Journal of Inorganic and General Chemistry

ZAAC

Zeitschrift für anorganische und allgemeine Chemie

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To be cited as: *Z. anorg. allg. Chem.* 10.1002/zaac.201700311

Link to VoR: http://dx.doi.org/10.1002/zaac.201700311

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Synthesis, Structural and Energetic properties of Copper(II) Perchlorate Complex with Aminoguanidine

Mohammad Mahdavi,*[a] Kamal Ghani,[a] and Keyvan Nosratzadegan[a]

Abstract: The complexation of copper(II) perchlorate with aminoguanidine hemesulfate (AGHS) yield related mononuclear complex bis(aminoguanidine)copper(II) perchlorate; $[Cu(AG)_2](ClO_4)_2$ (I). Characterization of complex was done by elemental analysis, electronic spectra, IR studies and x-ray studies. From analytical data, a stoichiometry of 1:2 of metal to ligand was determined for the complex. The structure consists of centrosymmetric square planar $[Cu(AG)_2]^{2+}$ cation and perchlorate counterion. The Cu(II) atom is four-coordinated by two imine N atoms and two amine N atoms from two aminoguanidine ligands, forming a slightly distorted square-planar coordination. In the crystal structure, molecules are linked through intermolecular N-H…O hydrogen bonds, forming a network. The thermal decomposition process of this complex was investigated through differential scanning calorimetry (DSC) and the sensitivities toward impact and friction were assessed using a BAM drophammer and a BAM friction tester.

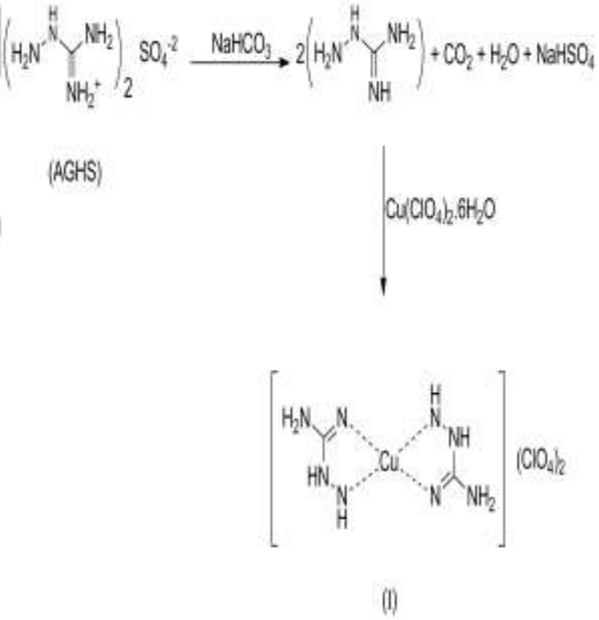
Introduction

Aminoguanidine and its derivatives have been the subjects for many important, interesting, and fruitful investigations. The researches on these substances, extending over a period of about fifty years, have occupied the time and energies of a great many chemists in several countries. One approach is the synthesis of nitrogen-rich compounds, which deliver their energy due to their high heat of formation. In addition to the common ammonium and toxic hydrazinium cations, guanidinium derivatives are used as nitrogen-rich cations in energetic salts. High-energetic salts have the main advantages of often possessing a high thermal stability, a low vapor pressure, and higher densities, due to their lattice energies.[1] These materials mostly combine facile syntheses and good thermal stabilities with energetic properties similar to that of the prominent primary explosive lead azide, which should be replaced because of its high toxicity.[2] The coordination chemistry of aminoguanidine(AG) has been described for a few transition metals. In one of the earliest studies, Thiele[3] described a complex salt of copper with the formula $[Cu(AG)_2](NO_3)_2$.[4, 5] Similar square-planar chelate structures have been attributed to complexes of nickel (II), platinum (II) and palladium(II).[6, 7] Many energetic nitrogen-rich Aminonitroguanidine (ANQ), containing transition metal salts, $M^{2+}(ANQ)_2X_2(H_2O)y$ with M^{2+} = Co, Ni, Cu, Zn and X = nitrate, perchlorate and dinitramide were synthesized and characterized as energetic materials.[8] Transition metal perchlorate complexes with nitrogen-rich ligands have attracted considerable attention, since they have superior explosive performances and can be widely used as lead-free primary explosives.[9–13] Furthermore, transition metal complexes with ligands derived from aminoguanidine represent an attractive field of research due to their special activities in pharmacology, physiology, and the wide range of applications, such as in clinical, analytical and catalytic areas.[14, 15] In this context, we describe the synthesis, structural characterization, spectroscopic behavior and energetic properties of mononuclear copper(II) perchlorate complex with aminoguanidine a chelating ligand.

