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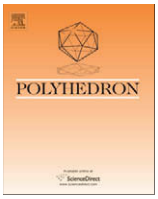

Synthesis, crystal structure, spectral and thermal characterization of bis(*o*-vanillinato)-triethylenglycoldiiminecopper(II) and bis[(R)-(−)-hydroxymethylpropylimine *o*-vanillinato]copper(II)

Figen Arslan [a], Mustafa Odabaşoğlu [b,*], Halis Ölmez [c], Orhan Büyükgüngör [d]

[a] *Department of Chemistry, Faculty of Arts and Sciences, Karabük University, TR78050 Karabük, Turkey*
[b] *Chemistry Program, Denizli Higher Vocational School, Pamukkale University, TR20159 Denizli, Turkey*
[c] *Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayis University, TR55139 Samsun, Turkey*
[d] *Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, TR55139 Samsun, Turkey*

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ABSTRACT

The novel complexes bis(*o*-vanillinato)-triethylenglycoldiiminecopper(II) (**1**) and bis[(R)-(−)-hydroxymethylpropylimine *o*-vanillinato]copper(II) (**2**) have been synthesized and characterized by elemental analysis, magnetic susceptibility, spectral methods (UV–Vis and FT-IR), simultaneous TG, DTA techniques and X-ray diffraction. The crystal structure of (**1**) determined that the Cu atom is coordinated by two imine N atoms and two phenol O atoms from the Schiff base ligand in a slightly distorted square-planar coordination. The *o*-vanillinato ligands moieties of the molecule are in a *trans* configuration and the dihedral angle between the aromatic ring planes is 43.97(14)°. Compound (**2**) crystallizes in the triclinic space group $P\bar{1}$ with unit-cell parameters $a = 8.054(7)$, $b = 8.684(7)$, $c = 10.258(8)$ Å, $\alpha = 79.452(6)°$, $\beta = 70.454(6)°$, $\gamma = 65.427(6)°$ and $Z = 1$. The crystal structure of (**2**) has indicated that the complex is slightly distorted square planar and is chelated by the two imine N atoms and two phenol O atoms from the Schiff base ligand. The *o*-vanillinato ligands moieties of (**2**) are in a *trans* configuration and the torsion angle between the aromatic ring planes is 60.5(3)°. The crystal packing involves both hydrogen-bonding and C–H···π interactions. Thermal analyses showed that the title compounds decompose in two stages over the temperature range 20–1000 °C in a static air atmosphere.

1. Introduction

Schiff bases have been used extensively as ligands in the field of coordination chemistry [1–5]. Chelating ligands containing O and N donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions [6]. Recent years have witnessed a great deal of interest in the synthesis and characterization of transition metal complexes containing Schiff bases as ligands due to their application as catalysts for many reactions [7–9], their relationship to synthetic and natural oxygen carriers [10] and also their use as new structural probes in nucleic acid chemistry and as therapeutic agents [11–14]. There is considerable interest in Schiff base ligands and their complexes in respect of their striking anticancer [15,16], antibacterial [17], antiviral [18], antifungal [19] and other biological properties [20,21]. Coordination complexes involving tetradentate (quadradentate) Schiff base ligands, abbreviated as H_2SB, have been studied extensively for more than 50 years [22]. Copper Schiff base complexes play an important role in both synthetic and structural research because they are useful stereochemical models in catalytic chemistry as a result of their preparative accessibility and structural variety [23]. The present study reports on bis(*o*-vanillinato)-triethylenglycoldiiminecopper(II), that was obtained by the reaction of *trans*-bisaquabis(*o*-vanillinato)copper(II) and 1,8-diamino-3,6-dioxaoctane, and bis[(R)-(−)-hydroxymethylpropylimine *o*-vanillinato]copper(II), that was obtained by the reaction of *trans*-diaquabis(*o*-vanillinato)copper(II) and (R)-(−)-2-amino-1-butanol. The aim this work was to prepare new *o*-vanillin Schiff base complexes with copper(II) and to characterize them by elemental analysis, magnetic susceptibility, UV–Vis, FT-IR spectroscopy, TG, DTA techniques and X-ray diffraction analysis.

2. Experimental

2.1. Preparation of the complexes

2.1.1. Synthesis of trans-bisaquabis(o-vanillinato)copper(II)

o-Vanillin (2.00 mmol, 0.30 g), dissolved in ethanol (50 ml), was added to a ethanol solution (50 ml) of copper acetate monohydrate (1.00 mmol, 0.19 g). The mixture was refluxed for 3 h, allowed to cool and then the solvent was removed. The resulting green

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* Corresponding author. Tel.: +90 258 212 37 88; fax: +90 258 211 80 65.
E-mail address: mustafaodabasoglu@gmail.com (M. Odabaşoğlu).

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powder was recrystallised in ethanol. Yield for the complex 90%, m.p. 249–251 °C. Elemental analysis, *Anal.* Calc. for $C_{16}H_{18}O_8Cu$: C, 47.82; H, 4.51. Found: C, 47.35; H, 4.78%.

2.1.2. Synthesis of (**1**) and (**2**)

Trans-bisaquabis(*o*-vanillinato)copper(II) (1 mmol, 0.4 g), dissolved in methanol (100 ml), was added dropwise with stirring at 50 °C to a suspension of 1,8-diamino-3,6-dioxaoctane (1 mmol, 0.15 g) or (R)-(−)-2-amino-1-butanol (2 mmol, 0.09 g) in methanol. The reaction mixture was then cooled to room temperature. The dark green crystals formed were filtered and washed with 10 ml of acetone. Yield: 68%, m.p. 184 °C for (**1**) and yield: 77%; m.p. 163 °C for (**2**).

