

TEMPLATE SYNTHESIS AND STRUCTURAL CHARACTERISATION OF FIVE DIFFERENT Co(II) COMPLEXES WITH THE SAME LIGAND

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abstract: A range of Co(II) complexes with Schiff bases obtained through condensation of salicylaldehyde with 2-aminothiazole has been synthesised. The stoichiometric formulas of the obtained complexes are: $[\text{Co}(\text{SATZ})_2\text{X}_2]$; $[\text{Co}(\text{SATZ})_2]\text{Cl}_2$ where: SATZ = salicylidene 2-aminothiazole; X = Cl⁻, CH₃COO⁻. Elemental analysis, molecular weight, magnetic susceptibility, molar conductivity determination, electronic and IR spectra were carried out. It has been found out that the ligand is NO bidentate, and the complexes are octahedral, except $[\text{Co}(\text{SATZ})_2]\text{Cl}_2$ which has a tetrahedral geometry.

Introduction

The importance for biological systems of 2-aminothiazole and its derivatives is well known /1, 2/. It is also known that the thiazolic ring is part of B₁ vitamin, and of some antibacterial drugs, those contain sulphathiazole. Even a range of penicillin contains in the molecule the hydrogenate thiazolic ring /3/.

The 2-aminothiazole and its derivative complexes with transitional metal ions, which are also interesting from biological point of view, have been synthesised and studied by some specialists /4-7/.

Upon these, we tried to obtain a range of Co(II) complexes with Schiff bases through condensation of 2-aminothiazole with salicylaldehyde. We must underline the fact that, this ligand can coordinate the metal ion through the N and S atoms from the thiazolic ring, but also through the N (azomethinic) and O (phenolic) atoms.

Experimental

All chemicals used are of p.a. produced by Merck.

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The electronic spectra were determined with a UNICAM UV-VIS 3-100, and the IR spectra with a spectrophotometer BIO-RAD FTS-135. The molar conductivity measurements were obtained through a conductivity bridge Elico CM-82.

Ligand synthesis

The Schiff base was obtained by mixing the salicyl aldehyde and 2-aminothiazole solutions in methanol, in molar ratio of 1:1. The obtained solution was refluxed for 6 hours and concentrated through distillation until the volume decreased to one third. The precipitate formed of light-brown colour was filtered off, washed with methanol and dried in vacuum over phosphorus pentaoxyde.

Complexes synthesis [Co(SATZ)₂(ac)₂] (I), (II)

A solution of 0,005 mols of salicylaldehyde in 50 ml of methanol is added by continuously stirring to that obtained of 0,005 mols of 2-aminothiazole and 100 ml methanol. After 20 minutes the solution is added through the same procedure at 0,0025 mols of Co(CH₃COO)₂·4H₂O dissolved in 50 ml of methanol. The solution colour is reddish. The mixture is refluxed for 3 hours and concentrated through until the volume is decreased to one third. After 24 hours a brick-reddish precipitate appears (compound I); this is filtered, washed with methanol and dried over in vacuum. Diethyl ether is added to the solution obtained through filtering. A brown-yellowish precipitate is obtained (compound II); this is filtered, washed with diethyl ether and dried over in vacuum.

Compound I is soluble in chloroform, acetone, benzene, half-soluble in ethanol, methanol and carbon tetrachloride and hard soluble in diethyl ether and toluene.

Compound II is half soluble in chloroform, acetone, benzene, hard soluble in benzene and not soluble in methanol, ethanol, toluene and carbon tetrachloride.

Analysis for I: calculated: Co 10,11; C 28,82; N 9,6; found: Co 12,03; C 27,45; N 10,9 and for II: calculated: Co 10,11; C 28,82; N 9,6; found: Co 11,4; C 26,77; N 11,1.

Obtaining of the [Co(SATZ)₂]Cl₂ (III) and [Co(SATZ)₂]Cl₂ (IV) complexes

A solution of 0,005 mols salicylaldehyde in 50 ml methanol is added through stirring to the solution obtained from 0,005 mols 2-aminothiazole and 100 ml methanol. After 20 minutes this solution is added through the same procedure to 0,0025 mols CoCl₂·6H₂O dissolved in 50 ml of methanol. The colour of the obtained solution is green-yellowish. The solution is refluxed for 4 hours and is concentrated until the volume decrease to one third. Even after 24 hours, any precipitate is not observed. Thus, diethyl ether is added to the clear solution and two layers are observed. The alcoholic layer is light-brown coloured and the etheric one is green. After separating the two layers, through evaporation from the alcoholic solution a blue precipitate is obtained. This is recrystallised from methanol. A light blue precipitate is obtained (compound III).

