

Crystal Structure and Vibrational Behaviour of Aqua Di(saccharinato)di(nicotinamide)copper(II)

Beatriz S. Parajón-Costa^a, Enrique J. Baran^a, Oscar E. Piro^b, and Eduardo E. Castellano^c

^a Centro de Química Inorgánica (CEQUINOR, CONICET/UNLP), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C. Correo 962, 1900 La Plata, Argentina

^b Departamento de Física and Instituto IFLP (CONICET), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 1900 La Plata, Argentina

^c Instituto de Física de São Carlos, Universidade de São Paulo, 13560 São Carlos (SP), Brazil

Reprint requests to Prof. Dr. E. J. Baran. E-mail: baran@quimica.unlp.edu.ar

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Copper(II)-saccharinate-nicotinamide, IR Spectra

The crystal structure of $[\text{Cu}(\text{sac})_2(\text{nic})_2(\text{H}_2\text{O})]$ (sac = saccharinate anion; nic = nicotinamide) has been determined by single-crystal X-ray diffraction. It crystallizes in the monoclinic space group $C2/c$ with $Z = 4$ and the Cu(II) ion presents a CuN_4O square pyramidal coordination. Some comparisons with related structures are made and the most important features of its IR spectrum were also discussed.

Introduction

A series of mixed-ligand saccharinato complexes of Cu(II), Co(II), Ni(II) and Zn(II) with nicotinamide were recently reported [1]. Although no structural information could be obtained, the spectroscopic characterization suggested that the Cu(II) complex was different from those of the other metal cations.

As a continuation of our own studies on mixed-ligand saccharinato complexes [2 - 6], and as the eventual incorporation of nicotinamide (vitamin B₃) to the coordination sphere of copper (II) presents an additional incentive from the biological point of view, we attempted to solve the structure of this complex and to analyze the most relevant aspects of its vibrational behaviour.

Experimental Section

Synthesis of the complex

Tetraaqua-bis(saccharinato)copper(II) dihydrate, $[\text{Cu}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2 \text{H}_2\text{O}$, prepared by literature methods [7, 8] was the starting material for the synthesis. One mmol of this complex was dissolved in 20 ml of distilled water over a water bath. To this solution, 2 mmol of solid nicotinamide was slowly added, under continuous stirring. After complete dissolution, the resulting solution was left to stand in air at room temperature. After two days, well formed, dark blue crystals were deposited.

They were separated and dried in air between sheets of filter paper.

Spectroscopic measurements

The IR spectra of the complex, and those of pure nicotinamide and sodium saccharinate monohydrate were recorded in the range between 4000 and 300 cm^{-1} on a Perkin Elmer 580B spectrophotometer, using the KBr pellet technique.

Crystal structure determination

Measurements were performed at 120 K, with a Kappa CCD diffractometer (graphite monochromated Mo- K_α radiation, $\lambda = 0.71073 \text{ \AA}$) and employing an Oxford Cryosystems low-temperature device. Crystal data, collection procedures and refinement results are summarized in Table 1 and bond distances and angles around the metal center are shown in Table 2. The structure was solved by direct and Fourier methods and the final molecular model obtained by anisotropic full-matrix least-squares refinement of the non-hydrogen atoms. All H-atoms were located in a difference Fourier map and refined isotropically. Intensity data were corrected for Lorentz, polarization and absorption effects [9]. The unit cell dimensions were obtained by least-squares refinement of the angular settings for 14517 reflections in the $1.70 < \theta < 26.00^\circ$ range. Programs used were DENZO and SCALEPACK [10] for data reduction and correction and SHELXS-97 [11] and SHELXL-97 [12] for structure solution and refinement, respectively.

