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[*N*-(3-Aminopropyl)-*N*-methyl-1,3-propanediamine- κ^3N]dichlorocopper(II)

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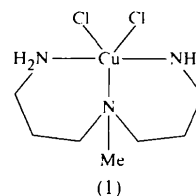
Abstract

The preparation and crystal structure of the title complex, [CuCl₂(C₇H₁₉N₃)], are described. The Cu^{II} ion has distorted tetragonal pyramidal geometry, with Cl axial;

the axial Cu—Cl distance [2.505(1) Å] is elongated compared with the basal Cu—Cl distance [2.400(1) Å]. In the basal plane, Cu—N(tertiary) [2.138(3) Å] is considerably longer than Cu—N(primary) [1.985(4) Å mean], presumably reflecting the reduced basicity of the ligand atom.

Comment

The title compound, (1), was synthesized during our mechanistic studies of metal template reactions involving 2,6-diacetylpyridine and 3'-diamino-*N*-methylpropylamine. The experimental conditions normally used for the synthesis of metal complexes of 2,7,12-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17),2,11,13,15-pentaene, (2), and analogous macrocyclic ligands suggest that such reactions are true template reactions involving substrates that are both coordinated to the metal ion concerned. This is supported by the failure of such reactions when the metal ion is present as its hydroxide, *i.e.* it is not coordinated by the triamine (Prince *et al.*, 1974). The title compound, (1), was isolated at an early stage in the preparation of the copper complex of (2). This further indicates that complexation of the metal by the triamine is required prior to forming the Schiff base linkages that complete the macrocycle.



Typical template syntheses of complexes of the tetradentate macrocycle (2) involve refluxing a metal salt with stoichiometric equivalents of the dicarbonyl and triamine for several hours in mixtures of ethanol and water (Karn & Busch, 1966; Caira *et al.*, 1975; Nelson *et al.*, 1981). The title compound was formed as the initial product of this reaction and the structure was determined to confirm its identity. Most of the structures already examined that share the CuN₃Cl₂ ligand set (from the Cambridge Structural Database; Allen & Kennard, 1993) are simple tris(monodentate ligand) complexes; all except one have trigonal bipyramidal geometry, with the bulkier Cl groups occupying the equatorial positions as expected [*e.g.* dichlorotrakis(1,2-dimethylimidazole)copper; Huq & Skapski, 1971]. One example only, dichlorotrakis(4-methylthiazole)copper (Cu₄MT) (Marsh *et al.*, 1988), has tetragonal pyramidal geometry, a difference attributed to the bulk of the thiazole ligand.

This geometry is also shown by the title compound (Fig. 1); it is probably preferred because the rigidity

of the backbone does not allow an N—Cu—N angle close to 180°, as needed for a trigonal bipyramid. In the title compound, this angle is 163.6(1)°, with the other *trans* angle in the basal plane [N(5)—Cu—Cl(1)] being 158.23(8)°. The Cu atom is 0.34(1) Å above the mean plane of the basal atoms [which deviate by ±0.08(1) Å from this plane]. The Cu—N distances to the terminal atoms in the ligand [mean 1.985(4) Å] are shorter than in most similar compounds [mean of 2.064 Å in Cu₄MT and mean of 2.036 Å for 12 four- to six-coordinate copper(II) compounds; Orpen *et al.*, 1989]. In contrast, the distance to the central tertiary N atom is considerably longer [2.138(3) Å], again unlike similar compounds in which bonds to tertiary amines differ by only 0.05 Å from those to primary and secondary amines. In general, this lengthening presumably reflects the reduced basicity of the tertiary nitrogen, but the additional lengthening in the title compound may reflect steric effects. In parallel to Cu₄MT, the axial Cu—Cl distance is considerably longer than the basal distance [2.505(1) and 2.400(1) Å, respectively]; this contrasts with the trigonal bipyramidal CuN₃Cl₂ complexes in which the two Cu—Cl distances are essentially identical.

The packing of the title compound shows no unusual close contacts.

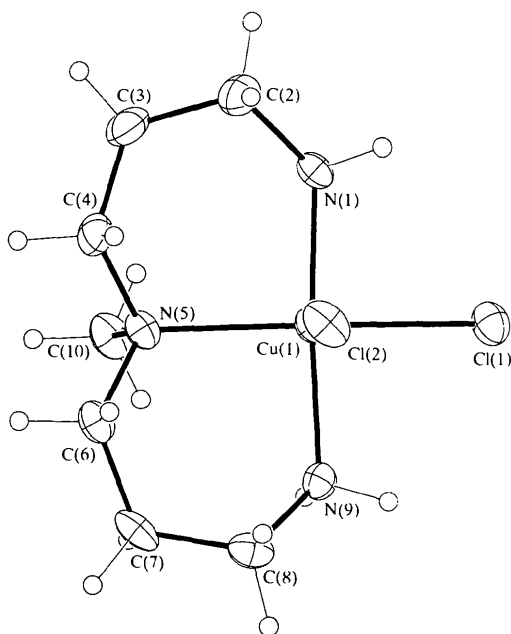


Fig. 1. View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compound, (1), was obtained from the reaction of equimolar amounts of CuCl₂, 2,6-diacetylpyridine and 3'-di-

amino-*N*-methylpropylamine at room temperature in ethanol and water (1:1). After 1 h, a portion of the reaction mixture was removed and concentrated *in vacuo*. The resulting blue-green solid was then recrystallized from methanol by slow evaporation. Both blue and green crystals were isolated but only the green crystals of (1) were suitable for X-ray study.