From the green ether solution through concentration, a brown-yellowish precipitate is obtained through concentration (compound IV). This is filtered washed with diethyl ether and dried over in vacuum.

Compound (III) is soluble in chloroform, benzene, acetone, half soluble in methanol and hard soluble in soluble in ethanol and diethyl ether.

Compound (IV) is soluble in ethanol and methanol, half soluble in chloroform, benzene, acetone and diethyl ether, hard soluble in the other usual solvents.

Analysis for III: calculated: Co 10,99; C 22,39; N 10,45; Cl 13,24; found Co 11,73; C 20,44; N 11,72; Cl 15,32 and for IV: calculated: Co 10,99; C 22,39; N 10,45; Cl 13,24; found Co 11,54; C 24,32; N 9,33; Cl 14,71.

Obtaining of the $[\text{Co}(\text{SATZ})_2\text{Cl}_2]$ (V) complex

The synthesis described above is repeated, until the separation of the two layers, ether and alcoholic. The alcoholic solution is evaporated and precipitate obtained is redissolved in acetone. After concentration of the solution, a green compound is obtained through evaporation (compound V), which is filtered, washed with acetone and dried over in vacuum. Analysis for V: calculated: Co 10,99; C 22,39; N 10,45; Cl 13,24; found Co 12,04; C 23,89; N 9,71; Cl 13,98.

Results and discussion

The molecular weight, magnetic susceptibility and molar conductivity determinations of the products are shown in Table 1. The molar conductivity determination in DMF 10^{-3} M indicates for compounds (I), (II), (IV), (V), low values between $15\text{-}25 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$, this showing the non-electrolytic nature of those compounds. The value of molar conductivity of the compound (III) solution indicates an 1:2 electrolyte.

Table 1. Molecular weight and conductivity determination (DMF 10^{-3} M)

No.	Compound Formula	M calc./det.	Λ ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	μ (B.M.)
(I)	$[\text{Co}(\text{SATZ})_2(\text{ac})_2]$	582,93/567,14	12,4	5,44
(II)	$[\text{Co}(\text{SATZ})_2(\text{ac})_2]$	582,93/571,18	21,5	5,51
(III)	$[\text{Co}(\text{SATZ})_2\text{Cl}_2]$	535,93/504,22	275,4	4,45
(IV)	$[\text{Co}(\text{SATZ})_2\text{Cl}_2]$	535,93/509,93	24,5	4,76
(V)	$[\text{Co}(\text{SATZ})_2\text{Cl}_2]$	535,93/512,4	18,5	5,04

The main band from the ligand and complex compounds IR spectra are presented in table 2.

Table 2. Spectral IR data of the ligand and of metal complexes with Co(II) (cm^{-1})

SATZ	(I)	(II)	(III)	(IV)	(V)	Assignments
3414	3333	3304	3308	3336	3284	$\nu_{\text{O-H}}$ phenolic
3111	3093	3122	3159	3114	3116	$\nu_{\text{C-H}}$ heterocyclic
2923	2910	2936		2905	2922	$\nu_{\text{C-H}}$ aromatic
1646	1627	1614	1629	1619	1604	$\nu_{\text{C=N}}$ azomethine
	1608	1580				ν_{COO^-} asymmetric
1535	1531	1540	1538	1527	1533	$\nu_{\text{C=N}}$ heterocyclic
1493	1478		1501	1512	1506	$\nu_{\text{C=C}}$ heterocyclic
1453	1454	1429	1429	1482		$\nu_{\text{C=C}}$ aromatic
	1439	1405				ν_{COO^-} symmetric
1273	1316	1291	1305	1298	1288	$\nu_{\text{C-N}}$ exocyclic
1109	1148	1151	1152	1149	1163	$\nu_{\text{C-O}}$ phenolic
759	743			756		$\chi_{\text{C-H}}$ heterocyclic
702		713	702	730	724	$\chi_{\text{C-H}}$ aromatic
675	666	671	683	680	679	$\nu_{\text{C-S}}$ heterocyclic

