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A novel copper(I) sulfamate π -complex based on the 5-(allylthio)-1-(3,5dimethylphenyl)-1*H*-tetrazole ligand: alternating-current electrochemical crystallization, DFT calculations, structural and NLO properties studies

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ABSTRACT

Using the alternating-current electrochemical technique, the novel π -complex [Cu¹(*m*-*dmphast*)NH₂SO₃] (**1**), based on the 5-(allylthio)-1-(3,5-dimethylphenyl)-1*H*-tetrazole (*m*-*dmphast*) ligand, was obtained and it was studied using single crystal X-ray diffraction as well as IR and UV–Vis spectroscopy. The structure **1** should be considered as the first known example of a metal sulfamate coordination compound with a tetrazole ligand. The copper(I) ion in **1** possesses a trigonal pyramidal environment, arranged from the N4 atom of the tetrazole core, the C=C bond from the S-allyl group of the same *m*-*dmphast* ligand and O and N atoms of the NH₂SO₃⁻ anion. The sulfamate anion is coordinated to the two neighboring Cu(I) ions in a bridged mode, occupying a basal plane (through the N atom) and an apical (through an O atom) position of the two neighboring metal trigonal pyramids. The bicolor coherent photoinduced treatment by a nanosecond Nd:YAG laser at a wavelength of 1064 nm caused the occurrence of charge density acentricity, which in turn favours an occurrence of second harmonic generation described by third rank polar tensors, that are usually forbidden for centrosymmerical crystals.

Keywords: tetrazole; copper(I) π -complex; crystal structure; *ac*-electrochemical technique; NLO properties

1. Introduction

Intensive efforts to search for and design compounds with organic molecules (chromophores) possessing enhanced non-linear optical (NLO) susceptibilities in a wide spectral range of transparency are of a special interest due to the development of laser optoelectronic devices [1,2]. Organometallic compounds with a large delocalized π conjugated electron system have potential applications in the field of non-linear optics due to their specific electronic absorptions, allowing them to be applied the typical lasers, facile preparation, large optical non-linearity (particularly third-order NLO properties) and the possibility of diverse ligand design and preparation [3-8]. The geometrically defined donormetal-acceptor arrangement of an organometallic fragment was found to be crucial for optical properties such as phosphorescence, quadratic and cubic non-linear optics, photoinduced effects etc. It was also shown that the photochromic properties could be readily tuned by varying the metal systems or by incorporating alternative donor centers in the organic ligand [8]. Among them, copper(I)-olefine complexes with alkenes have received considerable theoretical and practical interest because of their remarkable catalytic and luminescent activities, and other useful properties [9-12]. Also, the key role of heterocycles in the crystal engineering of copper π -compounds with extremely rare occurring inorganic fragments was found in recent years [13-15]. In contrast to solely σ -donor ligands, the coordination role of allyl derivatives in the stabilization of unusual Cu(I) compounds is in good accordance with the hard and soft acids and bases theory [13] (the olefin C=C bond acts as a soft base and the heterocyclic molecule donor atoms possess border-line basicity); the coordination of an allylic group as well as heterocyclic donor atoms to copper(I) ions causes specific interaction conditions between the π,σ -coordinated soft Cu⁺ acid, on the one hand, and hard bases (O, F), on the other. These specific coordination conditions are also caused by the contribution of a directed Cu(I)-olefin interaction (which includes σ -donor (Cu^I \leftarrow C=C) $_{\sigma}$ and π -dative $(Cu^{I} \rightarrow C = C)_{\pi}$ components) to the splitting of the copper atom's localized 3d orbitals (accompanying by a significant increase of the d_{z2} orbital energy), which leads to a significant distortion of the copper(I) tetrahedral coordination. Therefore, the synergy of a flexible allyl group and a conformationally rigid heterocyclic core plays an exceptionally crucial role in the stabilization of the unique fragments, resulting in the formation of compounds that exhibit a range of useful properties. Among the organic ligands possessing 6π -electron aromaticity, recently 1-allyloxybenzotriazole was found to be a good instrument for the design of a crystalline π -compound with enhanced non-linear optical susceptibilities [16]. Copper(I) complexes also have a couple of potential applications in advanced laser operated materials. For example, such compounds work as acid/base-induced "on-off" luminescence switch

