

# Crystal structure of dichloro-(3,5-dimethyl-1*H*-pyrazole-1-carboxamide-*N,N'*)copper(II), Cu(C<sub>6</sub>H<sub>10</sub>N<sub>4</sub>)Cl<sub>2</sub>

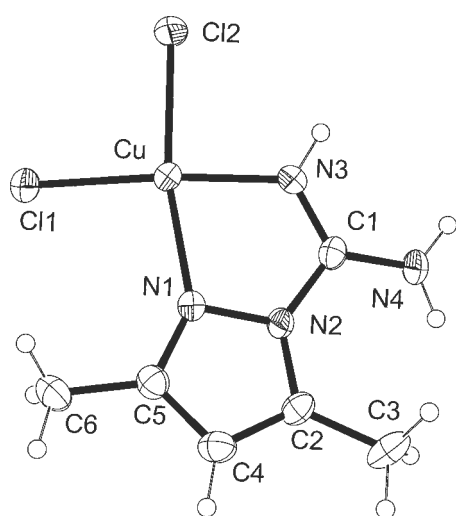
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## Abstract

C<sub>6</sub>H<sub>10</sub>Cl<sub>2</sub>CuN<sub>4</sub>, monoclinic, *P*2<sub>1</sub>/*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<sup>3</sup>, *Z* = 4, *R*<sub>gt</sub>(*F*) = 0.054, *wR*<sub>ref</sub>(*F*<sup>2</sup>) = 0.125, *T* = 293 K.

## Source of material

A mixture of 3,5-dimethyl-1-carboxamidinopyrazole (0.10 g, 0.5 mmol) and CuCl<sub>2</sub> · 2H<sub>2</sub>O (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<sub>6</sub>H<sub>10</sub>Cl<sub>2</sub>CuN<sub>4</sub>: 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*<sub>iso</sub>(H) = 1.2 *U*<sub>eq</sub>(N) and *U*<sub>iso</sub>(H) = 1.2 or 1.5 *U*<sub>eq</sub>(C<sub>methyl</sub>). 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-carboxamide (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 stud-

ies [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-carboxamide (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<sup>i</sup> distance of 3.297(5) Å, H4a···Cl1<sup>i</sup> distance of 2.64 Å, and N4—H4a···Cl1<sup>i</sup> 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<sup>ii</sup> distance is 3.495(5) Å, H4a···Cl2<sup>ii</sup> distance is 2.83 Å, N4—H4a···Cl2<sup>ii</sup> angle is 135°; N4···Cl2<sup>i</sup> distance is 3.382(5) Å, H4b···Cl2<sup>i</sup> distance is 2.76 Å, N4—H4b···Cl2<sup>i</sup> angle is 130°; N3···Cl2<sup>ii</sup> distance is 3.368(4) Å, H3···Cl2<sup>ii</sup> distance is 2.62 Å, N3—H3···Cl2<sup>ii</sup> 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 dichloro-(3,5-dimethyl-1*H*-pyrazole-1-carboxamide-*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 <i>K</i> <sub>α</sub> radiation (0.71073 Å)
<i>μ</i> :	27.01 cm <sup>-1</sup>
Diffractometer, scan mode:	Enraf-Nonius CAD-4, ω/2θ
2θ <sub>max</sub> :	58°
<i>N</i> ( <i>hkl</i> ) <sub>measured</sub> , <i>N</i> ( <i>hkl</i> ) <sub>unique</sub> :	2656, 2466
Criterion for <i>I</i> <sub>obs</sub> , <i>N</i> ( <i>hkl</i> ) <sub>gt</sub> :	<i>I</i> <sub>obs</sub> > 2 σ( <i>I</i> <sub>obs</sub> ), 1376
<i>N</i> ( <i>param</i> ) <sub>refined</sub> :	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<sup>2</sup>).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub>
H(3)	4e	0.4016	0.5495	0.3589	0.044
H(4A)	4e	0.4156	0.7017	0.3293	0.047
H(4B)	4e	0.3735	0.7323	0.1664	0.047
H(3A)	4e	0.2890	0.7717	-0.0749	0.067
H(3B)	4e	0.4084	0.7509	-0.1793	0.067

**Table 2.** Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub>
H(3C)	4e	0.5095	0.7407	0.0047	0.067
H(4)	4e	0.2519	0.6120	-0.3299	0.045
H(6A)	4e	0.2098	0.3961	-0.2355	0.070
H(6B)	4e	0.1586	0.4524	-0.3859	0.070
H(6C)	4e	-0.0008	0.4375	-0.3141	0.070

**Table 3.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
Cu	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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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## References

- Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
- Bogdanović, G. A.; Jačimović, Ž. K.; Leovac, V. M.: Transition metal complexes with pyrazole-based ligands. XXII. Di- $\mu$ -thiocyanato-bis[(3,5-dimethyl-1*H*-pyrazole-1-carboxamide- $\kappa^2N,N'$ )(thiocyanato- $\kappa N$ )copper(II)] and a redetermination of bis[(3,5-dimethyl-1*H*-pyrazole-1-carboxamide- $\kappa^2N,N'$ )bis(nitrate- $\kappa O$ )copper(II)]. *Acta Crystallogr.* **C61** (2005) m376-m379.
- Jačimović, Ž. K.; Leovac, V. M.; Mészáros Szécsényi, K.; Howard, J. A. K.; Radosavljević Evans, I.: Transition metal complexes with pyrazole-based ligands. XIX. Diaqua-bis(3,5-dimethyl-1*H*-pyrazole-1-carboxamide- $\kappa^2N,N'$ ) metal(II) dinitrate, with metal = Co and Ni. *Acta Crystallogr.* **C60** (2004) m467-m470.
- Podder, A.; Mukhopadhyay, B. P.; Saha, N.; Saha, A.; Stensland, B.: Crystal and molecular structure of diaqua-bis-(3,5-dimethyl-1-guanyl pyrazole)nickel(II) nitrate, [Ni(C<sub>6</sub>N<sub>4</sub>H<sub>10</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>. *J. Cryst. Spectrosc.* **19** (1989) 71-76.
- Barszcz, B.: Coordination properties of didentate *N,O* heterocyclic alcohols and aldehydes towards Cu(II), Co(II), Zn(II) and Cd(II) ions in the solid state and aqueous solution. *Coord. Chem. Rev.* **249** (2005) 2259-2276.
- Goslar, J.; Sczaniecki, P. B.; Strawiak, M. M.; Mrozinski, J.: Chemical properties, magnetic and e.p.r. studies of pyrazole copper(II) complexes. *Transit. Met. Chem.* **13** (1988) 81-86.
- Ding, L.; Grehn, L.; De Clercq, E.; Andrei, G.; Snoeck, R.; Balzarini, J.; Fransson, B.; Ragnarsson, U.: Synthesis and antiviral activity of three pyrazole analogues of distamycin A. *Acta Chem. Scand.* **48** (1994) 498-505.
- Vicentini, C. B.; Mares, D.; Tartari, A.; Manfrini, M.; Forlani, G.: Synthesis of Pyrazole Derivatives and Their Evaluation as Photosynthetic Electron Transport Inhibitors. *J. Agric. Food Chem.* **52** (2004) 1898-1906.
- Pogány, P.; Kovács, A.; Mészáros Szécsényi, K.; Leovac, V. M.: FT-IR and theoretical study of 3,5-dimethyl-1*H*-pyrazole-1-carboxamide (L) and the complexes CoL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>, NiL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>. *Spectrochim. Acta* **A71** (2008) 1466-1473.
- Mészáros Szécsényi, K.; Leovac, V. M.; Češljević, V. I.; Kovács, A.; Pokol, G.; Argay, Gy.; Kálmán, A.; Bogdanović, G. A.; Jačimović, Ž. K.; Spasojević-de Biré, A.: Reaction of copper(II) with 1-carboxamide-3,5-dimethylpyrazole, 1-carboxamide-3,5-dimethylpyrazole, 4-acetyl-3-amino-5-methylpyrazole and 5-amino-4-carboxamide-1-phenylpyrazole. *Inorg. Chim. Acta* **353** (2003) 253-262.
- Kovács, A.; Mészáros Szécsényi, K.; Leovac, V. M.; Tomić, Z. D.; Pokol, G.: Synthesis under self-controlled reaction conditions: Reaction of tetramminezinc(II) chloride with 3,5-dimethyl-1-thiocarboxamide pyrazole. *J. Organomet. Chem.* **692** (2007) 2582-2592.
- Mészáros Szécsényi, K.; Leovac, V. M.; Petković, R.; Jačimović, Ž. K.; Pokol, G.: Transition Metal Complexes with Pyrazole Based Ligands Part XXV. Deauration of isostructural cobalt(II) and nickel(II) complexes with 3,5-dimethylpyrazole-1-carboxamide. *J. Therm. Anal. Calorim.* **90** (2007) 899-902.
- Spek, A. L.: Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* **36** (2003) 7-13.
- Farrugia, L. J.: WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.* **32** (1999) 837-838.
- Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) *J. Appl. Crystallogr.* **30** (1997) 565.