Research Article

The Preparation and Structure of [(2,4-Dimethyl-8-ethyl-5,8-diazadec-4-ene-2-amine)chlorocopper(II)] Perchlorate

Neil F. Curtis¹ and Jan Wikaira²

¹ School of Chemical and Physical Sciences, Victoria University of Wellington, P.O. Box 600, Wellington 6140, New Zealand

² Department of Chemistry, University of Canterbury, P.O. Box 4800, Christchurch 8140, New Zealand

Correspondence should be addressed to Neil F. Curtis; neil.curtis@vuw.ac.nz

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Copper(II) chloride and perchlorate, *N,N*-diethylethane-1,2-diamine, react in (m)ethanol with acetone and ammonia to form [(2,4-dimethyl-8-ethyl-5,8-diazadec-4-ene-2-amine)chlorocopper(II)] perchlorate, $C_{12}H_{27}Cl_2CuN_3O_4$, $M_r = 411.81$, monoclinic, $C2/c$, (Hall- $C2/c$); a , 26.418(1), b , 9.7385(4); c , 14.0993(5) Å; β , 91.134(3)°. This has copper(II) in tetrahedrally distorted square-planar coordination by one primary, one tertiary, and one imine nitrogen atom and the chloride ion.

1. Introduction

Amine compounds of copper(II) and nickel(II) have been reported to react with 4-amino-4-methylpentan-2-one (diacetoneamine, amp) to form compounds with ligands which have primary amine groups condensed with amp, forming additional β -imino-amine chelate rings [1–3]. Compounds formed with ethane-1,2-diamine, propane-1,2-diamine, 1,5-diamino-3-azapentane (diethylenetriamine), 1,8-diamino-3,6-diazaoctane (triethylenetetramine), 1,7-diamino-4-azapentane (dipropylenetriamine), *N*-6-amino-4,6-dimethyl-3-azapent-3-enyl-piperazine, 2-aminoethyl-2-pyridine, and 2-amino-ethanol have been reported [1–3]. Structures of compounds formed with propane-1,2-diamine and 1,8-diamino-3,6-diazaoctane have been reported [4]. Related compounds have been prepared by reaction of copper metal, Reinecke's salt, $NH_4[Cr(NCS)_4(NH_3)_2] \cdot H_2O$, and acetone in DMF with tris(2-aminoethyl)amine [5] or *N,N*-dimethylethylene-1,2-diamine [6]. Copper(II) and nickel(II) ammine complexes react with acetone to form compounds of the simplest ligand of this type, 2-methyl-4-imine-pentan-2-amine, and

compounds of this ligand with a variety of metal ions have been described.

We now report the facile formation of [(2,4-dimethyl-8-ethyl-5,8-diazadec-4-ene-2-amine)chlorocopper(II)] perchlorate, $[Cu(deenim)Cl]ClO_4$, by reaction of (*N,N*-diethylethane-1,2-diamine), equimolar amounts of copper(II) chloride and perchlorate with acetone (or mesityl oxide) plus ammonia; see Figure 1. The compound is relatively resistant to hydrolysis and can be recrystallised from hot water. Compounds of other amines, such as those mentioned previously, which were prepared by using amp, can generally be more simply prepared by reacting the metal-amine compound in (m)ethanol with acetone and ammonia; the isolation of products for these labile systems is largely determined by the formation of polychelate ligands with additional aminoimine chelate rings, which better satisfy the optimal coordination number of the cation and the presence of appropriate counter ions which generate a low solubility product.

