

Synthesis, Crystal Structure and Spectroscopic Studies of a Mixed Ligand Copper (II) Complex: *trans*-Bis(succinimidato)-bis(benzylamino)Cu(II)

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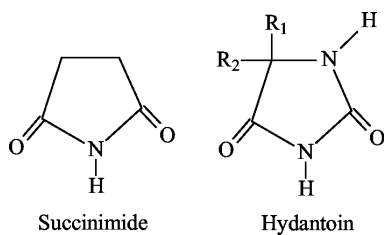
Z. Naturforsch. **61b**, 979–982 (2006); received December 28, 2005

The molecules of the title compound, $[\text{Cu}(\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_2)_2]$, lie across centres of inversion in space group $P2_1/c$ and are linked by intermolecular $\text{N-H}\cdots\text{O}$ and $\text{C-H}\cdots\text{O}$ hydrogen bonds. The central Cu atom has a slightly distorted square-planar coordination comprised of four N atoms. Cu–N bond distances are 1.975(2) and 2.020(2) Å. The interplanar angle between the phenyl and succinimidato ring is $87.34(10)^\circ$.

Key words: Succinimide, Succinimidato, Mixed Ligand Complex

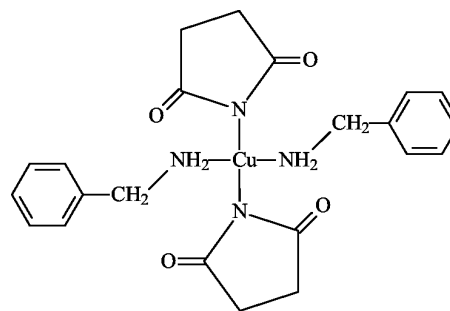
Introduction

The complexes of transition metals with five-membered heterocyclic imidate ligands such as hydantoin or succinimide (pyrrolidine-2,5-diones) (Scheme 1) possessing more than one donor atom, are of great interest in the chemistry of coordination compounds, since they can act either as neutral molecules or deprotonated as monoanions [1]. Imidate ligands are generally monodentate ligands having a deprotonated nitrogen atom.



Scheme 1. Imide ligands.

Various Cu(II) complex having imidate ligands have been synthesized and their crystal structures have been determined [2–8]. Especially, Akitsu *et al.* studied succinimide and 5,5-diphenylhydantoin complexes



Scheme 2. The structure of the title complex.

of copper(II) having alkyl amine ligands. The authors reported only $\text{N-H}\cdots\text{O}$ inter- and intra-molecular hydrogen bonds for these molecules. However, the complexes of imidates and alkylamines with aromatic substituents can also have other hydrogen bond systems. Therefore, the crystal structure determination of the title complex (Scheme 2) was carried out to search for different hydrogen bond interactions. The results are compared with those found in the related complex *trans*-bis(succinimidato)-bis(1,2-diphenylethylamine) copper(II) [4]. We also studied the IR spectra and the r. t. magnetic susceptibility of the title complex.

Experimental Section

Materials and measurements

Succinimide, benzylamine, and copper(II) acetate monohydrate were commercially available and were reagent grade. FT-IR spectra (4000–200 cm^{-1}) were recorded on a Jasco-430 FT-IR spectrophotometer with samples prepared as KBr pellets. The magnetic susceptibility of the complex was measured using a Sherwood scientific MX1 model Gouy magnetic susceptibility balance at r. t.

The crystal data were collected using ω - 2θ scan techniques on a Stoe IPDS-2 diffractometer with a graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Software programs used for data collection and cell refinement: X-Area [9]; for data reduction: X-RED32 [9]; to solve structure: SHELXS97 [10]; to refinement of structure: SHELXL97 [10]; for molecular graphics: ORTEPIII [11]; to prepare material for publication: WinGX [12].

