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The synthesis and characterization of nickel(II) and copper(II) complexes with the polydentate dialkyl dithiocarbamic acid ligand 3-dithiocarboxy-3-aza-5-aminopentanoate

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Square planar complexes of Ni(II) and Cu(II) with potassium 3-dithiocarboxy-3-aza-5-aminopentanoate have been prepared by direct synthesis. The obtained neutral complexes were characterized by elemental analysis, magnetic susceptibility measurements, infrared and electronic spectra. The thermal behaviour of both the Ni(II) and Cu(II) complexes, and the ligand itself was investigated by DSC and TG.

Keywords: nickel(II), copper(II), dithiocarbamate, synthesis, complexes, thermal analyses.

INTRODUCTION

A large number of transition metal complexes with various aliphatic and aromatic dithiocarbamate ligands have been synthesized until now.^{1–4} Complexes with dithiocarbamate ligands like dithiocarbamates themselves have practical application in agriculture, and in medicine for the treatment of alcoholism.^{5–6}

The dithiocarbamate ligands reported in the literature^{1–4} have only the dithiocarboxy group as the ligator group, so they behave like bidentate ligands in complexes. We have recently synthesized potassium 3-dithiocarboxy-3-aza-5-aminopentanoate dihydrate⁷ [K-DAAP · 2H₂O], a polydentate ligand of the dialkyldithiocarbamic acid type, the structure of which was determined by X-ray structure analysis.

The ligand K-DAAP · 2H₂O has five potential donor atoms: two sulfur atoms from the dithiocarboxy group, two nitrogen atoms, and an oxygen atom from the carboxylic group (Scheme 1). Therefore, the ligand can be coordinated to a central

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metal ion as a bidentate (*via* the two sulfur atoms) or as a tridentate ligand (*via* the two nitrogen atoms and the oxygen atom).

The first transition metal complex with K-DAAP · 2H₂O to be synthesized and characterized was the Co(II) complex.⁸ This complex with octahedral geometry has three dithiocarbamate ligands coordinated as bidentates. The thermal behaviour of the complex in temperature range from 20 °C to 600 °C indicated that on loss of crystal water and one ligand molecule, structural transformations occurred, *i.e.*, rearrangement from octahedral to square planar geometry. The obtained square planar cobalt(II) complex showed thermal stability until 600 °C.

The subject of this work was the synthesis and characterization of Ni(II) and Cu(II) complexes with potassium 3-dithiocarboxy-3-aza-5-aminopentanoate dihydrate, with particular accent on the thermal behaviour of both the ligand and the complexes.

EXPERIMENTAL

Materials

Ethylenediamine-*N*-monoacetic acid dihydrochloride was prepared according to the published procedure.⁹ All other substances were used without further purification.

Preparation of bis(3-dithiocarboxy-3-aza-5-aminopentanoato)-nickel(II), Ni(DAAP)₂

To a solution of 1 mmol (0.237 g) of NiCl₂ · 6H₂O in 5 ml of water, 2 mmol (0.536 g) of K-DAAP · 2H₂O were slowly added. The light-green Ni(DAAP)₂ precipitated immediately. The mixture was stirred for a further half an hour after which the precipitate of the complex was filtered off, washed several times with 1 × 10⁻³ mol/l HCl, then acetone, and finally air-dried. Yield: 0.3 g (67.5 %). Anal. Calcd. for Ni(DAAP)₂ = NiC₁₀H₁₈O₄N₄S₄ (FW = 444.70): C, 26.98; H, 4.05; N, 12.59. Found: C, 26.43; H, 4.42; N, 12.19. μ_{eff} = 0.00 BM.

Preparation of bis(3-dithiocarboxy-3-aza-5-aminopentanoato)-copper(II), Cu(DAAP)₂

To a solution of 1 mmol (0.370 g) of Cu(ClO₄)₂ · 6H₂O in 5 ml of water, 2 mmol (0.536 g) of K-DAAP · 2H₂O were slowly added. The brown Cu(DAAP)₂ was precipitated immediately. The mixture was stirred for a further half an hour after which the precipitate of the complex was filtered off, washed several times with 1 × 10⁻³ mol/l HCl, then acetone and finally air-dried. Yield: 0.41 g (91.2 %). Anal. Calcd. for Cu(DAAP)₂ = CuC₁₀H₁₈O₄N₄S₄ (FW = 449.50): C, 26.69; H, 4.00; N, 12.46; Cu, 14.12. Found: C, 27.37; H, 4.38; N, 11.98; Cu, 14.06. μ_{eff} = 1.79 BM.