The structure of $[Cu(deenim)Cl]ClO_4$ was determined by X-ray diffractometry; see the Experimental Section for details. The copper(II) ion is in tetrahedrally distorted

FIGURE 1: The formation of $[\text{Cu}(\text{deenim})\text{Cl}]\text{ClO}_4$. FIGURE 2: The asymmetrical unit of $[(2,4\text{-dimethyl-8-ethyl-5,8-diazadec-4-ene-2-amine})\text{chlorocopper(II)}]\text{ perchlorate}$, drawn [7] with displacement ellipsoids at 50% probability and with hydrogen atoms shown as circles of arbitrary radius.

square-planar coordination by primary amine N2, tertiary amine N8, and imine N5 nitrogen atoms of the tridentate ligand and chloride ion Cl1; see Figure 2. Displacements ($\text{\AA}$) of atoms from the best Cu1/N2/N5/N8/Cl1 plane are N2, -0.184 (1); N5, 0.199 (1); N8, -0.182 (1); Cl1, 0.167 (1); Cu1, -0.012 (1). See Table 1 for selected bond lengths and angles, which are normal for compounds of this type.

The six-membered chelate ring $\text{N2}\cdots\text{Cu1}\cdots\text{N5}$ has an asymmetrical conformation, similar to that observed for related compounds [4], with the conformation constrained by the near planarity of the imine function. Methyl substituents C21 and C41 are equatorially oriented and Cl axially oriented. The displacements ($\text{\AA}$) of atoms from the $\text{Cu1}\cdots\text{N2}\cdots\text{N5}$ chelate plane are Cl, 2.108 (4); C21,

-0.508 (5); C3, 0.084 (4); C4, 0.163 (4); C41, 0.462 (5); and the displacements ($\text{\AA}$) from the best plane of the imine function $\text{C3/Cu1/N5/C4/C6/C41}$ are C3, -0.062 (2); Cu1, 0.110 (1); N5, -0.096 (2); C4, -0.023 (2); C6, -0.052 (2); C41, 0.123 (2).

The five-membered chelate ring $\text{N2}\cdots\text{Cu1}\cdots\text{N5}$ has an asymmetrical gauche conformation with displacements ($\text{\AA}$) of atoms from the plane Cu1/N2/N5 of C6, 0.327 (4); C7, -0.321 (4); C9, -1.013 (4); C10, -2.347 (3); C81, 1.383 (3); C82, 1.630 (5).

The perchlorate ion is weakly coordinated axially by oxygen atom O1 and hydrogen bonded by the primary amine group, $\text{N2-H2A}\cdots\text{O2}$. Weak mutual interactions $\text{N2-H2B}\cdots\text{Cl1}$ ($-x + 1/2, -y + 1/2, -z + 1$) link adjacent molecules into dimers; see Table 2.

TABLE 1: Selected bond lengths (Å) and angles (°) for [Cu(deenim)Cl]ClO₄.

Atoms	Distance	Atoms	Angle
Cu1–Cl1	2.2631 (6)	N2–Cu1–Cl1	89.17 (6)
Cu1–N2	1.968 (2)	N2–Cu1–N5	92.79 (8)
Cu1–N5	1.986 (2)	N2–Cu1–N8	169.91 (8)
Cu1–N8	2.036 (2)	N5–Cu1–Cl1	169.34 (6)
Cu1–O1	2.890 (2)	N5–Cu1–N8	85.93 (8)
C4–N5	1.280 (3)	N8–Cu1–Cl1	93.93 (6)
		N2–Cu1–Cl1	89.17 (6)

TABLE 2: Weak mutual interactions (Å,°) for [Cu(deenim)Cl]ClO₄.

N–H...A	N–H	N...A	H...A	N–H...A
N2–H2A...O2	0.92	2.36	3.171 (3)	146.2
N2–H2B...Cl1 ^A	0.92	2.69	3.538 (2)	153.2

Symmetry operation ^A = $-x + (1/2), -y + (1/2), -z + 1$.

