Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Copper(I) and copper(II) complexes of an ethylene cross-bridged cyclam

Timothy J. Hubin,[a] Nathaniel W. Alcock[b]* and Daryle H. Busch[a]

[a]Department of Chemistry, University of Kansas, Lawrence, KS 66045, USA, and [b]Department of Chemistry, University of Warwick, Coventry CV4 7AL, England
Correspondence e-mail: msrbb@csv.warwick.ac.uk

Received 27 August 1999
Accepted 1 October 1999

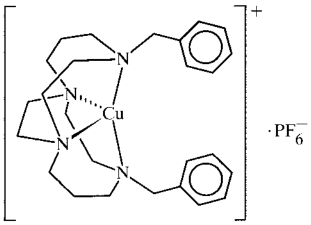
The preparation and crystal structures of (4,11-dibenzyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane-κ^4N)copper(I) hexafluorophosphate, $[Cu(C_{26}H_{38}N_4)]PF_6$, and acetonitrile(4,11-dibenzyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane-κ^4N)copper(II) bis(hexafluorophosphate), $[Cu(C_2H_3N)(C_{26}H_{38}N_4)](PF_6)_2$, are described. The Cu^I ion is tetracoordinated in a very distorted tetrahedron, while the Cu^{II} analogue is pentacoordinated in a square pyramid.

Comment

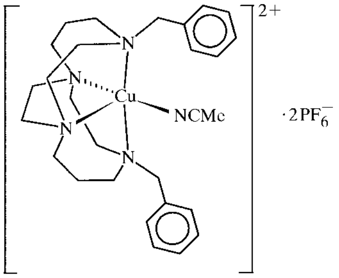
Ethylene cross-bridged tetraazamacrocycles have recently gained popularity as proton sponges (Weisman *et al.*, 1990; Bencini *et al.*, 1994; Miyahara *et al.*, 1999) but have been less well exploited as ligands for the coordination of transition metal ions (Weisman *et al.*, 1996; Hubin *et al.*, 1998). The short two-carbon cross-bridge imparts additional rigidity as well as topological constraints (Busch, 1993) to the parent macrocycle ligand. The resulting ligands are strongly basic, which causes coordination to transition metal ions to be difficult (Hubin *et al.*, 1998). However, these same attributes give the complexes valuable properties, such as remarkable kinetic stability in harsh aqueous conditions (Hubin *et al.*, 1998) and useful oxidizing ability (Busch *et al.*, 1998).

In further investigations of the properties of these interesting ligands, the copper(I) and copper(II) complexes of the benzyl disubstituted cross-bridged cyclam 4,11-dibenzyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane, *i.e.* (4,11-dibenzyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane-κ^4N)copper(I) hexafluorophosphate, (I), and [acetonitrile(4,11-dibenzyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane-κ^4N)]copper(II), (II), were prepared and then examined by X-ray crystallography, and their crystal structures are presented here.

In the Cu^I complex, (I) (Fig. 1), the Cu^+ ion was found to coordinate to all four tertiary N atoms of the bicyclic ligand, in what is best described as octahedral geometry with two vacant positions; the pendant benzyl groups appear to block the approach of ligands to these positions, with comparatively short Cu···C distances (Cu···C18, C19, C25 and C26 in the range 3.24–3.37 Å). The *trans* angle at Cu, N8—Cu1—N1, is 171.85 (5)°, with the other N—Cu—N bond angles in the range 85.17 (5)–97.96 (5)°. The N1—Cu1 and N8—Cu1 bond lengths [2.0204 (13) and 2.0105 (13) Å] are short compared with the other Cu—N bond lengths [N4—Cu1 2.1608 (13) and N11—Cu1 2.1715 (13) Å] and with the average four-coordinate copper(I) to tertiary-N bond length of 2.139 Å (Orpen *et al.*, 1989; Allen & Kennard, 1993). This short bond length indicates how difficult it is for the ligand cavity to accomodate Cu^+ in something approaching its preferred tetrahedral geometry.



(I)



(II)

Finally, it should be noted that (I) is the first structure of an ethylene cross-bridged cyclam in which the metal ion is completely enclosed within the ligand cavity (the Cu atom lies inside the N atoms subtending 172°), as opposed to the many other complexes (Hubin, 1999) with this size of cross-bridged ligand and small metal ions, such as Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+},

