Crystal structure of dichloro-*N,N*-bis(pyridine-2-ylmethyl)cyclohexamino copper(II), $C_{18}H_{23}Cl_2CuN_3$

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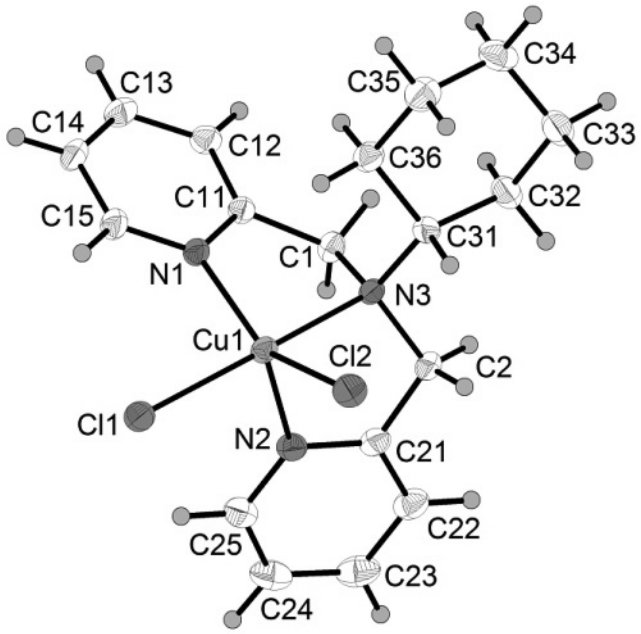

Abstract

$C_{18}H_{23}Cl_2CuN_3$, monoclinic, $P2_1/c$ (no. 14), a = 8.291(2) Å, b = 13.970(3) Å, c = 15.330(3) Å, β = 90.328(5)°, V = 1775.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.0272, $wR_{ref}(F^2)$ = 0.0736, T = 101 K.

Table 1. Data collection and handling.

Crystal:	green cuboids, size 0.469×0.578×0.601 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	15.36 cm^{-1}
Diffractometer, scan mode:	Bruker X8 ApexII 4K Kappa, ω and φ
$2\theta_{max}$:	55.99°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	39672, 4281
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3684
$N(param)_{refined}$:	217
Programs:	APEX2, SAINT-Plus, SADABS, SIR-97, DIAMOND, SHELX, WinGX [20–25]

Source of material

All chemicals were purchased from Sigma-Aldrich and used as received. *N*,*N*-Bis(pyridine-2-ylmethyl)cyclohexamine (1 mmol, 0.282 g) and copper (II) acetate (1 mmol, 0.183 g) were dissolved separately in methanol (5 ml). *N*,*N*-Bis(pyridine-2-ylmethyl)-cyclohexamine was added drop-wise to the copper(II) solution while stirring vigorously. Sodium chloride (3 mmol, 0.179 g) was added to the reaction mixture and stirred until all the sodium chloride was dissolved. The methanol was allowed to evaporate slowly to obtain the product as brilliant green crystals suitable for X-ray diffraction. Yield: 0.26 g, 61.90%.

Experimental details

In the structure all the H atoms were positioned geometrically and refined discemible using a riding model, with C–$H_{methine}$ = 1.00 Å; C–$H_{methylene}$ = 0.99 Å; C–$H_{aromatic}$ = 0.95 Å. The H atom isotropic displacement parameters were fixed; U_{iso}(H) = 1.2U_{eq}(C) for aromatic, methylene and methine, allowing them to ride on the parent atom.