materials or display high photocatalytic activity at ambient temperature [17]. Copper complexes exhibit considerable biochemical activities, ranging from antibacterial and antiinflammatory to cytostatic and enzyme inhibitory. Copper ions may be considered as multifunctional, participating in a broad spectrum of intracellular processes under normal and pathologic conditions [18]. Cu(I) complexes have been tested *in vitro* as potential anticancer drugs and have been found to be effective against A549 adenocarcinoma cells, which are resistant to the widely used anticancer drug, cisplatin [19]. Moreover, cancer progression is accompanied by increased ceruloplasmin and copper levels in various tissues, and the elevated copper levels and increased oxidative stress in cancer cells provide for the prospect of selective cancer treatment [20,21]. The exploration of their NLO features may be useful for the monitoring and clarification of the mentioned biochemical mechanisms.

Taking into account that most studied copper(I) coordination compounds for NLO properties are based on pyridine ligands [22], an investigation of the tetrazole containing system should attract enhanced attention. Moreover, an increase in the number of donor atoms in the heterocyclic ring should significantly contribute to the above conditions, that is why *N*-or *S*-allyl derivatives of tetrazoles (being practically unknown as ligands with respect to Cu(I) complexes) in this aspect appears to be of particular interest. So far, only five π -compounds (in accordance with the Cambridge Crystallographic Database (CCD) [23]) of ionic Cu(I) salts with allyl derivatives of tetrazole have been obtained and studied by X-ray crystallography [24-27]. In the present work, we have focused on the synthesis, structural characterization and optical properties of the novel copper(I) π -complex [Cu(*m*-*dmphast*)NH₂SO₃] (1), based on the 5-(allylthio)-1-(3,5-dimethylphenyl)-1*H*-tetrazole (*m*-*dmphast*) ligand. At present, the metal sulfamate coordination compound with a tetrazole ligand is studied for a first time. Particular attention will be devoted to the second non-linear optical features.

2. Experimental

2.1. Materials and instrumentation

Unless otherwise mentioned, all chemicals were obtained from commercial sources (Sigma Aldrich) and were used without further purification. The ¹H NMR spectrum of *m*-*dmphast* was recorded on a Varian Mercury 400 instrument (400 MHz) with deuterated solvent as an internal reference. IR spectra for m-C₁₂H₁₄N₄S and complex **1** were recorded in KBr pellets on a FT-IR Spectrum BX-II, PerkinElmer spectrometer in the 4000-400 cm⁻¹ range (see supplementary materials). Measurement of the electronic spectrum of complex **1** in

methanol was performed at 25 °C with a double-beam UV-VIS Spectrophotometer Spekol 2000 (Analytik Jena) in the wavelength range $\lambda = 190-1100$ nm (with a 1 nm step size). The solution was placed in quartz cuvette with a 10 mm thickness of the absorption layer and then the UV-Vis spectrum was recorded against methanol. Diffraction data for **1** were collected on a Kuma KM-4-CCD diffractometer with Mo K_a radiation ($\lambda = 0.71073$ Å).

