



Determination of fungicidal action of bis-(4-hydrocarboxy-2-nitroterephthalate) Cu(II) tetrahydrate on grapes

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Abstract

The paper deals with the two grape varieties– merlot and madrasa from the grape sites of the Ganja-Gazakh region of Azerbaijan. The determination of the residual amount of copper in these varieties was carried out in the laboratory of the Azerbaijan State Agricultural University. The qualitative determination of copper after using Cu (II) complexes, namely Cu-DNTA, synthesized from CuSO₄.5H₂O, nitro-substituted terephthalic acid, and N-donor ligands, based on the aforementioned factors and our experience with metal carboxylate by Atomic absorption spectroscopy according to the approved methods. Analyzes were performed on the Pin AAcle 500 Flame Atomic Absorption Spectrometer analyzer (PerkinElmer). The crystal structure of both compounds is determined by single crystal x-rays diffraction (SC-XRD) analysis which inferred that the coordination geometry is slightly distorted octahedral and square pyramidal in Cu-DNTA, respectively. The non-covalent interactions that are the main reason for the formation of the supramolecular assembly are explored by Hirshfeld surface analysis for both compounds and the propensity of each pair of chemical species to form crystal packing interactions is determined by enrichment ratio.

Keywords: grape, variety, SC-XRD, non-covalent interactions, determination

Introduction

Over the past 20 years, a great deal of research has been done on metal complexes based on benzene dicarboxylic acid to better understand their structural characteristics and diverse properties [1]. Dicarboxylates are frequently employed in the construction of coordination polymers with desirable topologies from a synthetic perspective due to their abundant coordination modes and potential to behave like hydrogen bonding acceptors and donors [2]. Because of the evenly spaced carboxylic groups, the stiffness of the phenyl skeleton, and particularly its different bridging modes, terephthalic acid, which has two carboxylate groups at the trans position, can be useful in the preparation of coordination polymers through complete and partial deprotonation [3].

Therefore, in this study, we describe Cu (II) complexes, namely Cu-DNTA, synthesized from CuSO₄.5H₂O, nitro-substituted terephthalic acid, and N-donor ligands, based on the aforementioned factors and our experience with metal carboxylates [4, 5].

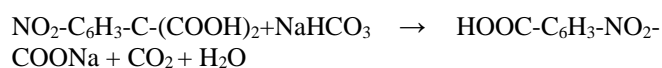
Material and Methods

In the current study, only commercially available reagent-grade chemicals were used. Samples' infra-red spectra (4000–450 cm⁻¹) by KBr pellets methods were measured on a Perkin-Elmer spectrum 100 FT-IR spectrophotometers. Thermal analysis was performed by the NETZSCH STA-409 PC/PG derivatograph. The DTA, TG, and DTG curves were taken in a static air atmosphere at an increasing heating rate of 10 °C/min from 20 to 800 °C by using

platinum crucibles. Element analysis (CHN) was performed using a Costech ECS 4010 CHNSO analyzer.

Synthesis of Bis-(4-hydrocarboxy-2-nitroterephthalate) Cu (II). tetrahydrate

First, we synthesized the sodium 4-hydrocarboxy-2-nitroterephthalate salt as shown in equation 1.



To do this, we look at 2.32g (0.01mol) 2-nitroterephthalic acid and a solution of 0.84g (0.01mol) of sodium bicarbonate so that one hydrogen of the carboxylic group would not be replaced by sodium metals.

2.33g (0.01mol) of sodium 4-hydrocarboxy-2-nitroterephthalate was dissolved in 25 mL of hot distilled water to which an aqueous solution (25 mL) of 2.50g (0.01mol) CuSO₄.5H₂O was added with continuous stirring and then left at room temperature. After a few days, bluish-colored prismatic crystals settled down. The crystals were filtered and dried in a desiccator over anhydrous ca₂ to a constant weight.

Yield 81.18%.

The elemental analysis C₁₆H₁₆CuN₂O₁₆ Calculated%: C; 34.53, H; 2.88, N; 5.04 Found%: C; 34.73, H; 2.65, N; 4.96.

SC-XRD of Cu-DNTA

The crystal structure of both compounds is determined by SC-XRD technique. Experimental details are listed in Table 1.