Table 1
Crystal data and structure refinement parameters of (**1**) and (**2**).

	(**1**)	(**2**)
Formula	$C_{22}H_{26}N_2O_6Cu$	$C_{24}H_{32}N_2O_6Cu$
Molecular weight	477.99	508.07
T (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
Crystal system	trigonal	triclinic
Symmetry space group name H–M	$R\bar{3}$	$P\bar{1}$
Symmetry int tables number	148	1
Unit cell dimensions		
a (Å)	30.105(3)	8.054(7)
b (Å)	30.105(3)	8.684(7)
c (Å)	12.3204(11)	10.258(8)
α (°)	90.00	79.452(6)
β (°)	90.00	70.454(6)
γ (°)	120.00	65.427(6)
V (Å³)	9669.9(16)	613.97(9)
Z	18	1
Calculated density (Mg m^{-3})	1.477	1.374
μ (mm^{-1})	1.058	0.930
F (0 0 0)	4482	267
Crystal size (mm)	0.260 × 0.190 × 0.140	
θ Range	1.35–26.07	2.6–29.5
Index ranges	$-36 \leqslant h \leqslant 36$	$-11 \leqslant h \leqslant 11$
	$-21 \leqslant k \leqslant 36$	$-11 \leqslant k \leqslant 11$
	$-13 \leqslant l \leqslant 15$	$-814 \leqslant l \leqslant 13$
Independent reflections	4147	13962
Reflections observed (>2*σ*)	1883	12888
Goodness-of-fit (GOF) on F^2	0.810	0.94
R, R_w [$I > 2\sigma(I)$]	0.0402, 0.0749	0.037, 0.086
R_{int} indices (all data)	0.0738	0.036, 0.085

Elemental analysis (%): *Anal.* Calc. for $C_{22}H_{26}N_2O_6Cu$ (**1**): C, 55.28; H, 5.48; N, 5.86. Found: C, 55.67; H, 5.34; N, 5.41%. *Anal.* Calc. for $C_{24}H_{32}N_2O_6Cu$ (**2**): C, 56.74; H, 6.35; N, 5.51. Found C, 56.67; H, 6.04; N, 5.28%.

2.2. Materials and measurements

Elemental analyses were performed by standard methods at TÜBİTAK (The Turkish Scientific Research Centre). The UV–Vis spectra were obtained for the methanol solution of the title complexes with a Unicam UV2 spectrometer in the range 900–200 nm. The IR spectra were recorded on a Jasco 430 FT/IR spectrophotometer using KBr pellets and operating at 4000–200 cm^{-1}. Magnetic susceptibility measurements at room temperature were performed using a Sherwood Scientific MXI model Gouy magnetic balance. A TG8110 thermal analyzer was used to record simultaneous TG and DTA curves in static air atmosphere at a heating rate of 10 K min^{-1} in the temperature range 20–1000 °C using platinum crucibles. Highly sintered α-Al_2O_3 was used as a reference and the DTG sensitivity was 0.05 mg s^{-1}.

2.3. Crystallographic analyses

For (**1**) and (**2**), all H atoms were refined using a riding model for C–H bonds with d(C–H) = 0.93–0.97 Å. The U_{iso} values for these H atoms were assigned to 1.2U_{eq}(C) [1.5U_{eq}(methyl C)]. A summary of the crystallographic data, experimental details and refinement results for (**1**) and (**2**) are given in Table 1.

Data collection: Stoe X-AREA [24]; cell refinement: Stoe X-AREA [24]; data reduction: Stoe X-RED [24]; program used to solve structures: SHELXS-97 [25]; program used to refine structures: SHELXL97 [25]; molecular graphics: ORTEP-3 for Windows [26]; software used to prepare material for publication: WINGX [27].

3. Results and discussion

3.1. UV–Vis spectra and magnetic properties

The electronic spectrum was measured at room temperature in methanol (10^{-4} M) for the dark green complex bis(*o*-vanillinato)-triethylenglycoldiiminecopper(II) (**1**), and it exhibited two absorption bands. The bands at 370 nm (ε = 9101 L mol^{-1} cm^{-1}) and 472 nm (ε = 1556 L mol^{-1} cm^{-1}) have been assigned to $\pi \rightarrow \pi^*$

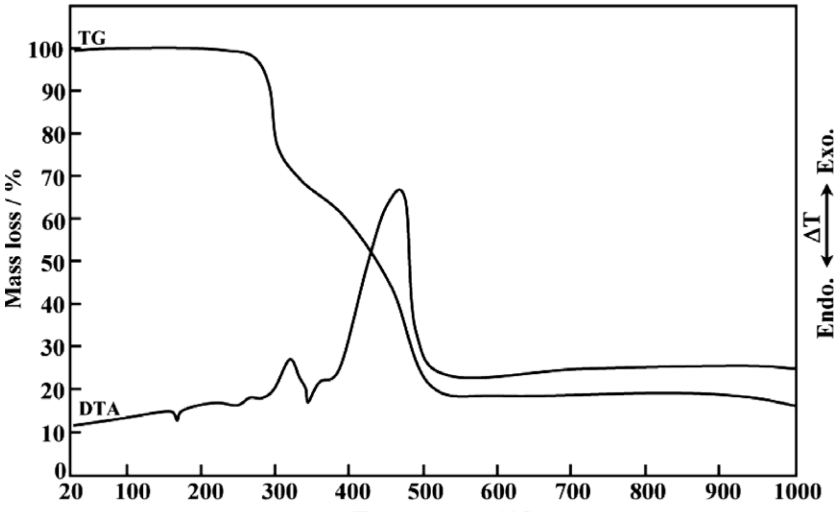

Fig. 1. TG and DTA curves of (**1**).