2O_9S_2$: C, 37.7; H, 4.1; N, 4.4%). FAB mass spectrum: *m/z* 536, $[Cu(ClO_4)L^{22}]^+$.

Molecular Mechanics Calculations.—Molecular mechanics has been used to model $[CuL^2(H_2O)]^+$ and $[CuL^{20}]^{2+}$ whose X-ray structures, as their corresponding perchlorate salts, were reported earlier.[12,13] The X-ray coordinates were used as the starting coordinates for the calculations; the latter were performed using the MOLMEC suite of programs described previously.[14] Allinger's MM2 force field[15] and subsequent additions[16] formed the basis for treating the organic parts of the structure while the parameters for those parts of the structure associated with the copper were largely based on those reported by Drew and co-workers,[17] but were modified where necessary in order to optimise the fit of the calculated structure to the X-ray data. It is noted that a slightly longer r_0 value was used for the axial Cu–S bond in $[CuL^{20}]^{2+}$ than employed by the above workers. This was to allow for the Jahn–Teller elongation present in this complex. In accordance with this, the r_0 value found necessary for modelling the (equatorial) Cu–S bonds in $[CuL^2(H_2O)]^{2+}$ and $[CuL^{20}]^+$ was shorter.

Results and Discussion

The macrocycles L^1–L^{24} represent a series in which the donor atom sequence and macrocyclic ring size vary in a stepwise manner. Each of these ligands reacts with copper(II) in solution to yield a 1 : 1 complex and a selection of these complexes has been isolated by treating copper(II) nitrate in boiling ethanol with the appropriate macrocycle, followed by addition of lithium perchlorate to the solution. Microanalysis of the solid products indicated that the complexes of L^5, L^{15} and L^{18} contain one nitrate and one perchlorate per metal ion, whereas the complexes of L^{20} and L^{22} contain two perchlorate anions per complex. Physical data for each of these species are presented in Table 1.

The infrared spectra of all complexes contain a strong absorption centred at approximately 1080 cm^{-1} confirming the presence of perchlorate ion. No clear splitting of this band was evident although it is quite asymmetric in most cases; from the infrared data it is difficult to decide whether or not the perchlorate ion is co-ordinated to the metal in individual complexes. The presence of peaks from the ligand partially mask the nitrate absorptions in each case and no attempt was made to assign these peaks. All spectra contained bands between 3200 and 3300 cm^{-1} arising from the presence of (co-ordinated) secondary amine groups. The spectra also confirmed the presence of water where it was suggested to be present from the microanalytical data.

The room-temperature magnetic moment of each complex falls in the range expected for copper(II) with $S = \frac{1}{2}$ (Table 1). The conductance data for the mixed-anion copper(II) complexes of L^5 and L^{15} indicate that they are 1 : 1 electrolytes in methanol[18] (Table 1), thus confirming that these complexes have one anion bound to the central metal ion in solution. In contrast, the complexes of L^{18}, L^{20} and L^{22} approach 2 : 1 electrolytes in the above solvent, indicating the ionic nature of both anions under the conditions employed for the measurements.

The solid-state and solution electronic spectra of the

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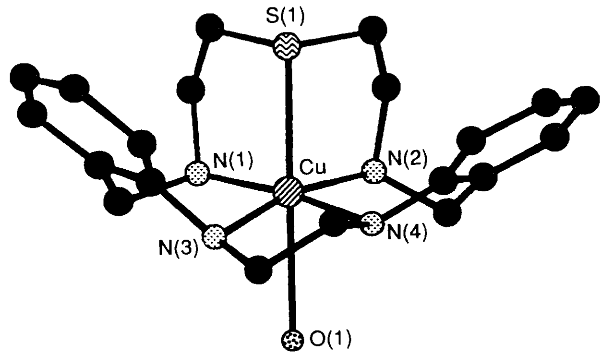
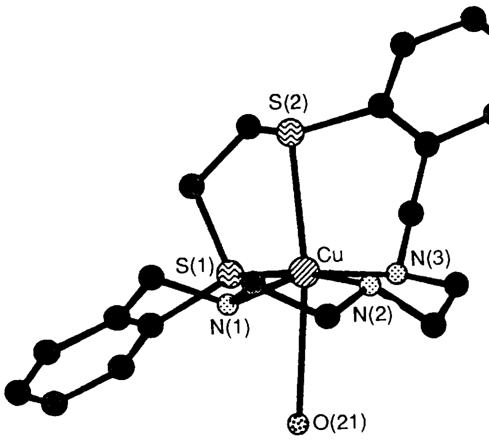
* **CAUTION**: perchlorates may be explosive.



