

Synthesis, Crystal Structure, Spectroscopic and Thermal Properties of a Novel Mixed Ligand Copper(II) Complex with 5,5-Dimethylhydantoin and Benzylamine

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The crystal structure of the newly synthesized complex, *trans*-aqua-bis(benzylamino)-bis(5,5-dimethylhydantoinato) copper(II) was determined by X-Ray single crystal data. The thermal analyses, FT-IR and magnetic susceptibility data are also presented. The complex crystallizes in the monoclinic system, space group *C*2. The complex features a distorted square pyramidal [CuN₄O] coordination with 5,5-dimethylhydantoinato, benzylamine and water ligands. The 5,5-dimethylhydantoinato anion is bonded to the copper(II) ion *via* its deprotonated N atom in the 3-position.

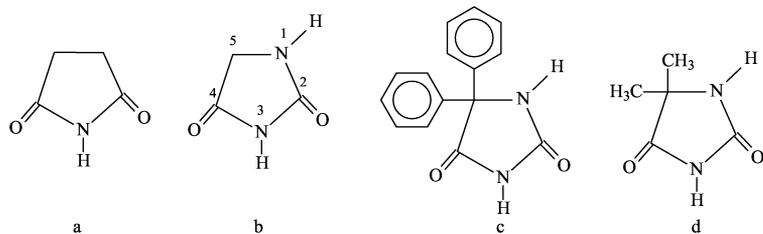
Key words: Hydantoin, Hydantoinato, 5,5-Dimethylhydantoin, Mixed Ligand Complex, Thermal Analyses

Introduction

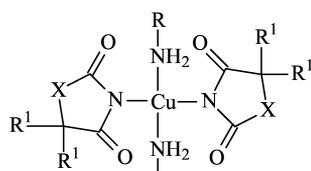
Hydantoin (2,4-imidazoline) is a compound in which an N-H replaced an CH₂ group of succinimide (Scheme 1 a) According to Oh *et al.*, the compound (2,4-imidazoline) (Scheme 1 b) was first discovered by Bayer in 1861 as a hydrogenation product of allantoin [1]. Since then hydantoin derivatives have been important intermediates in the synthesis of several amino acids. Due to their antimicrobial and anticonvulsant properties and their action against all types of epileptic form seizures they have been used with much clinical success [1–4]. Phenytoin (5,5-diphenylhydantoin) (Scheme 1 c), is another well-known hydantoin group of drug.

Complexes of transition metals with five-membered heterocyclic ligands such as hydantoin or succinimides (Scheme 1 a), possessing more than one donor

atom, are of great interest in the chemistry of coordination compounds. The ligands can act either as neutral molecules or deprotonated as monoanions [5]. As ligands, hydantoin (Scheme 1 b, c, d) contain several donor atoms and exhibit excellent coordination properties [6]. To date, various mixed ligand complexes of copper(II) having succinimide (Scheme 1 a) or phenytoin (Scheme 1 c) ligands and alkylamine ligands were prepared (Scheme 2) [7–10]. The X-ray data proved that the coordination to Cu(II) is realized *via* the endocyclic nitrogen atom N3 in Scheme 1 b, c, d of the monoanionic ligand (Scheme 2) [6–8]. The complexes have square planar [CuN₄] (reddish violet), distorted square planar [CuN₄] (blue-violet), and square pyramidal [CuN₄O] (blue) coordination geometries in the solid state and give deep blue or blue solutions accompanied by distinct spectral changes regardless of the structures in the solid states. The electronic and struc-



Scheme 1. a: Succinimide, b: hydantoin, c: 5,5-diphenylhydantoin, d: 5,5-dimethylhydantoin.

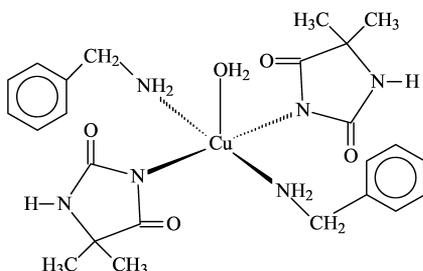


$R^1 = \text{H}$, $X = \text{CH}_2$, succinimide

$R^1 = \text{Phenyl}$, $X = \text{NH}$, 5,5-diphenylhydantoinate

$R = \text{Phanylalkyl}$

Scheme 2. Structure of the succinimide and 5,5-diphenylhydantoin complexes.



Scheme 3. The structure of the aqua-*trans*-bis-(benzylamino)-bis-(5,5-dimethylhydantoinato) copper(II) complex.

tural features of species in solutions have still not been elucidated [7].

