

Synthesis and X-Ray Structure of [N,N-Bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane](3,5-dimethylpyrazole)copper(II) dinitrate

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Abstract: The tridentate ligand N,N-Bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane (**L**) has been prepared in one step by condensation of two equivalents of 1-hydroxymethyl-3,5-dimethylpyrazole with one equivalent of 2-aminoethanol. This reaction is carried out under microwave irradiation (60 W) in the absence of solvent for 20 min [1]. Using this ligand **L** a new Cu(II) dinitrate complex has been prepared. The single-crystal X-ray structure of the title compound, [N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane] (3,5-dimethylpyrazole)copper(II) dinitrate, reveals that the copper (II) ion is coordinated to two pyrazole nitrogens, one tertiary amine nitrogen of the ligand **L** and 3,5-dimethylpyrazole, and in the apical position by an alcohol O atom.

Keywords: Structure, copper complex, tripod, pyrazole, tridentate ligand.

Introduction

Copper(II) complexes with nitrogen containing multipodal ligands are known and have been proposed as models for the type III copper proteins, as well as for the discovery of new catalyst precursors. Polypyrazolyl-containing molecules are used as models for copper proteins. A variety of nitrogen-containing ligands have been shown to promote novel catalytic transformations of organic substrates such as enantioselective catalysis and alkene polymerization [2-9].

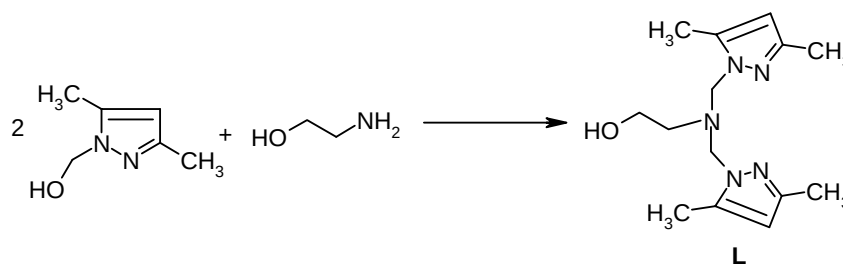
Copper (II) complexes of the ligand N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane (**L**, [10]) of the type $[\text{Cu}(\text{L})\text{X}]\text{Y}$ ($\text{X} = \text{Br}, \text{Cl}, \text{NO}_3, \text{N}_3$; $\text{Y} = \text{Cl}, \text{Br}, \text{BF}_4$) have been reported as mononuclear five-coordinate complexes by UV-Vis spectroscopy and Fast Atom Bombardment Mass Spectroscopy. The complexes were tested for their reactivity in the oxidation of catechol to quinone. The complexes show differing rates of reaction depending on the nature of the anion [11], however no structural analysis has been made on these complexes. For this reason we have been interested in studying the structure of the complex with $\text{X} = \text{Y} = \text{NO}_3$.

Results and Discussion

Synthesis of [N,N-Bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane] (**L**).

The synthesis of N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane was first carried out using the literature method [11] by condensation of 2 equivalents of 1-hydroxymethyl-3,5-dimethylpyrazole and one equivalent of 2-aminoethanol in acetonitrile with stirring in a closed vessel at room temperature for 4 days (Scheme 1, Method A). The product is isolated in 80% yield.

Scheme 1



Method	Time	Yield
A (25°C)	4 days	80%
B (60°C)	4 hrs.	88%
C (60W)	20 min.	90%

When this reaction was repeated in the absence of solvent (Method B, [1]) it required 4 hrs. at 60°C to reach apparent completion and gave the target compound in good yield (88%). In our laboratory similar reactions are carried out under microwave irradiation and without solvent, and typically afford high yields. The same substrate mixture placed in a microwave reactor and irradiated with microwaves (60 W) in the absence of solvent for 20 min. (Method C, [1]) gave the product **L** in excellent yield (90%).

