Complexes of Ligands providing Endogenous Bridges. Part 9.[1] Copper(II) Complexes of 1,11-Diamino-6-hydroxy-4,8-diazaundecane: the Use of Fast Atom Bombardment Mass Spectrometry to Monitor Exogenous Bridge Strength

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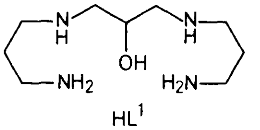
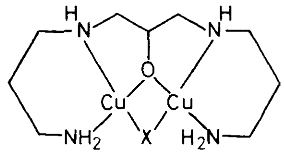
Homodinuclear copper(II) complexes of 1,11-diamino-6-hydroxy-4,8-diazaundecane (HL^1), $[Cu_2L^1(X)][ClO_4]_2$, have been prepared. The ligand is deprotonated thus generating a single-atom endogenous bridge and exogenous bridges (X) are provided by hydroxide, benzoate, 3,5-dimethylpyrazolate, and azide anions. The fast atom bombardment mass spectra of the complexes have been run and used to monitor the nature and strength of the exogenous bridge. For this system it appears that anions capable of binding in the μ-1,3 mode provide the best match with the dinuclear moiety.

The Michael addition of 2 equivalents of acrylonitrile to a primary amine is used as the first step in the synthesis of *N,N*-bis(3-aminopropyl)alkylamines.[2] By modifying the reaction conditions this approach can be used for the addition of 2 equivalents of acrylonitrile to primary diamines to form *N,N'*-bis(2-cyanoethyl)diaminoalkanes which can be reduced to give *N,N'*-bis(3-aminopropyl)diaminoalkanes.[3] Herein we report use of this reaction to prepare 1,11-diamino-6-hydroxy-4,8-diazaundecane (HL^1) together with the preparation and properties of some copper(II) complexes of this ligand. The binuclear complexes contain exogenous bridges of variable bonding mode and so the use of fast atom bombardment mass spectrometry (f.a.b.m.s.) to monitor the nature and strength of the bridge has been explored.



HL^1



(1)

X = OH, N_3, O_2CPh, or dmpz

Results and Discussion

The carefully controlled addition of acrylonitrile to a cooled methanolic solution of 1,3-diamino-2-hydroxypropane yields, on removal of the solvent, 1,9-dicyano-5-hydroxy-3,7-diazanonane (HL^2) as a clear oil. The progress of the reaction may be followed using i.r. spectra (for oils between NaCl plates) by monitoring the disappearance of the bands indicative of the primary diamine and the appearance of bands attributable to secondary amines and to the cyano-groups. The compound HL^2 is readily reduced to HL^1 by use of dissolving sodium metal in absolute ethanol.[4] The i.r. spectrum of HL^1 shows bands due to primary and secondary amines but no evidence of CN stretching frequencies.

Binuclear Copper Complexes.—Treatment of HL^1 with 2 equivalents of copper(II) perchlorate hexahydrate and 2 equivalents of lithium hydroxide in ethanol gives a deep blue solid characterised as the homodinuclear copper(II) complex $[Cu_2L^1(OH)][ClO_4]_2$. It is proposed, by analogy with related complexes derived from the 1,3-diamino-2-hydroxypropane moiety,[5–7] that the hydroxyl group on the ligand has been deprotonated such that the ensuing alkoxide provides an endogenous bridge at the dinuclear copper(II) centre, (**1**), and that the OH^- serves as an exogenous bridge. The i.r. spectrum shows that the ClO_4^- are non-co-ordinated.

The exogenous bridge may be readily changed by addition of an equivalent amount of the sodium salt of the required anion to the initial solution. The complexes $[Cu_2L^1(N_3)][ClO_4]_2\cdot EtOH\cdot H_2O$, $[Cu_2L^1(O_2CPh)][ClO_4]_2$, and $[Cu_2L^1(dmpz)][ClO_4]_2\cdot H_2O$, where dmpz is 3,5-dimethylpyrazolyl, have been prepared by this method.

The major i.r. peaks of interest are shown in Table 1; bands indicating the bridging groups are present as well as those of the perchlorate anions.

