

Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *NRCVAX*.

The authors thank Mr Shyh-Ming Chen for helping to plot the figure. They are also indebted to the National Tsing Hua University for financial support in the form of a postdoctoral fellowship for Bor-Hann Chen, who assisted this work and thanks the National Science Council for support under grants NSC86-2112-M007-028 and NSC86-2113-M007-017.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1071). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 1602–1604

A Copper(II) Complex of a Structurally Reinforced Chiral 14-Membered Aza-Macrocycle

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(Received 1 December 1997; accepted 11 February 1998)

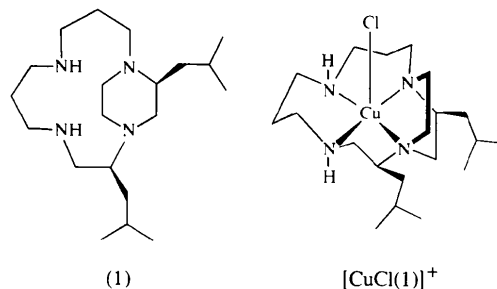
Abstract

The structure of a copper(II) complex cation of a reinforced chiral 14-membered aza-macrocycle, namely, chloro[(2*S*,13*S*)-2,13-diisobutyl-1,4,8,12-tetraazabicyclo[10.2.2]tetradecane-κ⁴N]copper(II), which crystallizes as a perchlorate hydrate, [CuCl(C₂₀H₄₂N₄)]ClO₄·H₂O, has been determined. The copper(II) cation lies in the macrocyclic cavity coordinated in a square-pyramidal

manner by the four N atoms of the aza-macrocycle, with the chloride anion in an apical position.

Comment

The syntheses of structurally reinforced macrocyclic polyamines and their metal complexes have been studied recently in areas such as molecular recognition and bio-inorganic chemistry (Mitewa & Bontchev, 1994). Although numerous structurally reinforced macrocyclic polyamines have been analyzed in many studies, carbon-backbone functionalized versions are less common (Aston *et al.*, 1994). Recently, we synthesized novel chiral and structurally reinforced 15-, 18- and 20-membered-ring polyamines, and their copper(II) complexes (Seki *et al.*, 1996; Yoshiki *et al.*, 1996). This paper describes the crystal structure of a copper(II) complex of a new chiral and structurally reinforced 14-membered polyamine, (2*S*,13*S*)-2,13-diisobutyl-1,4,8,12-tetraazabicyclo[10.2.2]tetradecane, (1).



A view of the complex is shown in Fig. 1. The copper complex cation is five-coordinate, bound to four N atoms of the macrocycle and to a chloride anion. The coordination geometry around the copper cation is best described as square pyramidal with the apical position being occupied by the chloride anion. The four N atoms of the macrocyclic ligand are approximately planar (within 0.0979 Å), with the copper(II) cation located in the direction of the chloride ligand, 0.310 Å from the N₄ plane. Both six-membered chelate rings in the complex (Cu1, N9, C10, C11, C12, N13 and Cu1, N13, C14, C15, C16, N3) have pseudo-chair forms. The absolute configurations of the N9 and N13 atoms are *R* and *S*, respectively, while the piperazine ring (C1, C2, N3, C4, C5, N6) is in a boat form. The Cu—N bond lengths are in the range 1.998 (7)–2.05 (1) Å, comparable to the strain-free *M*—N length (2.03 Å) for [Cu(1,4,8,11-tetraazacyclotetradecane)] (Hancock, 1989), and the average *M*—N lengths of 2.03 (2), 2.030 (7) and 2.033 (8) Å for [Cu₂(1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane)HCl₂]³⁺ or [Cu₂([30]-aneN₁₀)HCl₂]³⁺ (Bencini *et al.*, 1987), [Cu{(2*R*,5*R*,8*R*,11*R*)-1,4,7,10-tetraphenyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane}Cl]⁺ or [Cu(tecyclen)Cl]⁺ (Sakurai *et al.*, 1982), and [Cu(1,3,6,9,11,14-hexaazatricyclo-

[12.2.1.1^{6,9}octadecane)Cl]⁺ or [Cu(L)Cl]⁺ (Kim *et al.*, 1991), respectively. Also, the Cu—Cl bond length [2.478 (3) Å] is similar to the lengths of 2.43 (1), 2.42 (2) and 2.483 (4) Å in [Cu₂([30]-aneN₁₀)HCl₂]³⁺, [Cu(tecyclen)Cl]⁺ and [Cu(L)Cl]⁺, respectively.

