Structure of the Copper(II) Complex of a Highly Preorganised Tetradentate Ligand based on Bispidine (3,7-Diazabicyclo-[3.3.1]nonane)†

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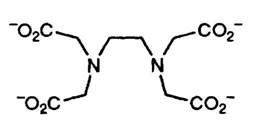
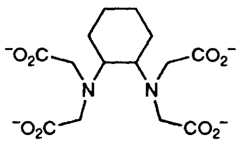
The structure of the complex of the reinforced ligand dpb {3,7-bis(2-pyridylmethyl)-3,7-diazabicyclo[3.3.1]nonane} with copper(II) perchlorate has been determined: space group *Pbcn* (no. 60), $a = 8.904(2)$, $b = 14.366(1)$, $c = 17.402(2)$ Å, $Z = 4$, $R = 0.0538$. The Cu–N bond lengths to the saturated nitrogens are 2.002(4) Å, and those to the aromatic nitrogens of dpb are 1.976(4) Å. The co-ordination geometry around Cu is considerably distorted away from the usual square-planar arrangement found with four nitrogen donor atoms, towards tetrahedral geometry, with the *trans* N–Cu–N angles being 161.1(2)° instead of the expected 180°. Molecular mechanics calculations showed that the distortion arises because of van der Waals repulsion between the two co-ordinated pyridyl groups of the ligand, particularly the hydrogen atoms *ortho* to the nitrogen donors. These calculations are also used to support the idea that the much greater thermodynamic stability of the complexes of dpb with smaller metal ions than is found for complexes of analogous unreinforced ligands is due to the rigid bispidine-type bridge of dpb.

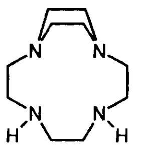
Macrocyclic ligands have interesting properties relating to the fact that they are highly preorganised. Preorganisation is a term coined by Cram *et al.*[1] to indicate ligands that are more nearly constrained to the conformation required for complexation of the target ion or molecule. The properties of macrocyclic ligands that are seen in their complexation of metal ions are (1) increased thermodynamic complex stability, the thermodynamic 'macrocyclic effect',[2] (2) altered selectivity patterns[3] and (3) much slower rates of metallation and demetallation,[4] as compared to their open-chain analogues. The macrocyclic structure constrains the ligand more nearly to the conformation observed in its complexes with metal ions, but there is no reason why a non-macrocyclic ligand cannot display all of the above properties. Indeed, many years ago Schwarzenbach *et al.*[5] found that a cyclohexylene bridge in *trans*-cdta (cyclohexane-1,2-diamine-*N,N,N′,N′*-tetraacetate) leads to an increase in the formation constant, log K_1, of some three log units as compared to the unreinforced analogue edta (ethylenediamine-*N,N,N′,N′*-tetraacetate), as well as slower rates of metallation and demetallation, and greatly altered selectivity patterns. *Reinforced* ligands[6] are those which contain bridges between the donor atoms that are more rigid than the simple ethylene or trimethylene bridges found, for example, in polyamine ligands. Thus, the reinforced macrocycle B-cyclen (1,4,7,10-tetraazabicyclo[8.2.2]tetradecane) shows[7] a very large thermodynamic macrocyclic effect as compared to its open-chain analogue B-trien [*N,N′*-bis(2-aminoethyl)-1,4-diazacyclohexane].



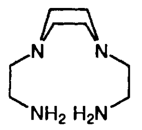
edta



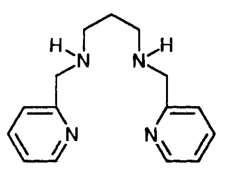
trans-cdta



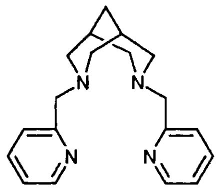
B-cyclen



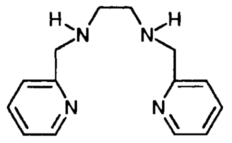
B-trien



dptn



dpb



dpen

We have reported briefly[8] on the complexing properties of the highly reinforced compound dpb, which is based on the bispidine (3,7-diazabicyclo[3.3.1]nonane) group. The bispidine group resembles the extremely rigid hydrocarbon adamantane once it has a metal ion co-ordinated between its two nitrogen donors. In this situation the metal ion is held in a fused double chelate ring which consists of two six-membered chair conformer rings. It has been shown[9] that six-membered chelate rings are of lowest strain energy with very small metal ions, in contrast to five-membered ones, which favour large metal ions. It thus seems clear that the very rigid bispidine group present in dpb should lead to a marked preference for small metal ions as compared to the non-reinforced analogues *N,N′*-bis(2-pyridylmethyl)-ethylenediamine and -trimethylenediamine (dpen and