The positive-ion f.a.b. mass spectra of the complexes have been recorded. The principal peaks are listed in Table 2 and give some insight into the nature and strength of the exogenous bridge. With the exception of that of the μ-hydroxy complex, all spectra show a major peak corresponding to $[Cu_2L^1(X)(ClO_4)]^+$. The spectrum of $[Cu_2L^1(OH)][ClO_4]_2$ does not show any peaks corresponding to species retaining the hydroxide anion; the highest peak found corresponds to $[Cu_2L^1(ClO_4)_2]^+$ which then loses the anions to give $[Cu_2L^1(ClO_4)]^+$ and $[Cu_2L^1]^+$. The remaining spectra fall into two groups; the benzoate and pyrazolate complexes follow one breakdown path and the azide follows a second path.

F.a.b.m.s. for the 3,5-dimethylpyrazolate and benzoate complexes shows initial loss of ClO_4^- from the neutral parent with retention of the exogenous bridge. The principal peak is $[Cu_2L^1(X)(ClO_4)]^+$ which then loses X^- to give $[Cu_2L^1(ClO_4)]^+$. The azido-complex exhibits two initial breakdown pathways; it loses either X^- to generate $[Cu_2L^1(ClO_4)_2]^+$ or ClO_4^- to yield $[Cu_2L^1(X)(ClO_4)]^+$. The relative strengths of the two peaks suggest that perchlorate loss is preferred. Further breakdown leads to $[Cu_2L^1(ClO_4)]^+$ by either X^- or ClO_4^- loss from the respective parent peaks.

The differences in the m.s. pathways may be rationalised in terms of the nature and strength of the exogenous bridge present

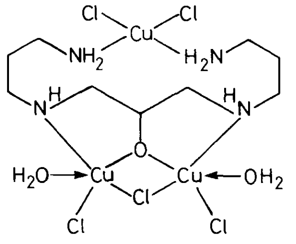
Table 1. Selected i.r. bands (cm^{-1}) for complexes (**1**)

	X^-			
	OH	N_3	dmpz	O_2CPh
NH stretches	3 315 3 260 3 175	3 315 3 250 3 160	3 335 3 260 3 160	3 335 3 250 3 160
NH bends	1 630 1 590	1 630 1 600	1 630 1 595	1 630 1 595
ClO_4^- stretch	1 100 624	1 100 624	1 100 624	1 100 624
X^-	3 550	2 040	1 525	1 600 1 580

The spectra were run as KBr discs.

Table 2. Principal m.s. peaks for complexes (**1**) with abundances (%) in parentheses

	X			
	OH	N_3	dmpz	O_2CPh
$[Cu_2L^1(ClO_4)_2]^+$	529 (31)	529 (28)		
$[Cu_2L^1(X)(ClO_4)]^+$		472 (62)	525 (100)	551 (100)
$[Cu_2L^1(ClO_4)]^+$	428 (51)	428 (60)	428 (15)	428 (15)
$[Cu_2L^1]^+$	329 (100)	329 (100)		



(**2**)

in the complex. It has been shown that for homodinuclear copper(II) complexes bearing a single-atom endogenous bridge an intermetallic separation of *ca.* 3.0 Å is required to support a μ-1,1-exogenous bridge whereas a longer separation of *ca.* 3.5 Å is needed for μ-1,2- and μ-1,3-exogenous bridges.[8] A flexible ligand should be capable of adapting itself to support either of these separations but the strength by which the exogenous bridge is bound is likely to be greater in the least conformationally strained (or best matched) system. The relief of any induced strain by the loss of the exogenous bridge may, in this case, account for the observed m.s. patterns.

