

Crystal structure of dichloro-(3,5-dimethyl-1*H*-pyrazole-1-carboxamidine-*N,N'*)copper(II), Cu(C₆H₁₀N₄)Cl₂

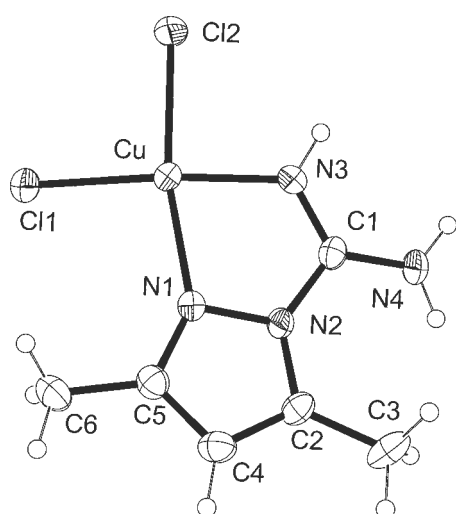
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Received July 21, 2009, accepted and available on-line September 8, 2009; CCDC no. 1267/2724



Abstract

C₆H₁₀Cl₂CuN₄, monoclinic, *P*2₁/*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 Å³, *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-carboxamidinopyrazole (0.10 g, 0.5 mmol) and CuCl₂ · 2H₂O (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 C₆H₁₀Cl₂CuN₄: 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 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-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...Cl1ⁱ distance of 3.297(5) Å, H4a...Cl1ⁱ distance of 2.64 Å, and N4–H4a...Cl1ⁱ 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...Cl2ⁱⁱ distance is 3.495(5) Å, H4a...Cl2ⁱⁱ distance is 2.83 Å, N4–H4a...Cl2ⁱⁱ angle is 135°; N4...Cl2ⁱ distance is 3.382(5) Å, H4b...Cl2ⁱ distance is 2.76 Å, N4–H4b...Cl2ⁱ angle is 130°; N3...Cl2ⁱⁱ distance is 3.368(4) Å, H3...Cl2ⁱⁱ distance is 2.62 Å, N3–H3...Cl2ⁱⁱ 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-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 <i>K</i> _α radiation (0.71073 Å)
μ:	27.01 cm ^{–1}
Diffractometer, scan mode:	Enraf-Nonius CAD-4, ω/2θ
2θ _{max} :	58°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	2656, 2466
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 1376
<i>N</i> (<i>param</i>) _{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 Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
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> _{iso}
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 Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
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)

Acknowledgment. This work was financially supported by the Ministry for Science and Technological Development of the Republic of Serbia (Projects 142010 and 142028).

References

- Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
- Bogdanović, G. A.; Jaćimović, Ž. K.; Leovac, V. M.: Transition metal complexes with pyrazole-based ligands. XXII. Di- μ -thiocyanato-bis[(3,5-dimethyl-1*H*-pyrazole-1-carboxamidine- κ^2N,N')(thiocyanato- κN)copper(II)] and a redetermination of bis(3,5-dimethyl-1*H*-pyrazole-1-carboxamidine- κ^2N,N')bis(nitrato- κO)copper(II). *Acta Crystallogr.* **C61** (2005) m376-m379.
- Jaćimović, 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-carboxamidine- κ^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(C₆N₄H₁₀)₂(H₂O)₂](NO₃)₂. *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-carboxamidine (L) and the complexes CoL₂(H₂O)₂(NO₃)₂, NiL₂(H₂O)₂(NO₃)₂. *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.; Jaćimović, Ž. K.; Spasojević-de Biré, A.: Reaction of copper(II) with 1-carboxamide-3,5-dimethylpyrazole, 1-carboxamidine-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 tetraamminezinc(II) chloride with 3,5-dimethyl-1-thiocarboxamide pyrazole. *J. Organomet. Chem.* **692** (2007) 2582-2592.
- Mészáros Szécsényi, K.; Leovac, V. M.; Petković, R.; Jaćimović, 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-carboxamidine. *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.