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SYNTHESIS AND STRUCTURAL STUDY OF COMPLEXES Sn(II) AND Co (II) WITH NITRODERIVATVES OF BENZOIC ACID

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ABSTRACT

The crystal structures of a new tin complex with nitrosalisilic acid were synthesized and studied. Single crystals were obtained by X-ray diffraction analysis. Crystallochemical data were obtained on an Entrat=Nonius CAD automated diffractometer, the molecular and crystal structures were deciphered using several programs. It was found that in the crystal structure of the title compound [$Sn(C_7H_4NO_5)_2 \cdot H_2O$], the coordination sphere around the Sn atom consises of four O atoms from two chelating carboxylate groups, one water O atom and two additional O atoms belonging to a carboxyl and a hydroxyi group of neibouring molecules. So, the coordination number of Sn complements to 7. The Sn – O distances are in the range 2,419 – 3,084 Å, the shortest distance being to a water O atom. Two inframolecular and two intermolecular hydrogen bonds are also observed in the polymeric structure. A new complex compound of cobalt with 5-nitro, 2-asetamido benzoic acid with the following composition $C_{28}H_{28}CoN_6O_{12}$ was synthesized. Single crystals of the new complex were obtained using an automatic diffractometr Bruker APEX CCD and crystallochemical parametrs were obtained. Crystal structures have been deciphered using special programs. Two pyridine molecules are coordinated by the cobalt (II) atom via donor nitrogen atoms in an axial position. With the help of donor oxygen atoms, two water molecules are coordinated to the central cobalt atom and complement its coordination number to four. The distance of cobalt (II) atom and the oxygen of the carboxyl groups is Co (1) – O (1) = 2,157Å, Co – N = 2,301Å, Co – H_2O=2,181Å.

INTRODUCTION

The presence of hydrophilic groups: OH, NH_2, COOH, NO_2 leads to the formation of complexes of trace elements as well as the heavy metal ions and chelate-structured complex compounds [6, 7,8].

In our early research work Ag (1) [9], Zn (II), Co (II) [10,11] metal complexes of p-nitrosalicylic acid which was used as ligands, were synthesized by us and their molecular structures were studied. As a continuation of the research work, single crystals of the complex compound with

the Sn(II) cation were synthesized and the molecular and crystal structures were studied by X-ray structural analysis.

In this research work another nitro derivative of benzoic acid, with Co (II) cation was synthesized and its molecular and crystal structures were studied.

The substituents in the ortho position in both ligands (2-OH and 2-CH3CONH) create an "ortho effect", that mobilizes the hydrogen cation of the carboxyl group and ensures easy substitution with metals.

Early we have synthesized the complex compounds of 5-nitro, 2-acetamido benzoic acid with Ni (II), Cu (II), Mn (II), Cd (II) metals and studied their molecular and crystal structures [13, 14].

As a continuation of the research work, the complex compound of this ligand with Co (II) cation was synthesized and single crystals of its pyridine adduct were obtained and their molecular and crystal structures were studied.

Experimental

Synthesis of bis-nitrosalicylate Sn (II) –hydrate –Sn(C7H4NO5)2·H2O (complex 1): 2.05 g (10 mmol) Na 2-nitrosalicylate salt is dissolved in 50 ml of distilled water, heated to 50 –

-60 0C. An aqueous solution of 1.4985 g (5 mmol) Sn(NO3)2 salt is added to the solution and stirred for 20 minutes at 80 0C on a magnetic stirrer. The boiling solution is filtered through filter paper and stored in the dark at room temperature. After a few days, prizmatic crystals precipitate.

Synthesis of the adduct complex compound bis-(5-nitro, 2-acetamidobenzoato) – di-(pyridine) Co (II) – dihydrate (complex 2): the sodium salt of the ligand, which is well soluble in water, is obtained according to the following reaction.

$$5-NO_2-CHNOCH_3-C_6H_3COOH+NaHCO_3 \rightarrow 5-NO_2-CHNOCH_3-C_6H_3COONa+CO_2\uparrow+H_2O$$

The obtained Na salt 2.41 (10 mmol) is dissolved in 50 ml of distilled water, 1.095 g (5 mmol) of CoCI2 · 4H2O and 10 mmol of pyridine are added to it and mixed with a magnetic stirrer at 80 0C for 20 minutes. The solution is filtered and stored in the dark at room temperature. After a few days, transparent crystals precipitate.