Results and Discussion

Synthesis

The reaction of aminogunidine hemisulfate (AGHS) in the presence of sodium bicarbonate ($NaHCO_3$), with copper(II) perchlorate in 1:1: molar ratio, afforded the bis(aminoguanidine)copper(II) perchlorate (I) product. As shown in scheme 1, the bidentate ligand aminoguanidine forms a chelate complex with the copper ion. Chelation results in the formation of a five-membered CuN_4 ring. To dissolve the AGHS, the pH of the solution was raised to 8.5 by adding several drops of an aqueous solution of sodium bicarbonate.



Scheme 1. Synthesis of $[Cu(AG)_2](ClO_4)_2$ (I)

Spectral characterization

Infrared spectroscopy was applying to identify the structure of the title coordination compound. The IR spectrum of the free ligand (AGHS) exhibits the characteristic bands of imine and sulfate anion, which appears at 1683 and 1115 cm^{-1}. The imine band is shifted to lower frequencies in the IR spectra of complex due to the coordination of the imine nitrogen.[16] Free ClO_4^- ion belongs to a high symmetry point group Td. The tetrahedral symmetry of the free ion, ClO_4^- is reduced to C_{3v} on unidentate coordination of the ion to a metal. The symmetry is further lowered to C_{2v} if the anion binds to a metal as bidentate, either as a chelate or as a bridging ligand. The uncoordinated ClO_4^- ion shows

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10.1002/zaac.201700311

two sharp bands at 1100 (ν_3) and 629 (ν_4) cm^{-1}.[17] As a result of complexation, typical perchlorate vibrations of I (*vas* (ClO_4^-)=1076 cm^{-1} and *vs* (ClO_4^-)=627 cm^{-1}) are redshifted compared to those of noncoordinating perchlorate anions (Fig. 1). The ultraviolet and visible spectroscopy (UV–Vis) was an important technique for the characterization. UV spectrums of the samples were recorded in water solution. Aminogunidine hemisulfate shows UV maximum in water at 212 nm. Absorption maximum at 212 nm is attributed to the high energy $n\rightarrow\pi^*$ transition originating in the -CH=N- chromophore.[18] The spectra of the complex this band is shifted to lower energy. The ultraviolet and visible spectral of AGHS and complex (I) are presented in figure 2. The absorption observed at 275 nm and attributed to the ligand-metal charge transition. This demonstrates metal coordination with the ligand.

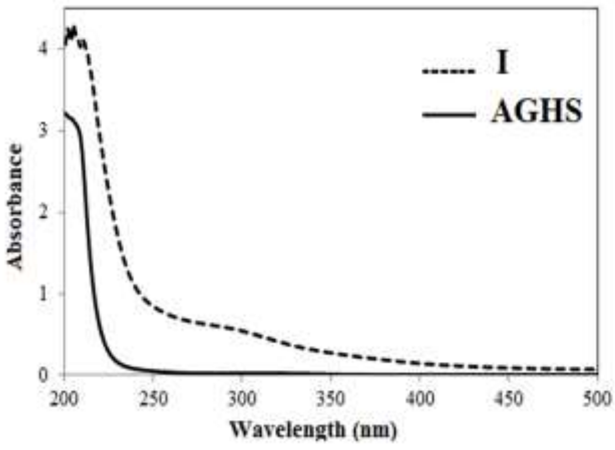

Figure 2: UV spectrum of AGHS and I in water.

