

O. V. QUINZANI<sup>2</sup>, S. H. TARULLI<sup>2</sup>, S. GARCIA-GRANDA<sup>3</sup>, C. MARCOS<sup>4</sup>,  
E. J. BARAN\*<sup>1</sup>

<sup>1</sup> Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina

<sup>2</sup> Departamento de Química, Universidad Nacional del Sur, Bahía Blanca, Argentina

<sup>3</sup> Facultad de Química, Universidad de Oviedo, Oviedo, Spain

<sup>4</sup> Facultad de Geología, Universidad de Oviedo, Oviedo, Spain

## Crystal structure and properties of [Cu(sac)<sub>2</sub>(py)<sub>3</sub>], a new example of a mononuclear complex with both N- and O-bonded saccharinate ligands

The crystal structure of the title complex has been determined by single X-ray diffraction methods and refined to an R-value of 0.0543. It crystallizes in the monoclinic  $P2_1/a$  space group with  $a = 21.1231(9)$ ,  $b = 9.4523(4)$ ,  $c = 16.1874(7)$  Å,  $\beta = 107.3706(3)^\circ$  and  $Z = 4$ . The compound represents only the second known example of a simple mononuclear metal complex containing simultaneously N- and O-bonded saccharinato ligands. Its infrared spectrum and thermal behavior are also briefly discussed.

Keywords: crystal structure, saccharinato complex, IR spectrum, thermal behavior

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### 1. Introduction

During the last years we have prepared and characterized a number of metal complexes containing simultaneously saccharinate and a second ligand in the coordination sphere (BARAN et al. 2000; QUINZANI et al. 1997, 1999; PARAJON-COSTA et al. 2002; WILLIAMS et al. 2000). In the case of Zn(II) and Ni(II) we could obtain and characterize mixed ligand complexes containing pyridine together with the saccharinato anion (QUINZANI et al. 1997, 1999). As a continuation of these studies, we could now obtain and characterize the interesting [Cu(sac)<sub>2</sub>(py)<sub>3</sub>] species, which presents an unexpected and rather uncommon coordination behavior of the saccharinato ligand. The crystal structure of this complex could be solved by single crystal X-ray diffractometry and we have also investigated its infrared spectrum and thermal behavior.

### 2. Experimental

The starting material for the synthesis of the new complex was bis(saccharinato) tetraquacopper(II) dihydrate, [Cu(sac)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>].2H<sub>2</sub>O, obtained by a well-known procedure (HAIDER et al. 1985). 0.0536 g (1 mmol) of this complex were dissolved in 30 mL of pyridine. The water was eliminated by azeotropic distillation, and the volume was reduced to 10 mL. After cooling, the solution was transferred, under a N<sub>2</sub> atmosphere, to a crystallization tube and 10 mL of totally anhydrous n-hexane were added, generating a

\* corresponding author: baran@quimica.unlp.edu.ar

double-layer system. Crystal formation began after three days and a number of well-developed single crystals adequate for diffractometric studies could be collected. They were mounted in liquid paraffin in order to preserve them from atmospheric humidity.

A well-formed blue crystal of dimensions 0.18x0.15x0.08 mm was used for the intensity data collection. Data collection was performed at room temperature (293(2) K) on a Nonius Kappa-CCD single crystal diffractometer, using Cu-K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). The reflections were corrected for Lorentz, polarization and absorption effects. Data reduction and cell refinements were performed with the programs HKL, Denzo and Scalepack (OTWINOWSKI & MINOR, 1997). Unit cell parameters were refined from 7746 reflections collected between  $\theta = 2.19$  and  $69.76^\circ$ .

The infrared spectra were recorded on a Spectrum GX FTIR instrument between 4000 and  $400 \text{ cm}^{-1}$ , using suspensions of the crystal powder in perfectly anhydrous Nujol. Measurements, using the KBr pellet technique, suggested partial decomposition or degradation of the samples, probably with generation of  $[\text{Cu}(\text{sac})_2(\text{py})_2(\text{H}_2\text{O})]$ .

The thermogravimetric analysis (TGA) was performed on a Rigaku Denki (Thermoflex model) analyzer, working under a  $\text{N}_2$  stream (30 mL/min) and at a heating rate of 5K/min.