Preparation of the complex

To a solution of copper(II) acetate monohydrate (0.499 g, 2.5 mmol) and succinimide (0.495 g, 5 mmol) in water (30 ml), benzylamine (0.54 g, 5 mmol) was added slowly and a light reddish-brown solid was precipitated. The mixture was stirred for 1 h at 50 °C. The solid was dissolved with the addition of a small amount of absolute ethanol to give a deep blue solution at 50 °C. The solution was slowly cooled to r. t. Light reddish-brown needles precipitated, were filtered and dried on air (Yield: 76.4%). FT-IR (KBr): $\bar{\nu} = 3259 - 3157 \nu(\text{NH}_2)$, $1770 \nu(\text{C=O})$, $1455 \nu(\text{C-N})$, $603 - 572 \nu(\text{Cu-N}) \text{ cm}^{-1}$. $\text{C}_{22}\text{H}_{26}\text{N}_4\text{O}_4\text{Cu}$ (474.01): calcd. C 55.75, H 5.53, N 11.82; found C 55.79, H 5.48, N 11.78

The complex exhibits an experimental magnetic moment of 1.82 BM corresponding to one unpaired electron.

Results and Discussion

Molecular structure of the complex

Crystallographic data of the title complex (Scheme 2) are summarized in Table 1. Selected bond lengths, angles and hydrogen bond geometries are listed and compared with data of *trans*-bis(succinimidato)-bis(1,2-diphenylethylamine)copper(II) in Table 2. The molecular structure and intra- and inter-molecular hydrogen bonds are shown in Figs. 1 and 2, respectively.

As the related complex, the title compound (Scheme 2) consists of benzylamine and succinimide moieties linked to the Cu atom. The copper ion in the complex lies in the center of a slightly distorted square-planar coordination, with N(2) of the benzylamine and N(1) of the pyrrolidine-2,5-dione (succinimidato). The

Table 1. Crystal data and structure refinement for the $[(\text{C}_{22}\text{H}_{26}\text{N}_4\text{O}_4)\text{Cu}]$.

Formula	$\text{C}_{22}\text{H}_{26}\text{N}_4\text{O}_4\text{Cu}$
Molecular weight	474.01
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	11.6302(10)
b [Å]	5.0138(3)
c [Å]	19.1276(18)
β [°]	99.020(7)
V [Å ³]	1101.57(16)
Z	2
D_{calc} [g/cm ³]	1.429
$F(000)$	494
μ (Mo- $K\alpha$) [Å]	0.71073
θ_{max} [°]	27.13
Crystal dimensions [mm]	0.400 × 0.303 × 0.303
Temperature [K]	293(2)
Number of measured reflections	12122
Number of unique reflections	9534
Number of reflections used in refinement	2405
Number of parameters	142
Goodness-of-fit	1.03
Final R indices $ F ^2 > 2\sigma(F ^2)$	$R_1 = 0.042$; $wR_2 = 0.103$
R indices (all data)	$R_1 = 0.060$; $wR_2 = 0.111$

Table 2. Selected interatomic distances (Å) and angles (°) for the title and related complex.

	Title complex	Related complex		
<i>Bonds:</i>				
Cu(1)-N(1)	1.976(2)	1.961(3)		
Cu(1)-N(2)	2.019(2)	2.032(4)		
O(1)-C(1)	1.222(4)	1.220(5)		
O(2)-C(4)	1.228(4)	1.225(4)		
N(1)-C(1)	1.359(4)	1.367(5)		
N(1)-C(4)	1.361(4)	1.371(5)		
N(2)-C(5)	1.481(4)	1.485(5)		
N(2)-H(1N)	0.80 (4)	0.89 (4)		
N(2)-H(2N)	0.83 (4)	0.89 (4)		
<i>Angles:</i>				
N(1)-Cu(1)-N(2)	90.6(1)	88.5(1)		
N(1)-Cu(1)-N(2) ⁱ	89.4(1)	91.5(1)		
N(1)-Cu(1)-N(1) ⁱ	180.0(2)	180		
N(2)-Cu(1)-N(2) ⁱ	180.0(2)	180		
<i>Hydrogen bonds:</i>				
D-H [Å]	H...A [Å]	D...A [Å]	D-H...A [°]	
C(5)-H(5B)...O(1)	0.97	2.82	3.567(4)	134.8
C(5)-H(5A)...O(2) ⁱ	0.97	2.75	3.615(5)	149.5
N(2)-H(2N)...O(2) ⁱⁱ	0.83(4)	2.19(4)	3.009(3)	171(3)
N(2)-H(1N)...O(1) ⁱⁱⁱ	0.80(4)	2.23(4)	3.031(4)	177(3)
C(2)-H(2B)...O(1) ^{iv}	0.97	2.53	3.413(4)	151.80
C(8)-H(8)...O(2) ^v	0.93	2.65	3.537(5)	159.8
C(11)-H(11)...O ⁱⁱⁱ	0.93	2.79	3.511(4)	134.8

ⁱ $1-x, -y, -z$; ⁱⁱ $1-x, 1-y, -z$; ⁱⁱⁱ $x, 1+y, z$; ^{iv} $1-x, 1/2+y, 1/2-z$, ^v $1+x, y, z$.