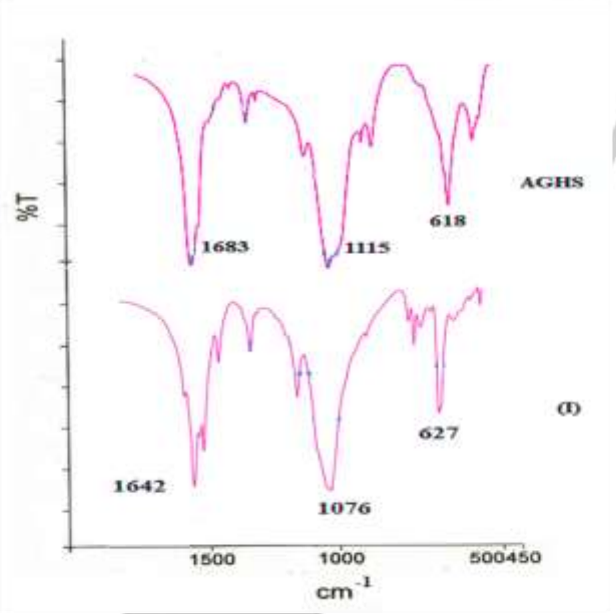

Figure 1: IR spectra of AGHS and $[Cu(AG)_2](ClO_4)_2$ (I).

Structure description

The molecular structure of I illustrated in figure 3, and selected bond distances and angles are given in table 1. In the cation of I, the Cu^{II} atom is four-coordinated by two imine N and two amine N atoms from two aminoguanidine (AG) ligands. The four coordinating atoms around Cu are approximately coplanar, giving a square-planar coordination. The two Trans angles at Cu1 are 180 °C and the other angles are ranging from 80.89 to 99.11°, which indicates a slightly distorted square-planar coordination of the Cu atom. The N3-C1 bond length is 1.291 Å, which is typical of C=N bonds. The Cu1-N1 bond (Table 1) is comparable to the corresponding value [1.982 Å] observed in $[Cu(ANQ)_2(H_2O)_2][ClO_4]_2$.[8] However, Cu1-N3 is slightly smaller than the corresponding value [2.032 Å]. The dihedral angle between the N1/Cu1/N3 and N3/C1/N2/N1 planes is 5.20°, showing that there is a significant copanarity of the CuN4 plane and the five-membered chelate ring. The dihedral angle between the two ligand coordination planes [Cu1/N1/N3 and Cu1/N1^i/N3^i; Symmetry code: (i) -x+1,-y+1,-z+1] is 0.0°. The molecule of the title copper (II) complex exist as monomer, with Cu…Cu separation of 5.080 Å, leading to no dimeric interaction. The Cl1-O1, Cl1-O2 bond lengths and O1-Cl1-O2 angle are 1.436(4), 1.428(7) Å and 109.1(5)°, respectively in the perchlorate counterion. In these and other respects there are no major differences between the perchlorate structures, the bond lengths and angles are similar to those of related salts found in the Cambridge Structural Database [19-22] Fischer et al. report the structural of 3-Amino-1-Nitroguanidinium Copper (II) perchlorate Complex.[8] In this report perchlorate containing complex as dehydrate, except for the copper complex of I, which crystallize water free. From our results, I crystallize in space group $P2_1/n$ with with a = 5.0795(10), b = 8.7977(18), c = 14.264(3)Å, α = 90, β = 93.87(3), γ = 90°, V = 636.0(2) $Å^3$, Z = 2. In I each perchlorate anion is surrounded by two nearest $copper^{II}$ cation so that each oxygen atom of perchlorate is hydrogen bonded to one hydrogen atoms. Conversely, in I each $copper^{II}$ cation is surrounded by four nearest perchlorate so that each hydrogen atoms of $copper^{II}$ cation is hydrogen bonded to one oxygen atoms. In the crystal packing, the ions are linked via N-H…O hydrogen bonds, involving uncoordinated perchlorate anions and NH, NH_2 groups of AG, to form a two-dimensional network (Figure 4). A view on the unit cell along the c axis is shown in figure 5. Thereby alternating columns can be found, which are mainly connected by “Van der Waals” forces.