The 3,5-dimethylpyrazolate and benzoate bridges each provide two donor atoms in the exogenous bridge (μ-1,2 and μ-1,3 respectively) and an intermetallic separation of *ca.* 3.5 Å is predicted, by analogy with related complexes.[8,9] These anions are not readily lost in the mass spectra whereas the OH^- anion, which as a single-atom bridge, would command a separation of *ca.* 3.0 Å, again by analogy,[8] is readily lost. This suggests that for HL^1, with which both bridging modes may be accommodated, the former are the better matched systems. The azide anion can act as either a μ-1,1 or a μ-1,3 bridge; the azide stretch is broad and centred on 2 040 cm^{-1} and is not diagnostic for the bridging mode. Both of the available breakdown patterns are noted in the mass spectrum suggesting that both bridging modes might be present in the bulk sample. The pathway retaining the azide anion appears to be favoured and this indicates that the μ-1,3 bridging mode is that providing the best match. A mixed μ-1,1 and μ-1,3 species has been noted for a dicopper(II) azido complex of a related flexible ligand, 4,4′-(3-hydroxypentane-1,5-diyl)dinitrilobis(2-pentanone) for which magnetic data were best fitted to a 19%:81% composition.[8]

From the above it can be seen that f.a.b.m.s. has the potential to provide a useful diagnostic test for the bridging mode and strength of interaction of the anions in dinuclear complexes and we are extending our investigations to related systems in order to test the generality of these observations.

A Trinuclear Copper(II) *Complex.*—Addition of 2 equivalents of copper(II) chloride monohydrate to a solution of HL^1 in methanol yields the trinuclear complex $[Cu_3L^1Cl_5]\cdot 2H_2O$, (**2**). In the i.r. NH stretches are observed at 3 280, 3 225, and 3 195 cm^{-1}. Positive-ion f.a.b.m.s. shows a highest peak at *m*/*z* 532 corresponding to $[Cu_3L^1Cl_4]^+$ with further chloride loss leading to $[Cu_3L^1Cl_3]^+$. No higher oligomers have been detected suggesting the discrete nature of the trinuclear species is retained during the m.s. experiment. Dinuclear intermediates such as $[Cu_2L^1Cl_2]^+$ and $[Cu_2L^1Cl]^+$ are also detected. It has not been possible to grow crystals of complex (**2**) but, in view of the recently reported structure of the ascorbate oxidase from zucchini in which a triangular array of copper atoms has been detected,[10] it is interesting to speculate on the nature of (**2**). In the metalloprotein the triangle is composed of a pair of copper atoms at 3.4 Å with the third copper atom 3.9 Å away. In (**2**) the ligand has been deprotonated and so a homodinuclear unit is likely to be present as indicated by the m.s. fragmentation pattern; by analogy a Cu ··· Cu separation of *ca.* 3.0 Å would be expected.[8] The third copper atom could then be co-ordinated in close proximity by the pendant arms of the ligand and so be easily lost in the m.s. experiment to leave the dinuclear fragment. Such an arrangement displays the basic features of the metalloprotein site but in the absence of a structure it is, of course, not possible to make a real comparison.

Experimental

Microanalyses were carried out by the University of Sheffield Microanalytical Service. I.r. spectra were recorded using a Perkin-Elmer 297 spectrophotometer, n.m.r. spectra on Bruker WH250 and WH400 spectrometers. F.a.b. mass spectra were recorded as previously described.[11]

1,9-*Dicyano*-5-*hydroxy*-3,7-*diazanonane.*—Acrylonitrile (0.10 mol) was added dropwise to a solution of 1,3-diamino-2-hydroxypropane (0.05 mol) in methanol (5 cm^3) at 0 °C over a period of *ca.* 30 min. On completion of the addition the solution was allowed to warm to ambient temperature and stirred (60 min). The methanol solvent was removed *in vacuo*, to allow isolation of the product as a clear oil which was characterised spectroscopically. I.r.: $\nu_{max.}$ 3 300, 3 260, 1 640, 1 580 (NH), and 2 250 cm^{-1} (CN) (oil between NaCl plates). $\delta_H(CDCl_3)$ 2.40 (3 H, br s, 2NH, OH), 2.48 (4 H, t, $2CH_2N$), 2.64 (4 H, m, $2NCH_2$), 2.88 (4 H, t, $2CH_2$), and 3.71 (1 H, spt, CHO). *m*/*z* (electron impact, e.i.) 197 ($[M + H]^+$, 14%); (chemical ionisation, c.i.) 197 ($[M + H]^+$, 100%).