In this work, we studied a mixed ligand copper(II) complex with 5,5-dimethylhydantoin (Scheme 1 d) and benzylamine (phenylmethylamine). Although, complexes of 5,5-diphenylhydantoin have been studied extensively, this is the first example of complexes of 5,5-dimethylhydantoin (Scheme 3).

Experimental Section

Materials and measurements

5,5-Dimethylhydantoin, benzylamine, and copper(II) acetate monohydrate were commercially available and were reagent grade. FT-IR spectra ($4000\text{--}200\text{ cm}^{-1}$) 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 room temperature. A Rigaku TG8110 thermal analyzer was used to record TG and DTA curves in static air atmosphere at a heating rate of 10 Kmin^{-1} in the temperature range of $20\text{--}1000\text{ }^\circ\text{C}$ using platinum crucibles. Highly sintered $\alpha\text{-Al}_2\text{O}_3$ was used as a reference.

The crystal data were collected using $\omega\text{-}2\theta$ scan techniques on a Stoe IPDS-2 diffractometer with a graphite-filtered $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Software programs used, for data collection and cell refinement:

Table 1. Crystal data and structure refinement for the $[\text{Cu}(\text{C}_5\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_7\text{H}_9\text{N})_2\text{H}_2\text{O}]$.

Empirical formula	$(\text{C}_{24}\text{H}_{34}\text{N}_6\text{O}_5)\text{Cu}$
Formula weight	550.11
Crystal dimensions /mm	$0.33 \times 0.30 \times 0.28$
Crystal shape	prism
Colour	blue-violet
Unit cell dimensions	$a = 19.2120 (13)\text{ \AA}$ $b = 5.6610 (3)\text{ \AA}$ $c = 24.5750 (15)\text{ \AA}$ $\beta = 96.143 (5)^\circ$
Volume	$2657.4 (3)\text{ \AA}^3$
Z	4
Crystal system, space group	monoclinic, $C2$
Density ρ_{calc}	1.375 g/cm^3
Absorption coefficient	0.87 mm^{-1}
Data collection	STOE IPDS 2 diffractometer
Temperature	$293 (2)\text{ K}$
Theta range	$1.67^\circ < \theta < 25^\circ$
Index ranges	$h = -22 \rightarrow 22$; $k = -6 \rightarrow 6$; $l = -29 \rightarrow 29$
Reflections collected	14182
Independent reflections	4682 ($R_{\text{int}} = 0.071$)
Reflections with $ F ^2 > 2\sigma(F ^2)$	4369
Flack parameter [20]	0.28(1)
Absorption correction	integration
$T_{\text{min}}, T_{\text{max}}$	0.763; 0.793
Restraints; parameters	4; 342
Largest diff. peak and hole [$\text{e}\text{\AA}^{-3}$]	0.36; -0.49
Final R indices $ F ^2 > 2\sigma(F ^2)$	$R_1 = 0.033$; $wR_2 = 0.078$
R indices (all data)	$R_1 = 0.035$; $wR_2 = 0.079$
Goodness-of-fit on $ F ^2$	1.017

X-AREA [11]; for data reduction: X-RED32 [11]; to solve structure: SHELXS97 [12]; to refinement structure: SHELXL97 [13]; for molecular graphics: ORTEPIII [14]; to prepare material for publication: WinGX [15].

Preparation of the complex

To a solution of copper(II) acetate monohydrate (0.50 g, 2.5 mmol) and 5,5-dimethylhydantoin (0.64 g, 5 mmol) in water (20 ml), benzylamine (0.54 g, 5 mmol) was added slowly and a blue solid was precipitated. The mixture was stirred for 1 h at $50\text{ }^\circ\text{C}$. The solid was dissolved with the addition of absolute ethanol to give a deep blue solution at $50\text{ }^\circ\text{C}$. The solution was cooled to room temperature. Blue-violet needles precipitated and were filtered and dried on air (Yield: 65.8%). FT-IR (KBr): $\tilde{\nu} = 3525\text{ } \nu(\text{N-H})$, $1697\text{--}1646\text{ } \nu(\text{C=O})$, 1465 and $1452\text{ } \nu(\text{C-N})$, $1608\text{ } \delta(\text{H}_2\text{O})$, $696\text{--}613\text{ } \nu(\text{Cu-N})$, $400\text{ } \nu(\text{Cu-O})\text{ cm}^{-1}$. $\text{C}_{24}\text{H}_{34}\text{N}_6\text{O}_5\text{Cu}$ (550.11): calcd. C 52.40, H 6.23, N 15.28; found C 52.59, H 6.37, N 15.35.

