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Synthesis and characterization of a dimeric complex of Cu^{II} with thiosalicylic acid and pyridine

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Abstract—The interaction between the Cu^{2+} cation and thiosalicylic acid was investigated. The solid complex is formed in methanolic solution and contains two Cu^{II} ions bridged by carboxylate groups of four ligand molecules and pyridine ligands that occupy the sixth coordination positions. Spectral measurements (IR, Raman and electronic spectra) show the lack of interaction of the —SH group in coordination. These results are supported by elemental and thermogravimetric analysis as well as magnetochemical measurements. © 1997 Elsevier Science Ltd

Keywords: copper(II); thiosalicylic acid; structure; spectroscopic data; thermal behavior; magnetic measurements.

The system Cu/thiosalicylic acid (H_2TSA), Fig. 1, was selected to continue our studies on the interaction of metals with ligands that contain biological and pharmacological activities; *cf.* the antimicrobial activities of the complexes generated between Ag^{I} and Au^{III} with H_2TSA for some bacteria, yeast and mold were demonstrated [1,2].

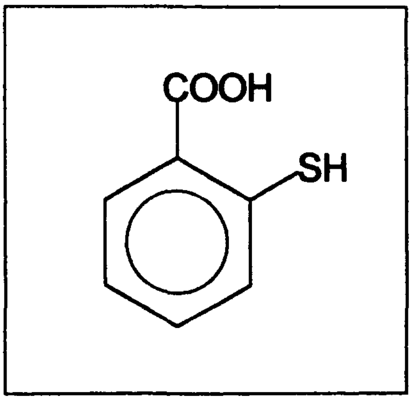

Fig. 1. Schematic structure of thiosalicylic acid (H_2TSA).

Previous work has reported the formation of a light blue complex with copper(II) and H_2TSA, in which the metal interacts with only one of the two potential binding sites of the ligand: the —SH group [3]. However, its characterization was incomplete.

We report in this work the synthesis and characterization of a new green complex containing Cu^{II}, H_2TSA and pyridine (py).

EXPERIMENTAL

Chemicals

All chemicals were used as received: $CuCl_2 \cdot 2H_2O$ (Riedel-de-Haën), H_2TSA (Sigma) and pyridine (Carlo-Erba).

Instrumentation

Room-temperature magnetic susceptibility was determined with a Cahn-2000 instrument, calibrated with $Hg[Co(SCN)_4]$ in the usual way, and magnetic field strength, 6 kG. Thermogravimetric (TG) and differential thermal analysis (DTA) were performed on a Shimadzu thermoanalytical system (models

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TG50 and DTA50). Alumina was used as a DTA standard.

The electronic absorption spectrum was obtained with a Hewlett–Packard 8452 diode-array spectrophotometer using 1 cm quartz cells. The diffuse reflectance spectrum of the solid complex was recorded with a Shimadzu UV-300 spectrophotometer using MgO as a standard. IR spectra were obtained with a Perkin–Elmer 580B spectrophotometer using the KBr pellet technique. The Raman spectrum was measured with a Spex-Ramalog Double Monochromator spectrometer, using the 514.5 nm line of an argon ion laser for excitation. Because the solid complex was burned by the laser light, the rotating disk technique was used.

Preparation

Na_2TSA was obtained mixing H_2TSA ($pK_{a1} = 5.44$; $pK_{a2} = 9.52$) [4] with NaOH in 1/2 ratio in aqueous solution. The disodium salt was precipitated with methanol. 2 mmol of H_2TSA were dissolved in 100 cm^3 of methanol and 0.8 cm^3 (10 mmol) of pyridine were added. $CuCl_2$ (1 mmol) was then added under agitation. The final pH value was 3.0. The solution turned its color from yellow to blue and finally a green precipitate was obtained; the solid was washed several times with methanol and stored in an oven at 60°C.

