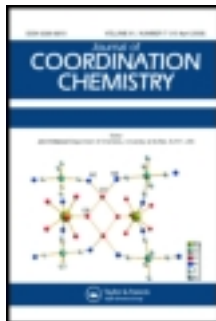


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COPPER CATALYZED HYDROLYSIS OF TRIAZINE: SYNTHESIS AND STRUCTURE OF $\text{Cu}(\text{HN} = \text{CHNHCH} = \text{NH})_2(\text{ClO}_4)_2$

Mark M. Turnbull^a, Ming Yi Wei^b & Roger D. Willett^b

^a Gustaf H. Carlson School of Chemistry, Clark University, Worcester, MA, 01610, USA

^b Department of Chemistry, Washington State University, Pullman, WA, 99164, USA

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COPPER CATALYZED HYDROLYSIS OF TRIAZINE: SYNTHESIS AND STRUCTURE OF $\text{Cu}(\text{HN} = \text{CHNHCH} = \text{NH})_2(\text{ClO}_4)_2$

MARK M. TURNBULL*

Gustaf H. Carlson School of Chemistry, Clark University, Worcester MA 01610, USA

MING YI WEI and ROGER D. WILLETT

Department of Chemistry, Washington State University, Pullman, WA 99164, USA

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Reaction of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with 1,3,5-triazine in 95% ethanol resulted in partial hydrolysis of the triazine ring and isolation of bis(1,3,5-triaza-1,4-pentadieno) copper(II) perchlorate, (1). Compound 1 crystallizes as violet needles. Crystal data for $\text{Cu}(\text{HN} = \text{CHNHCH} = \text{NH})_2(\text{ClO}_4)_2$ are: monoclinic, space group: C2/c , $a = 13.342(3)$, $b = 11.186(2)$, $c = 18.045(4)$ Å, $\beta = 99.09(3)^\circ$, $V = 2659.3(10)$ Å³, $Z = 8$, $D_{\text{calc}} = 2.021$ Mg/m³, $\mu = 2.096$ mm⁻¹, $F(000) = 1624$, MoK_α ($\lambda = 0.71069$ Å), $R = 0.063$ for 1597 unique observed [$|F| \geq 3\sigma(F)$] reflections and 196 parameters. The bis-chelated copper(II) ion contains a planar coordination geometry with $\text{Cu}-\text{N}_{(\text{ave})} = 1.97$ Å and the perchlorate ions weakly coordinated ($\text{Cu}-\text{O} = 2.84$ Å) in the axial positions.

KEYWORDS: triazine, copper, hydrolysis, crystal structure

INTRODUCTION

As a result of our interest in magnetic interactions in two-dimensional coordination lattices, we have been studying the coordination chemistry of a number of organic ligands with three-fold symmetry such as 1,3,5-triazine. Although the coordination chemistry of triazine has not been extensively investigated,¹ a number of complexes have been prepared.² Considerably more work has been done on the coordination chemistry of its pyridyl and pyrimidyl derivatives.³ For these complexes, coordination of an electrophile, such as H^+ or $\text{M}^{\text{n}+}$, catalyzes the hydrolysis of the triazine ring.⁴ The products isolated include coordinated formates and bis(heteroaryl)carbonyl amides, the expected products of ring hydrolysis. However, prior workers have not, to our knowledge, reported isolating the probable initial hydrolysis product of the triazine ring, 1,3,5-triazapentadiene. We describe here the Cu^{2+} catalyzed hydrolysis of 1,3,5-triazine and the isolation of the coordinated degradation product, 1,3,5-triaza-1,4-pentadiene.

* Author for correspondence.

EXPERIMENTAL

1,3,5-triazine was purchased from Aldrich Chemical and used without further purification. $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was purchased from Aesar and dried under vacuum prior to use. Ethanol refers to 95% ethanol. Infrared spectra were taken on a Perkin-Elmer 1330 spectrophotometer and calibrated against polystyrene. Elemental analyses were performed by the University Instrumentation Center, University of New Hampshire, Durham, NH.