In the ligand IR spectra, at 3414 cm^{-1} , a strong absorption band appears, assigned to the phenol O-H bond vibration which is shifted to lower frequencies in the complexes IR spectra. Also the absorption band characteristic for C-O bond, appears in the ligand IR spectrum at 1109 cm^{-1} . In the complexes IR spectra this band appears between $1148\text{-}1163\text{ cm}^{-1}$, shifted toward higher frequencies. These data indicates the O atom implication in coordination. The ligand shows in the IR spectra, a band of medium intensity, at 1646 cm^{-1} , attributed to the stretching frequencies $\nu(\text{C}=\text{N})$ (azomethine). In the complex compounds IR spectra, this band appears between $1604\text{-}1629\text{ cm}^{-1}$, shifted to lower frequencies, which indicates the implication of the azomethinic group nitrogen atom in coordination of the metal atom, with the forming of a chelate ring of six members. This fact is sustained also by the shift of the $\nu(\text{C}-\text{N})$ (exocyclic) stretching frequency from 1273 cm^{-1} , in the ligand spectrum, toward higher frequencies, in the complexes spectra inside the $1288\text{-}1316\text{ cm}^{-1}$ domain /8/. The small shifts of the stretching frequencies of C=N /9/ and C-S /4, 10/ bonds from the thiazolic ring in the complexes IR spectra, compared with the ligand, demonstrates that the N and S atoms from the thiazolic ring are not involve in the coordination. In the (I) and (II) complexes IR spectra, two absorption bands appears at $1608, 1580$ and $1439, 1405\text{ cm}^{-1}$. These could be ascribed to the stretching of the acetate groups (antisymmetric) respectively (symmetric). The difference between the two frequencies is of 139 cm^{-1} , for complex (I) and of 175 cm^{-1} for complex (II) afford us to considerate that the acetate groups are monodentate. The difference between two frequencies of acetate groups is too big to consider them to function in a bidentate way. As a conclusion, we can say that the ligand, saliciliden 2-aminothiazole is bidentate, of NO type, the phenolic oxygen and azomethinic nitrogen atoms taking part to the coordination of the metal ion. The N and S thiazolic atoms don't participate to this coordination.

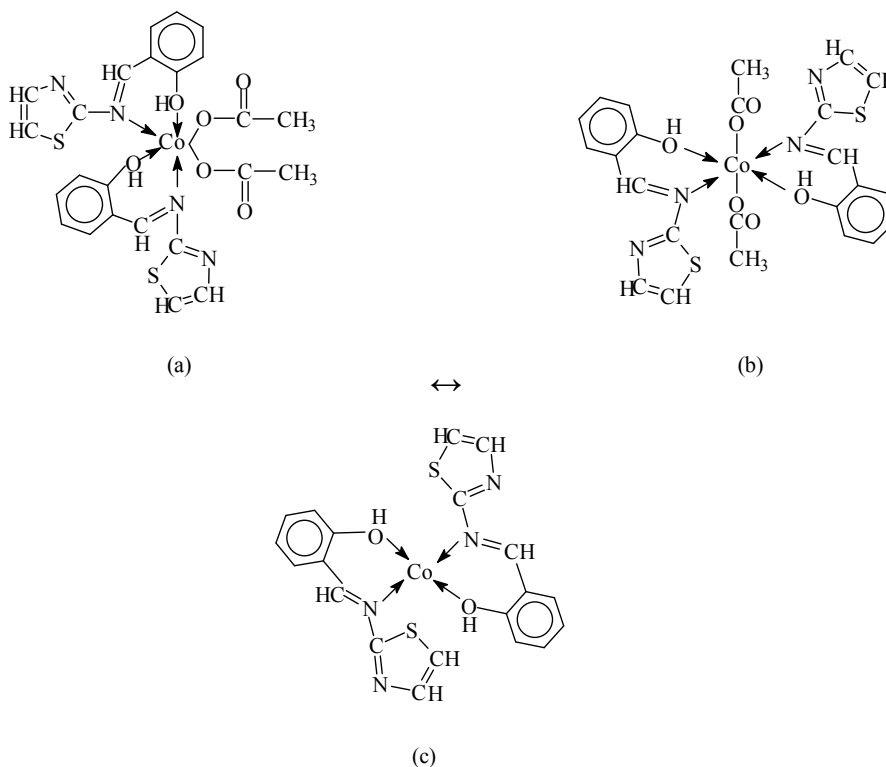
In Table 3, spectral UV-VIS data for ligand and complexes are presentate.

