

STRUCTURAL STUDY OF CADMIUM COMPLEXES WITH 2,2'-BIPYRIDINE AND SACCHARIN

O.Grupče¹, G. Jovanovski¹, B. Kaitner²

¹*Institute of Chemistry, Faculty of Sciences, PO Box 162, 91001 Skopje, Macedonia*

²*Laboratory of General and Inorganic Chemistry, University of Zagreb, kralja
Zvonimira 8, HR-10000 Zagreb, Croatia*

ABSTRACT: The crystal structure determination of the title compound revealed the formula $[\text{Cd}(\text{bpy})_2(\text{sac})_2]^*$. The compound is anhydrous, built up of discrete $[\text{Cd}(\text{bpy})_2(\text{sac})_2]$ molecules. The crystal structure packing is achieved through weak intermolecular contacts. Spectroscopic study of the title compound showed that there are actually two cadmium complexes with saccharin and 2,2'-bipyridine, hydrate form and anhydrous one. The hydrate compound is not stable and after a short period of time transforms into the anhydrous form. The loss of water is expectedly reflected on the appearance of the infrared spectra in the H-O-H region, but also causes changes in the vibrational region of CO and SO₂ groups.

Key words: Cd compounds, 2,2'-bipyridine saccharinato complexes, structural study

1. INTRODUCTION

Due to the everyday use of the saccharin as a food additive and its pronounced ability to form complexes with different metals, an extensive study on its ligation properties and possible effect on human health was done.

Systematic investigation of the ligation properties of saccharin in metal complexes with various mono- and polymembered ring bases has been a subject of our interest for a long period. Due to the structural characteristics of the saccharin molecule, extraordinary versatility in the coordination patterns was found.

Extensive structural and spectroscopic study of the metal (II) complexes with saccharin and 2,2'-bipyridine has taken place for some time, as well. Crystal structure determinations on the complexes with Mn(II), Cu(II), Co(II), Zn(II), Pb(II) and Hg(II) have been reported [1-7] as well as spectroscopic study on the complexes with Pb(II), Hg(II), Co, Ni(II) and Zn(II) [8-10]. The additional contribution to this issue is structural investigation of the $[\text{Cd}(\text{bpy})_2(\text{sac})_2]$.

2. EXPERIMENTAL

2.1. Synthesis

The title compound was prepared by adding an excess of cadmium(II) acetate to a warm, stirred, aqueous solution of stoichiometric amounts of saccharin and the 2,2'-bipyridine. Transparent, well-shaped, rectangular crystals were obtained from the mother liquor at room temperature. Water or ethanol was used for recrystallization of the crystals.

* sac stands for saccharinato ligand, bpy denotes 2,2'-bipyridine.

2.2. X-ray diffraction

The intensity data were collected at room temperature on a Philips PW 1100 diffractometer using graphite monochromatized MoK_α radiation [11]. Calculations were performed on IBM PC/AT microcomputer. PLUTON [12] programs were used to generate the illustrations.

2.3. Infrared spectra

The infrared spectra were recorded on a Perkin Elmer 2000 spectrophotometer, using KBr pellets and Nujol mull. The liquid nitrogen temperature infrared spectra were recorded using a variable RUC VLT-2 cell.

3. RESULTS AND DISCUSSION

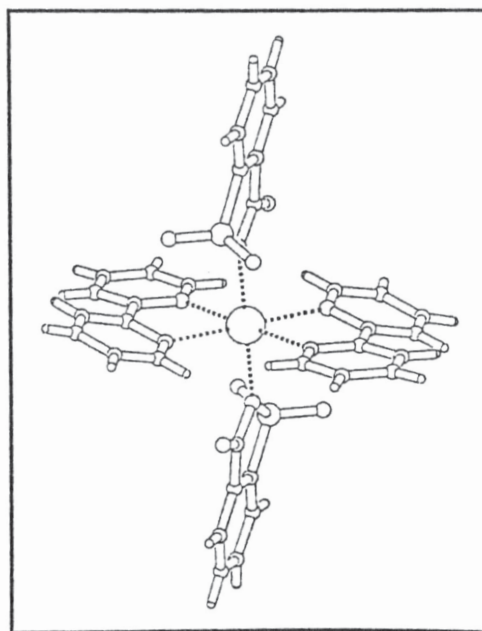
3.1. Crystal structure

Details concerning the crystal data, data collection and refinement conditions will be published elsewhere. Here, only the basic description of the crystal structure is given. Crystal data for $[\text{Cd}(\text{bpy})_2(\text{sac})_2]$ are given in Table 1. The complex is built up of discrete molecules held together by weak intermolecular contacts. The fragment of the structure is given in the Fig. 1.