(a)



(b)

Fig. 1 The X-ray diffraction structures of the cations in (a) $[CuL^2(H_2O)][ClO_4]_2$ (ref. 13) and (b) $[CuL^{20}][ClO_4]_2$ (ref. 12). The latter complex has a weak interaction between a perchlorate oxygen and the sixth (axial) site of the copper (see text)

complexes each show a broad envelope of bands in the region 500–1000 nm (Table 1). Because of the rather featureless nature of the spectra, it is inappropriate to attempt an assignment of co-ordination geometries from these data. However, it is noted that the copper(II) complexes of L^5 and L^{15} have very similar spectra in the solid state, suggesting that similar co-ordination geometries occur in the solid.

Previously,[13] we have published the results of an X-ray structural investigation of $[CuL^2(H_2O)][ClO_4]_2$ [prepared by a similar procedure to that used for the corresponding copper(II) perchlorate complex of L^{20}]. The structure [Fig. 1(a)] confirms that all macrocyclic donors (a N_4S-donor set) co-ordinate in the solid state; the macrocycle adopts a rather symmetrical square-pyramidal arrangement around the copper(II) which also has a water weakly bound (Cu–O, 2.638 Å) in the sixth position. The overall co-ordination geometry is distorted tetragonal with the copper slightly displaced (0.11 Å) from the N_4 equatorial plane towards the axial sulfur donor (Cu–S, 2.524 Å). The equatorial Cu–N bond distances (mean value of 2.050 Å) are unexceptional while the bonds to the axial donors are longer than usual. For the latter, a Jahn–Teller distortion undoubtedly contributes to the observed elongations.

More recently, the structure of $[CuL^{20}][ClO_4]_2$ has been reported [Fig. 1(b)].[12] The co-ordination geometry of the copper(II) also contains the macrocycle co-ordinated in an (approximate) square-pyramidal arrangement with the copper(II) ion lying 0.23 Å out of the N_3S-donor equatorial plane towards an axial sulfur donor. There is weak interaction between the copper(II) and a perchlorate oxygen in the remaining axial site (Cu–O, 2.851). The equatorial Cu–S distance of 2.346 Å is comparable with literature values while the corresponding axial distance of 2.590 Å is again somewhat elongated.

Table 2 Stability constants for the copper(II) complexes of L^1–L^{24} (95% MeOH, I = 0.1 mol dm^{-3}, NEt_4ClO_4 at 25 °C)

Ligand	Ring size	Donor set	Log K_{CuL}
L^1	17	N_5	≈16.3[a]
L^2	17	N_4S	14.5[b]
L^3	17	N_4O	14.5[c]
L^4	20	N_5	13.9[d]
L^5	16	N_3O_2	14.9
L^6	16	N_2O_2S	~6.9
L^7	16	N_2O_3	~7.0
L^8	17	N_3O_2	14.2[e] (14.4[f])
L^9	17	N_2O_2S	7.4
L^{10}	17	N_2O_3	6.5
L^{11}	18	N_3O_2	(14.0[f])
L^{12}	19	N_3O_2	11.0 (11.5[f])
L^{13}	19	N_3O_2	(10.5[f])
L^{14}	19	N_2O_2S	~7.8
L^{15}	19	N_3O_2	14.0
L^{16}	19	N_2O_2S	~7.2
L^{17}	19	N_2O_3	7.0
L^{18}	16	N_3S_2	14.3
L^{19}	16	N_2S_3	6.3
L^{20}	17	N_3S_2	~15.6
L^{21}	17	N_2S_3	6.9
L^{22}	17	N_2S_2O	11.0
L^{23}	19	N_3S_2	11.0
L^{24}	18	N_2S_3	7.3[g]

[a] Ligand: log K_1^H 9.69, log K_2^H 7.18, log K_3^H 2.20. [b] Ligand: log K_1^H 8.47, log K_2^H 6.67, log K_2^H 2.11. [c] Ligand: log K_1^H 9.14. log K_2^H 7.35. [d] Ligand: log K_1^H 9.91, log K_2^H 7.36, log K_3^H 5.96, log K_4^H 2.34, log K_5^H 1.64. [e] Ref. 19 reports that this complex has a log K_{CuL} value in water of 13.4 (I = 0.1 mol dm^{-3}, KNO_3) at 25 °C. [f] From refs. 4 and 9 (95% MeOH, I = 0.1 mol dm^{-3}, NMe_4Cl). [g] Ligand: log K_1^H 7.91, log K_2^H 6.70.

