

## Synthesis, Characterization and Thermal Decomposition of $[\text{Cu}(\text{H}_2\text{O})_2(\text{nia})_2\text{SO}_4]$ , nia = Nicotinamide

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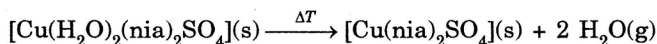
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$[\text{Cu}(\text{H}_2\text{O})_2(\text{nia})_2\text{SO}_4]$ , nia = nicotinamide, was prepared by the reaction between aqueous solutions of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and nicotinamide, and was characterized by standard chemical and physical methods. Thermal behaviour of the sample in inert atmosphere proceeds in several steps. The dehydration of the sample (330–445 K) with 8.3% of mass loss (theoretical value 8.2%) is followed by a strong exothermal peak in DTA curve at 462 K, which is not accompanied by any significant mass change. Changes in electronic spectra and powder patterns of residues indicate a recrystallization process. This suggestion was confirmed by the EPR spectra of powder samples recorded in the temperature range from 295 K to 473 K. Changes of  $g$  values reflect modifications of the coordination sphere around copper(II) in the temperature range from 295 K to 423 K. In this temperature range, the symmetry type of the complex should have remained the same. However, above 423 K EPR spectra reflect major structural alternations. Significant changes of IR spectra in 900–1250  $\text{cm}^{-1}$  region, where characteristic bands of  $\text{SO}_4^{2-}$  are present, indicate changes in the coordination mode of sulfate anion. All the observed results can be interpreted by slightly modified anation reaction in the solid state



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in which the loss of neutral volatile ligand  $\text{H}_2\text{O}$  is accompanied by rearrangement of coordinated ligands.

No significant change in fungicidal activity was observed for the title compound, as compared to the starting material  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

## INTRODUCTION

Transitional metal complexes with potential biological activity are being investigated more frequently now than ever before. Most of the first-row transition metals are biologically essential, with a number of the complexes demonstrating a range of bioactivities. Our interest in copper(II) carboxylate complexes evolves from their fungicidal and insecticidal implications.<sup>1</sup> During our work on coordination compounds of copper carboxylates with biologically important ligand nicotinamide<sup>2</sup> we have accidentally isolated the title compound. A routine thermogravimetric analysis revealed interesting properties, which was the reason for our undertaking a complete characterization and thermal decomposition study of the compound.

## EXPERIMENTAL

### *Synthesis*

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , nicotinamide (nia), and all solvents were purchased from commercial sources and used without further purification. The title compound was prepared after following procedure: 5.0 g (20 mmol) of finely ground  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was dissolved in 150 mL  $\text{H}_2\text{O}$ , acidified with a few drops of 20%  $\text{H}_2\text{SO}_4$  and mixed with a solution of 10.0 g (82 mmol) of nicotinamide in 90 mL  $\text{H}_2\text{O}$ . The obtained solution was left at room temperature for three days. The pale-blue product was filtered off, washed thoroughly with several portions of absolute ethanol, dried in air and over KOH under reduced pressure. Average yield: 70%. *Anal.* Calc. for  $[\text{Cu}(\text{H}_2\text{O})_2(\text{nia})_2\text{SO}_4]$  ( $M_r = 439.90$ ): Cu 14.4, C 32.8, H 3.67, N 12.7,  $\text{H}_2\text{O}$  8.2%; found Cu 13.7, C 32.5, H 3.32, N 12.9,  $\text{H}_2\text{O}$  8.3% (from TG analysis).  $\mu_{\text{eff}}(298 \text{ K}) = 1.83 \text{ BM}$ ; UV-VIS(Nujol)  $\lambda_{\text{max}}$ : 294 nm, 691 nm (broad). The measured  $d$  spacings with relative intensities are given in Table I.

### *Physical Measurements*

Interplanar spacings were obtained with the Guinier-de-Wolf camera (Enraf Nonius) and Cu- $K\alpha$  radiation. Infrared spectra were measured on mineral oil mulls between CsI plates using a Perkin-Elmer FT-IR 1720X spectrometer in the range 4000–220  $\text{cm}^{-1}$ . Electronic spectra (200–850 nm) were obtained on a Perkin-Elmer UV/VIS/NIR Spectrometer Lambda 19 with the solid compounds suspended in Nujol mulls. The mulls were smeared on filter paper and run against a reference consisting of a similar piece of filter paper soaked in Nujol. Room-temperature magnetic susceptibility measurements of powdered samples were performed with a Sherwood Scientific MSB-1 balance using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as a calibrant. Diamagnetic correc-

tions were applied using Pascal's constants and the effective magnetic moment was calculated from the expression:  $\mu_{\text{eff}} = 2.83(\chi_M T)^{1/2}$ .