The complex is slightly antiferromagnetic with an experimental magnetic moment of 1.29 BM corresponding to one unpaired electron.

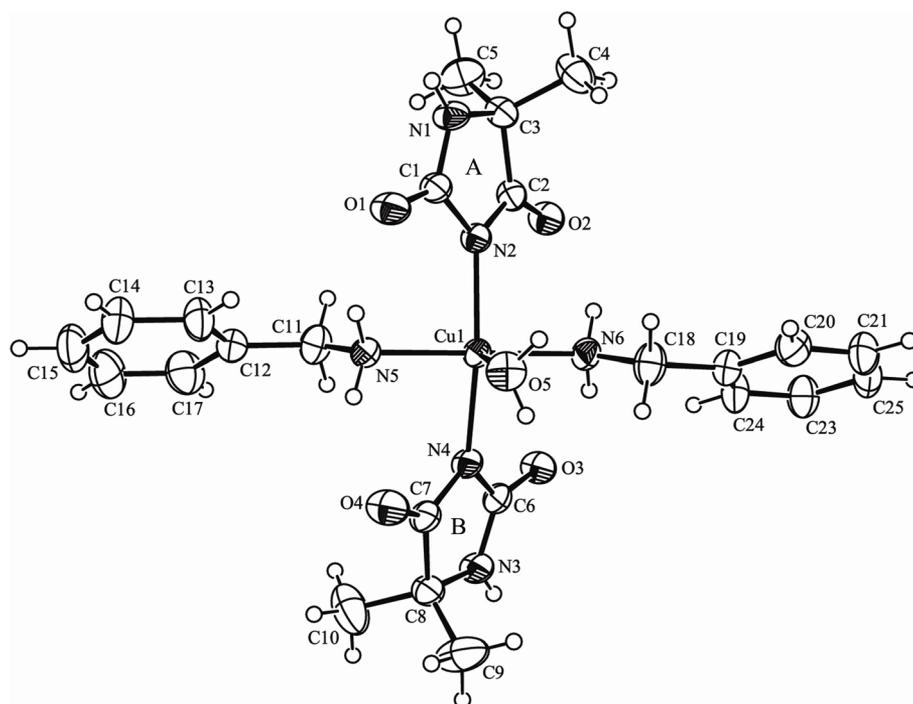


Fig. 1. ORTEP-III diagram with 40% probability ellipsoids of the aqua-*trans*-bis-(benzylamino)-bis-(5,5-dimethylhydantoinato) copper(II) complex.

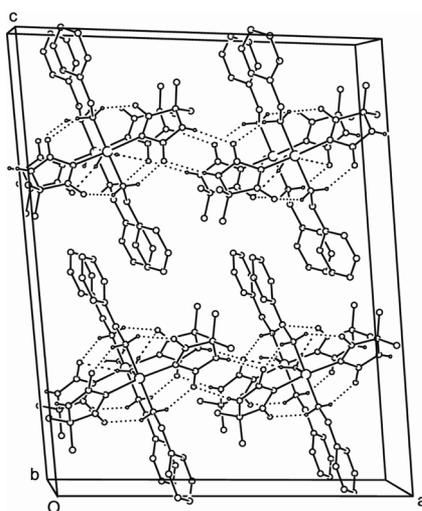


Fig. 2. Intra- and inter-molecular hydrogen bonds of the complex.

Results and Discussion

Molecular structure of the complex

Crystallographic data of the complex (Scheme 3) are summarized in Table 1. Selected bond lengths

and angles are listed and compared with data of 5,5-diphenylhydantoin complex in Table 2. Molecular structure and hydrogen bonds are shown in Figs 1 and 2, respectively.

The coordination around the Cu(II) atom is distorted square pyramidal [CuN₄O]. 5,5-Dimethylhydantoinato and benzylamine groups function as monodentate ligands, similar to the situation in related complexes having 5,5-diphenylhydantoinato and alkylamine ligands [7–10, 16]. The five-membered ring of the 5,5-dimethylhydantoinato group (A and B in Fig. 1) is nearly planar and the carbonyl O atoms lie in the plane. Maximum deviations were found for atom N(4) with 0.021(2) Å for ring A and for atom N(2) with –0.071(2) Å for ring B (Fig. 1). The 5,5-dimethylhydantoinato and benzylamine ligands are in *trans* positions at the basal plane of the pyramid, the water molecule is bonded to the metal atom in the axial position (Fig. 1).