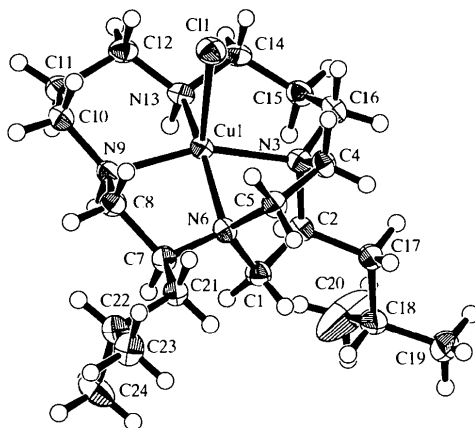


Fig. 1. ORTEP drawing (Johnson, 1976) of the [CuCl(C₂₀H₄₂N₄)]⁺ cation with the atom-numbering scheme. Ellipsoids for non-H atoms correspond to 50% probability.

Experimental

The cyclic ligand (1) was prepared by LiAlH₄ reduction in boiling THF for 48 h under an argon atmosphere of the cyclic pseudo-peptide *cyclo*(eLL-β-Ala-β-Ala), obtained by a method similar to that described in the literature [cyclic pseudo-peptide yield: 72% from Boc-eLL-β-Ala-β-Ala-OH; reduction yield: 52%; eLL is (2*S*,3'*S*)-2-(3'-isobutyl)-2'-oxo-piperazin-1'-yl)-4-methylpentanoic acid (Yoshiki *et al.*, 1996) and was purified by both basic silica-gel and activated alumina column chromatography (m.p. 445–452 K). Analysis: calculated for C₂₀H₄₂N₄·3.4HCl·3.25H₂O: C 46.1, H 10.0, N 10.8, Cl 23.1%; found: C 46.3, H 10.2, N 10.6, Cl 23.1%; [(C₂₀H₄₂N₄) + 1]⁺ = 339; [α]_D = +61° dm⁻¹ g⁻¹ cm³ (in CH₃OH). [CuCl(C₂₀H₄₂N₄)]Cl was prepared by the reaction of (1) and CuCl₂·2H₂O in methanol for 15 h at room temperature, and recrystallized from ethyl acetate (yield 75%, m.p. 401–407 K). Analysis: calculated for [CuCl(C₂₀H₄₂N₄)]·Cl·6.25H₂O: C 41.0, H 9.4, N 9.6%; found: C 41.3, H 9.1, N 9.3%; [CuCl(C₂₀H₄₂N₄)]⁺ = 436, [Cu(C₂₀H₄₂N₄)]⁺ = 401; [α]_D = -80° dm⁻¹ g⁻¹ cm³ (in CH₃OH). [CuCl(C₂₀H₄₂N₄)]·ClO₄ was prepared by the reaction of [CuCl(C₂₀H₄₂N₄)]Cl and AgClO₄ in methanol for 15 h at room temperature and violet crystals were obtained from hot water (yield 67%, m.p. 425–429 K). Analysis: calculated for [CuCl(C₂₀H₄₂N₄)]ClO₄·H₂O: C 43.3, H 8.0, N 10.1%; found: C 43.3, H 8.0, N 10.0%; [Cu(ClO₄)(C₂₀H₄₂N₄)]⁺ = 500, [CuCl(C₂₀H₄₂N₄)]⁺ = 436, [Cu(C₂₀H₄₂N₄)]⁺ = 401; [α]_D = +75° dm⁻¹ g⁻¹ cm³ (in CH₃OH).

Crystal data

[CuCl(C₂₀H₄₂N₄)]ClO₄·H₂O Mo Kα radiation
M_r = 555.04 λ = 0.7107 Å

Monoclinic
P2₁
a = 8.650 (4) Å
b = 14.309 (6) Å
c = 11.042 (3) Å
β = 105.83 (3)°
V = 1314.9 (8) Å³
Z = 2
D_x = 1.402 Mg m⁻³
D_m not measured

Data collection

Rigaku AFC-7R diffractometer
ω-2θ scans
Absorption correction:
ψ scans (North *et al.*, 1968)
T_{min} = 0.730, T_{max} = 0.852
4208 measured reflections
3979 independent reflections

Cell parameters from 25 reflections
θ = 14.8–15.0°
μ = 1.070 mm⁻¹
T = 150.0 K
Prism
0.30 × 0.20 × 0.15 mm
Violet

3170 reflections with I > σ(I)
R_{int} = 0.059
θ_{max} = 30°
h = -12 → 0
k = 0 → 20
l = -14 → 15
3 standard reflections
every 150 reflections
intensity decay: 2.51%

Refinement

Refinement on F
R = 0.046
wR = 0.053
S = 1.367
3414 reflections
290 parameters
H atoms not refined
w = 1/[σ²(F_o) + 0.00063|F_o|²]