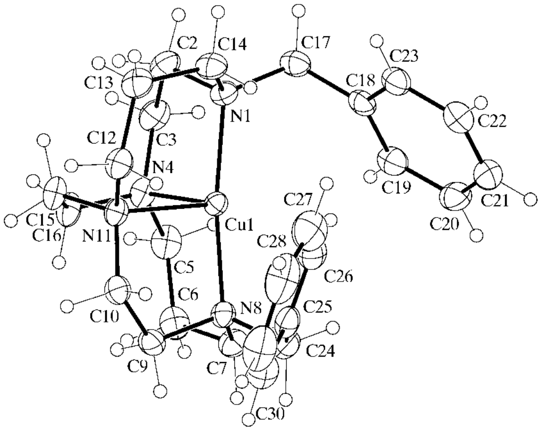


Figure 1
View of the cation of (I) showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

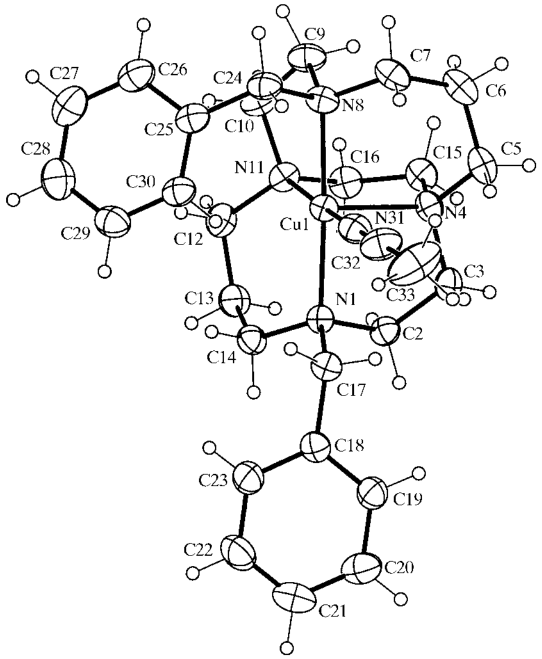


Figure 2

View of the cation of (II) showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

Zn^{2+}, Mn^{3+} and Fe^{3+}, in which the metal ion is situated outside the ligand cavity (axial $N-M-N$ bond angles < 180°, bent away from the ligand cavity). We believe the geometric preferences of the various metal ions underlie this difference.

The product of the air oxidation of (I) in acetonitrile is the green Cu^{2+} complex, (II), in which an acetonitrile molecule takes up a fifth position around the metal. This complex is similar to previous Cu^{2+} complexes of ethylene cross-bridged ligands, which tend to have square pyramidal coordination geometries, as does (II) (Fig. 2). The acetonitrile ligand and three of the macrobicyclic N atoms are the equatorial ligands, with one bridgehead N of the ligand acting as the axial ligand. The flexibility of the benzyl groups of this ligand is demonstrated in this structure, as one has been forced to rotate, folding away from the Cu^{II} ion, in order for the acetonitrile ligand to coordinate. In the Cu^{+} complex, (I), both benzyl groups are folded towards the metal ion, essentially occupying the empty fifth coordination site. Similarly, complex (II) has the metal ion completely engulfed, with an N1—Cu1—N8 bond angle of 177.34 (9)°.

Experimental

To prepare complex (I), $Cu(CH_3CN)\cdot PF_6$ (0.373 g, 0.001 mol) dissolved in pyridine (10 ml) was added to the ligand (0.406 g, 0.001 mol) dissolved in pyridine (10 ml) under a nitrogen atmosphere. The reaction mixture was stirred for 20 h, giving a clear pale-yellow solution. Filtration followed by solvent evaporation yielded pale green–yellow crystalline blocks of (I). To prepare complex (II), a solution of complex (I) in MeOH (15 ml) was stirred overnight while air was gently bubbled through it. The solution quickly turned dark green. Filtration followed by evaporation of the solvent yielded a dark-green crude product. Pure (II) was obtained on addition of excess NH_4PF_6 to an acetonitrile solution of the crude product. Ether diffusion into this solution yielded X-ray quality crystals.

Compound (I)

Crystal data

$[Cu(C_{26}H_{38}N_4)]PF_6$
$M_r = 615.11$
Monoclinic, $P2_1/n$
$a = 9.5684$ (2) Å
$b = 11.7898$ (2) Å
$c = 24.294$ (1) Å
$\beta = 90.684$ (1)°
$V = 2740.4$ (7) Å^3
$Z = 4$
$D_x = 1.491$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 5967 reflections
$\theta = 3$–20°
$\mu = 0.920$ mm^{-1}
$T = 180$ (2) K
Irregular block, pale green–yellow
0.6 × 0.5 × 0.4 mm

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.544$, $T_{max} = 0.692$
15 900 measured reflections
6434 independent reflections
5449 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 28.6$°
$h = -12 \rightarrow 11$
$k = -11 \rightarrow 15$
$l = -27 \rightarrow 32$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.078$
$S = 1.023$
6434 reflections
344 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.036P)^2 + 1.26P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.515$ e Å^{-3}
$\Delta\rho_{min} = -0.373$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0023 (2)