Crystal data

[CuCl₂(C₇H₁₉N₃)]

M_r = 279.69

Triclinic

P $\bar{1}$

a = 6.6583(5) Å

b = 9.4161(7) Å

c = 9.5481(7) Å

α = 96.087(2)°

β = 103.348(2)°

γ = 90.026(1)°

V = 578.97(7) Å³

Z = 2

D_x = 1.604 Mg m⁻³

D_m not measured

Mo K α radiation

λ = 0.71073 Å

Cell parameters from 2515 reflections

θ = 3–20°

μ = 2.310 mm⁻¹

T = 190(2) K

Block

0.3 × 0.2 × 0.1 mm

Blue–green

Data collection

Siemens SMART diffractometer

ω scans

Absorption correction:

multi-scan (SADABS;

Sheldrick, 1996a)

T_{min} = 0.39, *T_{max}* = 0.79

3532 measured reflections

2555 independent reflections

1750 reflections with

I > 2 σ (*I*)

R_{int} = 0.039

θ_{max} = 28.35°

h = –8 → 8

k = –11 → 12

l = –7 → 12

Intensity decay: none

Refinement

Refinement on *F*²

R[*F*² > 2 σ (*F*²)] = 0.045

wR(*F*²) = 0.097

S = 0.888

2555 reflections

118 parameters

H atoms treated by a mixture of independent and constrained refinement

w = 1/[$\sigma^2(F_o^2) + (0.0291P)^2$]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.006

$\Delta\rho_{max}$ = 0.749 e Å⁻³

$\Delta\rho_{min}$ = –0.914 e Å⁻³

Extinction correction: none

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu(1)—N(1)	1.980(4)	Cu(1)—Cl(1)	2.4004(11)
Cu(1)—N(9)	1.991(4)	Cu(1)—Cl(2)	2.5047(10)
Cu(1)—N(5)	2.138(3)		
N(1)—Cu(1)—N(9)	163.63(12)	N(5)—Cu(1)—Cl(1)	158.23(8)
N(1)—Cu(1)—N(5)	92.82(13)	N(1)—Cu(1)—Cl(2)	99.32(9)
N(9)—Cu(1)—N(5)	90.84(13)	N(9)—Cu(1)—Cl(2)	96.14(9)
N(1)—Cu(1)—Cl(1)	84.71(10)	N(5)—Cu(1)—Cl(2)	96.12(8)
N(9)—Cu(1)—Cl(1)	85.98(10)	Cl(1)—Cu(1)—Cl(2)	105.63(4)

The temperature of the crystal was controlled using the Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). The data collection nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures, with different φ angles for the crystal; each 10 s exposure covered 0.3° in ω . The crystal-to-detector distance was 5.0 cm.

Coverage of the unique set is over 97% complete to at least 26° in θ . Crystal decay was found to be negligible by repeating the initial frames at the end of data collection and analyzing the duplicate reflections. H atoms were added at calculated positions and refined using a riding model. Anisotropic temperature factors were used for all non-H atoms; H atoms were given isotropic temperature factors equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached.

Data collection: *SMART* (Siemens, 1994). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS96* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996b). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXTL/PC*.

We 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). EPSRC and Siemens plc generously supported the purchase of the SMART diffractometer. The Warwick–Kansas collaboration has been supported by NATO. AKM would like to thank the Department of Energy for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1028). Services for accessing these data are described at the back of the journal.

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3-Ferrocenyl-6-nitro-2-phenylquinoxaline: Cyclic Centrosymmetric Dimers Depending on both C—H···O Hydrogen Bonds and π – π Stacking Interactions†

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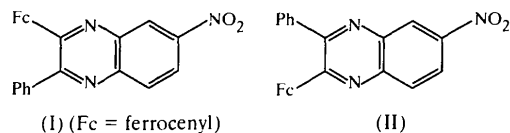
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Abstract

Molecules of 3-ferrocenyl-6-nitro-2-phenylquinoxaline, [Fe(C₅H₅)(C₁₉H₁₂N₃O₂)], are linked by C—H···O hydrogen bonds into centrosymmetric *R*₂²(22) dimers, reinforced by π – π stacking interactions. Two independent molecules form two such independent dimers which pack together in a pseudo-CsCl structure.

Comment

The reaction of 1-ferrocenyl-2-phenylethanedione with substituted 1,2-diaminobenzenes yields the corresponding substituted ferrocenyl(phenyl)quinoxalines as pairs of regioisomers, which are usually inseparable by chromatography (Zanello *et al.*, 1998). Thus, with 1,2-diamino-4-nitrobenzene, a mixture of two quinoxalines is formed with an isomer ratio of *ca* 3:1; the identity of the more abundant isomer could not be deduced from the NMR data. However, careful chromatography of this mixture afforded a crystalline material which appeared from NMR and TLC observations to consist of a single isomer, and the structure of this material is reported here. It proved, in fact, to be a 5:1 mixture of the two regioisomers, with 3-ferrocenyl-6-nitro-2-phenylquinoxaline, (I), as the major component and 2-ferrocenyl-6-nitro-3-phenylquinoxaline, (II), as the minor component.



The mixture crystallized in space group *P* $\bar{1}$ with two molecules in the asymmetric unit; because of

† Alternative name: (η^5 -cyclopentadienyl)[1-(6-nitro-2-phenylquinoxalin-3-yl)- η^5 -cyclopentadienyl]iron.