(Δ/σ)_{max} = 0.011
Δρ_{max} = 0.56 e Å⁻³
Δρ_{min} = -0.52 e Å⁻³
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu1—Cl1	2.478 (3)	Cu1—N9	1.998 (7)
Cu1—N3	2.04 (1)	Cu1—N13	2.006 (10)
Cu1—N6	2.05 (1)		
Cl1—Cu1—N3	95.9 (2)	N3—Cu1—N9	156.6 (5)
Cl1—Cu1—N6	107.6 (2)	N3—Cu1—N13	100.8 (3)
Cl1—Cu1—N9	98.1 (3)	N6—Cu1—N9	84.2 (3)
Cl1—Cu1—N13	95.4 (3)	N6—Cu1—N13	156.7 (2)
N3—Cu1—N6	73.7 (4)	N9—Cu1—N13	96.4 (4)

H atoms were introduced in the structure-factor calculations as fixed contributors, except for those of the water molecule. The absolute configuration of the molecule is derived from that of the ligand.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku Corporation, 1988). Cell refinement: *Rigaku/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR88* (Burla *et al.*, 1989) and *DIRDIF94* (Beurskens *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

We are grateful to Ms Rika Tanaka for elemental analysis and mass spectral measurements.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1052). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 1604–1605

Bis(methyl 3-pyridyl- κ N¹-carbamate)bis(propionato- κ O)copper(II)–Water (4/1)

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(Received 5 August 1997; accepted 1 May 1998)

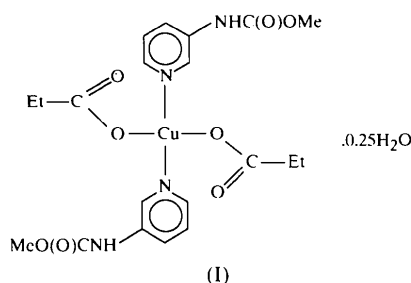
Abstract

The Cu^{II} centre in the title compound, [Cu(C₃H₅O₂)₂·(C₇H₈N₂O₂)₂].0.25H₂O, is situated on an inversion centre and has tetragonally distorted coordination. It is bonded in a *trans*-square-planar arrangement to the pyridyl N atoms of two methyl 3-pyridylcarbamate molecules [Cu—N1 2.025 (2) Å] and one carboxylate O atom from each of two propionate anions [Cu—O1 1.955 (2) Å]. The axial positions are occupied by

the other propionate O atoms [Cu···O2 2.653 (2) Å]. The propionate groups exhibit very small O1—Cu···O2 chelate angles of 54.23 (8)°.

Comment

While dimeric Cu₂(propionate)₄(substituted pyridine)₂ species have been reported previously (Borel & Leclaire, 1976*a,b*, 1978; Borel *et al.*, 1976, 1981; Smolander *et al.*, 1992; Melník *et al.*, 1998), the monomeric analogues have not. We report here such a monomer, namely, bis(methyl 3-pyridylcarbamate)bis(propionato)copper(II) 0.25-hydrate, (I).



The structure (Fig. 1) consists of discrete complex cations and H₂O molecules linked by hydrogen bonds [O4ⁱ···H8 2.520 Å and O2ⁱⁱ···H2 1.975 Å; symmetry codes: (i) $y, \frac{1}{2}-x, \frac{1}{2}-z$; (ii) $x, y, 1+z$] and van der Waals forces. The stereochemistry around the Cu^{II} centre may be described as axially elongated octahedral. Molecules of the cation lie on a crystallographic inversion centre, with the Cu^{II} atom coordinated by the pyridyl N atoms of two different methyl 3-pyridylcarbamate molecules and by an O atom from each of the two propionate anions to give a square-planar arrangement, with Cu—N1 and Cu—O1 bond lengths of 2.025 (2) and 1.955 (2) Å, respectively. The remaining carboxylate O atoms in each propionate anion participates in much longer axial bonding [Cu—O2

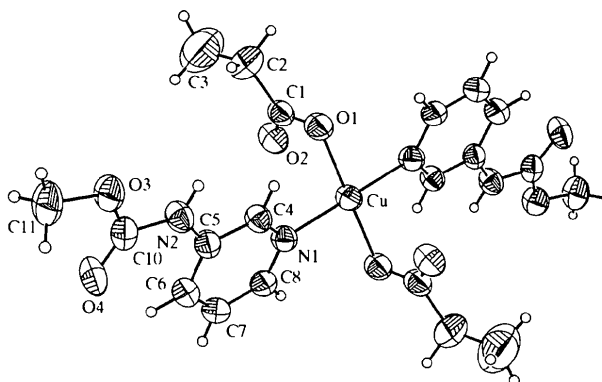


Fig. 1. A view of the title compound, without the hydrate molecule, showing displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.