1,11-*Diamino*-6-*hydroxy*-4,8-*diazaundecane.*—This compound was prepared by the reduction of 1,9-dicyano-5-hydroxy-3,7-diazanonane using the method described in ref. 4. Yield of HL^1 (94.0%); $\nu_{max.}$ 3 450 (OH), 3 290, 3 180, and 1 600 cm^{-1} (NH_2, NH) (oil between NaCl plates). $\delta_H(CDCl_3)$ 1.62 (4 H, qnt, $2CH_2$), 2.06 (7 H, br s, $2NH_2$, 2NH, OH), 2.65 (8 H, m, $2CH_2NCH_2$), 2.75 (4 H, t, $2CH_2$), and 3.78 (1 H, spt, CHO). *m*/*z* (e.i.) 205 ($[M + H]^+$, 12%); (c.i.) 205 ($[M + H]^+$, 100%).

Copper(II) *Complexes*.—$[Cu_3L^1Cl_5]\cdot 2H_2O$. A solution of $CuCl_2\cdot H_2O$ (2 mmol) in methanol (16 cm^3) was added dropwise to a stirred solution of HL^1 (1 mmol) in methanol (8 cm^3) at reflux temperature. The turquoise solution was heated at reflux temperature for *ca.* 15 min. The product was crystallised from the reaction solution by slow evaporation of the solvent at ambient temperature. It was collected by filtration and dried *in vacuo*, yield 81.0%, m.p. 158—159 °C (Found: C, 18.1; H, 4.4; Cl, 29.1; N, 8.8. $C_9H_{27}Cl_5Cu_3N_4O_3$ requires C, 17.8; H, 4.5; Cl, 29.2; N, 9.2%).

$[Cu_2L^1(OH)][ClO_4]_2$. A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (1.0 mmol) in ethanol (absolute, 30 cm^3) was added dropwise to a solution of HL^1 (0.5 mmol) in ethanol (absolute, 10 cm^3) at reflux temperature. The deep blue solution was heated at reflux temperature for *ca.* 15 min. Solid $LiOH\cdot H_2O$ (1 mmol) was added and the reaction mixture heated at reflux temperature (18 h). The product was removed from the hot suspension by filtration and dried *in vacuo*, yield 69.6% (Found: C, 20.2; H, 4.5; Cl, 13.0; N, 9.8. $C_9H_{24}Cl_2Cu_2N_4O_{10}$ requires C, 19.8; H, 4.4; Cl, 13.0; N, 10.2%).

$[Cu_2L^1(X)][ClO_4]_2$ ($X = N_3$, O_2CPh *or* dmpz). A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (1.0 mmol) in ethanol (absolute, 30 cm^3) was added dropwise to a solution of HL^1 (0.5 mmol) in ethanol (absolute, 10 cm^3) at reflux temperature. The blue solution was heated at reflux temperature for *ca.* 15 min. The salts $LiOH\cdot H_2O$ (0.5 mmol) and NaX (0.5 mmol) were added as solids and the mixture was heated at reflux temperature (*ca.* 20 h). The product was collected from the hot suspension by filtration, washed with ethanol (absolute, 2 × 6 cm^3), and dried *in vacuo*: $[Cu_2L^1(N_3)][ClO_4]_2\cdot EtOH\cdot H_2O$ (44.1%) (Found: C, 20.6; H, 4.5; Cl, 10.9; N, 15.3. $C_{11}H_{31}Cl_2Cu_2N_7O_{11}$ requires C, 20.8; H, 4.9; Cl, 11.2; N, 15.4%); $[Cu_2L^1(O_2CPh)][ClO_4]_2$ (62.3%) (Found: C, 29.6; H, 4.4; Cl, 10.6; N, 8.5. $C_{16}H_{28}Cl_2Cu_2N_4O_{11}$ requires C, 29.6; H, 4.3; Cl, 10.9; N, 8.6%); $[Cu_2L^1(dmpz)][ClO_4]_2\cdot H_2O$ (67.7%) (Found: C, 26.8; H, 4.9; Cl, 10.8; N, 12.7. $C_{14}H_{32}Cl_2Cu_2N_6O_{10}$ requires C, 26.2; H, 5.0; Cl, 11.0; N, 13.1%).

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