The crystals of both complexes are washed in water, ethyl alcohol and dried in a desiccator over anhydrous CaCI2. The yield of the reactions is 78% for complex 1 and 81.65% for complex 2.

The obtained single crystals are selected under a microscope, and high-quality single crystals are sent to the Bruker APEX CCD automated diffractometer operating at Samsun University, Republic of Turkey, for X-ray structure analysis. Based on the collected crystallographic data, molecular and crystal structures are revealed with the help of special programs [14,15,16]. The crystallographic parameters of complex compounds are as follows.

For **complex 1.** Formula: $Sn(C_7H_4NO_5)_2 \cdot H_2O$, molecular weight: 581,43, Singoni Triclinic: space groupe P-1, parametrs a=4,879Å, b=12,155Å, c=14,734Å, α=68,634^0, β=86,482^0, γ=78,770^0, V=796,68^0, Z=2, d=2,457 mq m^{-3}.

Data collection Enraf-Nonius CAD diffraktometr, measured reflex, 3610, independent reflex 2822, MoK$_\alpha$ – 0,71073Å, θ=9,92 – 18,12^0, crystal size: 0,35x0,20x0,10 mm, temperature -295K, R=0,027.

For complexs 2: Empirical formula - $C_{28}H_{28}CoN_6O_{12}$, molecular weight– 695,42, temperature at the time of measurement – 100(2)K, wavelengt - $M_0K_\alpha = 0{,}71073$, Singoni monoklinik - space group $P2_{1/n}$, parameters – a=10,485Å, b=19,675Å, c=8,214Å, angles $\alpha = \gamma = 90^0$, $\beta = 103{,}456^0$, $V = 1512{,}5\overset{0}{A}^3$, $Z = 2$, $\alpha = 1{,}543 q/sm^3$, monocrystaline dimensions: 0,28x0,19x0,21 mm^3, the number of all reflexes – 18589, the number of independent reflexes – 4698, R_{factor}=0,032.

Materials and measurements

$Sn(NO_3)_2{\cdot}4H_2O$ and $CoSO_4{\cdot}6H_2O$ was commerical product highest chemical grade (Aldrich). Solvents were purified according to standart procedures. IR spectra were recorded with a Perckin – Elmer 100 FT – IR spectrometer as KBr discs, in the range of 4000 – 400 cm^{-1}. Thermal analysis was perfomed by NETZSCH STA – 409 PC/PG derivatograph. The DTA, TG and DTG curves were taken in a static air atmosphere at an increasing heating rate of 10^0C/min from 20 to 800^0C by using platinium Crucibles.

IR spectral investigation of complexes (1) and (2)

The IR – spectra of complexes (1) showed new absorption bonds in the specific regions related to the bond asymmetric $\nu_S\left(COO^-\right) = 1635\, sm^{-1}$ and symetric $\nu_S\left(COO^{-1}\right) = 1450\, sm^{-1}$. The difference between the asymmetric (ν_{as}) and symmetric (ν_{sim}) carboxylate vibrations $\Delta\nu = \nu_{as}\left(COO^-\right) - \nu_S\left(COO\right)$ is often employed for the determination of models of coordination group (17-19) (Fig.1).