Reaction of copper metal, Reinecke's salt, NH₄[Cr(NCS)₄(NH₃)₂]·H₂O, *N,N*-dimethylethylene-1,2-diamine, and acetone in DMF produces [Cu(dmenim)(NCS)]·[*trans*-Cr(NCS)₄(NH₃)₂], where dmenim is a homologue [6]. The tridentate ligand dmenim is coordinated similarly to deenim, with N-bonded thiocyanate completing distorted square-planar coordination about the copper(II). The sulphur of a thiocyanato group N-coordinated to the chromium of the anion interacts weakly in the axial coordination site with Cu...S = 2.694 (4) Å. The one other structure in the CCDC database with a [Cu(L)X]⁺ cation, where L is a simple tridentate tri-aza ligand and X[−] a halide ion, is [Cu(dien)Br]Br (dien = 3-aza pentane-1,5-diamine) [8].

2. Experimental

[(2,4-Dimethyl-8-ethyl-5,8-diazadec-4-ene-2-amine)chlorocopper(II)] Perchlorate, [Cu(deenim)Cl]ClO₄. *N,N*-diethylethane-1,2-diamine (1.16 g), acetone or 4-methyl-pent-3-ene-2-one (mesityl oxide, 1.0 g), and ammonia (concd. aqueous, 0.5 cm³) were mixed in methanol (20 cm³). A solution of copper(II) perchlorate hexahydrate (1.7 g) and copper(II) chloride dihydrate (1.2 g) dissolved in ethanol (20 cm³) was added and the solution warmed, when the blue product crystallised. This was filtered off from the cold solution and recrystallised from hot water. The same product was formed when 4-amino-4-methylpentan-2-one (diacetoneamine, 1.2 g) was substituted for the mesityl oxide or acetone and ammonia. *Anal.* Calc for C₁₂H₂₇N₃Cl₂CuO₄; C, 35.0; H, 6.6; N, 10.2. Found: C35.3; H, 6.8; N, 10.2%. IR: ν(NH), 3303, 3219, 3146; ν(N=C), 1595 cm^{−1}.

3. Structure Determination

(2,4-Dimethyl-8-ethyl-5,8-diazadec-4-ene-2-amine)chlorocopper(II) perchlorate, C₁₂H₂₇N₃Cl₂CuN₃O₄, *M_r* = 411.81,

monoclinic, C2/c, (Hall-C2/c); *a*, 26.418 (1), *b*, 9.7385 (4); *c*, 14.0993 (5) Å; β, 91.134 (3)° (from 9900 refl., 2.23–25.23° at 113 (2) K). Violet coloured plate grown from water (0.05 × 0.18 × 0.72 mm), *F*(000), 1720; μ, 1.518. Data was collected at 113 (2) K by using a Bruker APEX-II CCD diffractometer (φ and ω scans) with fine focus Mo K_α radiation (0.71073 Å) and processed by using Bruker APEX2, SAINT and SAADABS-2 software [9] with multiscan absorption corrections, *T*_{max} 0.7452, *T*_{min} 0.6110, (−31 < *h* < 31; −11 < *k* < 11; −16 < *l* < 16); 2.65 < θ < 25°; 29186 reflns. (*R*_{equiv} 0.0360), 3201 unique refl., 3057 refl. with *I* > 2σ*I*.

The structure was solved by direct methods and refined on *F*² by using SHELTXL [7], with anisotropic parameters for all non-H-atoms. H-atoms are in calculated positions, refined by using the SHELXL default riding model. 203 params., 0 restraints. Data (*I* > 2σ*I*): *R*₁, 0.0299, *wR*, 0.0648; all data: *R*₁ = 0.0323, *wR* = 0.0659.

Supplementary Crystallographic Data

Supplementary crystallographic data for [Cu(deenim)Cl]ClO₄, CCDC 932478, can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, Cambridge, UK.

Highlights

Copper(II) amine compounds react with ammonia and acetone, or mesityl oxide, to form β-imino-amine compounds. [(2,4-Dimethyl-8-ethyl-5,8-diazadec-4-ene-2-amine)chlorocopper(II)] perchlorate is formed with *N,N*-diethylethane-1,2-diamine. This has copper(II) in square-planar coordination by a primary, tertiary, and imine nitrogen atom and a chloride ion.

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