2.2. Preparation of 5-(allylthio)-1-(3,5-dimethylphenyl)-1H-tetrazole

The target ligand IV (*m*-*dmphast*) was synthesized from the commercially available 3,5dimethylaniline I by several procedures (Scheme 1). The appropriate dimethylaniline I was converted into dimethylisothiocyanatobenzene II by the reaction with methanedithione, followed by the treatment with ethyl chlorocarbonate and HCl, according to a modified Kaluza method [28]. By the 1,3-dipolar cycloaddition reaction of the obtained dimethylisothiocyanatobenzene II with the azide ion, 1-(dimethylphenyl)-1*H*-tetrazole-5-thiol III was formed, which was then readily reacted with 3-bromoprop-1-ene in the presence of KOH, yielding the corresponding ligand IV [29,30]. 5-(Allylthio)-1-(3,5-dimethylphenyl)-1*H*tetrazole (*m*-*dmphast*, C₁₂H₁₄N₄S): ¹H NMR (400 MHz, DMSO-d₆), δ , ppm: 7.21 (s, 1H, H_{Ph}-4), 7.17 (s, 2H, H_{Ph}-2,6), 5.98 (dt, *J* = 16.8, 7.0 Hz, 1H, =CH), 5.37 (d, *J* = 16.8 Hz, 1H, CH₂=), 5.18 (d, *J* = 9.8 Hz, 1H, CH₂=), 4.00 (d, *J* = 7.0 Hz, 2H, CH₂), 2.40 (s, 6H, CH₃); IR (KBr, cm⁻¹): 3016 (w), 2975 (m), 2924 (m), 2858 (w, C_{sp3}–H), 1844 (w, C-C), 1732 (m, C-C), 1637 (w, C=C), 1614 (s, C–C, phenyl ring), 1595 (s, C–C, phenyl ring), 1475 (s, C=C and C=N, tetrazole ring), 1383, (vs, C–S), 1271 (s, C–N and N–N, tetrazole ring), 924 (s, C_{sp2}–H, allyl), 730 (m, C_{sp2}–H, allyl), 687 (s, C_{Ph}–H).



Scheme 1 Synthesis of *m*-dmphast

2.3 Synthesis of the copper(I) π -complex

For the synthesis of complex **1**, an alternating-current electrochemical synthesis [31,32] was chosen due to the possibility of large anion variety usage [14,33-35], contrary to the classic direct method.

Crystals of complex **1** were obtained starting from a water-alcohol solution of the appropriate organic ligand and the corresponding copper(II) salt. To 4.5 mL of a saturated water-alcohol (0.5mL of H₂O, 0.5 mL of C₂H₅OH and 3.5 mL of CH₃OH) solution of Cu(NH₂SO₃)₂ 0.15 g (0.61 mmol) of *m-dmphast* was added. Afterwards the mixture was carefully stirred. A copper wire was wrapped into a spiral of 1 cm diameter. A straight copper wire was placed inside the spiral. These copper electrodes were inserted in cork and immersed in the above mentioned solutions. The synthesis was performed using alternating current tension, providing the course of the following reactions:

K(-):
$$\operatorname{Cu}^{2+} + \bar{e} + m\text{-}dmphast + \operatorname{NH}_2\operatorname{SO}_3^{-} \longrightarrow [\operatorname{Cu}(m\text{-}dmphast)(\operatorname{NH}_2\operatorname{SO}_3)]$$

A(+): $\operatorname{Cu}^0 - \bar{e} + m\text{-}dmphast + \operatorname{NH}_2\operatorname{SO}_3^{-} \longrightarrow [\operatorname{Cu}(m\text{-}dmphast)(\operatorname{NH}_2\operatorname{SO}_3)]$

After application of an alternating-current tension (frequency 50 Hz) of 0.45 V for 7 days, good quality colorless crystals of **1** appeared on copper electrodes. The yield was about 75%. IR (KBr, cm⁻¹): 3266 (s), 3192 (s); 2972 (m), 2921 (s), 2858 (m, C_{sp3}–H), 1838 (vw, C-C), 1616 (m, C–C phenyl ring), 1594 (m, C–C phenyl ring), 1477 (m, C=C and C=N, tetrazole ring), 1433 (N–O, NO₃⁻), 1266 (vs), 1211 (vs), 1051 (vs), 1030 (vs, NH₂SO₃⁻), 915 (m, C_{sp2}–H, allyl), 772(s, N–S, NH₂SO₃⁻), 714 (m, C_{sp2}–H allyl), 690 (m, C_{Ph}–H).

2.4 Single crystal X-ray diffraction studies

The crystallographic parameters and summary of the data collection for **1** are presented in Table 1. The collected diffraction data for **1** were processed with the CrysAlis PRO program [36]. The structure was solved by the ShelXT program and refined by the least squares method on F^2 by the ShelXL program with the graphical user interface OLEX² [37-39]. Atomic displacements for non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms (except N-bonded H atoms) were placed in ideal positions and refined as riding atoms with their relative isotropic displacement parameters.