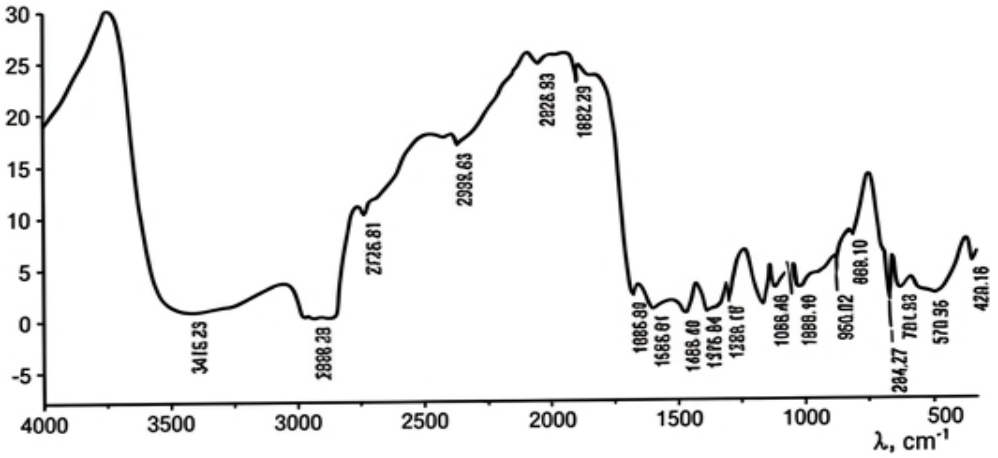

Figure 1. IR spectra of complex 2

The value of $\Delta\lambda = 185\, sm^{-1}$ is less than $200\, sm^{-1}$ in the complex (1) and indicated that the carboxylate groups participate at chelate type and bidantate-bridge manner, which is supported by the molecular structure Sn (II). $Ph - C = 1225\, sm^{-1}$, $Ph - NO_2 = 1365\, sm^{-1}$, $Sn - O(1) = 645\, sm^{-1}$, $Sn - H_2O = 825\, sm^{-1}$.

The IR-spectra of complexes (2) showed that bond of asymmetric - $\nu_S\left(COO^-\right) = 1663\, sm^{-1}$ and symmetric $\nu_S\left(COO^-\right) = 1453\, sm^{-1}$. The value of $\Delta\nu = 210\, sm^{-1}$ is more than $200\, sm^{-1}$, indicates that the carboxylate groups participate in a monodentate manner. Which is supported by the molecular structure Co(II).

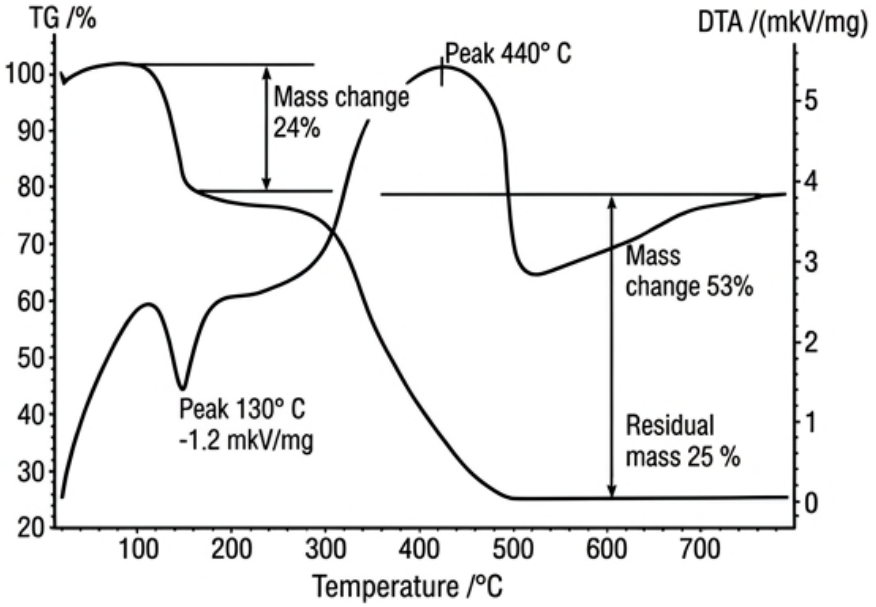

Figure 2. Termogravimetry of complex 2

Thermal analysis data for (1) showed that in both complexes thermic analyses proceeds in four stages.

In the first stage 148,8 to 205^{0}C mass loss for complex (1) equals 3,09%, for complex (2)- 24,02% (Fig. 2).

In the second stage at 220-350^{0}C, after the relase coordinated moleculs of water and pyridine, dimeric moleculas are formed that are stable. In the third stage 350-435^{0}C to the complexes the decomposition of carbon hydrate residues. In the fourth stage metal carbonates are formed (680^{0}C), that decomposes to metal oxides (750^{0}C).

Discussion of the crystal structures of complex 1 and 2.

Selected bond distances and $\left(d\ \overset{0}{A}\right)$ and angles $\left(\omega^0\right)$ for complex 1 have been shown in table 1.

Table 1. Selected bond distances (Å) and angles (^{o}) for (1).