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: cal = 4.184 J.

dptn). In this paper we report the crystal structure of the copper(II) complex of dpb, and a molecular mechanics (MM) analysis[10] of the selectivity patterns observed. The structure and MM calculations are reported to the formation constants of the complexes of dpb with Cu^{II}, Zn^{II}, Cd^{II} and Pb^{II}, which have been reported elsewhere.[9,11]

Experimental

Synthesis of the dpb Complex of Copper(II) *Perchlorate*.—The synthesis of dpb has been reported in detail elsewhere.[11] The copper(II) complex was prepared by dissolving $Cu(ClO_4)_2 \cdot 6H_2O$ (100 mg) in ethanol (20 cm^3), and adding 1 equivalent of dpb. Dark blue needles were deposited, which were recrystallised from water–ethanol (1 : 1). The λ_{max}(water) was at 598 nm, and prominent IR bands (KBr) at 3418m, 3160m, 2926, 1613m, 1402m, 1386m, 1147m, 1110s, 1089s and 625m cm^{-1} (Found: C, 40.35; H, 4.20; N, 9.85. $C_{19}H_{24}Cl_2CuN_4O_8$ requires C, 40.00; H, 4.35; N, 9.80%).

X-Ray Crystallography.—The crystal used for X-ray diffraction studies was a blue needle of approximate dimensions 0.52 × 0.25 × 0.31 mm. Oscillation and Weissenberg photographs were employed to determine the space group *Pbcn*, as well as the preliminary lattice constants. Diffraction data were collected on a four-circle Enraf-Nonius CAD4 automatic diffractometer with Mo-Kα radiation (λ = 0.710 69 Å) fitted with a graphite monochromator. An ω–2θ scan mode was used, with $2.5 \leqslant \theta \leqslant 27°$, and the index ranges were $-1 \leqslant h \leqslant 11$, $0 \leqslant k \leqslant 18$, $0 \leqslant l \leqslant 22$. The cell dimensions were obtained by least-squares refinement of 25 accurately measured reflections ($8 \leqslant \theta \leqslant 16°$). The maximum time allowed per reflection was 90 s. The structure was solved by heavy-atom methods, using the SHELX 86 program,[12] and refined using SHELX 76.[13] All hydrogen atoms were placed at geometrically calculated positions, except for those bonded to the carbon bridge, which were found on the Fourier-difference map. The parameters relating to the solution of the structure of $[Cu(dpb)][ClO_4]_2$ are given in Table 1. The atomic coordinates are given in Table 2 and selected bond lengths and angles in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Molecular Mechanics Calculations.—These were carried out using the program SYBYL,[14] as described previously[15] for the analysis of steric problems in co-ordination chemistry. The calculations were carried out using the TAFF force field[14] present in SYBYL. The geometry around the Cu^{II} was modelled with an ideal Cu–N bond length of 2.00 Å and force constant of 200 kcal mol^{-1} Å^{-1}. The N–Cu–N angle bending force constants were set at 0.008 kcal mol^{-1} deg^{-1} with ideal angles of 90° for *cis* and 180° for *trans* nitrogens. The Cu–N–C angle bending constants were set at 0.008 kcal mol^{-1} deg^{-1}, with ideal Cu–N–C angles involving the sp^3-hybridised nitrogens of the bispidine groups of 109.5° and 120° for those involving the aromatic nitrogens of the pyridyl groups.

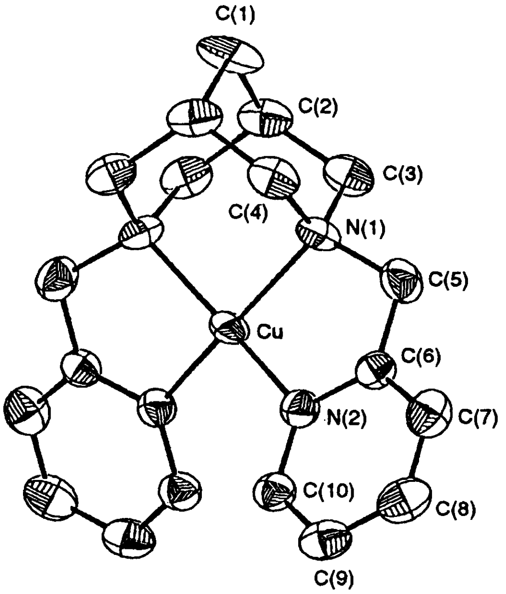

Fig. 1 Structure of the complex cation $[Cu(dpb)]^{2+}$, showing the atom numbering scheme