NETZSCH STA 409 apparatus was used for TG/DTG/DTA measurements. Analyses were carried out under the following conditions: initial  $T = 293$  K, heating rate  $2 \text{ K min}^{-1}$ , purge gas dry argon, flow rate  $6 \text{ L h}^{-1}$ , initial mass about 35 mg, reference material  $\text{Al}_2\text{O}_3$ , crucible 0.3 mL  $\alpha\text{-Al}_2\text{O}_3$ . For EGA (TG/MS) analysis, NETZSCH STA 409 apparatus was connected with a capillary coupling system to a quadrupole mass spectrometer LEYBOLD HERAEUS QUADREX 200. Conditions at TG measurements were the same as for TG/DTG/DTA analysis, except for the initial mass being 250 mg. The connecting capillary was heated up to 473 K. Inlet pressure to mass spectrometer was 1 mbar, pressure in MS was  $1.2 \times 10^{-5}$  bar. Masses from 1 to 100 were detected.

EPR spectra of powdered samples were recorded on a Bruker ESP-300 X-band spectrometer in the temperature range from 295 to 473 K. Temperature was regulated by heating and by blowing nitrogen through the Bruker flow Dewar with a sample. In order to ensure uniform heating of samples, capillaries with powder were left for five minutes at the selected temperature under a gas stream before each measurement.

## RESULTS AND DISCUSSION

During our studies of complex formation between copper(II) benzoate and nicotinamide (nia) in aqueous solution, we isolated, at low molar proportions of copper and benzoate ligand in the presence of (nia) ( $\text{Cu}(\text{II}) : \text{C}_6\text{H}_5\text{COO}^- \leq 1 : 1$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{NaC}_6\text{H}_5\text{COO}$  as starting materials), compound **1** in the form of pale-blue needles. IR spectrum of the isolated compound **1** gives evidence for the presence of water, nicotinamide and sulfate anion, but none of the characteristic vibration modes of benzoate ligands were observed. Therefore, we repeated the synthesis without addition of sodium benzoate and the same compound was obtained. Optimized conditions for the preparation are given in the experimental section. Analytical data and the evidence of water content obtained with TG analysis are consistent with the formulation of compound **1** as  $[\text{Cu}(\text{H}_2\text{O})_2(\text{nia})_2\text{SO}_4]$ , indicating the difference with already described compound  $[\text{Cu}(\text{nia})_2\text{SO}_4]$ .<sup>3</sup> The IR spectrum clearly indicates the presence of coordinated sulfato groups. The sequence of three very strong bands at 1147, 1100 and  $1063 \text{ cm}^{-1}$  in the  $\nu_3$  fundamental region of the sulfato group (labelling after Nakamoto *et al.*)<sup>4</sup> indicates bidentate bridging or chelating sulfato coordination. Due to the presence of four other ligands (2 nia and 2  $\text{H}_2\text{O}$ ), the bridging bidentate coordination is more probable. Bi- or poly-nuclear bridged  $\text{Cu}(\text{II})$  complexes usually exhibit subnormal magnetic moments, attributable to spin-spin coupling occurring *via* a superexchange mechanism operating through the orbitals of the bridging atoms. The magnetic moment measured for **1** is 1.83 BM, slightly higher compared to the spin only magnetic moment of 1.73 BM,

and characteristic of the monomeric Cu(II) complexes. We believe that this is not in contrast with the bridging nature of sulfato group, because super-exchange through the Cu-(OS(O<sub>2</sub>)O)-Cu bridges would be rather unlikely.<sup>5</sup>

The broad maximum centred at 691 nm in the electronic spectrum of the title compound (d-d transition) strongly supports a distorted octahedral stereochemistry. 294 nm band has been assigned to nicotinamide  $\pi \rightarrow \pi^*$  transition. Therefore, we believe that two molecules of (nia) and two molecules of H<sub>2</sub>O are coordinated to Cu(II) in the equatorial plane through *N*- and *O*-atoms, respectively, while the sulfato group connects these entities through apical positions into an infinite chain.