Solubility tests showed that the complex was not soluble in water and organic solvents (and mixtures of both) either at room or boiling temperatures. It was only solubilized in hot DMSO. Found : C, 51.3; H, 3.9; N, 3.6; S, 14.9%. Calc. for $C_{38}H_{30}S_4Cu_2N_2O_8$: C, 50.8; H, 3.3; N, 3.1; S, 14.3%.

RESULTS AND DISCUSSION

UV–vis and diffuse reflectance spectra

As mentioned above, solution studies could only be performed using DMSO as solvent. The complex showed a poorly resolved broad electron absorption band at 825 nm, suggesting coordination through the —COO^- group [5]. The relatively high ε value (70 M^{-1} cm^{-1}) agrees with a structure where the octahedra suffered a tetragonal distortion because of the Jahn–Teller effect.

The solid complex showed bands at 775, 433 and 395 nm; the first band has been identified with a *d–d* transition of the copper ions. The origin of the latter bands has been subjected to controversial analysis. The assignment can be due to a transition between Cu—Cu or to a bridging system. In the first case the odd electron in the $d_{x^2-y^2}$ orbital of each copper forms a δ bond and in the second, the interaction occurs between two metal centers of copper (II) interconnected by COO^- groups [5]. It can be concluded that such absorption is "characteristic of binuclear copper".

Evidently, DMSO produces a break of the carboxylate bridge and also acts as ligand in the sixth coordination position, generating the observed shift in the electronic spectrum.

IR and Raman spectra

Table 1 shows IR spectra of H_2TSA, Na_2TSA (thiosalicylic acid, disodium salt), Cu/TSA and the Raman spectrum of Cu/TSA.

In the sodium salt the stretching mode associated with the S—H group, ν(SH), is not observed. In the solid complex this band is weak and denotes no interaction of this group with the metal centers. In the free ligand, ν(COOH) appears at 1678 cm^{-1}. In the sodium salt, however, this band is replaced by two new bands at 1575 and 1449 cm^{-1}, which are assigned to the asymmetric and symmetric stretching frequencies of the deprotonated carboxylate groups [1,2]. In the $[Cu(TSA)_2py]_2$ complex these bands shift to higher frequencies, showing coordination through this group. The characteristic bands of the coordinated pyridine molecules appear at 3057(w), 1447(m) and 1067(w) cm^{-1} [6,7]. The strong IR band located at 1400 cm^{-1} (of lower intensity in the Raman spectrum) could be assigned to aromatic ring vibrations [8]. The new band that appears at 282 cm^{-1} (w, IR) and 287, 274 cm^{-1} (w, Ra) is probably due to ν(Cu—N) [9].

Magnetic and thermal behavior

The low value of μ_{eff} at room temperature (1.46 BM) is indicative of an antiferromagnetic interaction between the two metal centers typical of binuclear carboxylates of copper(II) of the type: $[Cu(R—COO)_2L]_2$ [10–12].

The TG/DTA traces are shown in Fig. 2. The first weight loss of 17.6%, associated with a weak exothermic peak at 192°C could be due to the loss of two pyridine molecules:

$$[Cu(TSA)_2py]_2 \xrightarrow{\phi, O_2} 2Cu(TSA)_2 + 2py$$

with a theoretical value of 17.6%.

In a second step the decomposition occurs in the

Table 1. Comparison of IR data for H_2TSA, Na_2TSA and Cu/TSA system and Raman spectrum of Cu/TSA system[a]

	IR			Raman
Assignment	H_2TSA	Na_2TSA	Cu/TSA	Cu/TSA
ν (S—H)	2520 (m)		2556 (w)	2562 (w)
ν (COOH)	1678 (s)			
ν_a (COO^-)		1575 (s)	1614 (s)	1614 (vw)
ν_s (COO^-)		1449 (m)	1455 (m)	1461 (vs)
ν (M—N)			282 (w)	287,274 (w)

[a] Band positions in cm^{-1}. vs: very strong; s: strong; m: medium; w: weak; vw: very weak.