Distanses	d, Å	Distans	d, Å
Sn – O (1)	2,452 (4)	Sn – O (11)	2,416 (4)
Sn – O (2)	2,691 (3)	O (1) – C (7)	1,269 (3)
Sn – O (5)	3,084 (4)	O (7) – C (7)	1,235 (4)
Sn – O (6)	2,428 (5)	O (6) – C (14)	1,284 (7)
Sn – O (7)	2,727 (4)	O (7) – C (14)	1,245 (8)
Sn – O (8)	2,872 (4)	C (II) – NO_2	1,436 (7)
O (1) – Sn – O (1)	50,1	O (2) – Sn – O (5)	60,7
O (1) – Sn – O (6)	89,1	O (11) – Sn – O (5)	94,5
O (1) – Sn – O (7)	75,9	O (6) – Sn – O (7)	81,3
O (1) – Sn – O (11)	74,2	O (11) – Sn – O (7)	121,2
O (2) – Sn – O (6)	133,9	Sn – O (1) – O (7)	99,2
O (2) – Sn – O (7)	120,9	Sn – O (6) – O (14)	98,5
O (2) – Sn – O (1)	74,6	O (1) – C (7) – O (2)	121,7

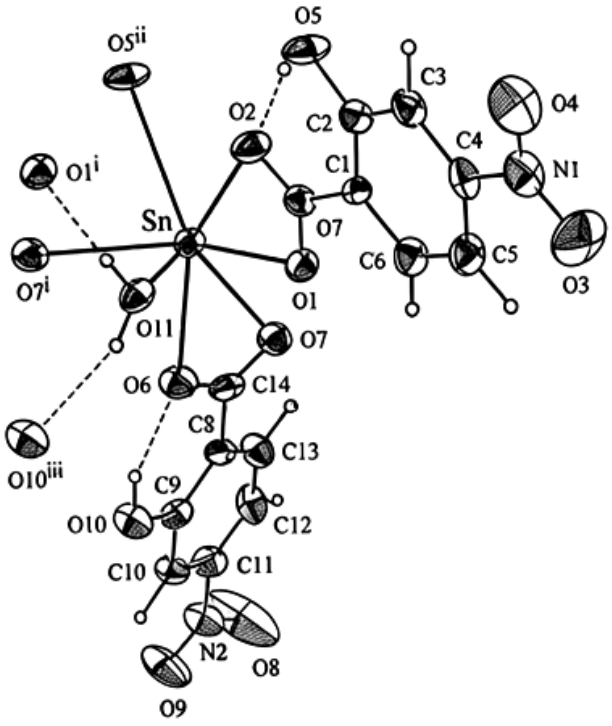

Figure 3. Molecular structure of $Sn(C_7H_4NO_5)_2 \cdot H_2O$ [complex 1]

Is can be seen brow Fig. 4 the coordination of the Sn (II) atom involves three primary bonds: carboxyl O (1) – 2,452Å, carboxyl O (6) – 2,428Å, and aqua O (11) atoms – 2,419Å, while secondary interaction with carboxyl O (2) – 2,691Å and O (7) – 2,727Å on the same molecular complex the chelate rings (Fig. 1). Two additional weaker intermolecular contacts with carboxyl O (7^1) – 2,691Å and hydroxyl O (5^1) – 3,084Å. All other O atoms are more than 3,35Å from the tin atom. The seven-coordinate geometry is highly irregular and leaves a substantial empty region on one side of the Sn atom, which can be attributed to a sterochemically-active ion pair of electrons, typical for Sn(II) [18, 19].

The two hydroxyl groups in the molecule, O (5) and O (10), are involved in inframolecular hydrogen bonds to the carboxyl O (2) and O (6) atoms, respectively. The water molecule is involved in two intermolecular hydrogen bonds to the carboxyl O (1) and hydroxy O (10) atoms.

Selected bond distances $\left(d\ \overset{0}{A}\right)$ and angles $\left(\omega^0\right)$ for complex 2 have been shown in table 2.

Table 2. Selected bond distances (Å) and angles (^{0}) for complex (2)

Distance	$\overset{0}{d}, A$	Distance	$\overset{0}{d}, A$
$Co(1)-O(1)$	2,157	$O(4)-N(2)$	1,227
$Co(1)-O(1)$	2157	$N(1)-C(8)$	1,357
$Co(1)-O(H_2O)$	1,181	$N(1)-C(3)$	1,395
$Co(1)-N(1)$	2,301	$N(2)-C(6)$	1,463
$C(1)-O(1)$	1,279	$C(1)-C(2)$	1,515
$C(1)-O(2)$	1,240	$C(3)-C(4)$	1,401
$C(8)-O(3)$	1,221	$C(2)-C(7)$	1,386