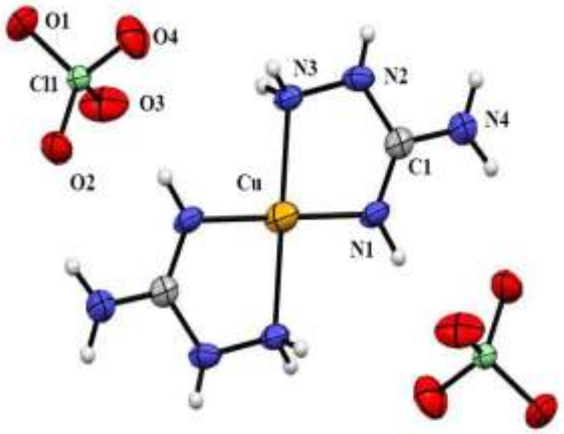

Figure 3. Molecular structure and labeling scheme for the complex (I), thermal ellipsoids are shown at the 50% probability level

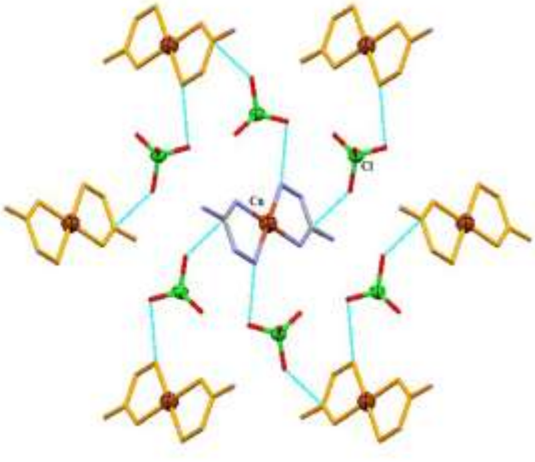

Figure 4. N-H...O hydrogen bonds network in I

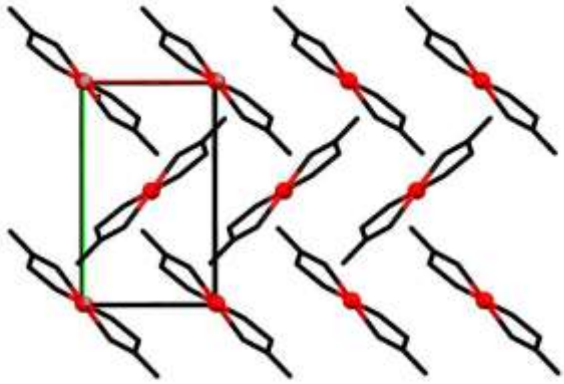

Figure 5. The crystal packing in I, viewed along the c axis.

Table 1. Selected geometric parameters (Å, °) for I.

Bond lengths	Å	Bond angle	°
Cu(1)-N(1)	1.937(7)	N(3)-Cu(1)-N(3)[a]	180.0(2)
Cu(1)-N(3)	2.030(6)	N(1)-Cu(1)-N(1)[a]	180.0(3)
C(1)-N(1)	1.291(10)	N(3)-Cu(1)-N(1)[a]	99.1(3)
C(1)-N(4)	1.315(11)	N(1)-C(1)-N(4)	124.5(7)
C(1)-N(2)	1.345(10)	N(4)-C(1)-N(2)	116.8(7)
Cl(1)-O(1)	1.436(6)	O(1)-Cl(1)-O(2)	109.1(5)
Cl(1)-O(2)	1.428(7)	O(1)-Cl(1)-O(3)	109.1(4)