$\text{Cu}(\text{HN} = \text{CHNHCH} = \text{NH})_2(\text{ClO}_4)_2$ (1) — triazine (0.41 g, 5.1 mmol) was dissolved in 15 mL of ethanol with stirring and a solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.85 g, 5.00 mmol) in 10 mL of ethanol was added dropwise through a glass wool plug (to remove traces of insoluble material). When the addition was complete a red-violet powder had formed which was recovered by filtration, washed with ethanol and air-dried to give 0.25 g (25%). The filtrate was left to evaporate to one-half its original volume. The resulting purple needles were collected by filtration to give an additional 0.30 g (30%, 55% total). Infrared spectroscopy showed them to be identical to the initial powder. *Anal.* Calcd. for $\text{C}_4\text{H}_{10}\text{Cl}_2\text{CuN}_6\text{O}_7$: C, 11.87; H, 2.49; N, 20.77. Found: C, 11.45; H, 2.64; N, 20.81. IR (KBr) ν 3360 sh, 3330 s, 3310 sh, 1690 s, 1540 s, 1435 ms, 1100 vs br, 620 m (cm^{-1}) [s = strong, m = medium, br = broad, sh = shoulder].

CAUTION: Although we have not encountered any difficulties in working with this compound, the potential for explosion with perchlorate salts is well documented.

X-ray Structure Determination

Data collection was carried out on a Siemens R3m/V diffractometer employing $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$) and a graphite monochromator. Three standard reflections were monitored every 97 reflections. The intensities of 3677 reflections were measured by using an omega scan (0.9° range) with speeds varying from 3 to $60^\circ/\text{min}$. Following the data reduction 3064 unique reflections remained, with 1597 having $|F| > 3\sigma$. The solution was obtained *via* direct methods. Final refinement gave $R = 0.0630$ and $R_w = 0.0512$ (all data; $R = 0.1268$, $R_w = 0.0607$). The final refinement included 196 least-squares parameters with a mean value of $|\Delta/\sigma| = 0.005$. The goodness of fit was 1.21. The hydrogen atoms were refined as a riding model with fixed isotropic U 's. An absorption coefficient of 2.096 mm^{-1} was calculated. All data reduction, structure solution and refinement, and graphics were performed by using SHELXTL PLUS (VMS) software. Crystallographic data may be found in Table 1. Atomic coordinates and isotropic thermal parameters are

Table 1 Crystallographic data for $\text{Cu}(\text{HN} = \text{CHNHCH} = \text{NH})_2(\text{ClO}_4)_2$ (1)

Formula: $\text{C}_4\text{H}_{10}\text{Cl}_2\text{CuN}_6\text{O}_7$	Space group: C2/c
Fw = 404.6	T = 295 K
$a = 13.342(3)\text{\AA}$	$\lambda = 0.71069\text{\AA}$
$b = 11.186(2)\text{\AA}$	$D_{\text{calc}} = 2.021 \text{ Mg/m}^3$
$c = 18.045(4)\text{\AA}$	$\mu = 2.096 \text{ mm}^{-1}$
$\beta = 99.09(3)^\circ$	
$V = 2659.3(10)\text{\AA}^3$	$R(F_o) = 0.0630$
Z = 8	$R_w(F_o) = 0.0512$

Table 2 Atomic coordinates and equivalent isotropic thermal parameters

for Cu(HN = CHNHCH = NH) ₂ (ClO ₄) ₂ (1)				
	x	y	z	U(eq)
Cu(1)	3772(1)	7295(1)	6219(1)	31(1)
N(11)	3705(5)	6340(6)	5309(3)	39(2)
C(12)	3743(6)	5219(7)	5253(4)	41(3)
N(13)	3801(5)	4437(5)	5824(4)	47(3)
C(14)	3783(7)	4750(8)	6560(5)	43(3)
N(15)	3787(5)	5788(6)	6802(3)	36(2)
N(16)	3823(5)	8786(6)	5640(3)	36(2)
C(17)	3790(7)	9848(7)	5869(5)	46(3)
N(18)	3704(6)	10158(6)	6589(4)	50(3)
C(19)	3690(6)	9388(8)	7160(4)	43(3)
N(20)	3763(5)	8281(6)	7116(3)	38(2)
Cl(2)	6419(2)	7673(2)	5882(1)	36(1)
O(21)	7397(5)	7181(6)	5864(3)	55(2)
O(22)	5912(4)	6987(6)	6396(3)	54(2)
O(23)	6511(5)	8891(5)	6124(3)	63(3)
O(24)	5831(5)	7617(5)	5143(3)	47(2)
Cl(1)	1142(2)	7565(2)	6655(1)	36(1)
O(11)	1624(5)	7100(6)	6059(3)	63(3)
O(12)	101(5)	7221(6)	6543(3)	67(3)
O(13)	1202(5)	8854(5)	6639(3)	69(3)
O(14)	1672(5)	7132(6)	7358(3)	52(2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 3 Selected bond lengths (Å) for Cu(HN = CHNHCH = NH)₂ (ClO₄)₂ (1)