Table 1

	CCDC number	1816413	
	Empirical formula	$C_{12}H_{16}CuN_5O_3S_2$	
	Formula weight	405.96 g/mol	
	Temperature, K	150(2)	
	Wavelength, Å	0.71073	
	Crystal system,	orthorhombic	
	space group	Pbca	
	Unit cell dimensions		O
	<i>a</i> , Å	7.737(3)	6
	b, Å	14.866(4)	
	<i>c</i> , Å	27.640(8)	
	V, Å ³	3179.1(17)	
	Ζ	8	
	Calculated density, g/cm ³	1.70	
	Absorption coeff., mm ⁻¹	1.658	
	F(000)	1664	
	Crystal size, mm	$0.47 \times 0.22 \times 0.17$	
	Color	Colorless	
	Diffractometer	Kuma KM-4-CCD	
	θ range, °	3.01 - 28.74	
	Limiting indices	$-10 \le h \le 5, -19 \le k \le 18,$	
		$-35 \le l \le 35$	
	Refinement method	Full-matrix least-squares	
	U	on F ²	
1	Measured reflections	15060	
	Used in refinement	3829	
	Free parameters	218	
	Goodness-of-fit on F ²	1.036	
	$R(F_0^2 > 2\sigma(F_0^2))$	$R_1 = 0.0457, wR_1 = 0.1209$	
	R (all)	$R_1 = 0.0516, wR_2 = 0.1269$	
	Largest diff. peak and	0.87 and -0.64	
	hole, e Å ⁻³		

Selected crystal data and structure refinement parameters of ${\bf 1}$

r

2.5 Theoretical quantum chemical calculations

For the dimer fragment in 1 of the $\{Cu(m-dmphast)NH_2SO_3\}_2$ composition (Fig. 6a), quantum chemical calculations of the dipole additional moment, first order hyperpolarizability (β) at 1064 nm as well as simulations of the HOMO and LUMO, and UV-Vis spectra were performed using the Gaussian W09 package [40]. Calculation of the dipole moment, average first order hyperpolarizability (β), HOMO and LUMO shape were performed using the DFT and B3LYP functional methods supplemented with the standard 6-31G(d) basis set for H, C, N, O and S atoms and LANL2DZ ECP for the Cu atom. The UV-VIS spectrum was simulated using TD-DFT and B3LYP with 6-31G(d) (H, C, N, O, S) and LANL2DZ ECP (Cu) basis sets. A primary model derived from the structure obtained by Xray diffraction was used.

3. Results and discussion

3.1. Crystal structure

The crystal structure of $[Cu(m-dmphast)NH_2SO_3]$ (1) demonstrates the only example to date of a metal sulfamate coordination compound with a tetrazole ligand (Fig. 1). The π complex 1 crystallizes in the orthorhombic centrosymmetric space group *Pbca*, with one copper(I) ion, one NH₂SO₃⁻ ion and one *m*-dmphast molecule in the asymmetric unit. In 1, the Cu(I) ion possesses a trigonal pyramidal environment, coordinated by the N4 atom of the tetrazole core, a C=C bond from the S-allyl group of the same ligand and O and N atoms of the NH₂SO₃⁻ anion (Fig. 1). The sulfamate anion is coordinated to the two neighboring Cu(I) ions in a bridging mode, occupying a basal plane (through the N atom) and an apical position (through an O atom) of the two neighboring metal trigonal pyramids. Thus, an infinite coordination {Cu(*m*-dmphast)NH₂SO₃}_n polymer is formed in 1 (Fig. 2). Two hydrogen atoms of the sulfamate anion participate in N-H....O hydrogen bonding with two neighbouring anions and it provides stabilization of the organometallic chain (Table 2).



Fig. 1. Fragment of the crystal structure **1**. Symmetry codes: (*i*) 0.5+x, y, 1.5-z; (*ii*) -0.5+x, y, 1.5-z. Selected bond length (Å) and angle (deg) values: Cu–N4 1.994(2), Cu–N5 2.015(2), Cu–O1 2.444(2), C1–C2 1.369(4), Cu–*m* 1.927(3) (*m* - middle point of the C1=C2 bond), C1-Cu-C2 39.1(1), *m*-Cu-N4 116.7(1), *m*-Cu-N5 139.7(1), N4-Cu-N5 103.10(9), N4-Cu-O1 94.5(1).