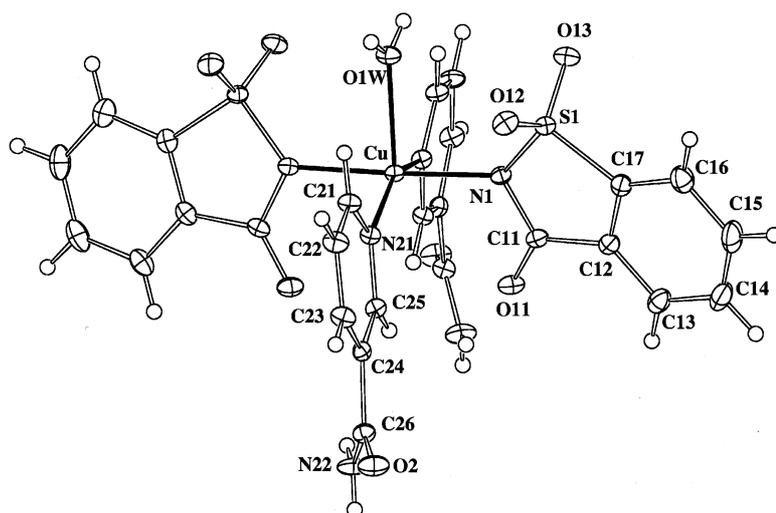


Fig. 1. ORTEP plot of the $[\text{Cu}(\text{sac})_2(\text{nic})_2(\text{H}_2\text{O})]$ complex showing the labelling scheme of the non-H atoms and their displacement ellipsoids at 50% probability level. Full lines emphasize copper-ligand bonds.

Table 1. Crystal data and structure refinement for $[\text{Cu}(\text{sac})_2(\text{nic})_2(\text{H}_2\text{O})]$.

Empirical formula	$\text{C}_{26}\text{H}_{22}\text{O}_9\text{N}_6\text{S}_2\text{Cu}$
Formula weight	690.16
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	20.7680(3)
b (Å)	14.8480(3)
c (Å)	9.4630(2)
β (°)	103.8870(7)
Z	4
Volume (Å ³)	2832.75(9)
D_c (g·cm ⁻³)	1.618
Reflections collected	14517
Independent reflections	2799 [R(int) = 0.023]
Observed refls [$I > 2\sigma(I)$]	2705
Data / restraints / params	2799 / 0 / 212
Goodness-of-fit on F^2	1.271
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0271, wR2 = 0.0872
Final R indices (all data)	R1 = 0.0307, wR2 = 0.1032
Largest peak and hole (e·Å ⁻³)	0.465 -0.778

Table 2. Interatomic bond distances (Å) and angles (°) around Cu(II) in $[\text{Cu}(\text{sac})_2(\text{nic})_2(\text{H}_2\text{O})]^a$.

Cu-N(1)	1.998(2)	Cu-N(21)	2.027(2)
Cu-O(1w)	2.321(2)		
N(1)-Cu-N(1')	177.38(9)	N(1)-Cu-N(21')	90.84(6)
N(1)-Cu-N(21)	89.77(6)	N(21)-Cu-N(21')	153.14(9)
N(1)-Cu-O(1w)	88.69(4)	N(21)-Cu-O(1w)	103.43(5)

^a Primed atoms are obtained from unprimed ones by the two-fold axis symmetry $-x, y, -z - 1/2$.

Tables containing complete information on atomic coordinates and equivalent isotropic displacement param-

eters, bond distances and angles, anisotropic displacement parameters and hydrogen coordinates are available from the authors upon request and have been deposited at the Cambridge Crystallographic Data Centre, reference number CCDC-173603.

Results and Discussion

Crystal structure

An ORTEP [13] drawing of the structure is presented in Fig. 1. The Cu(II) ion sits on a crystallographic two-fold axis in a square pyramidal environment, equatorially coordinated to the nitrogen atoms of the two saccharinate moieties [$d(\text{Cu}-\text{N}(1)) = 1.998(2)$ Å] and the pyridine nitrogen atoms of the nicotinamide ligands [$d(\text{Cu}-\text{N}(21)) = 2.027(2)$ Å]. The five-fold coordination is completed with a water molecule located at the pyramid apex [$d(\text{Cu}-\text{O}(1w)) = 2.321(2)$ Å]. The Cu(II) cation departs from the mean plane defined by the four nitrogen atoms of the pyramidal basis by 0.313(1) Å towards the axial water ligand.

The Cu-N(sac) distances are only slightly shorter than those found in the recently reported mixed-ligand complex $[\text{Cu}(\text{sac})_2(\text{bzim})_2(\text{H}_2\text{O})]$ (bzim = benzimidazole) whereas the Cu-OH₂ distances are practically equal in both complexes [5]. The obtained Cu-N distances are also comparable to those reported for the Zn-N(sac) and Zn-N(py) bonds (1.977 and 2.033 Å, respectively) in the $[\text{Zn}(\text{sac})_2(\text{py})_2]$ complex (py = pyridine) [2].