### 3. Structure analysis

Crystal structure was solved by direct methods, using the program SHELXS-97 (SHELDRICK 1997a), and phase expansion using the options PHASEX of the DIRDIF package (BEURSKENS et al. 1996). Anisotropic least-squares refinement was carried out with the program SHELXL-97 (SHELDRICK 1997b). All non-hydrogen atoms were anisotropically refined. The hydrogen atoms were treated by a mixture of independent and constrained refinements. The analysis also revealed the presence of pyridine as a crystallization molecule placed disordered around of a symmetry center. Therefore, the true formula of the complex may be written as  $[\text{Cu}(\text{sac})_2(\text{py})_3] \cdot 1/2\text{py}$ . Notwithstanding, the crystallization pyridine is rapidly lost if the crystals are conserved in a dry environment at ambient temperature and also if the crystals were crushed before the spectroscopic and thermal studies. Crystallographic data and structure refinement details are shown in Table 1.

Table 1: Crystal data and structure refinement details for  $[\text{Cu}(\text{sac})_2(\text{py})_3] \cdot 1/2\text{py}$

Empirical formula	$\text{C}_{31.5}\text{H}_{25.5}\text{CuN}_{5.5}\text{O}_6\text{S}_2$
Formula weight	704.24
Crystal system, space group	Monoclinic, $\text{P}2_1/a$
Unit cell dimensions	$a = 21.1231(9)$ , $b = 9.4523(4)$ , $c = 16.1874(7) \text{ \AA}$ , $\beta = 107.3706(3)^\circ$
Volume	$3084.6(2) \text{ \AA}^3$
Z, Calculated density	4, $1.516 \text{ Mg/m}^3$
Absorption coefficient	$2.722 \text{ mm}^{-1}$
F(000)	1448
$\theta$ -range for data collection	$2.19$ to $69.76^\circ$
Index ranges	$-25 \leq h \leq 24$ , $0 \leq k \leq 11$ , $0 \leq l \leq 19$
Reflections collected/unique	5785/5785 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on $F^2$

Data / restraints / parameters	5785 / 0 / 420
Goodness-of-fit on $F^2$	1.069
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0406$ , $wR2 = 0.1065$
R indices (all data)	$R1 = 0.0543$ , $wR2 = 0.1170$
Largest diff. peak and hole	0.496 and $-0.298 \text{ e } \text{\AA}^{-3}$

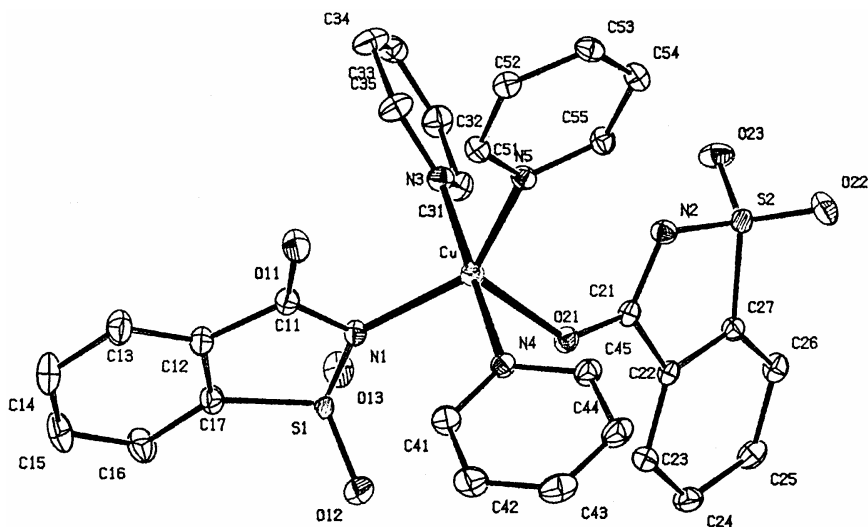


Fig. 1: Molecular structure of  $[\text{Cu}(\text{sac})_2(\text{py})_3]$  showing the labeling scheme of the non-H atoms and their displacement ellipsoids at 30% probability level. Full lines emphasize the copper-ligand bonds.

### 3. Crystal Structure of $[\text{Cu}(\text{sac})_2(\text{py})_3] \cdot 1/2\text{py}$

The compound presents a structure containing isolated molecules that presents only weak hydrogen bonds to other similar units, involving the saccharinato O-atoms and H-atoms of pyridine molecules. A PLATON plot (SPEK 2000) of the structure of the complex is shown in Fig.1. Select bond distances and angles are shown in Table 2.