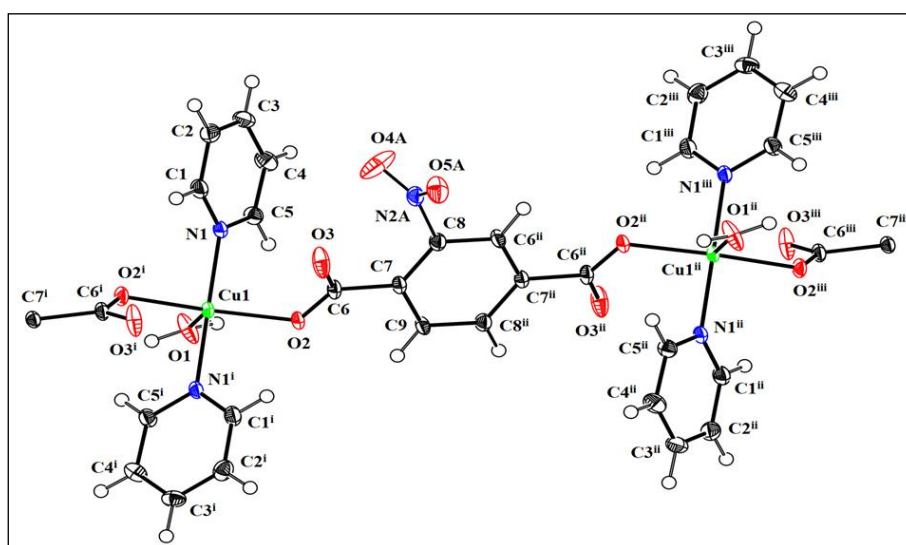
Table 1: SC-XRD experimental details of Cu-DNTA.

Crystal Parameters	Cu-DNTA
Chemical formula	C ₁₈ H ₁₅ CuN ₃ O ₇
CCDC	2192299
<i>M_r</i>	231.67
Crystal system, space group	Monoclinic, C ₂ /c
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	15.0291 (13), 5.8680 (5), 21.9408 (18)
<i>α</i> , <i>β</i> , <i>γ</i> (°)	90, 104.359 (3), 90
<i>V</i> (Å ³)	1874.5 (3)
<i>Z</i>	4
Radiation type	Mo K α
μ (mm ⁻¹)	1.213
Crystal size (mm)	0.25 × 0.20 × 0.03
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2007)
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	16281, 3432, 2427
<i>R</i> _{int}	0.113
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.759
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.051, 0.104, 1.05
No. of reflections	3432
No. of parameters	150
No. of restraints	-
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.53, -0.74

(i) $-x+1/2, -y+5/2, -z+1/2$. The central Cu-atom is coordinated by four water molecules and two non-chelating 4-carboxy-2-nitrobenzoate. The coordination sphere around Cu-atom consists of four O-atoms from the waters and two O-atoms from the two non-chelating 4-carboxy-2-nitrobenzoate.

In coordination sphere, the bond lengths range from 1.9219 (11) to 2.5164 (11) Å and bond angles range from 87.34 (5)° to 180.0° (Table 1) which indicates that the coordination geometry is slightly distorted octahedral. The phenyl ring A makes the dihedral angle of 41.9 (1)°, 5.9 (2)° and 47.3 (9)° with the first carboxylate group B (C1/O4/O5), second carboxylate group C (C8/O5/O6) and nitro group C (N1/O7/O8), respectively.

The crystal structure of Cu-DNTA (Figure 1, Table 1) is a one dimensional polymeric form that extend along *c*-axis. The central Cu-atom is penta coordinated by the O-atom of the non-chelating 2-nitroterephthalate ligand, N-atom of pyridine ring and O-atom of water. The important bond lengths and bond angles are listed in Table 1. In order to find the coordination geometry, the value of geometry index τ_s is calculated. The value of τ_s is zero and one for the square pyramidal geometry and trigonal bipyramidal geometry. For Cu-DNTA, the value of the geometry index is 0.00066 which indicates that the geometry is square pyramidal with the oxygen atom (O1) occupy axial site. The Cu-atom is deviated by 0.122 Å from the basal plane defined by (N1/N1¹/O2/O2¹) atoms. 5.8682(14)Å.