Compound (II)

Crystal data

$[Cu(C_2H_3N)(C_{26}H_{38}N_4)](PF_6)_2$
$M_r = 801.14$
Triclinic, $P\overline{1}$
$a = 9.9695$ (4) Å
$b = 10.5610$ (5) Å
$c = 17.7607$ (8) Å
$\alpha = 101.236$ (1)°
$\beta = 101.105$ (1)°
$\gamma = 109.157$ (1)°
$V = 1664.83$ (13) Å^3
$Z = 2$
$D_x = 1.598$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7334 reflections
$\theta = 3$–20°
$\mu = 0.849$ mm^{-1}
$T = 180$ (2) K
Block, dark green
0.4 × 0.2 × 0.2 mm

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.774$, $T_{max} = 0.881$
10 176 measured reflections
7384 independent reflections
6457 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 28.53$°
$h = -12 \rightarrow 13$
$k = -14 \rightarrow 13$
$l = -20 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.146$
$S = 1.051$
7384 reflections
434 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2 + 3.3905P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max} = 1.087$ e Å^{-3}
$\Delta\rho_{min} = -0.882$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1—N8	2.0105 (13)	Cu1—N4	2.1608 (13)
Cu1—N1	2.0204 (13)	Cu1—N11	2.1715 (13)
N8—Cu1—N1	171.85 (5)	N8—Cu1—N11	89.04 (5)
N8—Cu1—N4	97.96 (5)	N1—Cu1—N11	96.92 (5)
N1—Cu1—N4	88.12 (5)	N4—Cu1—N11	85.17 (5)

Table 2
Selected geometric parameters (Å, °) for (II).

Cu1—N31	2.049 (3)	Cu1—N1	2.116 (2)
Cu1—N8	2.056 (3)	Cu1—N4	2.142 (3)
Cu1—N11	2.088 (2)		
N31—Cu1—N8	88.19 (10)	N11—Cu1—N1	93.35 (9)
N31—Cu1—N11	173.04 (10)	N31—Cu1—N4	97.76 (10)
N8—Cu1—N11	86.28 (10)	N8—Cu1—N4	95.25 (10)
N31—Cu1—N1	91.98 (10)	N11—Cu1—N4	86.96 (10)
N8—Cu1—N1	177.33 (10)	N1—Cu1—N4	87.37 (10)

For both compounds, data collection: *SMART* (Siemens, 1994); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990) for (I); *SHELXTL* (Sheldrick, 1997*b*) for (II). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*) for (I); *SHELXTL* for (II). For both compounds, molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We thank Procter & Gamble for their generous support of this research. TJH thanks the Madison A. and Lila Self Graduate Fellowship of the University of Kansas for financial support. EPSRC and Siemens plc generously supported the purchase of the SMART diffractometer. The Warwick–Kansas collaboration has been supported by NATO. We also wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury Laboratory (Fletcher *et al.*, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1270). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Bencini, A., Bianchi, A., Bazzicalupi, C., Ciampolini, M., Fusi, V., Micheloni, M., Nardi, N., Paoli, P. & Valtancoli, B. (1994). *Supramol. Chem.* **3**, 141–146.

Busch, D. H. (1993). *Chem. Rev.* **93**, 847–860.

Busch, D. H., Collinson, S. R. & Hubin, T. J. (1998). *Catalysts and Methods for Catalytic Oxidation*, Patent WO 98/39098, September 11, 1998.

Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.

Hubin, T. J. (1999). PhD thesis, University of Kansas, USA.

Hubin, T. J., McCormick, J. M., Collinson, S. R., Alcock, N. W. & Busch, D. H. (1998). *J. Chem. Soc. Chem. Commun.* pp. 1675–1676.

Miyahara, Y., Tanaka, Y., Amimoto, K., Akazawa, T., Sakuragi, T., Kobayashi, H., Kubota, K., Suenaga, M., Koyama, H. & Inazu, T. (1999). *Angew. Chem. Int. Ed. Engl.* **38**, 956–959.

Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1—83.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*a*). *SHELXL*97. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXTL. Structure Determination Programs*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1994). *SMART. Software Reference Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1995). *SAINT. Software Reference Manual.* Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Weisman, G. R., Rogers, M. E., Wong, E. H., Jasinski, J. P. & Paight, E. S. (1990). *J. Am. Chem. Soc.* **112**, 8604–8605.

Weisman, G. R., Wong, E. H., Hill, D. C., Rogers, M. E., Reed, D. P. & Calabrese, J. C. (1996). *J. Chem. Soc. Chem. Commun.* pp. 947–948.