Cu(1)–O(11)	2.843 (6)	Cu(1)–O(22)	2.844 (6)
Cu(1)–N(11)	1.948 (6)	Cu(1)–N(15)	1.986 (6)
Cu(1)–N(16)	1.975 (6)	Cu(1)–N(20)	1.961 (6)
N(11)–C(12)	1.260 (10)	C(12)–N(13)	1.344 (10)
N(13)–C(14)	1.378 (11)	C(14)–N(15)	1.241 (11)
N(16)–C(17)	1.261 (10)	C(17)–N(18)	1.368 (11)
N(18)–C(19)	1.344 (11)	C(19)–N(20)	1.246 (11)
Cl(2)–O(21)	1.421 (7)	Cl(2)–O(22)	1.452 (6)
Cl(2)–O(23)	1.430 (6)	Cl(2)–O(24)	1.437 (5)
Cl(1)–O(11)	1.436 (7)	Cl(1)–O(12)	1.423 (7)
Cl(1)–O(13)	1.445 (6)	Cl(1)–O(14)	1.436 (5)

Table 4 Selected bond angles (°) for Cu(HN = CHNHCH = NH)₂ (ClO₄)₂ (1)

N(11)–Cu(1)–N(15)	88.7(3)	N(11)–Cu(1)–N(16)	91.0(3)
N(15)–Cu(1)–N(16)	177.5(3)	N(11)–Cu(1)–N(20)	176.9(3)
N(15)–Cu(1)–N(20)	92.4(3)	N(16)–Cu(1)–N(20)	88.1(3)
Cu(1)–N(11)–C(12)	128.0(5)	N(11)–C(12)–N(13)	125.8(7)
C(12)–N(13)–C(14)	124.4(7)	N(13)–C(14)–N(15)	125.3(8)
Cu(1)–N(15)–C(17)	127.5(6)	Cu(1)–N(16)–C(17)	128.1(6)
N(16)–C(17)–N(18)	124.2(8)	C(17)–N(18)–C(19)	125.4(7)
N(18)–C(19)–N(20)	125.2(7)	Cu(1)–N(20)–C(19)	128.5(5)
O(21)–Cl(2)–O(22)	109.4(4)	O(21)–Cl(2)–O(23)	110.0(4)
O(22)–Cl(2)–O(23)	109.5(4)	O(21)–Cl(2)–O(24)	109.3(4)
O(22)–Cl(2)–O(24)	109.2(3)	O(23)–Cl(2)–O(24)	109.5(3)
O(11)–Cl(1)–O(12)	109.7(4)	O(11)–Cl(1)–O(13)	108.3(4)
O(12)–Cl(1)–O(13)	108.9(4)	O(11)–Cl(1)–O(14)	108.9(4)
O(12)–Cl(1)–O(14)	111.6(4)	O(13)–Cl(1)–O(14)	109.5(4)

listed in Table 2; selected bond distances and angles are given in Tables 3 and 4 respectively. Observed and calculated structure factors, anisotropic thermal parameters, and H-atom positions and isotropic thermal parameters may be found in the supplementary material.

RESULTS AND DISCUSSION

Reaction of copper(II) perchlorate with triazine in 95% ethanol gave bis(1,3,5-triaza-1,4-pentadieno) copper(II) perchlorate in 55% isolated yield. The first