Thermal decomposition of the sample in inert atmosphere proceeds in several steps (Figure 1). All the characteristic data on thermal decomposition are gathered in Table II. The temperature interval of the first process – dehydration of the sample – is rather high, confirming the coordination of water molecules to copper atoms. Dehydration of the sample is followed by a strong exothermal peak in DTA curve at 462 K, which is not accompanied by any significant mass change, and only traces of H<sub>2</sub>O were detected by the EGA analysis. A well characterized change in the diffraction pattern

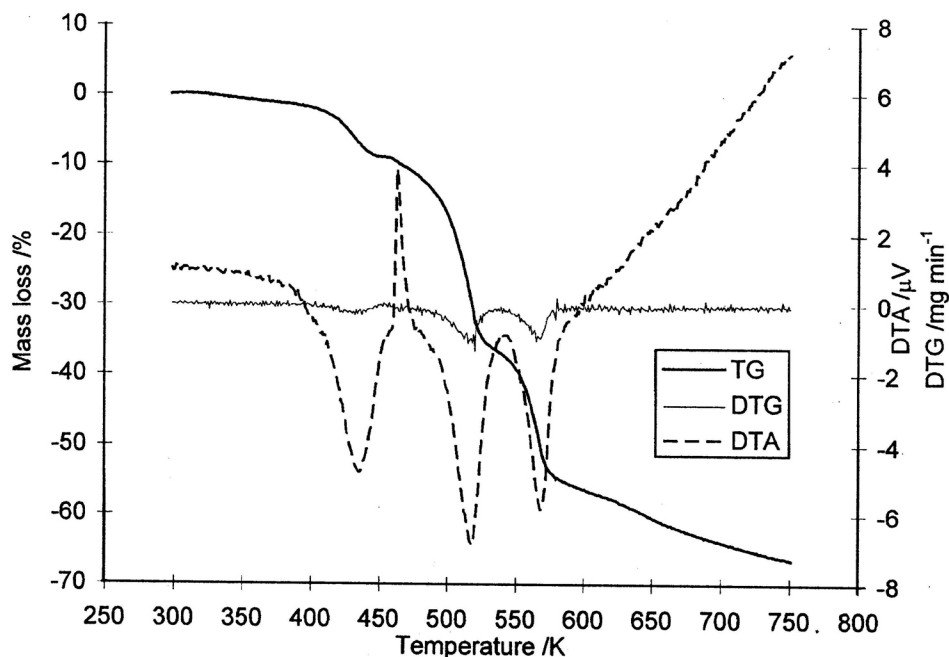


Figure 1. TG/DTG/DTA curves for thermal decomposition of [Cu(H<sub>2</sub>O)<sub>2</sub>(nia)<sub>2</sub>SO<sub>4</sub>] (1) in inert atmosphere.

of residue **2** (see Table I) suggests that the phase transition is a recrystallization process, in which the loss of  $\text{H}_2\text{O}$  ligands is followed by rearrangement of coordinated ligands. This rearrangement leads to formation of compound  $[\text{Cu}(\text{nia})_2\text{SO}_4]$ , which stoichiometry was confirmed by the results of elemental analysis. This type of solid-state reaction of coordination compounds is well known.<sup>6</sup>

TABLE I

Measured  $d$ -values with relative intensities ( $I/I_0$ ) for  $[\text{Cu}(\text{H}_2\text{O})_2(\text{nia})_2\text{SO}_4]$  (**1**) and  $[\text{Cu}(\text{nia})_2\text{SO}_4]$  (**2**)

<b>1</b>	$d_{\text{meas}}/\text{\AA}$	10.9	7.95	7.45	5.75	5.39	4.94	4.70	3.93	3.88	3.70
	$I/I_0$	4	5	1	4	2	10	3	1	9	1
<b>2</b>	$d_{\text{meas}}/\text{\AA}$	11.1	6.3	6.2	5.57	4.76	4.62	4.22	4.15	3.94	3.76
	$I/I_0$	10	1	4	3	8	1	3	3	7	1

