A New Series of Quinquedentate Macrocycles Exhibiting Systematic Donor-Atom Variation: Equilibrium and X-Ray Structural Data for their Interaction with Copper(II)

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A series of nine seventeen-membered macrocyclic ligands in which the donor atom set varies systematically is reported; each ligand reacts with Cu^{II} to yield a 1:1 complex, the stability of which is markedly dependent on the donor atom pattern; the X-ray structure of the Cu^{II} complex of the N_4S donor confirms that all its donor atoms co-ordinate in the solid state; the structure of this metal-free macrocycle is also reported.

The use of macrocyclic ligands for selective complex formation is of considerable current interest,[1] particularly with regard to the factors that favour selectivity.[2] As part of such a study, we have prepared the well defined ligand series (1)—(9) in which the donor atom sequence varies systematically. Taken together, compounds (1)—(9) represent an extensive new series of ligands of which only (3) has been reported previously.[3] The ligand (3) forms the parent compound of a number of O_2N_3 donor analogues of various ring sizes which exhibit metal-ion recognition behaviour; with these ligands, ring-size control has been used to alter the thermodynamic stabilities of the complexes of a number of heavy metal ions.[4] The macrocyclic ligand series (1)—(9) was synthesised in order to investigate the effects of donor-atom variation on complex stabilities. The results of an investigation of interaction with Cu^{II} are now reported.

The free macrocycles were synthesised (in 30—70% yield) via reduction (with $NaBH_4$ or $LiAlH_4$) of their corresponding di-imine precursors, and characterised by elemental analysis, ^1H and ^{13}C n.m.r., i.r., and mass spectroscopy. An X-ray diffraction study† of (8) confirmed the structure and indicated that this ligand adopts the rather symmetrical arrangement shown in Figure 1.

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† Crystal data: $C_{20}H_{28}N_4S$ (8), $M = 356.5$, triclinic, space group $P\bar{1}$, $a = 15.819(3)$, $b = 11.717(2)$, $c = 5.285(2)$ Å, $\alpha = 103.24(2)$, $\beta = 95.07(2)$, $\gamma = 91.15(2)°$, $U = 949.0$ Å^3, $Z = 2$, $D_c = 1.25$ g cm^{-3}, $F(000) = 384$, $\mu(Mo-K_\alpha) = 1.42$ cm^{-1}; 1939 unique data with $I \geqslant 3\sigma(I)$ gave final $R = 0.114$ and $R' = 0.128$. There is evidence for disorder in the structure along $C(8b)–C(10b)$.

$[CuL(H_2O)](ClO_4)_2$ $[L = (8)]$, $C_{20}H_{30}Cl_2CuN_4O_9S$, $M = 637.0$, orthorhombic, space group $P2_12_12_1$, $a = 16.793(3)$, $b = 14.530(2)$, $c = 10.393(2)$ Å, $U = 2535.9$ Å^3, $Z = 4$, $D_c = 1.67$ g cm^{-3}, $F(000) = 1316$, $\mu(Mo-K_\alpha) = 11.39$ cm^{-1}; 1634 unique data with $I \geqslant 3\sigma(I)$ gave final $R = 0.062$ and $R' = 0.065$ (weighting scheme $w = 1/[\sigma^2(F_o)]$). Reversing the 'hand' of the structure gave $R = 0.068$ and $R' = 0.072$ confirming that the correct enantiomorph had been chosen. Data were collected with a Phillips PW1100 diffractometer in the θ range 3—25°.

Atomic co-ordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.
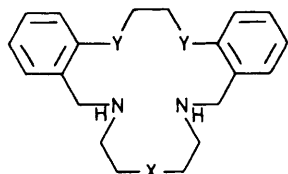
(1) Y = O, X = O   (6) Y = S, X = NH
(2) Y = O, X = S   (7) Y = NH, X = O
(3) Y = O, X = NH   (8) Y = NH, X = S
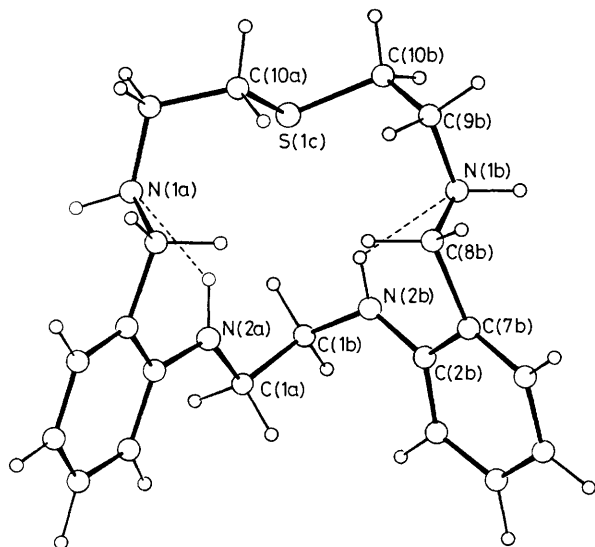(4) Y = S, X = O   (9) Y = NH, X = NH
(5) Y = S, X = S