As it can be seen from the figure, Cu(II) presents a five coordinated environment with an approximately bipyramidal triangular geometry. The most interesting aspect of this coordination sphere is the fact that the two bonded saccharinato moieties interact in a different way with the metallic center. One bond occurs through the imine N-atom whereas the other involves the carbonylic O-atom. This peculiar situation was so far only observed in another mixed-ligand saccharinato complex, namely  $[\text{Cu}(\text{dipyridilamine})(\text{sac})_2(\text{H}_2\text{O})]$ , recently reported independently by two different research groups (DENG et al. 2001; NAUMOV et al. 2001).

An analysis of the coordination sphere in the present case shows that in the equatorial plane the Cu(II) center is bonded to the N atom of one saccharinato anion at a  $\text{N}(1)\text{-Cu}$  distance of  $2.038 \text{ \AA}$  while the second, O-bonded, ligand  $[\text{O}(21)\text{-Cu}]$  is at  $2.136 \text{ \AA}$  and the N-atom of one of the pyridine molecules  $[\text{N}(5)\text{-Cu}]$  is at  $2.044 \text{ \AA}$ . The value of the bond angle between the two saccharinato ligands  $[\text{N}(1)\text{-Cu-O}(21)]$  is, with  $105.57^\circ$ , somewhat lower as

the theoretically expected one, whereas that between the N-bonded saccharinato and the equatorially bonded pyridine [N(1)-Cu-N(5)] is rather large (140.22 °), probably conditioned by the spatial orientation of the pyridine molecule. The axial positions are occupied by the other two pyridine N-atoms at N(3)-Cu = 2.022 Å and N(4)-Cu = 2.039 Å, generating a N(3)-Cu-N(4) angle of 177.01°. On the other hand, the angles conformed by these axial ligands, the Cu(II) cation and the equatorial ligands are all around 90°, as expected for the bipyramidal geometry.

Table 2: Interatomic bond distances (Å) and angles (°) around Cu(II) in [Cu(sac)<sub>2</sub>(py)<sub>2</sub>].1/2py

Cu-N(3)	2.022(2)	Cu-N(1)	2.038(2)
Cu-N(4)	2.039(2)	Cu-N(5)	2.044(2)
Cu-O(21)#1	2.1362(17)	S(1)-N(1)	1.621(2)
S(2)-N(2)	1.621(2)	C(11)-O(11)	1.226(3)
C(21)-O(21)	1.255(3)	C(11)-N(1)	1.368(3)
C(21)-N(2)	1.333(3)		
N(3)-Cu-N(1)	88.04(8)	N(3)-Cu-N(4)	177.01(9)
N(1)-Cu-N(4)	92.89(8)	N(3)-Cu-N(5)	88.99(8)
N(1)-Cu-N(5)	140.22(9)	N(4)-Cu-N(5)	88.47(8)
N(3)-Cu-O(21)#1	95.63(8)	N(1)-Cu-O(21)#1	105.57(8)
N(4)-Cu-O(21)#1	86.86(7)	N(5)-Cu-O(21)#1	114.20(8)
C(21)-O(21)-Cu#2	133.92(17)	C(11)-N(1)-Cu	113.81(17)
(S1)-N(1)-Cu	133.39(12)	O(22)-S(2)-O(23)	115.61(13)
O(12)-S(1)-O(13)	115.89(13)	N(1)-S(1)-C(17)	95.62(12)
C(11)-N(1)-S(1)	112.46(18)	C(21)-N(2)-S(2)	110.96(18)
C(27)-C(22)-C(21)	111.1(2)	C(17)-C(12)-C(11)	111.6(2)

Symmetry transformations used to generate equivalent atoms: #1: x, -y-1/2, z+1/2; #2: x, -y-1/2, z-1/2

The relatively similar values of the equatorial Cu-O and Cu-N bonds suggest that there is a little difference in the strength of these two bonds, although N-coordination is usually preferred by this ligand in transition metal complexes. The only examples of O-coordination previously reported in mononuclear compounds are in [V(sac)<sub>2</sub>py<sub>4</sub>].2py (COTTON et al. 1986) and [Ni(sac)<sub>2</sub>py<sub>4</sub>].2py (QUINZANI et al. 1999).

Besides, the Cu-N and Cu-O distances found in the present case are comparable to those reported in the [Cu(dipyridilamine)(sac)<sub>2</sub>(H<sub>2</sub>O)] complex (DENG et al. 2001; NAUMOV et al. 2001), although in this case d(Cu-N) > d(Cu-O). Also the Cu-N(py) distances found here are comparable to those reported in the dipyridilamine complex.