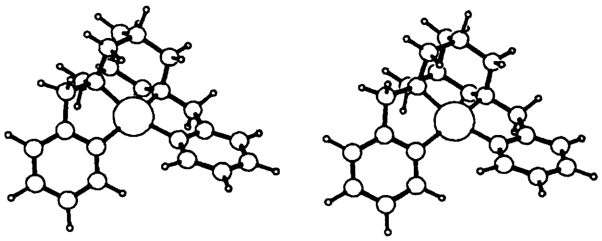

Fig. 2 Stereoview of the complex cation $[Cu(dpb)]^{2+}$

Table 1 Crystal data for $[Cu(dpb)][ClO_4]_2$

Chemical formula	$C_{19}H_{24}Cl_2CuN_4O_8$
M	570.88
T/°C	22
Space group	*Pbcn* (no. 60)
a/Å	8.904(2)
b/Å	14.366(1)
c/Å	17.402(2)
μ/cm^{-1}	12.04
Z	4
U/Å^3	2225.84
D_c/g cm^{-3}	1.70
D_m/g cm^{-3}	1.69
R'*	0.0506
R	0.0538

* $w = 2.2340/(\sigma_F^2)$.

Results and Discussion

The structure of the complex cation $[Cu(dpb)]^{2+}$ is shown in Fig. 1, and Fig. 2 shows a stereoview. The Cu–N bond lengths are normal for square-planar Cu^{II}, at 2.002 Å for the sp^3-hybridised nitrogens and 1.976 Å for the aromatic nitrogens. A striking feature of the structure, seen clearly in Fig. 2, is the distortion of the co-ordination geometry, with the *trans* N–Cu–N angles at 161.1° instead of the 180° expected for square-planar geometry. Inspection of the structure suggests that the cause of the distortion is steric interaction between the *o*-hydrogens of the pyridyl groups and the aromatic carbons of the opposing co-ordinated pyridyl group. Also of interest here is the rigid adamantane-like bispidine bridge, which it was anticipated would greatly sharpen the preference of dpb for small relative to large metal ions, as compared to the analogous ligand dptn.

Molecular Mechanics Calculations.—The MM calculations reproduced the structure of the copper(II) complex of dpb reasonably well, as seen in Table 4, where calculated and observed bond lengths and angles are shown. A useful type of calculation that can be carried out using MM is[10,15] to scan the energy of the complex as a function of the strain-free M–N bond length. In such calculations all the force-field parameters are kept constant except for the ideal M–N bond length, which is varied at suitable intervals, typically 0.1 Å, over a range, here 1.98–2.5 Å. The results of this calculation for the complexes of dpb and its open-chain analogue dptn are seen in Fig. 3. This shows that the strain energy of dpb complexes rises much more rapidly with increasing size than is true for the complexes of dptn, reflecting the rigid structure of the bispidine bridge. Bispidine, once it has a metal ion coordinated between its two nitrogen donors, resembles the very rigid hydrocarbon adamantane in structure, and would be of minimum strain energy with a metal ion the size of an sp^3-hybridised carbon held between the two nitrogens. The sharper selectivity for small metal ions of dpb as compared to its unreinforced analogue dptn is seen in the formation constants[8,9] of dpb complexes compared to those[16] of dptn (Table 5).

Table 2 Fractional atomic coordinates ($\times 10^4$) for $[Cu(dpb)][ClO_4]_2$

Atom	*X/a*	*Y/b*	*Z/c*
Cu	0	400(1)	2500(0)
N(1)	1123(5)	−589(2)	1928(2)
N(2)	645(4)	1245(3)	1667(2)
C(1)	0	−2399(5)	2500(0)
C(2)	−959(7)	−1766(3)	2003(3)
C(3)	23(7)	−1160(3)	1477(3)
C(4)	2013(6)	−1186(3)	2454(3)
C(5)	2200(6)	−102(4)	1411(3)
C(6)	1600(5)	840(3)	1173(3)
C(7)	2060(6)	1287(4)	506(3)
C(8)	1530(7)	1264(4)	353(3)
C(9)	523(6)	2575(3)	851(3)
C(10)	106(1)	2093(3)	1500(3)
Cl(1)	6627(1)	648(1)	1088(1)
O(1)	7203(1)	847(1)	1844(1)
O(2)	5879(1)	−240(1)	1095(1)
O(3)	7875(1)	624(1)	548(1)
O(4)	5579(1)	1362(1)	868(1)
O(5)	7279(1)	834(1)	1831(1)
O(6)	6227(1)	−315(1)	1042(1)
O(7)	5326(1)	1222(1)	992(1)
O(8)	7714(1)	865(1)	498(1)