TABLE I. Crystal data for $[\text{Cd}(\text{bpy})_2(\text{sac})_2]$

Empirical formula	$\text{C}_{34}\text{H}_{24}\text{CdN}_6\text{O}_6\text{S}_2$
M_r	789.15
Crystal system	triclinic
Space group	$P\bar{1}$
$a/\text{\AA}$	8.5784
$b/\text{\AA}$	9.4939
$c/\text{\AA}$	10.9027
?	67.6740
?	73.4650
?	78.1960
$V/\text{\AA}^3$	782.74
Z	1
$(\text{MoK}\alpha)/\text{\AA}$	0.7107
Final R	0.0675

Fig. 1. The structure of $[\text{Cd}(\text{bpy})_2(\text{sac})_2]$



The cadmium atom lies on the inversion center and is octahedrally coordinated by four 2,2'-bipyridine nitrogens and two saccharinato nitrogen atoms. Four 2,2'-bipyridine nitrogens form an "equatorial" plane. Saccharinato ligands are sited perpendicularly above and below the equatorial plane, occupying the axial positions.

3.2. Infrared spectra

Two types of infrared spectra were obtained concerning the title compound – one that characterizes the complex as hydrate and the other for the anhydrous complex. The hydrate form is not stable and after a short period of time transforms into the anhydrous one. The loss of water in the anhydrous compound expectedly changes the appearance of the infrared spectra in the H-O-H region, but also is reflected on the vibrational region of CO and SO₂ groups.

The appearance of the single bands due to the stretchings of the CO and SO₂ groups of the saccharinato ligands in the spectrum of the anhydrous complex is consistent with the existence of a single type of saccharinato ligands in the crystal structure. On the other hand, the bands due to the stretchings of the CO and SO₂ groups in the spectrum of the hydrate form appeared doubled. It indicates that the presence of the water molecules in the complex provokes the existence of nonequivalent saccharinato ligands in the structure.

The frequencies of the CO and SO₂ stretchings in the cadmium complex are similar to the corresponding modes found in the spectra of the other metal(II) 2,2'-bipyridine saccharinato complexes [8-10].

4. CONCLUSION

Two types of complexes of cadmium with saccharin and 2,2'-bipyridine exist - the hydrate form and the anhydrous one. The anhydrous compound has the formula [Cd(bpy)₂(sac)₂]. The appearance of the infrared spectrum of the anhydrous complex is in agreement with the data obtained by crystal structure determination.

5. LITERATURE

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Апстракт. Продолжувајќи го испитувањето на 2,2'-бипиридин сахаринатните комплекси со различни метали, синтетизиран е комплексот на кадмиум со сахарин и 2,2'-бипиридин. Структурните испитувања се вршени, користејќи инфрацрвена спектроскопија и рендгенска дифракција. Кристалната структура на безводниот комплекс е решена и уточнета до $R = 0.0675$. Најдено е дека кадмиумот е октаедарски координиран со четири бипиридински азотни атоми и два атоми на азот што припаѓаат на сахаринатните лиганди. Користејќи инфрацрвена спектроскопија, заклучено е дека комплексот всушност сејавува во две форми - како хидрат и безводен. Хидратната форма е нестабилна и со стоење ја губи кристалната вода, додека безводниот комплекс е стабилен и не си го менува својот изглед. Промените што настануваат со губење на кристалната вода влијаат на изгледот на инфрацрвениот спектар, не само во областа на вибрациите на водата, туку и во подрачјето на лентите што потекнуваат од вибрации на CO и SO₂ групите. Сознанијата добиени со анализа на инфрацрвените спектри се корелирани со првичните резултати за кристалната структура на безводниот комплекс на кадмиумот како и со структурните податоци за различни метал 2,2'-бипиридин сахаринатни комплекси [метал = Hg(II), Cu(II), Co(II), Ni(II), Zn(II), Pb(II)].

Клучни зборови: Cd соединенија, 2,2'-бипиридин сахаринатни комплекси, структурни испитувања