SCRI

The organic molecule *m*-*dmphast* in the structure of **1** adopts N,(C=C)-bidentate and chelate functions, being attached to the metal centre through the S-allylic C=C bond and the most nucleophilic N atom of the tetrazole ring. Such a bidentate π , σ -coordination behavior of 1-aryl substituted 5-(allylthio)-1*H*-tetrazoles with regard to ionic Cu(I) salts is observed for the first time, while the previously studied 1-phenyl- (*phast*), 1-(4-chlorophenyl)- (*clphast*) and 1-[2-(trifluoromethyl)phenyl]- (*trifphast*) substituted 5-(allylthio)-1*H*-tetrazoles showed a dominant tendency to be bound with copper(I) ions by means of two N3 and N4 tetrazole atoms, forming stable {Cu₂(L)₂}²⁺ dimers [23-25]. The dihedral angle between the planes of the tetrazole and phenyl rings equals 39.06(7)°.

SCRI



Fig. 2. The organometallic $\{Cu(m-dmphast)NH_2SO_3\}_n$ chain in **1**.

Table 2

Geometry of selected hydrogen bonds in the crystal structure of 1

Atoms involved	Symmetry	Distances, Å		Angle, deg	
D–H···A		D-H	H···A	D····A	D−H…A
N5-H5A…O3	-0.5+x, y, 1.5-z	0.82(3)	2.13(4)	2.939(3)	167(3)
N5−H5B…O2	0.5+x, y, 1.5-z	0.89(4)	2.26(4)	3.096(3)	157(3)

The allylic C=C bond is slightly elongated to 1.369(4) Å (due to a back-donation from an occupied 3*d* metal orbital to a low-lying empty π^* orbital of the olefin) in contrast to the values for free ethylene: 1.338(1) Å gas phase [41], 1.3142(3) Å at 85 K [42]. The efficiency of the Cu(I)–(C=C) interaction in **1** is also confirmed by the fact that the Cu(I) ion deviates from the base of the trigonal pyramid by 0.086(1) Å, as well as by the relatively small angle between the C=C bond and the polyhedron base plane (14.2(1)°). A rather short Cu–*m* (*m* = mid-point of the C=C bond) bond distance and large C-Cu-C angle also confirm this conclusion. A comparison of the vibrational spectra of the pure ligand and the corresponding π -compound shows a significant frequency decrease of the C=C band, caused by the effective Cu(I)–(C=C) interaction. In the IR spectrum of the pure *m*-*dmphast* ligand the C=C stretching mode is observed at 1637 cm⁻¹, while the band arising from the C=C vibrations of the allyl group coordinated to the copper ion in **1** is bathochromically shifted and disguised by the C-C

stretching bands of the phenyl ring. The deformational vibration C-H band of the $-CH=CH_2$ group, observed at 730 cm⁻¹, is also shifted to lower frequencies by 14 cm⁻¹.

3.2. Non-linear optical effects

It is well known that optical second harmonic generation (SHG) is forbidden in centrosymmetric media, including crystals. The presence of Cu(I) ions possessing localized *3d*-states and an additional absorption in visible light spectra may favor the performance of bicolor coherent stimulated material treatment. The process of the treatment by two coherent beams of the fundamental and doubled frequency leads to the occurrence of a long lived reversible dc-electric field [43]. During the treatment by the two coherent beams, which are space separated, features similar to single-axis crystals appear [44]. The corresponding mechanisms are theoretically well described in detail in the literature [45].



Fig. 3. Principal set-up for performance of bicolor coherent laser treatment.

