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Crystal structure of dicholoro-(3,5-dimethyl-1*H*-pyrazole-1-carboxamidine-*N*,*N*′)copper(II), $Cu(C_6H_{10}N_4)Cl_2$

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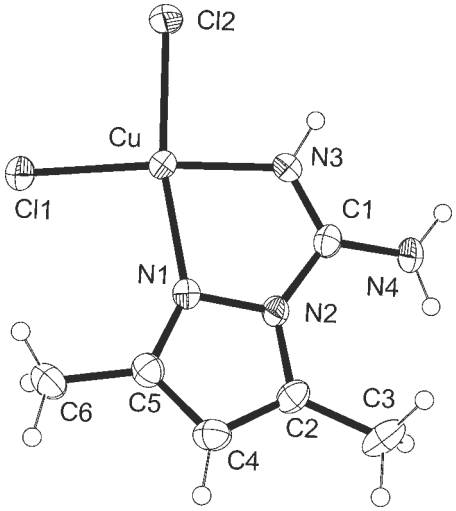

Abstract

$C_6H_{10}Cl_2CuN_4$, monoclinic, $P2_1/n$ (no. 14), a = 7.316(2) Å, b = 16.002(2) Å, c = 9.202(6) Å, β = 113.15(2)°, V = 990.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.054, $wR_{ref}(F^2)$ = 0.125, T = 293 K.

Source of material

A mixture of 3,5-dimethyl-1-carboxamidinepyrazole (0.10 g, 0.5 mmol) and $CuCl_2 \cdot 2H_2O$ (0.04 g, 0.2 mmol) was dissolved under heating in ethanol (5 ml). After two days dark-blue crystals were obtained. Elemental analysis — found: C, 26.08 %; N, 20.70 %; H, 3.59 %; calculated for $C_6H_{10}Cl_2CuN_4$: C, 26.43 %; N, 20.55 %; H, 3.70 %.

Experimental details

All H atoms were placed at calculated positions and treated using a riding model, with U_{iso}(H) = 1.2 U_{eq}(N) and U_{iso}(H) = 1.2 or 1.5 U_{eq}(C_{methyl}). The positions of methyl H atoms were defined by HFIX 137 command in SHELXL-97 [1]. The number of H atoms and their positions are in agreement to elemental analysis and known crystal structures of transition metal complexes with the same 3,5-dimethyl-1*H*-pyrazole-1-carboxamidine (HL) ligand [2-4].

Discussion

Pyrazole ligands have a wide variety of applications in coordination chemistry [5-8] and are therefore part of our systematic studies [9-12]. Herein we focus on the transition metal complex with pyrazole-based ligand. To date there are several structures [2-4] published with transition metal complexes containing 3,5-dimethyl-1*H*-pyrazole-1-carboxamidine (HL) ligand with this particular being the first square-planar mononuclear complex.

The HL ligand coordinates copper *via* two nitrogen atoms, forming a five-membered chelate ring (N1–N2–C1–N3–Cu). The Cl atoms are in *cis*-position with the Cu—Cl1 bond (2.206(2) Å) being shorter than the Cu—Cl2 bond (2.264(2) Å), which can be explained by the difference in H-bonding of the two Cl atoms to the neighboring molecules. The Cl1 atom forms only one hydrogen bond with N4···Cl1^i distance of 3.297(5) Å, H4a···Cl1^i distance of 2.64 Å, and N4 H4a···Cl1^i angle of 134° (symmetry code i: –*x*+0.5,*y*+0.5,–*z*+0.5). The Cl2 atom forms three H bonds having the following geometrical parameters: N4···Cl2^{ii} distance is 3.495(5) Å, H4a···Cl2^{ii} distance is 2.83 Å, N4–H4a···Cl2^{ii} angle is 135°; N4···Cl2^i distance is 3.382(5) Å, H4b···Cl2^i distance is 2.76 Å, N4–H4b···Cl2^i angle is 130°; N3···Cl2^{ii} distance is 3.368(4) Å, H3···Cl2^{ii} distance is 2.62 Å, N3–H3···Cl2^{ii} angle is 145° (symmetry code ii: –*x*+1,–*y*+1,–*z*+1). Another difference to previously known structures containing HL ligands [2-4] is in the chelate ring which usually lies in a distinct plane. In the case of dicholoro-(3,5-dimethyl-1*H*-pyrazole-1-carboxamidine-*N*,*N*′)-copper(II) the chelate ring is deformed by a twist on the N2—C1 bond with a torsion angle (N1–N2–C1–N3) of 12.6(7)°. This is significantly larger than 6° which is the largest of all torsion angles in the chelate ring in the five structures with the same ligand [2-4]. The angles ∠Cl1–Cu–N3 and ∠Cl2–Cu–N1 between the donor atoms in *trans*-positions differ from 180°, with values of 172.3(1) and 167.8(1)°, respectively. All bond lengths in the pyrazole ring are shorter than expected for single bonds, but still longer than the value for double bond. This indicates a partial electron delocalization inside of the pyrazole ring.