Table 3 Selected bond lengths (Å) and angles (°) for $[Cu(dpb)][ClO_4]_2$

Cu–N(1)	2.002(4)	C(1)–C(2)	1.517(6)
Cu–N(2)	1.976(4)	C(2)–C(3)	1.536(7)
N(1)–C(3)	1.499(6)	C(5)–C(6)	1.513(6)
N(1)–C(4)	1.485(6)	C(6)–C(7)	1.388(6)
N(1)–C(5)	1.488(6)	C(7)–C(8)	1.372(7)
N(2)–C(6)	1.341(6)	C(8)–C(9)	1.379(8)
N(2)–C(10)	1.341(6)	C(9)–C(10)	1.376(7)
N(1)–Cu–N(2)	85.7(2)	N(1)–Cu–N(1′)	89.6(2)
N(2)–Cu–N(2′)	104.2(2)	N(1)–Cu–N(2′)	161.1(2)
Cu–N(1)–C(3)	108.8(3)	Cu–N(1)–C(4)	111.7(3)
Cu–N(1)–C(5)	106.8(3)	Cu–N(2)–C(6)	112.8(3)
Cu–N(2)–C(10)	127.8(3)	C(2)–C(1)–C(2′)	106.4(6)

The results presented here show how the rigid bispidine bridge is able to sharpen selectivity for smaller metal ions relative to the selectivity for small metal ions displayed by the less rigid dptn, and indicate how further ligands based on the bispidine bridge may in the future display useful metal-ion selectivities.

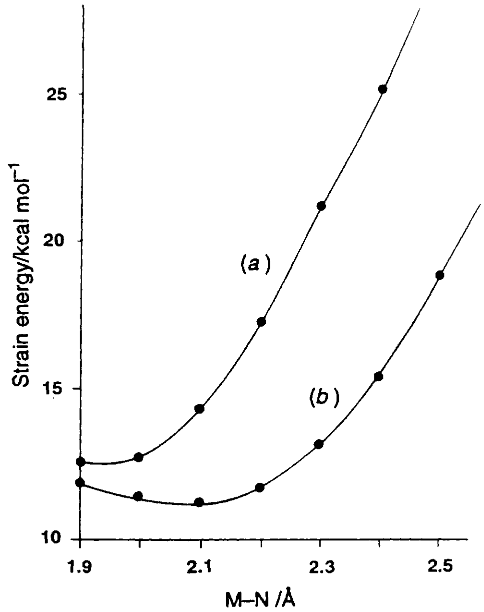

Fig. 3 Variation of strain energy (ΣU) of (*a*) the $[M(dpb)]^{n+}$ and (*b*) the $[Cu(dptn)]^{n+}$ complex cations, calculated as a function of the strain-free M–N bond length using the molecular mechanics program SYBYL[14] as described in the text. The diagram shows that ΣU rises much more rapidly for $[M(dpb)]^{n+}$ than for $[Cu(dptn)]^{n+}$ complexes as M–N increases, accounting for the much sharper selectivity[8] of dpb for small metal ions than is true for dptn complexes

Table 5 Comparison of the change in log K_1, produced by reinforcement of the chelate ring in dpb complexes as compared to the unreinforced dptn analogues, shown as a function of metal-ion radius

	M				
	Cu^{II}	Ni^{II}	Zn^{II}	Cd^{II}	Pb^{II}
Ionic radius[a]/Å	0.57	0.69	0.74	0.95	1.19
log K_1 (dpb)[b]	23.0	15.8	12.0	11.3	*c*
log K_1 (dptn)[d]	18.35	14.2	10.33	8.58	6.4
Δlog *K*[e]	4.6	1.6	1.7	2.7	—

[a] From ref. 17. [b] From ref. 8 and 9. [c] No evidence of complex. [d] From ref. 16. [e] Difference in log K_1 for dpb and dptn complexes, showing how selectivity for the small copper(II) ion is sharpened by the reinforced bispidine bridge of dpb.

Table 4 Structural parameters (bond lengths in Å, angles in °) for $[Cu(dbp)]^{2+}$, obtained by MM calculation as described, compared with the crystallographically determined values reported *

	Calc.	Obs.		Calc.	Obs.
Cu–N(1)	1.996	2.002	Cu–N(2)	1.981	1.976
N(1)–Cu–N(2′) (*trans*)	160.7	161.1	N(1)–Cu–N(2) (*cis*)	87.7	85.7
N(2)–Cu–N(2′)	96.7	104.2	N(1)–Cu–N(1′)	94.3	89.6
Cu–N(1)–C(3)	106.6	108.8	Cu–N(1)–C(5)	105.7	106.8
Cu–N(1)–C(4)	107.4	111.7	Cu–N(2)–C(6)	110.3	112.8
Cu–N(2)–C(10)	127.1	127.8	C(2)–C(1)–C(2′)	106.3	106.4

* The atom numbering scheme is in Fig. 1.

Acknowledgements

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