Synthesis of [N,N-Bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane] (3,5dimethylpyrazole)copper(II) dinitrate: [Cu(L)(L_o)(NO₃)₂]

Suitable crystals of the title complex [N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane](3,5dimethylpyrazole) copper(II) dinitrate were obtained by treating a solution of N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane (**L**) in ethanol with a solution of copper(II) dinitrate [Cu(NO₃)₂ · 3H₂O] in ethanol at 25°C. Partial hydrolysis of the ligand N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane (**L**) in its solution with the metal salt resulted in the formation of 3,5-dimethyl pyrazole (**L_o**) [10, 12, 13].

X-ray structure analysis

The sample was studied on an automatic CAD4 Enraf-Nonius diffractometer with graphite monochromated MoK α radiation (ω -2 θ) scan. The cell parameters were obtained by fitting a set of 25 high-theta reflections. The measured intensities were corrected for Lorentz and polarisation effects. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre [14]. All crystallographic and data collection parameters are summarized in Table 1.

Table 1: Crystal and experimental data of Copper(II) complex CuLL_o(NO₃)₂.

Empirical formula	C ₁₉ H ₃₁ CuN ₉ O ₇
Formula weight	561.07
Temperature	293(2)K
Radiation	MoK α
Wavelength	0.71073 Å
Crystal system, Space group	triclinic; P-1
Unit cell dimensions	
a = 8.4404(8) Å	alpha = 88.914(2) deg.
b = 11.3445(8) Å	beta = 76.177(3) deg.
c = 13.7384(15) Å	gamma = 85.254(4) deg.
Volume	1273.0(2) Å ³
Z	2

Table 1. Cont.

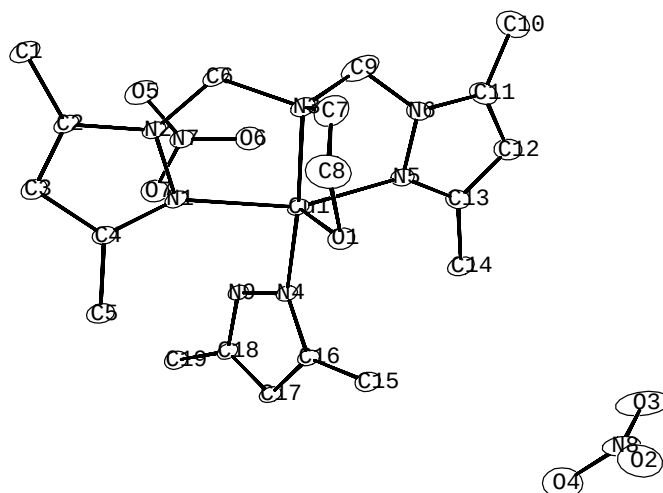
Calculated density	1.464 Mg/m ³
Absorption coefficient	0.915 mm ⁻¹
F(000)	586
Theta range for data collection	2.36 to 27.50 deg.
Limiting indices	-9<=h<=10 , -14<=k<=14 , -11<=l<=17
Reflections collected / unique	5555/
Independent reflections	4246 [R(int) = 0.0488]
Completeness to theta	0.726
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4246 / 0 /326
Goodness-of-fit on F ²	0.994
Final R indices [I>2sigma(I)]	R1 = 0.0702, wR2 = 0.1680
R indices (all data)	R1 = 0.1347, wR2 = 0.2094
Largest diff. peak and hole	0.433 and -0.301 e.Å ⁻³
W=1/[s ² (Fo ²)+(0.100)P ²]	where P = (Fo ² +2Fc ²)/3