Stability Constants.—Ligand protonation constants (in 95% methanol, I = 0.1 mol dm^{-3}, NEt_4ClO_4; 25 °C) for L^5–L^{23} have been reported previously[6] and those for L^1–L^4 and L^{24} are listed in footnotes to Table 2. Stability constants for the 1 : 1 (L : M) complexes of the macrocyclic ligands were determined potentiometrically. The values are listed in Table 2; for completeness, some previously published log K data for the complexes of L^8 and L^{11}–L^{13} in 95% methanol (I = 0.1 mol dm^{-3}, NMe_4Cl; 25 °C)[4,9] as well as the complex of L^8 in water (I = 0.1 mol dm^{-3}, KNO_3; 25 °C)[19] have also been included.

In undertaking this study it was of particular interest to observe the effect of the structural variation embodied in L^1–L^{24} on the stabilities of the corresponding complexes. For convenience, it is useful to divide the macrocycles into three categories based on whether X = NH, O or S. For each category, Y may be NH, O or S. Further, for each donor set combination, the overall macrocyclic ring size may also vary, providing a third variable that may be employed for tuning the stabilities of individual complexes.

Conceptionally it has proved useful to consider the respective macrocycles to form part of a three-dimensional structural matrix (each of the variables just mentioned corresponding to a dimension). The tuning process then amounts to stepwise movement within the matrix until the required stability is achieved. More importantly, when two or more metal ions are involved, the stepwise procedure may be employed to maximise a stability difference between ions of interest. In addition to the implication for metal-ion discrimination, the investigation of systems showing a regular variation in structure tends to lead to a more complete understanding of individual complexation

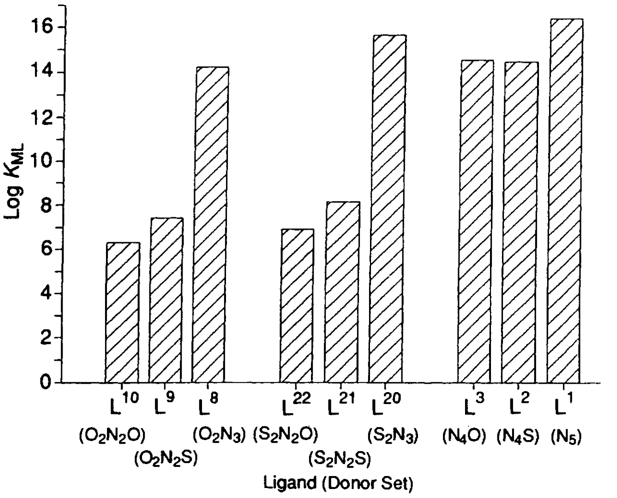


Fig. 2 The relative log K_{ML} values for the copper(II) complexes of the 17-membered macrocycles, L^{10}, L^9, L^8, L^{22}, L^{21}, L^{20}, L^3, L^2 and L^1

behaviour than would occur if the study was restricted to isolated systems.

The data in Table 2 clearly show the stability dependence of the copper complexes on the nature of the donor atom at the Y position. Thus, when Y = NH (to yield a N_3-donor backbone), the stabilities of the corresponding complexes are consistently high and it is apparent that the other donor types have less effect on the overall stability.

It is instructive to consider the stability pattern for the 17-membered rings listed in Table 2 (these may be considered to make up one layer of the matrix). The relative values are shown diagrammatically in Fig. 2. The following observations may be made. First, the figure illustrates the strong dependence of the respective stabilities on the donor atom set present, with the constants varying by up to ten orders of magnitude along the series. Secondly, it is clear that the magnitude of a particular log K value is strongly influenced by the number of nitrogen donors present. Thirdly, the contribution of the respective donor atom types to the overall complex stability falls in the order: NH(aliphatic) > NH(anilino) > S > O.