In the basal coordination plane formed by the N atoms, the Cu–N distances are not equivalent and are in the range from 2.000(2) to 2.039(2) Å. According to CSD [17], the average Cu–N_{hyd} and Cu–N_{amine} bond lengths are 1.99 and 2.03 Å, respectively [7].

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

	Title complex	Related complex*
<i>Bonds:</i>		
Cu(1)-N(6)	2.037(2)	2.030(3)
Cu(1)-N(5)	2.000(2)	2.032(4)
Cu(1)-N(2)	2.039(2)	1.990(4)
Cu(1)-N(4)	2.025(2)	2.026(4)
N(2)-C(1)	1.400(3)	1.405(6)
N(2)-C(2)	1.352(4)	1.345(7)
N(1)-C(1)	1.332(4)	1.343(7)
N(1)-C(3)	1.450(4)	1.459(7)
N(3)-C(6)	1.321(4)	1.340(7)
N(3)-C(8)	1.457(4)	1.457(7)
N(4)-C(6)	1.387(4)	1.392(5)
N(4)-C(7)	1.367(4)	1.374(7)
O(1)-C(1)	1.236(3)	1.238(7)
O(2)-C(2)	1.232(3)	1.232(6)
O(3)-C(6)	1.252(3)	1.237(7)
O(4)-C(7)	1.228(3)	1.232(6)
Cu(1)-O(5)	2.371(2)	2.397(4)
<i>Angles:</i>		
N(5)-Cu(1)-N(4)	88.5(1)	89.2(2)
N(5)-Cu(1)-N(6)	176.4(1)	175.0(2)
N(4)-Cu(1)-N(6)	90.5(1)	93.7(2)
N(5)-Cu(1)-N(2)	89.5(1)	89.1(2)
N(4)-Cu(1)-N(2)	165.7(1)	163.5(2)
N(6)-Cu(1)-N(2)	90.6(1)	86.9(2)
N(5)-Cu(1)-O(5)	88.0(1)	91.9(1)
N(4)-Cu(1)-O(5)	95.7(1)	86.7(1)
N(6)-Cu(1)-O(5)	95.6(1)	92.2(1)
N(2)-Cu(1)-O(5)	98.3(1)	109.8(1)
N(6)-Cu(1)-N(5)-C(11)	-8.1(2)	58.6(4)
O(5)-Cu(1)-N(5)-C(11)	-178.5(2)	-154.2(5)

* (5,5-Diphenylhydantoinato)₂(2,2-diphenyl-ethylamine)₂Cu [16].

The *trans*-N_{hyd}-Cu-N_{hyd} and *trans*-N_{amine}-Cu-N_{amine} bond angles are 165.7(1) and 176.3(1)°, respectively (Table 2). N_{hyd}-Cu-N_{amine} bond angles lie between 88.5(1) and 90.6(1)° (Table 2). O(5)-Cu-N(2)_{hyd}, O(5)-Cu-N(4)_{hyd}, O(5)-Cu-N(5)_{amine} and O(5)-Cu-N(6)_{amine} bond angles are 98.3(1), 95.7(1), 88.0(1) and 95.6(1)°, respectively. While the dihedral angle between the two phenyl rings is 3.7(2)°, the dihedral angle between the two 5,5-dimethylhydantoinato planes is 11.7(1)°. It is clear that these planes are nearly parallel to each another. Owing to the steric interaction between the substituents the atoms N(2), N(5), N(4) and N(6) (Fig. 1) are not coplanar and the Cu atom also slightly deviates from this plane by -0.173(1) Å. The amine ligands are in the *E*-conformation (Fig. 1, Table 2). The C(1)-N(2)-C(2) and C(6)-N(4)-C(7) angles are 106.9(2) and 107.0(2)° and indicate *sp*² character of the deprotonated N(2) and N(4) atoms; the angles of O(1)-C(1)-N(2), O(2)-C(2)-N(2), O(3)-C(6)-N(4) and O(4)-C(7)-N(4) of 124.3(3), 126.1(3), 123.9(3), and

Table 3. Hydrogen-bonding geometry for the complex.