N(2)ⁱ and N(1)ⁱ atoms are related by symmetry [code: (i) $1-x, -y, -z$] (Fig. 1).

Succinimidato and benzylamine groups function as monodentate ligands, similar to the situation in the re-

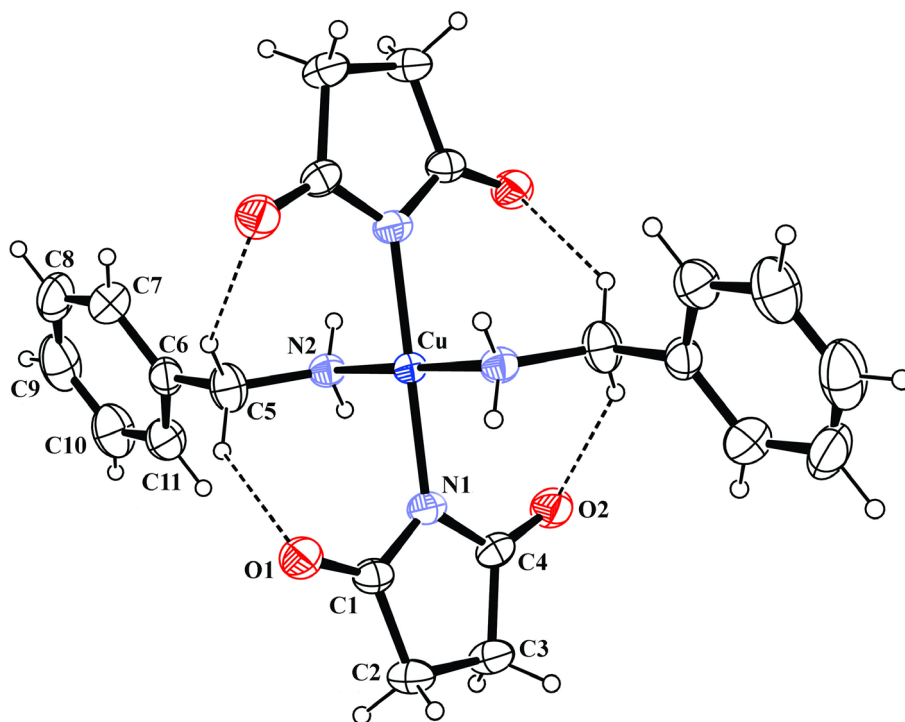


Fig. 1. The intramolecular H-bonds and the Ortep-III diagram with 30% probability ellipsoids of the title complex.

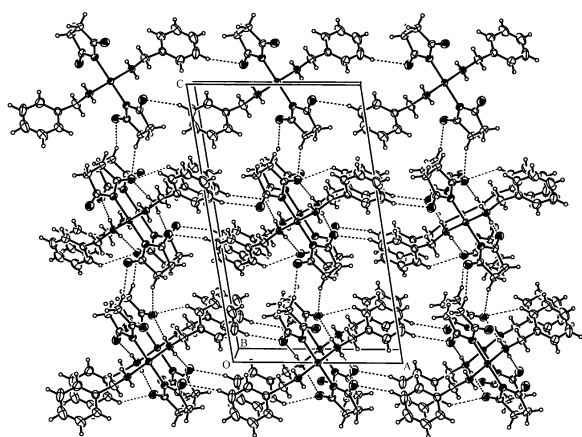


Fig. 2. Intermolecular hydrogen bonds in the title complex.