Physical measurements

Analyses for C, H, and N were performed out by conventional methods at the Laboratory for Microanalysis of The Faculty of Chemistry, Belgrade. The Cu content was determined by atomic absorption spectrometry using a Perkin Elmer spectrophotometer model 1100-B.

The infrared spectra in the 4000–400 cm⁻¹ range were measured on a Perkin Elmer FTIR 317 25X spectrophotometer using the KBr technique. The far IR spectra were measured on a Perkin Elmer 983 spectrophotometer using Nujol mull supported between CsI sheets.

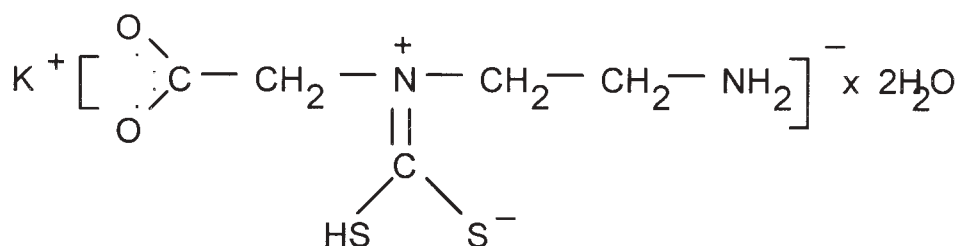
The electronic absorption spectrum of Cu(DAAP)₂ was recorded on a GBC UV/VIS 911A spectrophotometer (8 × 10⁻⁵ mol/l aqueous solution). The electronic absorption reflection spectrum of solid Ni(DAAP)₂ was recorded on Cary 2300 spectrophotometer at the Dipartimento di Chimiche e Technologie Inorganiche e Metallorganiche, Università di Cagliari, 09124 Cagliari, Italy.

The magnetic susceptibilities were determined at room temperature using a magnetic susceptibility balance MSB-MKI. The data were corrected for diamagnetism.

Thermal analysis was performed on a thermoanalyzer Du Pont 1090. DSC and TG curves were obtained in nitrogen at a scan rate of 20 °/min.

RESULTS AND DISCUSSION

Potassium 3-dithiocarboxy-3-aza-5-aminopentanoate (K-DAAP) (Scheme 1), the ligand with a large number of possible donor atoms (two sulfur atoms, two nitrogen atoms and one oxygen atom from the deprotonated COOH group), was obtained by direct synthesis.



Scheme 1. The structure of the K-DAAP · 2H₂O molecule.

The DAAP ligand could be coordinated to transition metal ions as either a tridentate O,N,N' ligand or a bidentate S,S' ligand. The complexes of Ni(II) and Cu(II) with 3-dithiocarboxy-3-aza-5-aminopentanoate were prepared by direct synthesis and characterized by elemental analysis, infrared and electron absorption spectroscopy, and magnetic susceptibility measurements. The behavior of these complexes during thermal decomposition was also studied.

Spectroscopic characterization of the complexes

The most significant bands recorded in the IR spectra of the DAAP ligand, as potassium salt, and corresponding Ni(II) and Cu(II) complexes are shown in Table I.

TABLE I. The most important infrared absorption bands (cm⁻¹)

	COO ⁻		C-N ^a	C-S	S-H	M-S
	ν_{as}	ν_s				
K-DAAP	1597	1414	1453	963	2631	
Ni(DAAP) ₂	1605	1420	1480	960		390
Cu(DAAP) ₂	1608	1412	1480	951		370

^aCarbon atom of the dithiocarbamate group

All the examined substances show bands in the 1500–1450 cm⁻¹ range (Table I). These bands can be assigned to carbon-nitrogen bonds, and lie between $\nu(C=N)$ (1680 – 1640 cm⁻¹) and $\nu(C-N)$ (1350–1250 cm⁻¹) ranges,^{4,10} suggesting a considerable double bond character of the C–N bond in the dithiocarbamate group. As the double bond character is more pronounced in the complexes (larger wave numbers), it can be concluded that the ligand is coordinated *via* S,S' atoms. The lack of S–H band in the complexes confirms such a mode of coordination.

The presence of asymmetric stretching vibrations of carboxylate groups at 1610–1590 cm^{-1} suggests that the carboxylic groups are deprotonated both in the DAAP ligand, and the corresponding Ni(II) and Cu(II) complexes.^{11–13} Based on the spectral data and elemental analysis, it is obvious that the amino group is protonated, *i.e.*, that the uncoordinated part of the DAAP molecule is in the zwitter ion form.

In the far-IR region, the bands of the ligand are mostly unchanged in the spectra of the complexes but new bands at 390 cm^{-1} (for the Ni(DAAP)₂ complex) and at 370 cm^{-1} (for the Cu(DAAP)₂ complex) due to $\nu(\text{M-S})$ stretching modes^{2–4,10} appear.