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
O(5)-H(10)...O(2) ⁱ	0.817(10)	2.141(15)	2.945(3)	168(5)
O(5)-H(20)...O(3) ⁱ	0.819(10)	2.29(2)	3.086(4)	163(6)
N(1)-H(1)...O(3) ⁱⁱ	0.76(3)	2.26(3)	3.023(3)	174(3)
N(3)-H(2)...O(1) ⁱⁱⁱ	0.70(3)	2.18(3)	2.861(4)	168(3)
N(5)-H(5A)...O(4)	0.90	2.04	2.828(3)	145.9
N(5)-H(5B)...O(1)	0.90	2.01	2.802(3)	146.7
N(6)-H(6A)...O(3)	0.90	2.04	2.850(3)	148.7
N(6)-H(6B)...O(2)	0.90	2.08	2.878(3)	146.9
C(16)-H(16)...Cg1 ^{iv}	0.930	3.173	3.784(6)	124.96
C(20)-H(20)...Cg2 ^v	0.930	3.029	3.655(4)	126.13

ⁱ $x, 1 + y, z$; ⁱⁱ $1/2 + x, 1/2 + y, z$; ⁱⁱⁱ $-1/2 + x, -1/2 + y, z$; ^{iv} $1/2 - x, -1/2 + y, -z$; ^v $1/2 - x, 1/2 + y, 1 - z$; Cg1: atoms [C(12)-C(17)] and Cg2: atoms [C(19)-C(24)].

126.6(3)°, respectively, also reflect electron delocalization in the π -conjugated system (Table 2) [10]. The Cu-N_{hyd} distances of the 5,5-dimethylhydantoin are longer than those of the 5,5-diphenylhydantoin in the complexes.

Hydrogen bonds link the molecular units into a two-dimensionally network (Table 3). In particular one may notice that the coordinated water molecule O(5) of unit x, y, z is bifurcated hydrogen bonded to carboxyl oxygen atoms O(2) and O(3) in unit $x, n + y, z$ (n is an integer) (Fig. 2). These hydrogen bonds result in the formation of polymeric chains along the (010) axis. Additionally, the nitrogen atoms N(1), N(3) act as donors for hydrogen bonds, giving rise to the formation of N-H...O intermolecular hydrogen bonds with carbonyl oxygen atoms O(3) in unit $1/2 + x, 1/2 + y, z$ and O(1) in unit $-1/2 + x, -1/2 + y, z$ (Table 3, Fig. 2). All these intermolecular interactions result in the formation of sheets of molecules lying parallel to the [110] axis. There are also intramolecular N-H...O hydrogen bonds formed between benzylamine hydrogen atoms and carbonyl oxygen atoms of the 5,5-dimethylhydantoinato ligands (Fig. 2). Similar intramolecular hydrogen bonds are also found in related distorted square planar [CuN₄] complexes [7–10, 16]. Therefore, intramolecular hydrogen bonds appear to play a supplementary role in stabilizing distorted square pyramidal [CuN₄O] complexes in the solid state (Fig. 2).

As different from related complexes, there are also weak C-H- π interactions in the molecular sheets. Intermolecular C-H- π interactions between the C(16)-H(16) group and the ring center of Cg1(C12-17) and between the C(20)-H(20) group and the ring center of Cg2(C19-24) are observed. These C-H- π interactions

link the sheets of molecules to each other (parameters summarized in Table 3).

IR spectra of the complex

5,5-Dimethylhydantoin shows two bands at 3527 and 3467 cm^{-1} for N-H stretching vibrations. The higher wave number band corresponds to the stretching vibration of the N(1)-H bond adjacent to a carbonyl group and the lower band is attributed to the N(3)-H bond surrounded by two carbonyl groups (Scheme 3 d) [18]. C=O vibrations of 5,5-dimethylhydantoin appear at 1770 and 1735 cm^{-1} as sharp and strong bands.