The bicolor treatment and registration of the photoinduced SHG was performed using the principal set-up shown in Fig. 3. A light beam from a pulsed Nd:YAG nanosecond laser with a frequency repetition of about 10 Hz was incident on the single non-linear crystals of BiB₃O₆ (BiBO) cut under the phase matching angle. After the crystals, two coherent beams at wavelengths ω =1064 nm and doubled frequency 2ω =532 nm were incident on the set of mirrors M2 and M3, forming two optical channels. The first channel at 1064 nm was the fundamental channel and the doubled frequency channel at 2 ω formed a writing channel. A set of polarizers P1/P2 and lenses L1/L2 form two coherent beams with different intensities. Additionally using a set of polarizers and lenses gives an opportunity to tune the power densities of the fundamental ω and writing 2 ω beams. The photoinduced process contains two

stages. The first one is the bicolor photopolarization, realized using simultaneous illumination by two bicolor beams. This process has a duration of up to 2-3 mins and its efficiency and saturation were controlled using continuous wave (CW) low power He-Ne laser diffraction gratings. During this step, a non-centrosymmetric charge density is created. The second step (measurements of the photoinduced SHG) requires switching off the writing channels and only performing registration for the output SHG using a set of green interferometer filters. The polarizers operate by light polarizations of the angles between the laser beams based on the ratio between the fundamental and the writing beams. The SHG efficiency was determined using the photomultiplier with the ratio of the corresponding intensities. Additionally, for space control of the SHG we analyzed the SHG space distribution using a CCD camera.

The principal mechanisms of the bicolor coherent treatment are explained by the occurrence of gratings. Generally, in our case some optically induced electrostatic field occurs due to photocarrier charge separation, which is more prominent for the 3*d*-localized Cu states. The electrostatic field favors an occurrence of second order optical susceptibilities through the equations $\chi_{ijk}^{(2)} = \chi_{ijkl}^{(2)} E_{0l}$, where $\chi_{ijk}^{(2)}$ corresponds to third rank polar tensors requiring charge density acentricity and $\chi_{ijkl}^{(2)}$ corresponds to fourth rank tensors describing the effects which do not need space density acentricity. Additionally, the bicolor coherent interaction leads to the occurrence of birefringence of the Δn_{ij} gratings, which is responsible for the existence of the SHG [46].

For the non-linear optical studies, the powders were embedded into polyvinyl alcohol (PVA) photopolymer matrices. Among the different concentrations, 35% was optimal. All the solidified processes were carried out similarly to that described in the literature [47]. To evaluate the efficiency of the second order susceptibilities, we have used the reference organic samples studied earlier [1]. These crystals are among the best for observing photoinduced second order NLO effects. For example, in many materials [48-52] studied under the same experimental conditions by us, the effect was less than 15 %.

The effective second order susceptibility, determined by the ratio of the corresponding maximal SHG intensities, versus the fundamental power density is given in Fig. 4.



Fig. 4. Dependence of the laser induced second order susceptibilities versus the laser induced power density for the two output polarization of the SHG with respect to the fundamental ones.

The optical treatment was performed by two bicolor coherent beams at angles varying within 20-21 degrees for the two polarizations with respect to the fundamental beams. Fig. 4 shows an increase of the second order susceptibility with enhancement of the laser induced power density up to 20 MW/cm². To avoid the influence of the parasitic fluorescence background, two filters at wavelengths of 528 and 535 nm have been used. The further increase of the SHG was limited by the samples photo-thermal destruction. The effect disappeared over 2-3 minutes after switching off the two bicolor beams, however some irreversible SHG remains (up to 10 %).



Fig. 5. The beam profile of the output SHG for the different ratios of the photoinduced ω to 2 ω beam powers. The left (*a*) corresponds to a ratio of 4:1 and the right one (*b*), 6:1.

Fig. 5 clearly confirms that some space gratings occur, and the gratings are also directly related to the SHG efficiency and the laser stimulated gratings absorption. The higher space frequency favors higher SHG intensities and it is closely connected to the photoinduced gratings. During the measurements we varied the ratio between the fundamental and the doubled frequency intensities within the range 3:1 to 10:1. It appeared that the maximal signal was achieved for the ratio 6:1. This confirms the huge role of the laser induced gratings. Additionally, it is necessary to empathize that a similar treatment of the optical lead containing glasses [53-56] gives an effect a least half an order less. This may indicate the principal role of the Cu-containing bonds to the effect observed. Additionally, disordered oxide materials, even with Cu, are more stable and are not sensitive to laser induced changes [57].