Table 3. Spectral UV-VIS data for ligand and complexes (cm^{-1})			
No.	Compound	Absorption band	Assignments
	SATZ	46082	$\pi \rightarrow \pi^*$
		37593	$\eta \rightarrow \pi^*$
(I)	$[\text{Co}(\text{SATZ})_2(\text{ac})_2]$	46340	$\pi \rightarrow \pi^*$
		39270	$\eta \rightarrow \pi^*$
		27027	${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$
		22220	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$
(II)	$[\text{Co}(\text{SATZ})_2(\text{ac})_2]$	47619	$\pi \rightarrow \pi^*$
		39840	$\eta \rightarrow \pi^*$
		25000	${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$
		22321	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$
(III)	$[\text{Co}(\text{SATZ})_2]\text{Cl}_2$	46790	$\pi \rightarrow \pi^*$
		38461	$\eta \rightarrow \pi^*$
		21276	${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$
(IV)	$[\text{Co}(\text{SATZ})_2]\text{Cl}_2$	44440	$\pi \rightarrow \pi^*$
		35087	$\eta \rightarrow \pi^*$
		21739	${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$
		19762	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$
(V)	$[\text{Co}(\text{SATZ})_2]\text{Cl}_2$	45662	$\pi \rightarrow \pi^*$
		35971	$\eta \rightarrow \pi^*$
		20920	${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$
		18656	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$

In the UV-VIS spectra of the $[\text{Co}(\text{SATZ})_2(\text{ac})_2]$ complex compounds the absorption bands from 27027 and 25000 cm^{-1} are generated by the electronic transition. Also, the bands from 22220 and 22321 cm^{-1} , that appears in the electronic spectra of complexes (I) and (II) are ascribed to the ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_2) transition, these data indicates that those complexes have distorted octahedral geometry (Figure 1 a,b).

The absorption band at 21276 cm^{-1} of the $[\text{Co}(\text{SATZ})_2]\text{Cl}_2$ (III) UV-VIS spectrum, could be ascribed to the electronic transition ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ /9/ and also to the low symmetry components may be due to spin-orbital coupling. As a conclusion, we could say that this blue complex has a tetrahedral geometry (Figure 1 c).

The absorption bands from 21739 and 19762 cm^{-1} , that appears in the complex (IV) electronic spectrum are ascribed to the ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\nu_3)$ electronic transition and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_2). The same type of transition has as a result the appearance of the absorption bands from 20920 and 18656 cm^{-1} from the complex (V) electronic spectrum. This is giving us the opportunity to say that these complexes have a distorted octahedral geometry (Figure 1 d,e).



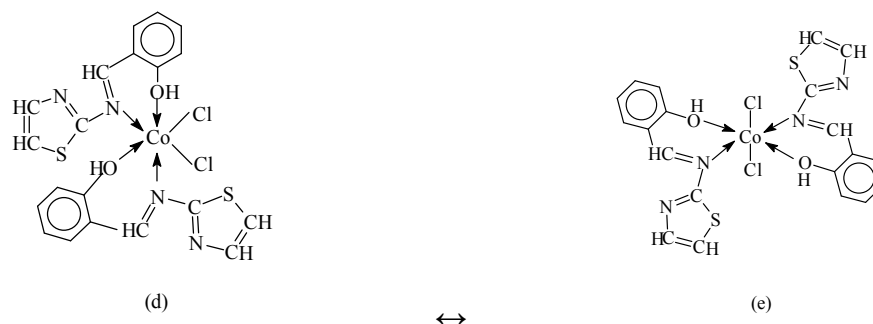


Fig. 1 The geometric formulas of Co(II) complex compounds.

Conclusions

As a conclusion, five Co(II) complexes compounds with salicylidene 2-aminothiazole have been synthesised, the ligand is acting as a bidentate by coordinating to the metal ion through the nitrogen (azomethine) and oxygen (phenol) atoms. The complexes (I) and (II) have a distorted octahedral geometry and they can be cis-trans isomers, complex (III) shows a tetrahedral geometry, and complexes (IV) and (V) have also a distorted octahedral geometry and they possible be cis-trans isomers.

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