X-ray Structure Determination and Crystal Structure

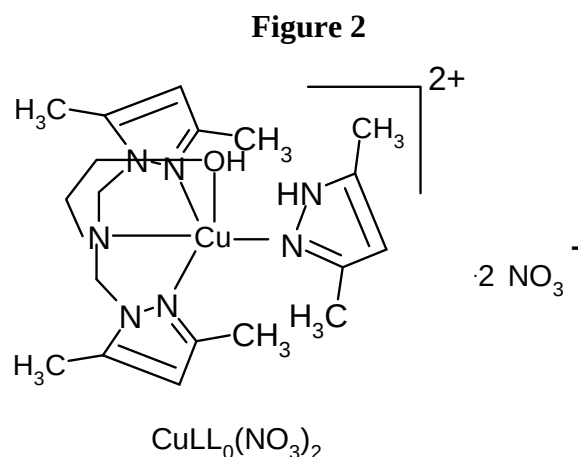
The crystal structure solution of the title compound was carried out with SHELXS-97 [15] using direct methods in space group P. Non-hydrogen atoms were found by Fourier and difference synthesis. The atomic parameters and anisotropic temperature factors were refined in space group P-1 using full-matrix least squares methods of SHELXL-97 [16]. Hydrogen atoms were positioned via HFIX. The final agreement factor is 0.0702. Molecular view used is ORTEPIII [17].

The asymmetric unit of the crystal structure of the title compound is constituted by one molecule based on a copper ion and two isolated nitrate groups (Figure 1).

Figure 1: Molecular structure of CuLL₀(NO₃)₂. H atoms have been omitted for clarity.



This structure reveals that the copper (II) ion is in a distorted square-pyramidal environment of four N atoms and one O atom. The two pyrazole N atoms and the amine N atom of N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane (**L**) and the 3,5-dimethylpyrazole (**L**₀) N atom form the base of pyramid. The alcohol O atom is in the apical position [18] (Figure 2).



The Cu-N bond distances are similar to those found in other N,N-bis (pyrazolyl-1-ylmethyl)amine complexes of copper [18,19] and [N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane](3,5-dimethylpyrazole) copper(II) diperchlorate [20]. Least-squares planes calculation show that the copper(II) ion lies slightly outside of the plane defined by N1, N3, N5, and N4 toward O1 with a Cu-O distance of 2.304 Å, similar of that observed (2.273 Å) when the oxygen anion is part of a perchlorate moiety [20].

Table 1: Selected Cu-N and Cu-O bond distances (Å) for $\text{CuLL}_0(\text{NO}_3)_2$ and $\text{CuLL}_0(\text{ClO}_4)_2$ [20].

Bond	NO_3^-	ClO_4^- [20]
Cu-N ₁	2.005(5)	1.980(2)
Cu-N ₃	2.091(6)	2.073(2)
Cu-N ₄	1.980(5)	1.968(2)
Cu-N ₅	2.005(6)	1.977(2)
Cu-O ₁	2.304(5)	2.273(2)

This distance is shorter than observed in other pyramidal complexes with coordinated alcohols (2.33–2.382 Å) [21–23], where the corresponding out of plane displacement of the copper ion is smaller. In a related structure, the [N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)amine](pyrazole)bis (tetrafluoroborate) complex [18], a F atom of one of BF_4^- anions is in the apical position with a Cu-F distance of 2.517 Å and the copper(II) ion is coplanar with the base of the pyramid.

If the angles formed by the copper and the three nitrogens of **L** are similar to those found when the anion is an perchlorate we notice a difference at the level of the apical position and the free pyrazole (L_o) (Table 2) [20]. The some observations show that the nature of the anion affect the geometry of the copper complex of the flexible ligand **L** and therefore its catalytic activity in the oxidation of catechol to quinone[11].

Table 2: Selected angles(°) for $CuLL_o(NO_3)_2$ and $CuLL_o(ClO_4)_2$ [20].