Another closely related Cu(II) complex is [Cu(sac)<sub>2</sub>(py)<sub>2</sub>(H<sub>2</sub>O)], adopting a slightly distorted square pyramidal configuration, with the four Cu-N bonds in the equatorial plane and the Cu-O bond, involving the water molecule, at the apex (JOVANOVSKI et al. 1998). Also in this case the Cu-N bonds ranged between 2.03 and 2.04 Å.

#### 4. Infrared Spectrum and Thermal Behavior

Some of the most characteristic IR bands of the complex are presented in Table 3. As expected, the ν(C=O) vibrations of the two saccharinato moieties appear clearly separated.

The one corresponding to the N-bonded ligand is seen as a doublet at higher frequencies (1683/1668 cm<sup>-1</sup>) whereas the one bonded through the O-atom is found at 1628 cm<sup>-1</sup>, in agreement with the determined bond distances for both groups (cf. Table 2). The value for the O-bonded group compares well with that found in the case of the [Ni(sac)<sub>2</sub>py<sub>4</sub>] complex (1614 cm<sup>-1</sup>) in which the saccharinato anions are also O-bonded to Ni(II) (QUINZANI et al. 1999).

Table 3: Assignment of the most characteristic IR bands of [Cu(sac)<sub>2</sub>(py)<sub>3</sub>].1/2py (band positions in cm<sup>-1</sup>)

IR-band	Assignment	IR-band	Assignment
1683 vs/1668 vs	$\nu(\text{C}=\text{O})$ <b>1</b>	1171 s	$\nu_s(\text{SO}_2)$
1628 m	$\nu(\text{C}=\text{O})$ <b>2</b>	1153 s	$\nu_s(\text{SO}_2)$
1607 m	$\nu(\text{C}-\text{C})$ py	1068 m	$\delta(\text{CH})$ py
1597 s	$\nu(\text{C}-\text{C})$ sac	959 vs	$\nu_{as}(\text{CNS})$
1583 w	$\nu(\text{C}-\text{C})$ sac	951 s	$\nu_{as}(\text{CNS})$
1489 m	$\nu(\text{C}-\text{C})$ py	799 w	$\delta(\text{C}=\text{O})$ <b>2</b>
1443 s	$\nu(\text{C}-\text{C})$ py	786 m	$\gamma(\text{C}-\text{H})$
1297 m	$\nu_{as}(\text{SO}_2)$	782 m	$\gamma(\text{C}-\text{H})$
1288 vs	$\nu_{as}(\text{SO}_2)$	770 w	$\delta(\text{C}=\text{O})$ <b>1</b>
1219 m	$\delta(\text{CH})$ py	700 vs	$\gamma(\text{CH})$ (py)

vs: very strong; s: strong; m: medium; w: weak.

**1:** N-coordinated saccharinato moiety; **2:** O-coordinated saccharinato moiety

The stretching vibrations of the SO<sub>2</sub> –groups appear clearly separated as doublets, despite the fact that its S-O distances and angles are nearly identical. Their frequencies lie in the same range as found for this group in other saccharinato complexes in which they show similar O-S-O angles (JOVANOVSKI et al. 1995). Besides, the  $\nu_{as}(\text{CNS})$  modes are also observed as doublets, whereas the corresponding symmetric modes could not be identified with certainty.

Some of the characteristic pyridine bands are found in the same regions and with comparable intensities as in the other previously investigated saccharinato-pyridine complexes (QUINZANI et al. 1997, 1999).

The thermal behavior was investigated by thermogravimetric measurements. As stated in the experimental part, the crystallization pyridine molecule is partially or totally lost during the sample preparation for these measurements.

The experiments clearly show that the three pyridine molecules are lost in three successive steps between 110-160, 160-240 and 240-315 °C, respectively. The total mass loss observed was of 36.5% in excellent agreement with the theoretical expectations (35.7%). The following degradation involves two steps more, the first one between 315 and 400 °C, followed immediately by the other that extends up to about 650 °C, temperature at which weight constancy is attained. In these consecutive processes the two saccharinato ligands are lost. The total observed mass loss of 88% is in excellent agreement with the expected one (88.1%) if the final solid residue is CuO. The generation of this residue was definitively confirmed by IR spectroscopy.

## 5. Conclusions

The present study allowed the characterization of a new mixed ligand metal complex containing two saccharinate anions and three pyridine molecules bonded to Cu(II), with the peculiarity that one of the saccharinato ligands interacts through its N-atom and the other through the carbonylic O-atom. The results of the IR spectroscopic study and of the thermal analysis are in good agreement with the reported structural results.

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