Electronic spectra

The electronic spectra data are given in Table II.

TABLE II. Electronic spectra data for the Ni(DAAP)₂ and Cu(DAAP)₂ complexes

Complex	Transition	$\lambda_{\text{max}}/\text{nm}$
Ni(DAAP) ₂	$d_{xy} \rightarrow d_{x^2-y^2}$	640
	$d_z^2 \rightarrow d_{x^2-y^2}$	490
	L \rightarrow M	440
	L \rightarrow M	410
	$\pi \rightarrow \pi^*$	320
	$\pi \rightarrow \pi^*$	230
Cu(DAAP) ₂	$d_{xy} \rightarrow d_{xz}$	438

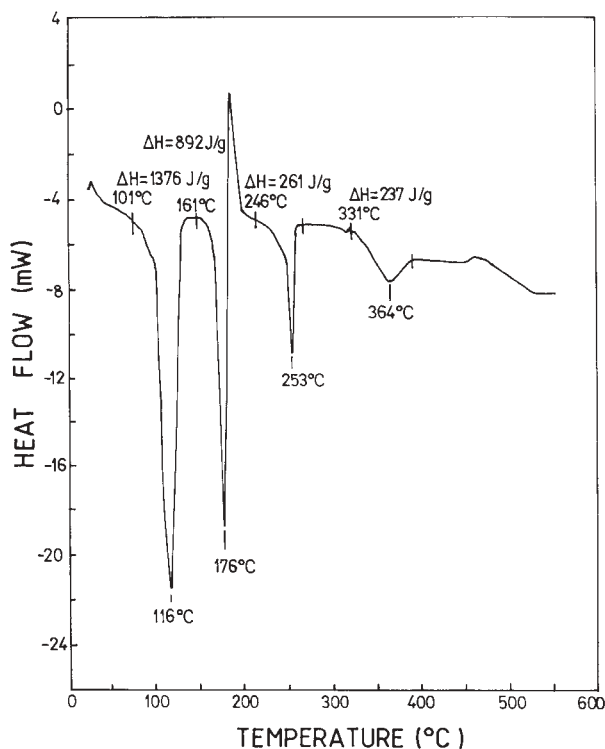
The expected local symmetry around the nickel(II) ion is not strictly D_{4h}, but D_{2h} symmetry, as the S–S distances between the two sulphur atoms belonging to the same dithiocarbamate ligand are usually shorter than the distances between the two sulphur atoms in the *cis* positions belonging to two ligands.

Four bands are to be expected for Ni(II) complexes with D_{2h} symmetry,^{4,10} but in the case of the Ni(DAAP)₂ complex six bands were recorded. According to results published earlier,^{4,10,14–16} the low intensities of the first two bands (at 640 and 490 nm) indicate that these bands could be assigned to d-d, Laporte forbidden, spin-allowed transitions of the Ni(II) ion. The medium-intensity bands (at 440 and 410 nm) are due to metal-ligand charge transfer processes.¹⁶ The last two bands (at 320 and 230 nm) are usually ascribed to transitions in the ligand.

According to other authors,^{4,17} two bands (at about 660 and 460 nm) are to be expected for Cu(II) complexes with D_{2h} symmetry. These bands are due to $d_{xy} \rightarrow d_z^2$ and $d_{xy} \rightarrow d_{xz}$ transitions. The isolated Cu(DAAP)₂ complex shows only one very broad and intense band (at 438 nm) with no indication of resolution. This band could be ascribed to $d_{xy} \rightarrow d_{xz}$ transitions of the Cu(II) ion but the band originating from $d_{xy} \rightarrow d_z^2$ transitions was not recorded because of its low intensity and the insolubility of the Cu(DAAP)₂ complex.

Magnetic measurements

The nickel(II) complex with the DAAP ligand is diamagnetic ($\mu_{\text{eff}} = 0.00$ BM) indicating the square-planar structure of the complex. The copper(II) complex with a

Fig. 1. DSC curve of K-DAAP·2H₂O.