Angle	NO_3^-	ClO_4^- [20]
N_1-Cu-N_3	82.4(2)	81.97(9)
N_1-Cu-N_4	94.9(2)	94.62(9)
N_1-Cu-O_1	94.00(19)	103.40(9)
N_1-Cu-N_5	155.5(2)	155.86(9)
N_3-Cu-N_4	174.35(19)	169.23(9)
N_3-Cu-N_5	81.8(3)	82.62(9)
N_3-Cu-O_1	81.4(2)	81.53(8)
N_4-Cu-N_5	98.9(2)	97.10(10)
N_4-Cu-O_1	103.82(19)	109.22(9)
N_5-Cu-O_1	102.1(2)	92.55(9)

Conclusions

The structure of a new complex has been determined. The comparison of the structure of this complex and that with a perchlorate anion show that the nature of the anion affects the geometry of the copper complex of the flexible ligand **L**. this factor can contribute to the explanation of the catalytic activity dependence in the oxidization of catechol in quinone of the nature of the anion [11].

Experimental

General

The melting point was measured on a BUCHI 510 apparatus and is uncorrected. The proton NMR spectra of the compound **L** dissolved in $CDCl_3$ was obtained with an AC 250 MHz Bruker spectrometer. The infrared spectrum was recorded in KBr pellets using a Perkin-Elmer 1310 infrared spectrophotometer. Mass spectra were determined on a Platform II Micromass instrument (ESI+, CH_3CN/H_2O : 50/50). Elemental analyses were determined by the CNRS Service Central d'Analyse Vernaison (France). Microwave irradiations were carried out using a Prolabo Maxidigest MX 350 focused monomode system (100% power = 300 W).

Synthesis of [N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane] using Method C.

A mixture of 1-hydroxymethyl-3,5-dimethylpyrazole (2.52 g, 20 mmol) and aminoethanol (0.61g, 10 mmol) was introduced into a Pyrex tube, which was then placed in a microwave reactor and irradiated with microwaves (60W) in the absence of solvent for 20 min. The reaction mixture was extracted with dichloromethane and washed with water to eliminate the residual ethanolamine. The organic solution was dried and the solvent was removed under reduced pressure. The resulting solid was crystallised from ethyl acetate to give white crystals (2.5 g, 90%); melting point: 82-84°C (ethyl acetate); IR (cm⁻¹): 3259.2, 2923.9, 2858.7, 1548.5, 1457.1, 1365.1, 1333.6, 1294.6, 1245.6, 1135.9, 1070.8, 1051.8, 797.1, 784.7, 736.3; ¹H-NMR (δ ppm): 2.20 (s, 6H, 2CH₃), 2.25 (s, 6H, 2CH₃), 2.95 (t, 2H, CH₂-N, J=5.43Hz), 3.65 (t, 2H, CH₂-OH, J=5.43Hz), 4.95 (s, 4H, N-CH₂-N), 5.80(s, 2H, pz-H); Anal. Calc. for C₁₄H₂₃N₅O: C: 60.62, H: 8.28, N: 25.25; Found: C: 60.45, H: 8.36, N: 25.07; MS: [M+H⁺]= 278, 236, 214, 182, 172, 144, 118, 97 (100%), 86.

Synthesis of [N,N-Bis(3,5-dimethylpyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane](3,5dimethylpyrazole) copper(II) dinitrate

The copper(II) complex was prepared by the addition of a solution of tridentate ligand (0.277 g; 1mmol) in ethanol (3 mL) to a solution of copper(II) dinitrate [Cu(NO₃)₂·3H₂O] (0.2415 g, 1mmol) in ethanol (3 mL). The resulting solution was filtered and allowed to stand at 25°C. Blue crystals formed after a few days, which were filtered and washed with small amounts of cold ethanol and dried in air; melting point: 188-190 °C (ethanol); IR (cm⁻¹): 3120, 2940, 2860, 1550, 1585, 1465, 1425, 1380, 1330, 1290, 1260, 1135, 1060, 830.

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14. CCDC 211606 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via the <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336033; e-mail: deposit@ccdc.cam.ac.uk)
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Sample availability: Available from MDPI

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