Table 1. Values of log K for formation of the 1:1 complexes of Cu^{II} with (1)—(9).[a]

Compd.	(1)	(2)	(3)	(4)	(5)	(6)
log K	6.4	7.4	14.2	6.9	8.1	15.6
Compd.		(7)	(8)	(9)		
log K		14.5	14.5	16.3		

[a] The stabilities were obtained potentiometrically in 95% methanol (I = 0.1M; Et_4NClO_4) at 25 °C. Each value is the mean of between 2 and 5 individual determinations at varying metal : ligand ratios. For the log K values of less than 9 the error is ±0.1; for values above 14 the error is ±0.3 log units.

Figure 1. The structure of the macrocycle (8). There are two intramolecular hydrogen bonds: N(2a)H · · · N(1a) 2.30, and N(2b)H · · · N(1b) 2.29 Å.
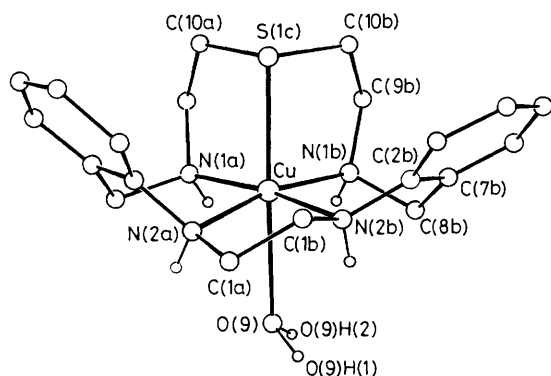

Figure 2. The structure of the cation $[CuL(H_2O)](ClO_4)_2$ [L = (8)]. Bond lengths to Cu^{II} are S(1c) 2.525(4), N(1a) 2.037(11), N(2a) 2.049(10), N(1b) 2.065(10), N(2b) 2.047(10), O(9) 2.638(9) Å. There are several strong hydrogen-bonding interactions to the perchlorate anions with N(1a)H · · · O(1) 2.14, N(2a)H · · · O(8) 2.08, N(1b)H · · · O(4) 2.27, and O(9)H(2) · · · O(2) 2.00 Å.

Stability constants have been determined for the 1:1 copper complexes in 95% methanol (I = 0.1 M; Et_4NClO_4) at 25 °C. A summary of the values is given in Table 1. As expected, the stabilities depend on the donor atom set; in fact, the constants

vary by up to ten orders of magnitude along the series. Clearly, the magnitude of a particular log K value is strongly influenced by the number of nitrogen donor atoms. Whenever X = NH (to yield an aliphatic N_3 donor backbone), the stabilities of the Cu^{II} complexes are high. From Table 2, the contribution of the various donor atom types to the overall complex stability is seen to fall in the order NH(aliphatic) > NH(anilino) > S > O.

The X-ray structure of the Cu^{II} complex of (8),† containing the N_4S donor set, confirms that all five donor atoms of the macrocycle co-ordinate in the solid state. The ligand adopts a configuration different from that in the uncomplexed state (Figure 1). Thus, the macrocycle occupies a square pyramidal arrangement around the Cu^{II}, which also has a water molecule weakly bound in the sixth position (Figure 2). The overall co-ordination geometry is distorted tetragonal and contains the copper slightly displaced (0.11 Å) from the N_4 equatorial plane towards the axial sulphur donor. The equatorial Cu–N bond distances [mean 2.050(5) Å] are unexceptional; the bonds to the axial ligands are both longer than usual. A Jahn–Teller distortion undoubtedly contributes to the observed elongations.

In summary, the present study demonstrates the extremely large stability differential (up to 10^{10} for Cu^{II}) that may be achieved solely through donor atom variation within the ligand framework employed. In conjunction with ring-size variation, it appears likely that such donor-atom variation will provide a valuable additional means of achieving metal-ion discrimination of the type already mentioned. Studies in this area involving a range of heavy metal ions are in progress.

References

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