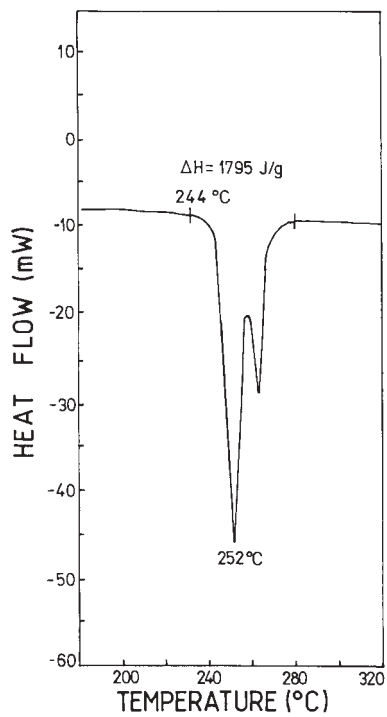
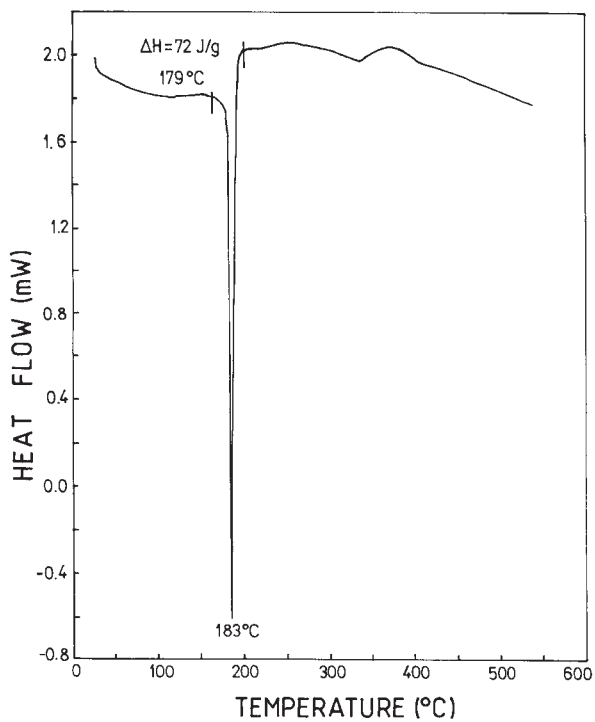
DAAP ligand is paramagnetic ($\mu_{\text{eff}} = 1.79 \text{ BM}$) confirming the presence of one unpaired electron¹⁸ but not probably the square-planar geometry of the complex.

Thermal analysis

The thermal behavior of the potassium salts of the ligand, as well as of the Ni(II) and Cu(II) complexes with 3-dithiocarboxy-3-aza-5-aminopentanoate was also studied. The thermal behaviour was studied using DSC and TG thermograms in the temperature range from 20 °C to 600 °C in a nitrogen stream.

The thermal decomposition of the ligand (K-DAAP·2H₂O) starts with the loss of crystal water. Between 144.4 °C and 159.5 °C an endothermic process, immediately followed by an exothermic process occurs, corresponding to the loss of a molecule of hydrogen sulfide. The resulting product is stable until 334.4 °C. The product is presumably potassium salt of 1-carboxymethyl-2-imidazolidinethione, an ethylenethiourea derivate. It is well known that thioureas can be prepared by heating amine salts of dithiocarbamic acids.¹⁹ In this particular case, the reaction, being intramolecular, would be particularly favored. At higher temperatures decomposition of the ligand proceeds in two endothermic steps (Fig. 1).

The square planar complexes of Ni(II) and Cu(II) have different thermal stabilities, although they are structurally similar. The Ni(II) complex is thermally stable until 243.7 °C, *i.e.*, is more stable than the ligand (Fig. 2). At higher temperatures stepwise

Fig. 2. DSC curve of [Ni(DAAP)₂].Fig. 3. DSC curve of [Cu(DAAP)₂].

endothermic decomposition takes place, but the steps are not separated sufficiently for the individual mass losses to be identified. The Cu(II) complex is less stable, and its degradation occurs in two well-separated steps, that do not proceed at an equal rate. Its swift decomposition starts at 179.8 °C, giving rise to a sharp endothermic peak, indicates a concomitant melting process (Fig. 3). The other, much slower step takes place in the temperature range 250 °C to 350 °C.

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ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА НИКАЛ(II) И БАКАР(II) КОМПЛЕКСА СА ПОЛИДЕНТАТНИМ ДИАЛКИЛ ДИТИОКАРБАМИНСКИМ ЛИГАНДОМ 3-ДИТИОКАРБОКСИ-3-АЗА-5-АМИНОПЕНТАНОАТОМ

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Директном синтезом између никал(II)- и бакар(II)- соли и калијум 3-дитиокарбоксо-3-аза-5-аминопентаноата наглађени су одговарајући комплекси квадратно-планарне структуре. Изоловани неутрални комплекси карактерисани су елементарном анализом, инфрацрвеном и електронском апсорпционом спектроскопијом, као и мерењем магнетних суцептибилитета. Термичко понашање комплекса и лиганда испитивано је применом DSC и TG метода.

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