As expected, the molecular skeleton of the saccharinate ligands is nearly planar (the rms deviation of atoms from the mean plane is of 0.028 Å) and these ligands are nearly perpendicular to the equatorial plane generated by the four N-atoms of the ligands (dihedral angle of 81.66(3)°). Also the pyridine rings are nearly perpendicular to this equatorial plane (inter-planar angle of 83.47(5)°) and subtend an angle of 72.95(4)° with the saccharinate plane. The plane of the terminal nicotinamide C(C=O)NH₂ group is tilted by 25.00(9)° from the pyridine plane.

It is worth to mention that the determined saccharinate N-C and N-S bond distances (1.367(2) and 1.635(2) Å, respectively) are closer to the bond lengths found in the neutral saccharin molecule (1.375 and 1.663 Å, respectively [14]) than to the corresponding values found in the saccharinate anion (for example, 1.354 and 1.596 Å, respectively, in the corresponding sodium salt [15]).

The crystal structure is further stabilized by a net of intermolecular N-H...O bonds [d(NH(1)...O(2)) = 2.18 Å, d(NH(2)...O(11)) = 2.08 Å; ∠(N(22)-NH(1)...O) = 136.6°, ∠(N(22)-NH(2)...O(11)) = 176.4°] and O(1w)-H...O bonds [d(O(1w)H...O(12)) = 2.22 Å, ∠(O(1w)H...O(12)) = 167.1°].

Finally, it is also interesting to mention that using the same experimental conditions as those reported here, but apparently by a longer heating of the reaction mixture, Naumov et al. obtained a similar complex in which nicotinamide was oxidized to nicotinic acid, i.e. [Cu(sac)₂(nicotinic acid)₂(H₂O)] [16]. Although it crystallizes in a different space group (P2₁/n) the overall geometric features around the metal center are comparable. The Cu-N bond distances in this complex are slightly longer than those reported here whereas the Cu-OH₂ bond is somewhat shorter.

Infrared spectrum

The assignment of some of the most characteristic IR bands of the complex are shown in Table 3, together with those of sodium saccharinate monohydrate and nicotinamide, recorded for comparative purposes and to facilitate the spectral analysis. Some aspects of this assignment are commented as follows:

Table 3. Assignment of the most characteristic IR bands of sodium saccharinate monohydrate [Na(sac) · H₂O], nicotinamide and of [Cu(sac)₂(nic)₂(H₂O)] (band positions in cm⁻¹).

Na(sac) · H ₂ O	Nicotinamide	[Cu(sac) ₂ (nic) ₂ (H ₂ O)]	Assignment
	3368 vs	3421 vs	ν _{as} (NH ₂)
	3169 vs	3260 vs	ν _s (NH ₂)
	1682 vs	1660 vs	ν(C=O)
1642 vs		1692 sh	ν(C=O)
	1623 s	1625 w	δ(NH ₂)
	1593m,	1586 m	ν(CN) + ν(CC)
	1574 m		ring
	1399 vs	1399 vs	ν(CN) amide
1258 vs		1255 s	ν _{as} (SO ₂)
1150 vs		1160 vs	ν _s (SO ₂)
	1124 m	1119 m	ρ(NH ₂)
950 m		970 vs	ν _{as} (CNS)
	624 m	641 m	δ(ring)
	411 m	436 w	δ(ring)

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

- The region involving the carbonyl stretching vibrations is relatively complex, as both the C=O vibrations of saccharin and of the amide group lie close together and also the bending mode of the coordinated water molecule is expected in the same region [17]. In the complex, the ν(C=O) mode of the bonded saccharinato is only observed as a shoulder but displaced, as expected [16], to higher frequency in relation to its position in the free anion.

- Some of the typical nicotinamide bands are only slightly displaced after coordination, remaining in their characteristic absorption regions.

- The ν_{as}(CNS) mode of the saccharinate is clearly displaced to higher frequency after coordination, as usually observed when coordination takes place through the N-atom of this moiety [2]. The corresponding symmetric mode, located at 1336 cm⁻¹ in sodium saccharinate, is apparently overlapped with a strong nicotinamide band found at 1339 cm⁻¹ in the complex.

- The two bands located at 624 and 411 cm⁻¹ and related to deformational modes of the heterocycle are displaced to higher frequencies after coordination showing a similar behaviour as observed in the case of pyridine complexes [2, 15].

- Vibrations related to the Cu-N vibrations could not be found. They are expected to lie below 300 cm⁻¹.

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