Significant changes in SO stretching bands are observed when **1** is heated to the temperature where the exothermic DTA peak described above appears. A broad very strong absorption band at  $1118\text{ cm}^{-1}$  (with well defined shoulder at  $\approx 1125\text{ cm}^{-1}$ ) in the IR spectrum of residue **2** can be identified as  $\nu_3$  mode due to the sulfato group with  $T_d$  symmetry, indicating that a regular coordination by all four oxygens of the sulfato group is present. A polymeric structure similar to that of  $[\text{Cu}(\text{isn})_2\text{SO}_4]$ , (isn) = isonicotinamide (structure H in Ref. 3) is tentatively assigned to product **2**. The broad band centred at  $692\text{ nm}$  in the electronic spectrum and effective magnetic moment of  $1.90\text{ BM}$  are in agreement with such proposition, which was confirmed by the EPR spectra of powder samples recorded in the temperature range from  $295$  to  $473\text{ K}$ . At room temperature, as well as at temperatures up to  $423\text{ K}$ , axial EPR spectra were observed (Figure 2). Such spectra are expected for rhombic symmetry around copper(II) with slight misalignment of the »tetragonal« axes ( $G < 4.0$ ). The determined  $g$  values reflect  $d_{x^2-y^2}$  ground state of copper(II). In the temperature range up to  $423\text{ K}$ ,  $g_{\parallel}$  increases from  $2.306 \pm 0.002$  to  $2.326 \pm 0.002$  and  $g_{\perp}$  remains unchanged at  $2.076 \pm 0.003$ . The changes in  $g$  values reflect modifications of the coordination sphere around copper(II), probably caused by emission of water molecules from the sample, which was already proved by thermal analysis. However, the symmetry type must have remained the same. On heating above  $423\text{ K}$ , the EPR spectrum alters from axial to nearly isotropic with  $g_0 = 2.26 - 2.27$  (Figure 2), implying major structural changes of the studied compound. Various stereochemical features can result in broad isotropic EPR line shapes, but the most common reasons for the observation of such spec-

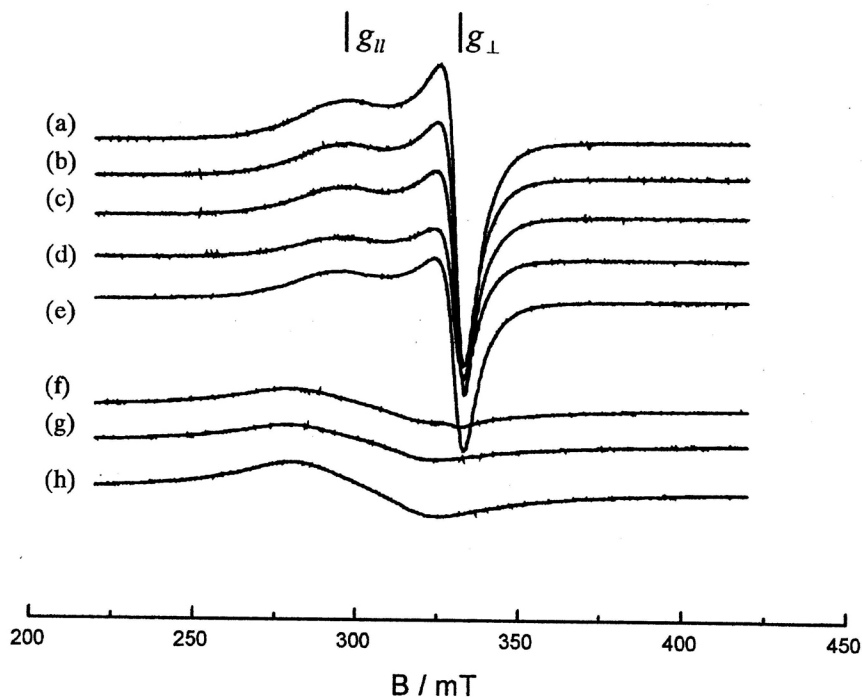


Figure 2. EPR spectra of  $[\text{Cu}(\text{H}_2\text{O})_2(\text{nia})_2\text{SO}_4]$  (1) recorded at room temperature (a), 353 K (b), 373 K (c), 393 K (d), 423 K (e), 433 K (f), 473 K (g) and after cooling back to room temperature (h); (microwave power: 20 mW, modulation frequency: 100 KHz, modulation amplitude: 4.113 G).