Table 1. Data collection and handling.

Crystal:	dark-blue prism, size 0.20 × 0.23 × 0.23 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	27.01 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD-4, $\omega/2\theta$
$2\theta_{max}$:	58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2656, 2466
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1376
$N(param)_{refined}$:	120
Programs:	SHELXL-97 [1], PLATON [13], WinGX [14], ORTEP-III [15]

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

Atom	Site	x	y	z	U_{iso}
H(3)	4*e*	0.4016	0.5495	0.3589	0.044
H(4A)	4*e*	0.4156	0.7017	0.3293	0.047
H(4B)	4*e*	0.3735	0.7323	0.1664	0.047
H(3A)	4*e*	0.2890	0.7717	–0.0749	0.067
H(3B)	4*e*	0.4084	0.7509	–0.1793	0.067
H(3C)	4*e*	0.5095	0.7407	0.0047	0.067
H(4)	4*e*	0.2519	0.6120	–0.3299	0.045
H(6A)	4*e*	0.2098	0.3961	–0.2355	0.070
H(6B)	4*e*	0.1586	0.4524	–0.3859	0.070
H(6C)	4*e*	–0.0008	0.4375	–0.3141	0.070

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	4*e*	0.2685(1)	0.44301(4)	0.15002(8)	0.0347(3)	0.0229(3)	0.0273(3)	–0.0019(3)	0.0102(3)	0.0007(3)
Cl(1)	4*e*	0.1284(2)	0.33138(9)	0.0098(2)	0.0467(8)	0.0295(7)	0.0359(8)	–0.0079(6)	0.0091(7)	–0.0028(6)
Cl(2)	4*e*	0.3426(3)	0.3788(1)	0.3856(2)	0.078(1)	0.0373(8)	0.0283(7)	–0.0160(8)	0.0132(7)	0.0045(7)
N(1)	4*e*	0.2435(7)	0.5197(3)	–0.0339(5)	0.037(3)	0.025(2)	0.028(2)	–0.002(2)	0.011(2)	–0.002(2)
N(2)	4*e*	0.3074(6)	0.5995(2)	0.0173(5)	0.032(2)	0.020(2)	0.028(2)	0.004(2)	0.010(2)	–0.003(2)
N(3)	4*e*	0.3567(7)	0.5473(3)	0.2574(5)	0.050(3)	0.030(3)	0.023(2)	–0.004(2)	0.008(2)	–0.001(2)
N(4)	4*e*	0.3832(7)	0.6918(3)	0.2304(6)	0.054(3)	0.023(2)	0.035(3)	–0.003(2)	0.012(2)	–0.008(2)
C(1)	4*e*	0.3483(8)	0.6144(3)	0.1769(6)	0.025(2)	0.025(3)	0.036(3)	–0.001(2)	0.011(2)	–0.002(2)
C(2)	4*e*	0.3163(8)	0.6473(3)	–0.1013(7)	0.034(3)	0.024(3)	0.041(3)	0.005(2)	0.018(3)	0.004(2)
C(3)	4*e*	0.3871(9)	0.7355(3)	–0.0864(8)	0.054(4)	0.029(3)	0.064(4)	0.008(3)	0.036(3)	0.015(3)
C(4)	4*e*	0.2589(9)	0.5971(4)	–0.2301(7)	0.045(3)	0.039(3)	0.033(3)	0.007(3)	0.020(3)	0.005(3)
C(5)	4*e*	0.2126(8)	0.5196(3)	–0.1869(6)	0.033(3)	0.034(3)	0.033(3)	0.002(2)	0.014(3)	–0.002(2)
C(6)	4*e*	0.139(1)	0.4447(4)	–0.2897(7)	0.061(4)	0.049(4)	0.030(3)	–0.010(4)	0.019(3)	–0.007(3)

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