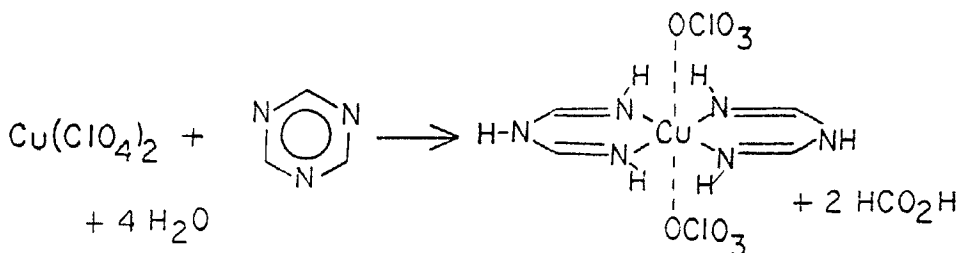


Figure 1 Reaction of copper(II) perchlorate with triazine gives bis(1,3,5-triaza-1,4-pentadieno) copper(II) perchlorate.

evidence that the ligand had been hydrolyzed came from the infrared spectrum. New strong, sharp absorbances were observed at 3330, 1690, and 1540 cm^{-1} in distinct contrast to the starting material, but in good agreement with related biguanide complexes.⁵ Combustion analysis gave a carbon/nitrogen ratio of 2/3, indicating the loss of a carbon, and was consistent with a molecular formula of $\text{C}_4\text{H}_{10}\text{Cl}_2\text{CuN}_6\text{O}_7$. The exact structure was confirmed by single crystal X-ray diffraction. Figure 2 shows an ORTEP drawing of the molecule while Figure 3 is a stereodrawing showing the packing in the unit cell. The compound is best described as tetragonal with four N-atoms, two from each of the chelating ligands, occupying the equatorial positions ($\text{Cu}-\text{N}_{\text{avg}} = 1.97\text{\AA}$). Perchlorate anions sit above and below the Cu in the axial positions with very long Cu—O distances of 2.84Å suggesting semi-coordinate bonds.

The N—Cu—N bond angles (88.7° , 88.1°) within the chelate rings are somewhat less than 90° and slightly larger between rings (92.4° , 91.0°) as expected. The Cu-atom and the triazapentadiene rings are all coplanar. Although there is resonance delocalization, the C—N bond lengths within the rings reflect the different bond orders. The average C—N distance of coordinated N-atoms (nominally C = N) is 1.252Å compared to a C—N distance of 1.359Å for bonds to the uncoordinated N-atoms (nominally C—N). The overall structure resembles that of the related complex bis(biguanide)nickel(II) chloride.⁶

We believe the reaction proceeds *via* coordination of the Cu^{2+} ion to one of the triazine N-atoms. Subsequent nucleophilic attack by water and hydrolysis would allow for loss of a carbon as formate ion followed by formation of one chelate ring. A second sequence of triazine coordination, nucleophilic attack and chelation would lead to formation of 1. When the reaction was run by addition of the triazine

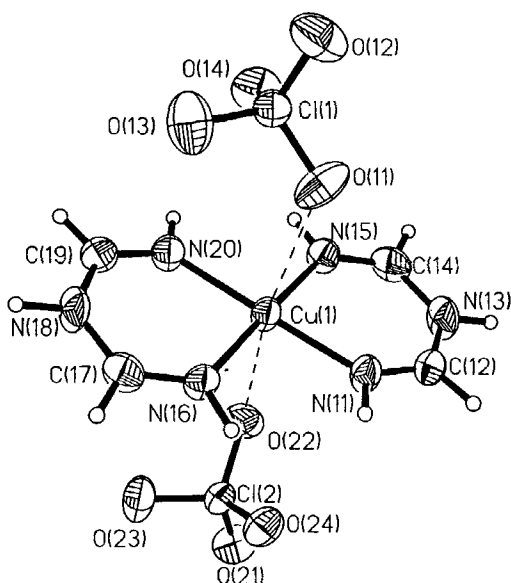


Figure 2 Ortep Drawing of $\text{Cu}(\text{HN}=\text{CHNHCH}=\text{NH})_2(\text{ClO}_4)_2$ (1) showing 50% probability clipsoids with H-atoms in calculated positions.

solution to the Cu^{2+} solution, a blue powder was formed initially and isolated by filtration. The compound was identified as copper(II) formate based on its infrared spectrum and combustion analysis, supporting the idea that formate ion is formed during the hydrolysis. The filtrate from the inverse addition subsequently yielded crystals of 1.