TABLE II

Thermal decomposition data for  $[\text{Cu}(\text{H}_2\text{O})_2(\text{nia})_2\text{SO}_4]$  (1)

T range/K	$\Delta m/\%$	DTG peak/K	DTA peak/K	MS/AMU
330–445	8.3	428	434.5 <i>endo</i>	18 – $\text{H}_2\text{O}$
445–465	0.4	–	462 <i>exo</i>	18 – $\text{H}_2\text{O}$
465–535	27.9	515	517 <i>endo</i>	18 – $\text{H}_2\text{O}$ ; 26 – CN 44 – $\text{CO}_2/\text{CONH}_2$ ; 50 – $\text{C}_4\text{H}_2$ ; 77 – $\text{C}_5\text{H}_3\text{N}$
535–575	17.4	568	568 <i>endo</i>	18 – $\text{H}_2\text{O}$ ; 26 – CN; 44 – $\text{CO}_2/\text{CONH}_2$ ; 64 – $\text{SO}_2$
580–750	12.4	–	–	–

tra are dynamically distorted octahedral stereochemistry or grossly misaligned local »tetragonal« axes in the structure.<sup>7</sup> We believe that the structural changes described above, which occur upon heating above 423 K, are the possible reason for the changes of EPR line shapes. Small differences in temperatures of the observed changes are most probably due to the different experimental techniques used.

Further steps of thermal decomposition are more complex and the interpretation not straightforward. Results of the TG and EGA analyses suggest elimination of one nicotinamide molecule in the third temperature interval and the sulfato group in the fourth one.

Fungicidal activity was estimated visually by measuring the fungal growth retardation, as described previously.<sup>1a</sup> No significant change in fungicidal activity was observed for  $[\text{Cu}(\text{H}_2\text{O})_2(\text{nia})_2\text{SO}_4]$ , as compared to the starting material  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

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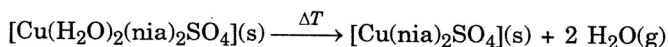
## SAŽETAK

**Sinteza, karakterizacija i toplinska razgradnja**  
**[Cu(H<sub>2</sub>O)<sub>2</sub>(nia)<sub>2</sub>SO<sub>4</sub>], nia = nikotinamid**

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[Cu(H<sub>2</sub>O)<sub>2</sub>(nia)<sub>2</sub>SO<sub>4</sub>], nia = nikotinamid pripremljen je reakcijom vodene otopine CuSO<sub>4</sub> · 5H<sub>2</sub>O i nikotinamida i karakteriziran standardnim kemijskim i fizikalnim metodama.

Promjene pri zagrijavanju uzorka u inertnoj atmosferi stupnjevite su: nakon dehidriranja uzorka (330–445 K) uz 8,3% gubitka mase (teorijska vijednost 8,2%) slijedi jak egzotermni maksimum u krivulji DTA, pri 462 K, koji nije popraćen znatnijim gubitkom mase. Promjene u elektronskim spektrima i rentgenskim difraktogramima praška ostatka ukazuju na rekristalizacijski proces. To je potvrđeno spektrima ESR praškastih uzoraka snimljenih u temperaturnom području od 295 K do 473 K. Promjene vrijednosti *g* odražavaju modificiranje koordinacijske sfere bakra(II) u temperaturnom području od 295 K do 423 K. U tom je temperaturnom području kompleks trebao zadržati istu simetriju. Međutim, iznad 423 K spektri ESR odražavaju strukturnu promjenu. Znatne promjene IR spektra u području 900–1250 cm<sup>-1</sup>, gdje su prisutne karakteristične vrpce SO<sub>4</sub><sup>2-</sup>, upućuju na promjene koordinacijskog moda sulfatnog aniona. Svi dobiveni rezultati mogu se objasniti modificiranom reakcijom zamjene koordinirane vode anionskim ligandom u čvrstom stanju



u kojoj je gubitak neutralnog hlapivog liganda H<sub>2</sub>O popraćen premještanjem koordiniranih liganada.

Nije uočena značajna promjena u fungicidnoj aktivnosti navedenog spoja u usporedbi s polaznim spojem CuSO<sub>4</sub> · 5H<sub>2</sub>O.