lated complex. Cu-N(1) bond distances are 1.976(2) and Cu-N(2) bond distances are 2.019(2) Å. The interplanar angle between the phenyl and the succinimidato (pyrrolidine-2,5-dione) ring is 87.34(10)°; *i.e.* these rings are nearly perpendicular to each other. The rings have an approximately planar structure, with the largest deviation from the plane being that of atom C(3) [−0.027(3) Å]. Cu-N_{amine} [2.019(2) Å] bond lengths are slightly shorter and Cu-N_{imidate}

[1.976(2)] bond lengths are slightly longer than this in the reference complex [2.032(4) and 1.961(3) Å, respectively] [4]. The *cis*-N-Cu-N bond angles are 89.4(1) and 90.6(1)° and the *trans*-N-Cu-N angles are 180.0(2)° for the title complex (Fig. 1). The corresponding bond angles are 88.5(1), 91.5(1) and 180° for the related complex [4]. Akitsu *et al.* reported only one type of hydrogen bonds which is formed between an amine hydrogen atom of 1,2-diphenylethylamine and a carbonyl oxygen atom of the succinimidato ligand for the related complex [4]. The N(2)-H(2N)···O(2) intramolecular hydrogen bond angle was reported as 133° and the bond length was reported as 2.966(4) Å [4]. No intermolecular hydrogen bonds have been reported this reference complex [4].

The possibility of hydrogen bonds was explored for the title complex by the statistical criterion proposed by Taylor and Kenrad [13]. Two of four possible N-H···O and five C-H···O hydrogen bonds have been detected (Fig. 2, Table 2). The N(2) atom of benzylamine at (*x*, *y*, *z*) acts as a hydrogen bond donor, *via* the H(1N) atoms, to an O(1) atom of a succinimidate at (*x*, 1 + *y*, *z*) and *via* the H(2N) atom to the O(2) atom of the succinimidate at (1 − *x*, 1 − *y*, −*z*), so generating by translation two different chains running approx-

imately parallel to the [010] direction. In this way, the special position of the Cu(II) ion is centered at $(m + 1/2, n + 1/2, k)$ and $(m + 1/2, n, k + 1/2)$ (where m , n and k independently take the value zero and integer). Also, the C(2) atom of the succinimidato ring acts as a hydrogen bond donor, *via* the H(2B) atom to the O(1) atom of the succinimide ligand at $(1 - x, 1/2 + y, 1/2 - z)$. The benzene ring acts as a hydrogen bond donor *via* C(8)-H(8) to O(2) of the succinimide at $(1 + x, y, z)$. So, C-H...O bonds result in the formation of sheets of molecules lying parallel to the (100) axis, and the N-H...O bonds link the sheets of molecules to each other. In addition, C(11) acts as a hydrogen bond donor *via* H(11) to O(1) at $(x, 1 + y, z)$, and the C(2)-H(2B) atoms at $(1 - x, 1/2 + y, 1/2 + z)$ give intermolecular hydrogen bonds with an O(1) atom at $(x, 1 + y, z)$ (Fig. 2, Table 2).

The intramolecular hydrogen bond between N(2) of 1,2-diphenylethylamine and an oxygen atom of the succinimide ligand hydrogens occurs between C(5) of benzylamine and a carbonyl oxygen atom of the succinimide at $(1 - x, -y, -z)$ (Fig. 1, Table 2) as a difference from the related complex. The results obtained in this work indicate that there are significant differences in the molecular packing between the two complexes.

Ir spectra of the complex

The IR spectrum of succinimide reveals a band at 3450 cm^{-1} , ascribed to the N-H vibrations and a C=O peaks can be seen at 1770 cm^{-1} .

The N-H stretching vibration of the succinimide has disappeared in the complex, indicating deprotonation upon complex formation. Two new sharp peaks appear for the NH₂ group of benzylamine at 3259 and 3157 cm^{-1} . The peak for $\nu(\text{C}=\text{O})$ remains non-shifted indicating that the C=O unit is non-coordinated to the copper(II) ion. The $\nu(\text{C}-\text{N})$ mode at 1429 cm^{-1} for the succinimide is shifted to higher wave number and appears at 1455 cm^{-1} in the complex indicating thereby imidate formation and coordination to the metal ion [14]. Metal-nitrogen coordination bands were seen at $603 - 572 \text{ cm}^{-1}$.

Supplementary Data

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication No. CCDC 267836. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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