[a] Symmetry code: -x+1,-y+1,-z+1

Energetic properties

DSC measurements for determining the thermal behavior of the AGHS and I were performed in covered Al-containers with a nitrogen flow of 20 mL min^{-1} on a Perkin-Elmer Pyris 6 DSC, at a heating rate of 10 °C min^{-1}. I show a well-defined decomposition point at 215 °C (Figure 6), while the neutral AGHS melt at an onset temperature of 200 °C.[2] Fischer et al. report the structural of Perchlorate-Based 3-Amino-1-Nitroguanidinium (ANQ) Complexes (Co, Ni, Zn and Cu).[8] These complexes crystallize isotypically as dehydrates in the crystal system. Two water molecules participate in the coordination sphere (Co, Ni and Zn complexes), while water molecules are connected to the ANQ by formation of hydrogen bonds in copper (II) complex. The crystal water containing complexes (Co, Ni, Zn and Cu) can be dehydrated after heating, indicated by an endothermic peak in the DSC curve, which is well-separated from the exothermic decomposition event. The complex (I) decomposes violently mostly without prior melting point. One of the most important properties for new energetic materials is sensitivity. The drop weight sensivitie of I is 4 J. A summary of the impact, friction and electrostatic sensitivity of I is given in Table 2. The friction sensitivity results for I is 20 N. The observation shows that the fraction sensitivity of I much more than that of RDX (157 N) and ADN (72 N).[23]

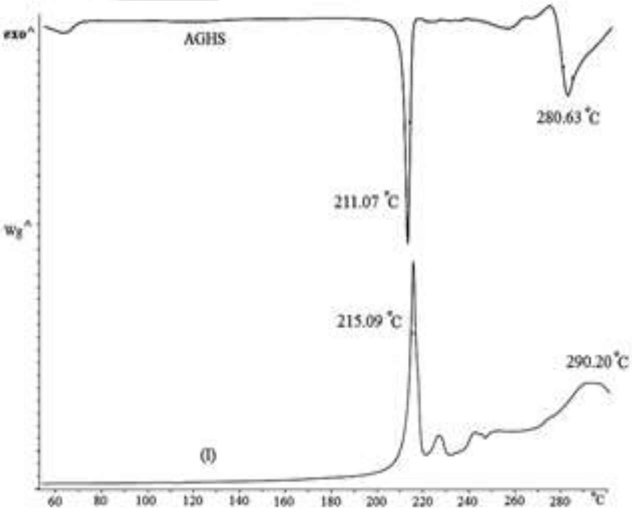

Figure 6. DSC spectrum of AGHS and I at a heating rate of 10 °C min^{-1} in N^{2} atmosphere.

Table 2. Sensitivities and thermal behavior.

Complexes	IS (J)	FS (N)	ESD (J)	T_{dehydr} (°C)	T_{dec} (°C)
$[Cu(AG)_2](ClO_4)_2$ (I)	4	20	0.45	-	215
$[Zn(ANQ)^b{}_2(H_2O)_2](ClO_4)_2$ [8]	3	28	0.3	108, 154	198
$[Co(ANQ)^b{}_2(H_2O)_2](ClO_4)_2$ [8]	3	10	0.03	170^a	176
$[Ni(ANQ)^b{}_2(H_2O)_2](ClO_4)_2$ [8]	3	10	0.04	162	230
$[Cu(ANQ)^b{}_2(ClO_4)_2](H_2O)_2$ [8]	<1	16	0.5	120^a	134

[a] Decomposition (exothermic) occurs immediately after dehydration (endothermic)

[b] 3-amino-1-nitroguanidine

Conclusions

The energetic coordination compound, $[Cu(AG)_2](ClO_4)_2$, was prepared and characterized. A perchlorate containing complex crystallizes water free. The structure consists of centrosymmetric square planar $[Cu(AG)_2]^{2+}$ cation and perchlorate counterion. The copper (II) complex decomposes at relatively high temperature (210 °C). This complex bearing energetic counterion show enhanced sensitivities toward impact and friction, which especially applies to the solvate water free copper complex with values of 4 J (IS) and 20 N (FS).