It is of interest to note the effect of macrocyclic ring size (and concomitant chelate ring size) variation on complex stability. The log K value for the complex of the 16-membered O_2N_3-donor ligand L^5 is only marginally different to that of its 17-membered analogue L^8. If all donors co-ordinate in each of these complexes, the formation of a four-membered chelate ring (involving both ether donors) in the former complex would be expected to result in lower stability relative to the complex of the 17-membered ring, L^8, in which the corresponding chelate ring would be five-membered. However, this is not the case; although other possibilities exist, the results are in accord with non co-ordination of the ether donors in one or both of these complexes. Non-co-ordination of ether donors in the solid state has been demonstrated previously by X-ray diffraction for the complex of the corresponding 18-membered ligand, L^{11}.[9]

In contrast to the above, the stability of the complex of the S_2N_3-donor ligand L^{18} (16-membered) is significantly less than for the complex of the corresponding 17-membered ring system, L^{20}. The order thus follows that expected from chelate ring size considerations and suggests that the thioether donors are co-ordinated to the copper(II) in this latter complex—an observation in accordance with its solid-state structure.[12]

The higher stability of the copper(II) complex of the 17-membered dithia macrocycle L^{20} relative to the complex of the related dioxa macrocycle L^8 probably reflects the documented preference of copper(II) for thioether over ether donors.[19] However, the absence of similar behaviour for the copper(II) complexes of the 16-membered macrocycles L^5 and L^{18} is more difficult to rationalise but may imply that the X donors do not co-ordinate in either of these complexes (in preference to forming four-membered rings on co-ordination).

Table 3 Force-field parameters for copper(II) complexes of co-ordinated quinquedentate macrocycles

Non-bonded parameters[a]

Atom	r^*/Å	ε/kJ mol^{-1}
Cu	2.30	0.711

Bond stretching parameters and bond moments

Bond type	r_0/Å	k_r/mdyn Å^{-1} molecule^{-1}	μ/D
Cu–N	2.00	3.00	0.000
Cu–N (anilino)	2.00	1.50	0.000
Cu–S (axial)	2.58	2.00	0.000
Cu–S (in-plane)	2.40	2.00	0.000
S–Lp[b]	0.60	5.30	0.800
C(sp^3)–N(sp^3)	1.46	4.00	0.027

Bond bending parameters

Bond angle	θ_0/°	k_θ/mdyn Å rad^{-2} molecule^{-1}
Cu–N–C	109.5	0.50
Cu–N–H	109.5	0.50
Cu–S–C	100.0	0.50
Cu–S–Lp	115.0	0.50
N–Cu–N	90.0	0.30
N–Cu–O	90.0	0.30
N–Cu–S	90.0	0.30
O–Cu–S	90.0	0.30
S–Cu–S	90.0	0.30

Stretch-bend constants

Bond angle	k_{sb}/mdyn rad^{-1} molecule^{-1}
C–N–Cu	0.12
H–N–Cu	0.09
C–O–Cu	0.12
C–S–Cu	0.25

Torsional constants

Torsion	V_1/kJ mol^{-1}	V_2/kJ mol^{-1}	V_3/kJ mol^{-1}
C–C–N–Cu	−0.84	3.05	3.35
H–C–N–Cu	0.00	0.00	2.18
C–C–O–Cu	1.67	2.18	1.95
H–C–O–Cu	0.00	0.00	2.22
C–C–S–Cu	−2.59	1.26	1.05
H–C–S–Cu	0.00	0.00	2.26

[a] The same values were used by Drew and co-workers.[17] [b] Lp = Lone pair.