Discussion

The bidentate ligand, 2,2-dipyridylamine is considered one of the classical ligands and has been the subject of numerous studies since the 1980's [1]. The ligand can be readily derivatised to form tridentate ligands [2] with various functionalities bonded to the central nitrogen atom, including that utilised in this study [3]. The ligands of 2,2-dipyridylamine and derivatives thereof have an affinity for various transition metals such as platinum [4], iron [5], palladium [6] and a variety of others [7–8]. The interest in these ligands and complexes thereof, is due to their potential applications as anti-cancer agents [9–10] and catalysts [11–13]. The dichloro-*N,N*-bis(pyridine-2-ylmethyl)cyclohexamino copper(II) (Figure 1) complex crystallized in the monoclinic space group $P2_1/c$, with four molecules per unit cell. Thus the asymmetric unit consists of a Cu(II) atom coordinated to one tridentate *N,N*-bis(pyridine-2-ylmethyl)cyclohexamino ligand and two chlorine atoms to form a distorted trigonal bipyramid. The distortion is illustrated by the N1–Cu1–Cl2 bond angle of 146.84(4)°, deviating significantly from the ideal 120°. The *N,N*-bis(pyridine-2-ylmethyl)cyclohexamino ligand coordinates tridentally to the copper metal centre, forming two adjacent five-membered rings, through the coordination of the Cu with the nitrogen atoms N1, N2 and N3. The N2–Cu1–N3, N3–Cu1–N1 and $N1_{pyridine}$–Cu1–$N2_{pyridine}$ bite angles of 77.91(6)°, 82.31(6)° and 105.18(6)° respectively, correlates well with similar complexes of dipyridylamine ligands with Cu(II). All the bond distances and angles in the title structure fall within the range of similar complexes [14–18], with the exception of a closely related blue Cu(II) complex containing a dichloromethane solvate which crystallized in the *C*2/*c* space group [19].

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.3149	0.8341	0.4506	0.024
H(1B)	4*e*	0.4736	0.8139	0.5077	0.024
H(2A)	4*e*	0.5645	0.9441	0.3065	0.025
H(2B)	4*e*	0.4845	0.9653	0.3993	0.025
H(12)	4*e*	0.3436	0.6753	0.5852	0.026
H(13)	4*e*	0.2684	0.5135	0.5773	0.031
H(14)	4*e*	0.2631	0.4374	0.4409	0.030

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Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(15)	4*e*	0.3309	0.5240	0.3169	0.027
H(22)	4*e*	0.2795	1.0724	0.3237	0.033
H(23)	4*e*	0.0236	1.0737	0.2576	0.040
H(24)	4*e*	–0.0820	0.9299	0.2021	0.039
H(25)	4*e*	0.0734	0.7917	0.2085	0.032
H(31)	4*e*	0.7562	0.8343	0.3416	0.023
H(32A)	4*e*	0.7317	0.9528	0.4483	0.033
H(32B)	4*e*	0.6909	0.8745	0.5214	0.033

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(33A)	4*e*	0.9957	0.8928	0.4343	0.036
H(33B)	4*e*	0.9651	0.9166	0.5351	0.036
H(34A)	4*e*	0.9138	0.7532	0.5637	0.037
H(34B)	4*e*	1.0896	0.7654	0.5222	0.037
H(35A)	4*e*	0.9520	0.6376	0.4528	0.036
H(35B)	4*e*	0.9873	0.7209	0.3834	0.036
H(36A)	4*e*	0.6838	0.6913	0.4692	0.029
H(36B)	4*e*	0.7161	0.6712	0.3679	0.029