3.3. Quantum chemical calculations

HOMO and LUMO space distribution plots for compound **1** are presented in Fig. 6. In the calculated UV-Vis spectra in the range 250-700 nm, the electronic transitions are presented mainly by three peaks – a main peak at an approximate wavelength of 255 nm and two weak absorption maxima at around 279 and 297 nm (Fig 7). The last two mentioned peaks mainly correspond to the electronic transitions from HOMO-1 (MO 197) to the MOs which are located near ligand molecules, which is associated with a charge transfer from the $NH_2SO_3^-$ anion and Cu^+ cation donor fragments to the rest of the ligand molecule (Tables 3 and S1). One can conclude that we deal with a clear donor-acceptor space separation defining a principal charge transfer from the $NH_2SO_3^-$ anion to the ligand molecule.

Excitation	CI expansion	Excitation	Calculated	Oscillator
	coefficient	energy (eV)	wavelength (nm)	strength (f)
	Singlet-A	4.1801	296.60	0.0120
197 ->205	-0.27001			
197 ->206	0.59886			
197 ->208	0.15688			
	Singlet-A	4.4434	279.03	0.0102
193 ->200	0.51946			
194 ->200	-0.23470			
197 ->204	-0.11137			
197 ->205	0.30556			
197 ->206	0.16581			
197 ->208	-0.12269			

Table 3

Selected calculated absorption wavelengths, energies and oscillator strengths of 1

Since the samples were prepared in the form of microcrystalline powders, characteristic SHG properties could be described using average first-order hyperpolarizability. First-order hyperpolarizability (β) is a third order tensor which can be described by a 3 × 3 × 3 matrix with 27 components, which can be reduced to 10 components due to the Kleinman symmetry. Using *x*, *y* and *z* components, the hyperpolarizability (β) could be written as follows:

 $\beta = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}$ $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$ $\beta_y = \beta_{yyy} + \beta_{yxx} + \beta_{yzz}$ $\beta_y = \beta_{zzz} + \beta_{zxx} + \beta_{zyy}$

The (β) components of the GAUSSIAN 09 output are reported in atomic units and therefore the calculated values are converted into esu units (1a.u =8.6393 × 10⁻³³esu). The computed values of the dipole moment μ and the average hyperpolarizability (β) for **1** equals 20.79 D and 3.92×10⁻²⁹esu.



Fig. 6. {Cu(*m*-*dmphast*)NH₂SO₃}₂ fragment (*a*) and its HOMO-1 (*b*), HOMO (*c*) and LUMO (*d*) plots.



Fig. 7. Experimental (*a*) and theoretically calculated (*b*) UV-VIS spectra of compound 1.

4. Conclusions

We have synthesized and determined the crystal structure of a novel copper(I) π complex, [Cu^I(*m*-*dmphast*)NH₂SO₃] (1), with the 5-(allylthio)-1-(3,5-dimethylphenyl)-1*H*tetrazole (*m*-*dmphast*) ligand. It is the only example to date of a metal sulfamate coordination

compound with a tetrazole ligand. *m-Dmphast* acts as a chelate π,σ -ligand, being attached to the Cu(I) ion by means of the allylic C=C bond and one tetrazole N atom. In complex **1**, the sulfamate anion is coordinated to two neighboring Cu(I) ions in the bridged mode, occupying a basal plane (through the N atom) and an apical position (through an O atom) of two neighboring metal trigonal pyramids. A high efficiency of the studied material for optical treatment by an external bicolor laser nanosecond light at 1064 nm was established. The effect is almost independent of the polarization and is higher than for known non-linear optical lead containing glasses. The principal role here is played by highly localized *3dCu* states.

Appendix A. Supplementary data

CCDC 1816413 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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A novel crystalline π -complex, [Cu^I(C₁₂H₁₄N₄S)NH₂SO₃], was grown.

The complex was studied by single crystal X-ray diffraction, IR- and UV-VIS spectroscopy.

The structure is considered as the first known example of a metal sulfamate coordination compound with a tetrazole ligand.

Quantum chemical calculations were performed using DFT and the B3LYP functional Effective laser operated non-linear optics are found