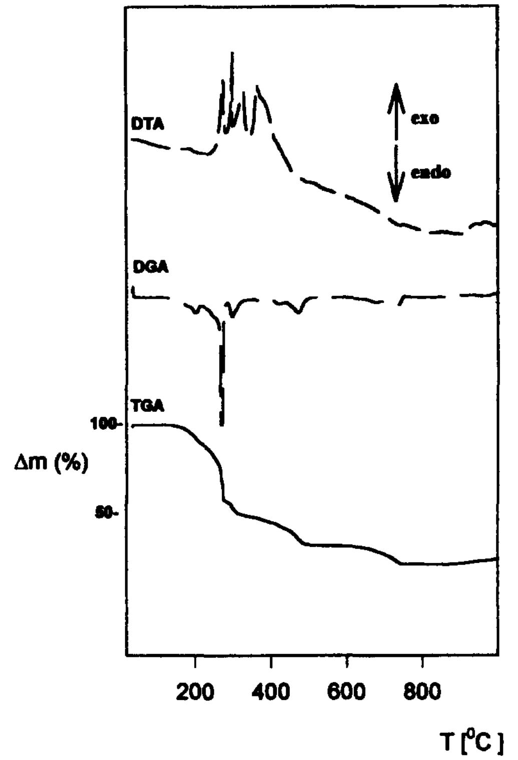

Fig. 2. TG, DGA and DTA traces for the thermal decomposition of Cu/TSA system (O_2-flow = 60 cm^3 min^{-1}; heating rate = 10°C min^{-1}).

range 200–500°C, showing that there are at least four chemical processes in progress, associated with four exothermic signals of medium intensity.

At 600°C the formation of $CuSO_4$ and CuO (70.5 and 29.5%, respectively) could be detected by IR spectroscopy; at 700°C the remainder $CuSO_4$ decomposes with the formation of the final products CuO and SO_3.

It follows that the final product is CuO that could be identified based on its IR spectrum. The final formation of CuO entails $\Delta\omega = 17.7\%$ in agreement with the experimental determination (18.1%).

Therefore, the following general decomposition scheme can be formulated:

$$[Cu(TSA)_2py]_2+\frac{101}{2}O_2\xrightarrow{\phi, O_2}2CuO$$

$$+4SO_3+38CO_2+15H_2O+2NO_2$$

Previous works on the system Cu/TSA conclude on the formation of mononuclear compounds of the type $[Cu(H_2TSA)_2]SO_4$ [3]. This study clearly proves the formation of a new dimeric copper(II) compound. The physicochemical characterization allows us to postulate the following structure: $[Cu(TSA)_2py]_2$ (Fig. 3).

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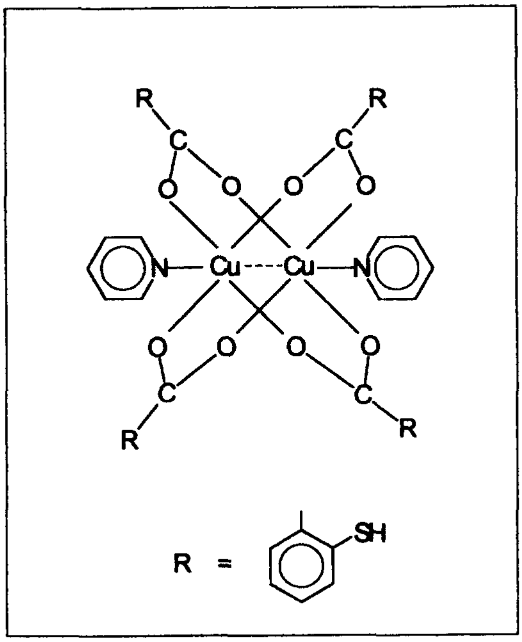

Fig. 3. Schematic structure proposed for the $[Cu(TSA)_2py]_2$ complex.

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