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	4*e*	0.43917(2)	0.73277(2)	0.27445(2)	0.0232(1)	0.0157(1)	0.0146(1)	–0.00098(8)	0.00051(8)	0.00048(8)
N(1)	4*e*	0.3732(2)	0.6482(1)	0.37581(9)	0.0229(7)	0.0162(7)	0.0169(7)	–0.0014(6)	–0.0006(6)	–0.0004(5)
N(2)	4*e*	0.2606(2)	0.8479(1)	0.2709(1)	0.0230(7)	0.0205(7)	0.0203(7)	0.0021(6)	–0.0014(6)	0.0002(6)
N(3)	4*e*	0.5196(2)	0.8230(1)	0.37643(9)	0.0201(7)	0.0147(6)	0.0162(7)	–0.0005(5)	0.0001(5)	0.0013(5)
Cl(1)	4*e*	0.31406(6)	0.63857(3)	0.17408(3)	0.0380(3)	0.0209(2)	0.0183(2)	–0.0023(2)	–0.0038(2)	–0.0016(2)
Cl(2)	4*e*	0.64294(6)	0.78026(3)	0.18289(3)	0.0282(2)	0.0334(2)	0.0191(2)	–0.0040(2)	0.0049(2)	0.0024(2)
C(1)	4*e*	0.4163(2)	0.7968(1)	0.4531(1)	0.0238(8)	0.0177(8)	0.0185(8)	–0.0016(7)	0.0032(7)	–0.0012(6)
C(2)	4*e*	0.4813(2)	0.9222(1)	0.3480(1)	0.0263(9)	0.0143(8)	0.0224(9)	–0.0014(7)	–0.0021(7)	0.0009(7)
C(11)	4*e*	0.3770(2)	0.6915(1)	0.4540(1)	0.0177(8)	0.0174(8)	0.0171(8)	–0.0001(6)	0.0002(6)	0.0000(6)
C(12)	4*e*	0.3394(2)	0.6433(1)	0.5306(1)	0.0252(9)	0.0237(9)	0.0165(8)	–0.0001(7)	0.0005(7)	0.0008(7)
C(13)	4*e*	0.2957(2)	0.5477(1)	0.5260(1)	0.031(1)	0.0250(9)	0.0210(9)	–0.0021(8)	0.0014(7)	0.0068(7)
C(14)	4*e*	0.2924(2)	0.5029(1)	0.4456(1)	0.033(1)	0.0164(8)	0.026(1)	–0.0046(7)	–0.0013(8)	0.0034(7)
C(15)	4*e*	0.3323(2)	0.5551(1)	0.3721(1)	0.0301(9)	0.0176(8)	0.0210(9)	–0.0035(7)	–0.0014(7)	–0.0012(7)
C(21)	4*e*	0.3184(2)	0.9291(1)	0.3053(1)	0.0252(9)	0.0195(8)	0.0181(8)	0.0011(7)	0.0018(7)	0.0021(7)
C(22)	4*e*	0.2343(2)	1.0152(1)	0.3005(1)	0.036(1)	0.0204(9)	0.025(1)	0.0051(8)	–0.0003(8)	0.0004(7)
C(23)	4*e*	0.0839(3)	1.0160(2)	0.2615(1)	0.038(1)	0.031(1)	0.032(1)	0.0152(9)	–0.0007(9)	0.0033(8)
C(24)	4*e*	0.0223(2)	0.9315(2)	0.2280(1)	0.0266(9)	0.041(1)	0.030(1)	0.0082(9)	–0.0046(8)	0.0044(9)
C(25)	4*e*	0.1148(2)	0.8492(1)	0.2329(1)	0.0261(9)	0.029(1)	0.0234(9)	0.0005(8)	–0.0026(7)	0.0008(7)
C(31)	4*e*	0.6980(2)	0.8164(1)	0.3962(1)	0.0195(8)	0.0204(8)	0.0172(8)	–0.0017(6)	–0.0014(6)	0.0018(6)
C(32)	4*e*	0.7530(2)	0.8863(1)	0.4675(1)	0.0271(9)	0.0259(9)	0.029(1)	–0.0015(8)	–0.0076(8)	–0.0037(8)
C(33)	4*e*	0.9332(2)	0.8740(2)	0.4864(1)	0.0259(9)	0.036(1)	0.027(1)	–0.0070(8)	–0.0042(8)	–0.0009(8)
C(34)	4*e*	0.9726(2)	0.7713(2)	0.5102(1)	0.0195(9)	0.045(1)	0.029(1)	0.0007(8)	–0.0022(8)	0.0073(9)
C(35)	4*e*	0.9256(2)	0.7044(2)	0.4364(1)	0.0226(9)	0.030(1)	0.037(1)	0.0037(8)	0.0016(8)	0.0051(8)
C(36)	4*e*	0.7450(2)	0.7131(1)	0.4176(1)	0.0224(9)	0.0206(9)	0.029(1)	0.0013(7)	–0.0008(7)	0.0035(7)

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