Experimental Section

Caution! The herein described metal complexes of perchlorate are energetic materials with increased sensitivities toward shock and friction. Therefore, proper safety precautions (safety glass, face shield, earthed equipment and shoes, Kevlar gloves, and ear plugs) have to be applied while synthesizing and handling the described compounds.

Materials and physical measurements

All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros). Infrared spectra were measured using a Perkin-Elmer Spectrum One FT-IR spectrometer as KBr pellets. The UV/Vis/NIR reflectance of the solid samples was measured with a Varian Cary 500 spectrometer in the wavelength range 350–1300 nm. The impact and friction sensitivity tests were performed according to standard methods by using a BAM (Bundesanstalt fur Materialforschung) drop hammer and a BAM friction tester. The sensitivity toward electrostatic discharge was tested by using an OZM Research electric spark tester ESD 2010 EN.

Synthesis of $[Cu(AG)_2][ClO_4]_2$ (I)

At ambient temperature, a water solution (5 ml) of sodium carbonate (20 mg) was added to aminogunidine hemesulfate (AGHS) (1 g, 4 mmol) in water (10 ml) with stirring. After half an hour, $Cu(ClO_4)_2.6H_2O$ (1 gr, 4 mmol) in water (5 ml) was added to the above solution, which was stirred for an additional 20 min. Slow evaporation of the solvent gave the title complex (I) as dark violet crystals and dried in a desiccator. Anal Calc. for $C_2H_{12}Cl_2CuN_8O_8$ (%); C, 5.85; N, 27.29; H, 2.95; Found C, 5.91; N, 27.10; H, 3.01.

X-ray Crystal structure determination

Single-crystal diffraction for (I) were measured at 298 K on a Stoe IPDS-II diffractometer with Mo Ka radiation (0.71073 Å); absorption corrections were based on repeated and symmetry-equivalent data. The structure was solved by direct methods and refined on all unique F^2 values, with anisotropic displacement parameters and with constrained riding isotropic H atoms. Violet crystal, 0.31 × 0.27 × 0.25 mm; $C_2H_{12}Cl_2CuN_8O_8$, M = 410.64; monoclinic, space group $P2_1/n$, $a = 5.0795(10)$, $b = 8.7977(18)$, $c = 14.264(3)$ Å, $\alpha = 90$, $\beta = 93.87(3)$, $\gamma = 90°$, $V = 636.0(2)$ Å^3, Z = 2. 1100 reflections measured, 1100 unique, $R_{int} = 0.0318$, 1100 reflections with $F^2 > 2\sigma$, data 99.4 % complete to $\theta = 25°$. 101 refined parameters, R [F, $F^2 > 2r$] = 0.0722, R_w [F^2, all data] = 0.2148, goodness of fit = 1.256 on F^2, final difference map extremes +0.722 and -1.698 e Å^3. Computer Programs was X-AREA for data collection and processing, SHELXTL for structure solution, refinement and graphics.[24, 25]

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1498520 for (I). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors acknowledge a reviewer who provided helpful insights.

Keywords:

Aminoguanidine; Perchlorate Anion; Energetic Complex; Nitrogen-Rich Compound

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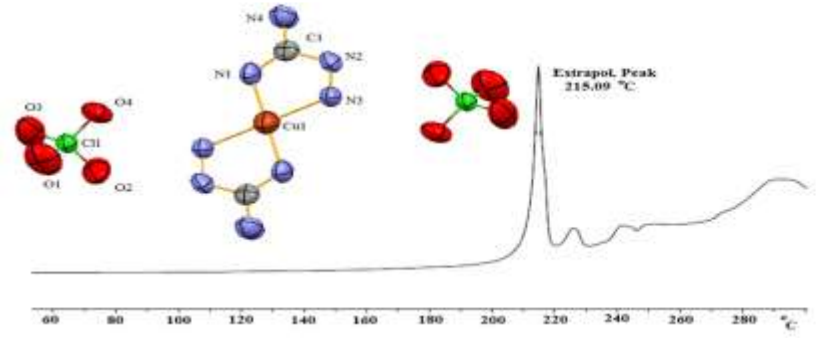

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