$O(1)-Co-O(2)$	180,00	$O(4)-N(2)-O(5)$	123,81
$O(1)-Co-O(H_2O)$	84,14	$O(4)-N(2)-C(6)$	118,11
$O(1)-Co-N(1)$	91,39	$O(2)-C(1)-O(2)$	125,10
$N(1)-Co-N(13)$	90,08	$C(7)-C(2)-C(1)$	117,12
$C(1)-O(1)-Co(1)$	133,86	$C(7)-C(6)-N(2)$	119,28
$C(8)-N(1)-C(3)$	129,21	$C(5)-C(6)-N(2)$	119,62

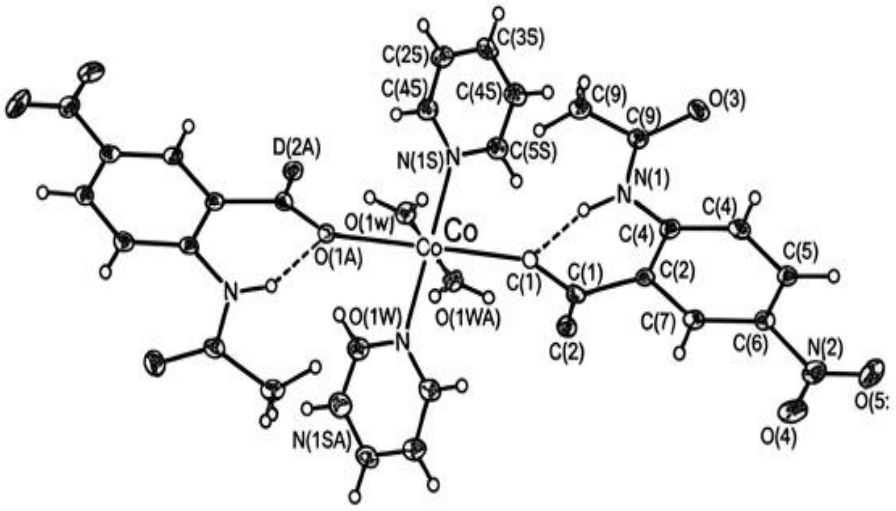

Figure 4. Molecular structure of Co (II) [complex 2]

As can be seen fig. 4, the central atom Co(II) coordinated with the oxygens atoms of the carboxyl group at monodentate bond.

The bond between the central atom and the oxygen of the carboxyl group $Co(1)-O(1)=2;157\overset{0}{A}$, it is compatible other Co(II) complexes.

The pyridin molecules enter in the structure and form the adduct which is coordinated by the donor nitrogen atoms and the central cobalt atom is coordinated throught donor-acceptor type.

The length of this bond - $Co(1)-N(1)=2,301\overset{0}{A}$ and corresponds to the other cobalt-nitrogen bonds [10].

Two molecules of water from a donor oxygen atoms and a donor-acceptor bond with the cobalt atom, completing its coordination number to six. The length of this bond is $Co(1)-O(H_2O)=1,181\overset{0}{A}$ and similar to other aqua complexes of Cobalt [11].

The phenyl carbon bond $(C(2)-C(3))=1,543(6)\overset{0}{A}$ is similar to other derivatives benzoic acid .

The phenyl ring and substituents are located on a plane, which is due to the ionic structure.

The bond length between the carbons forming both the benzene and pyridine

C – C=1,385Å, the same as the bond length in other benzoic acid derivativers.

The length of the C – NO_2 bond is 1,436 Å, which is the same as in other nitrobenzoate complexes. Molecules are linked together by strong hydrogen bonds $O\cdots HO=2,89\overset{0}{A}$.

Conclusion

It has been synthesized and deciphered the molecular structure of new complex bis-(p-nitrosalysilato) Sn · H_2O. It was established that the central Sn atom is coordinated by the oxygen atoms of the carboxyl group and the oxygen atom of the hydroxyl group. The water molecule in the complex, via a donor oxygen atom, coordinates with the central atom and increases its coordination number to seven. The carboxyl oxygens form chelate bonds. It has been synthesized and deciphered molecular structure of new complex bis-(5-nitro, 2-asetamidobenzoata)-di-(pyridine) cobalt(II)-dihydrate. It was established that the central cobalt atom is coordinated by the oxygen atoms of the carboxylic group by monodentate type. Two molecules forming the adduct are coordinated by donor nitrogen atoms of pyridine to the central atom via a donor-acceptor bond. The water molecule in the complexes, via a donor oxygen atom, coordinates the central atom and increases its coordination number to four.

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