Molecular Mechanics Calculations.—The complexes, $[CuL^2(H_2O)][ClO_4]_2$ and $[CuL^{20}][ClO_4]_2$, whose X-ray structures were reported earlier,[12,13] were modelled successfully using the molecular mechanics technique. The modifications and additions to the basic MM2 force field employed are listed in Table 3. A comparison of the copper to donor bond distances and angles about copper for the respective calculated and X-ray structures is given in Table 4. The position of the co-ordinated water molecule in $[CuL^2(H_2O)][ClO_4]_2$ was not refined but rather its atom positions were fixed in space (relative to the copper) at the X-ray positions while the remainder of the molecule was allowed to refine. Similarly, the weakly co-ordinated perchlorate group (Cu–O, 2.851 Å), which interacts in the remaining axial site in $[CuL^{20}]^{2+}$, was also fixed in space at its X-ray position. Although both complex cations were generally modelled satisfactorily by the chosen parameter set, it

Table 4 Bond distances (Å) and angles (°) involving copper(II) in the X-ray structures and the structures calculated using molecular mechanics[a]

$[CuL^2(H_2O)][ClO_4]_2$

Distance	X-Ray	Calc.[b]	Angle	X-Ray	Calc[c]
Cu–N(1)	2.04	2.05	N(1)–Cu–N(2)	94	95
Cu–N(2)	2.07	2.04	N(1)–Cu–N(3)	90	91
Cu–N(3)	2.05	2.06	N(1)–Cu–N(4)	172	173
Cu–N(4)	2.05	2.07	N(1)–Cu–S(1)	86	84
Cu–S(1)	2.53	2.57	N(2)–Cu–N(3)	168	169
			N(2)–Cu–N(4)	93	92
			N(2)–Cu–S(1)	86	85
			N(3)–Cu–N(4)	83	83
			N(3)–Cu–S(1)	105	106
			N(4)–Cu–S(1)	99	94

$[CuL^{20}][ClO_4]_2$

Distance	X-Ray	Calc.[d]	Angle	X-Ray	Calc[e]
Cu–S(1)	2.34	2.37	S(1)–Cu–S(2)	85	81
Cu–S(2)	2.59	2.54	S(1)–Cu–N(1)	93	95
Cu–N(1)	2.02	2.02	S(1)–Cu–N(2)	172	178
Cu–N(2)	2.01	2.01	S(1)–Cu–N(3)	95	98
Cu–N(3)	2.01	2.02	S(2)–Cu–N(1)	106	107
			S(2)–Cu–N(2)	103	98
			S(2)–Cu–N(3)	93	94
			N(1)–Cu–N(2)	85	83
			N(1)–Cu–N(3)	160	157
			N(2)–Cu–N(3)	84	83

[a] Atom labels correspond to those in Fig. 1. [b] The root-mean-square (r.m.s.) difference for the metal to donor bonds is 0.026 Å (for all bonds in the structure it is 0.033 Å). [c] The r.m.s. difference for the angles around copper is 1.9° (for all angles in the structure it is 2.4°). [d] The r.m.s. difference for the metal to donor bonds is 0.027 Å (for all bonds in the structure it is 0.032 Å). [e] The r.m.s. difference for the angles around copper is 3.4° (for all angles in the structure it is 2.7°).

is important to note that the parts of the force field involving the copper have been calibrated using a limited amount of structural data. These components of the force field should thus be considered as still somewhat tentative.

In modelling other complexes of the present type care also needs to be exercised in treating the varying nature of the Jahn–Teller distortions which will occur as different donor atom types occupy the axial co-ordination positions. Thus, for example, it may be necessary to assign different parameters to particular donor atoms depending on whether they are axial or equatorial in the co-ordination sphere; as indeed was the case for the two Cu–S bonds in $[CuL^{20}][ClO_4]_2$. In view of this, no attempt was made to compare the strain energies of the various possible co-ordination isomers for the above complex cations. That is, each isomer may need to be represented by a (slightly) different parameter set as the axial donor is changed, making direct comparison of relative steric strains invalid. Clearly, this limits the usefulness of molecular mechanics for predicting the co-ordination behaviour of the present and related polydentate ligands towards copper(II).

Conclusion

The present study demonstrates the extremely large stability differential (up to 10^{10}) that may be achieved for complexes of the present type solely through donor atom variation within the ligand framework employed for this study. It also confirms that relatively minor variation in the donor set (and/or macrocyclic ring size) may be reflected by major changes within the co-ordination spheres of particular complexes. Taken together with the results of our earlier studies of the corresponding cobalt(II) and nickel(II) complexes, the results provide an additional background upon which the design of new reagents for metal-ion discrimination may be based. Studies involving the use of the present macrocyclic systems for selective heavy-metal-ion extraction as well as membrane transport will be reported in future.

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