Of particular interest is the fact that hydrolysis stops after loss of a single carbon and formation of the coordinated triazapentadiene (or diamidide⁷). Triazine hydrolyzes readily to formamidine and subsequently ammonia and formic acid.⁸ The reaction is catalyzed by both acid and base.⁹ Triazapentadiene is a proposed intermediate in the hydrolysis and in the reaction of triazine with nitrogen bases.¹⁰ We are aware of one previous report showing that the hydrolysis of a sulfur substituted derivative can be controlled under certain conditions. Fischer and co-workers¹¹ showed that treatment of 2,4,6-trichloro-2-thiatriazine with Raney-Nickel and H_2 in water gave the neutral nickel complex $\text{Ni}(\text{C}_2\text{H}_4\text{N}_3)_2$. The Ni^{2+} ion is chelated by the conjugate base of triazapentadiene, formed via hydrogenolysis of the C—Cl bonds and excision of the sulfur atom. The compound is presumed square planar and therefore has a structure similar to that of our Cu complex (with the perchlorates absent).

Metal promoted hydrolyses have been suggested to occur *via* several pathways.¹² Lippard^{4b} has suggested that the Cu^{2+} catalyzed hydrolyses of tripyridyl- and tripyrimidyl-triazine occur *via* both Lewis acid and coordination activation. In the latter case, he observes that coordination of the copper ion to one of the tripyridyl-like binding sites causes deformation of the bond angles about the triazine carbons, inducing strain and therefore making the ring more susceptible to

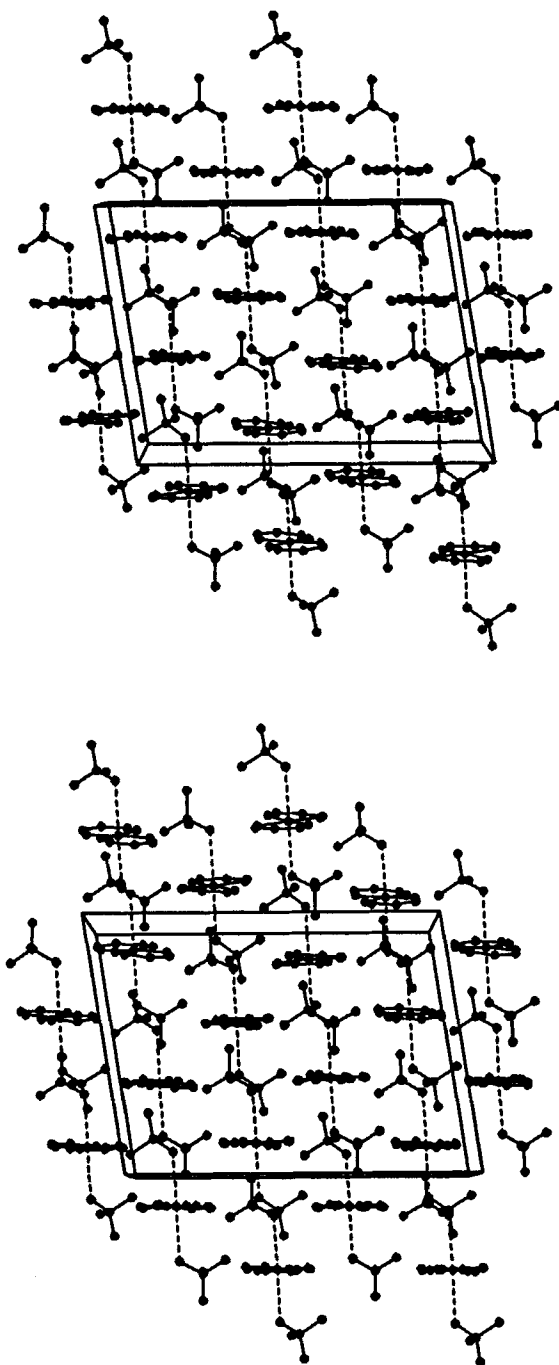


Figure 3 Stereodrawing of 1 showing the unit cell packing.

nucleophilic attack. No such deformation can occur in the present system and we conclude that the metal promotes the hydrolysis solely *via* Lewis acid activation.

We have demonstrated reaction conditions for the controlled hydrolysis of triazine to the corresponding triazapentadiene, isolated as the Cu^{2+} complex. Further work is in progress to determine the stability of this complex and its suitability for the preparation of site-ordered heterometallic coordination polymers.

Acknowledgement

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