The distinction between O and N coordination of imides (succinimide and hydantoin) is not readily made by infrared spectra because shifts in $\nu(\text{C}=\text{O})$ may result either from coordination through carbonyl oxygen or from the deprotonation and coordination of the imide nitrogen atoms [19]. It is expected that coordination will occur preferentially through the deprotonated N(3) nitrogen atom [6, 19]. Coordination through the carbonyl oxygen and N(1) nitrogen atoms (Scheme 1 b–d) is inhibited by steric hindrance [19]. In the title complex $\nu(\text{C}=\text{O})$ appears at 1697–1646 cm^{-1} whereas it is seen at 1770 and 1735 cm^{-1} in free 5,5-dimethylhydantoin. The $\nu(\text{C}-\text{N}(1))$ mode at 1471 cm^{-1} for the 5,5-dimethylhydantoin shifts to lower wave numbers and appears at 1465 cm^{-1} indicating that the N(1) atom is non-coordinated, while the $\nu(\text{C}-\text{N}(3))$ mode at 1440 cm^{-1} for the 5,5-dimethylhydantoin shifts to higher wave number and appears at 1452 cm^{-1} in the complex indicating N^- formation and coordination *via* the N(3) atom [19]. The $\nu(\text{N}(3)\text{H})$ band (Scheme 1 d) appearing at 3467 cm^{-1} in the free 5,5-dimethylhydantoin should be absent in the spectrum of the complex, but this region is obscured by $\nu(\text{O}-\text{H})$ from coordinated water. After heating for 2 h at 110 $^{\circ}\text{C}$, there is no band for N(3)H and H_2O which indicates the removal of the proton of N(3) upon complex formation. The $\nu(\text{N}(1)\text{H})$ band at 3527 cm^{-1} in the free 5,5-dimethylhydantoin is seen at 3525 cm^{-1} as a shoulder next to the $\nu(\text{O}-\text{H})$ vibration in the complex. After heating for 2 h at 110 $^{\circ}\text{C}$ the shoulder sharpened as a peak. This result suggests that the proton of N(1) was not separated upon complex formation. The $\nu(\text{NH}_2)$ peaks of the benzylamine ligands are obscured by $\nu(\text{O}-\text{H})$ of coordinated water. As expected, after

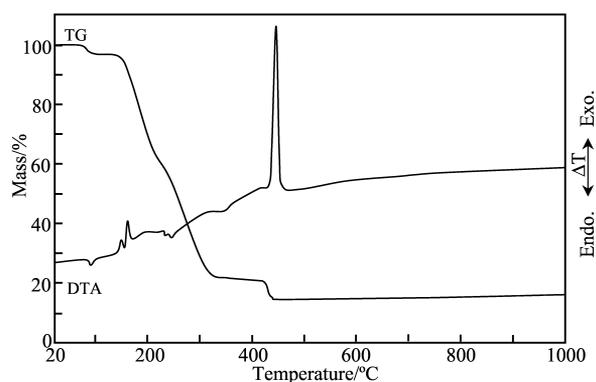


Fig. 3. TG and DTA curves of the complex.

heating the $\nu(\text{NH}_2)$ peak of benzylamine occurred at 3260–3150 cm^{-1} . The $\delta(\text{H}_2\text{O})$ peak at 1608 cm^{-1} for the complex suggests the presence of a coordinated water molecule inside the coordination sphere [19]. Metal nitrogen bond vibrations were seen at 696 and 613 cm^{-1} , and the metal oxygen bond vibrations at 400 cm^{-1} .

Thermal analyses of the complex

The title complex undergoes endothermic and exothermic decomposition in five stages (Fig. 3). The first stage in the range 80–138 $^{\circ}\text{C}$ is related to the endothermic removal (DTA_{max} 97 $^{\circ}\text{C}$) of 1 mole coordinated water (calcd. 3.28%; found 3.36%). The second stage between 139 and 217 $^{\circ}\text{C}$ is accompanied by a mass loss of 32.42% (calcd. 33.13%) and corresponds to the removal of two benzyl ($\text{C}_6\text{H}_5\text{-CH}_2$) radicals. In this stage, exothermic reactions take place at 159 and 165 $^{\circ}\text{C}$, and endothermic reaction occurs at 162 $^{\circ}\text{C}$, indicating the release of the benzyl radicals in parallel with melting and decomposition. At the third stage of decomposition between 217 and 269 $^{\circ}\text{C}$, the mass loss was found to be 5.53% (calcd. 5.82%), corresponding to endothermic removal of two NH_2 radicals. Immediately after this stage, in the region 269–351 $^{\circ}\text{C}$ the fourth stage of pyrolysis was accompanied by a mass loss of 35.67% and in the last stage, the organic residue was burned in a highly exothermic reaction between 351 and 470 $^{\circ}\text{C}$ (DTA_{max} 460 $^{\circ}\text{C}$; loss of weight: 8.28%). Total loss of weight in the fourth and fifth stages correspond to pyrolysing of 5,5-dimethylhydantoinato ligands (found 43.95%; calcd. 43.31%). In the fourth and fifth stages 85.26% of the complex are removed to leave CuO (calcd. 85.54%), identified by IR spectroscopy.

Supplementary Data

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication No. CCDC 276037. Copies of the data can be obtained, free of charge, on appli-

cation 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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