**Fig 1:** ORTEP diagram of Cu-DNTA that is drawn at a probability level of 50%

H-atoms are shown by small circles of arbitrary radii. The major part of the disordered nitro group and disordered hydrogen attached to the carbon atom (C8) are shown for clarity.

The synthesized complex of bis-(2nitroterephthalato) di-(pyridine) Cu(2) tetrahydrate was applied to two grape varieties: Merlo and Madrasa. An active effect of this complex compound on *Plasmopara viticola* was established

[5]. After the application of this compound, the residual amount of copper in grape varieties was determined by Atomic absorption spectroscopy. Below are the absorbances of quantitative analysis of copper after using the synthesized complex of Bis-(4-hydrocarboxy-2-nitroterephthalate) Cu (II) tetrahydrate:

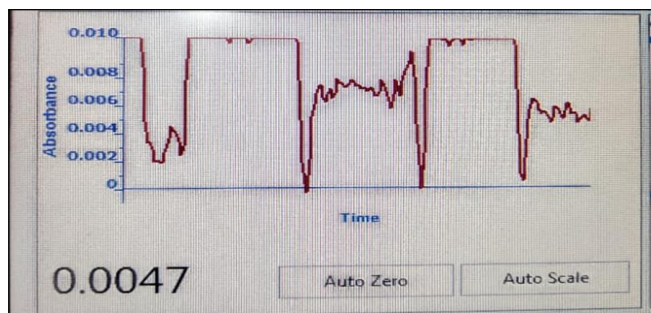


Fig 2: The absorbance of residual amount of copper in grape variety Merlo after using the synthesized complex



Fig 3: The absorbance of residual amount of copper in grape variety Merlo after using the Bordo compound

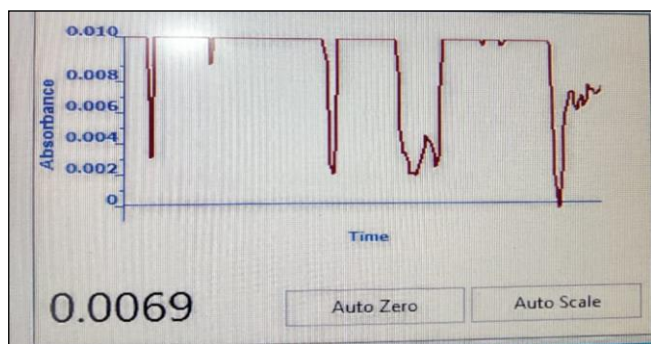


Fig 4: The absorbance of residual amount of copper in grape variety Madrasa after using the synthesized complex

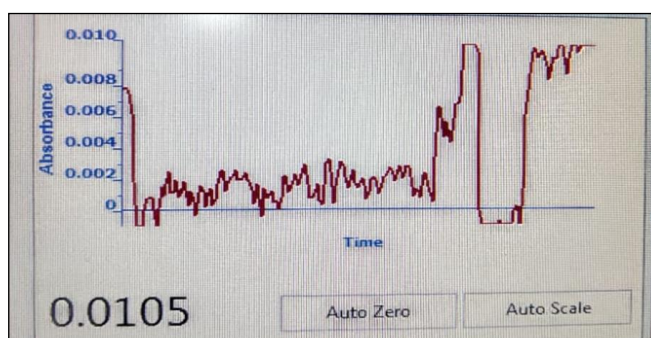


Fig 5: The absorbance of residual amount of copper in grape variety Madrasa after using the Bordo compound

Table 2: The residual amount of copper in grape variety Merlo and Madrasa

Variety of grapes	With complex of copper	Without of complex of copper
Madrasa	0.0069 ppm	0.0107 ppm
Merlo	0.0047ppm	0.0105 ppm

Conclusion

In the paper two grape varieties – merlot and madrasa from the grape sites of the Ganja-Gazakh zone of Azerbaijan are studied, and the residual amount of copper is determined in the considered samples. An active effect of bis-(2-nitroterephthalate)-di-(pyridine) Cu (II) monohydrate compound on *Plasmopara viticola* was established. Analysis of the quantitative determination of copper is carried out in the considered samples. Qualitative determinations of copper in grapes after using Cu-DNTA are lower than in grape varieties after the application of the Bordeaux blend.

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