Preparation and Characterization of Cobalt (II)-Complexes of 4-Hydroxybenzaldehyde Semicarbazone and Amino Acid Esters Ligands

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الخلاصة

حضرت معقدات الكوبلت (II) مع مزيج من الليكندات التي تتضمن 4-هيدروكسي بنزالديهايد سميكاربازون (HBSCH) واسترات الاحماض الامينية (A) [فينول كلايسين استر (GlyP) وفينول الانين استر (AlaP) و 2-امينو فينول كلايسين استر (GlyA) و 2-امينو فينول الانين استر (AlaA)]. وشخصت باستخدام تقنيات فيزيائية-كيميائية. اقترحت الصيغ العامة $[Co(HBSCH)(A)_2(NO_3)]NO_3$ و $[Co(HBSCH)(A)_2(NO_3)_2]$ و $[Co(HBSCH)_2(A)(NO_3)]NO_3$ و $[Co(HBSCH)_2(A)(NO_3)_2]$ للمعقدات المحضرة في الوسط المتعادل. في حين اقترحت الصيغ العامة $[Co(HBSC)(A)_2]$ و $[Co(HBSC)_2(A)]$ للمعقدات المحضرة في الوسط القاعدي (حيث HBSC = الليكاند HBSCH مزال منه بروتون او بروتونين). اقترحت الدراسة ان جميع المعقدات ذات بنية ثمانية السطوح.

ABSTRACT

Cobalt (II) complexes with mixed ligands including 4-hydroxybenzaldehyde semicarbazone (HBSCH) and esters of amino acids - A {phenol glycine ester (GlyP), phenol alanine ester (AlaP), 2-aminophenol glycine ester (GlyA) and 2-aminophenol alanine ester (AlaA)} have been prepared and characterized by physical chemical techniques. General formulaes $[Co(HBSCH)(A)_2(NO_3)]NO_3$, $[Co(HBSCH)(A)_2(NO_3)_2]$, $[Co(HBSCH)_2(A)(NO_3)]NO_3$ and $[Co(HBSCH)_2(A)(NO_3)_2]$ have been proposed for the complexes prepared in neutral medium. Whereas, the

formulaes [Co(HBSC)(A)$_2$] and [Co(HBSC)$_2$(A)] have been proposed for the complexes prepared in basic medium (where HBSC = deprotonated HBSCH ligand). The study suggested that all the complexes had octahedral geometries.

INTRODUCTION

Cobalt is known to be one of the trace elements essential to human nutrition. It is present in meat and dairy products and in vitamin B$_{12}$. It is an important substance that can prevented the disease known as precious anemia, in which the blood was depleted of a dequate numbers of its carrying red cells [1].

The chemistry of transition metal complexes of semicarbazones has been receiving considerable attention because of their biological activities and providing models for metal ligand bonding sites in several enzymes [2-4]. In the solid state, these semicarbazones were existed in the keto form (Figure 1a). In solution, however, they were known to tautomerize into the enol form (Figure 1b). Complexation usually took place through the N and O donor atoms [2,5-8], resulting in the formation of a five-membered chelate ring (Figure 1c and 1d).

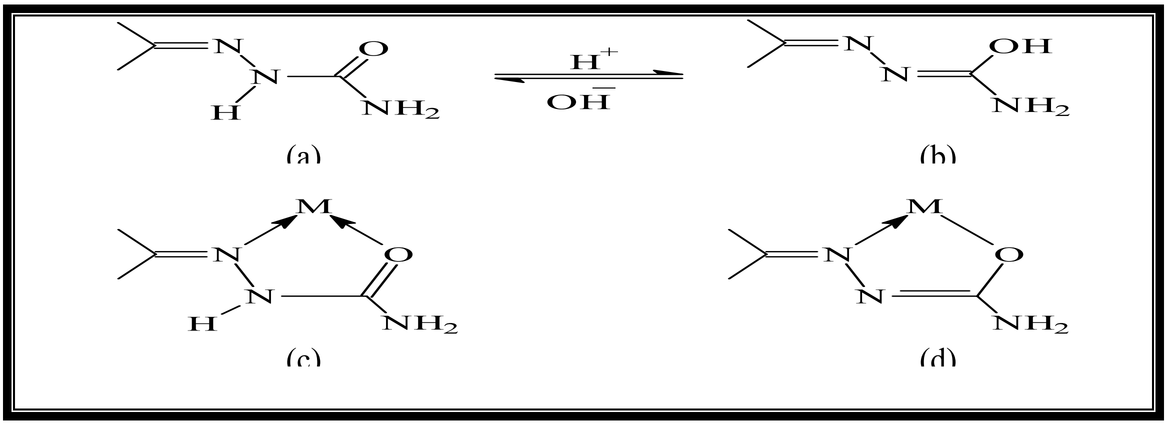


Figure 1: Semicarbazone ligand and its coordination compound

Amino acids and their derivatives have been used for different purposes [9-13]. A good deal of work has been reported on the formation of amino acid esters chelates involving ligands containing different donating atoms such as nitrogen, oxygen and sulfur [14-20].

Coordination compounds of mixed ligands were of a considerable importance in the field of metalloenzymes and biological activities in addition to other purpose [21-26]. Hence a large number of coordination compounds containing mixed ligands with transition and non-transition metal ions have been reported recently [27-30]. Due to the importance of semicarbazone, amino acid esters and mixed ligands complexes we took a humble part in the chemistry of their complexes. Recently, some articles have been published concerning their coordination chemistry with transition and non-transition metal ions [31-36].

In the present work new cobalt (II) complexes with mixed ligands 4-hydroxybenzaldehyde semicarbazone and amino acid esters (Figure 2) has been prepared and characterized physico-chemically.

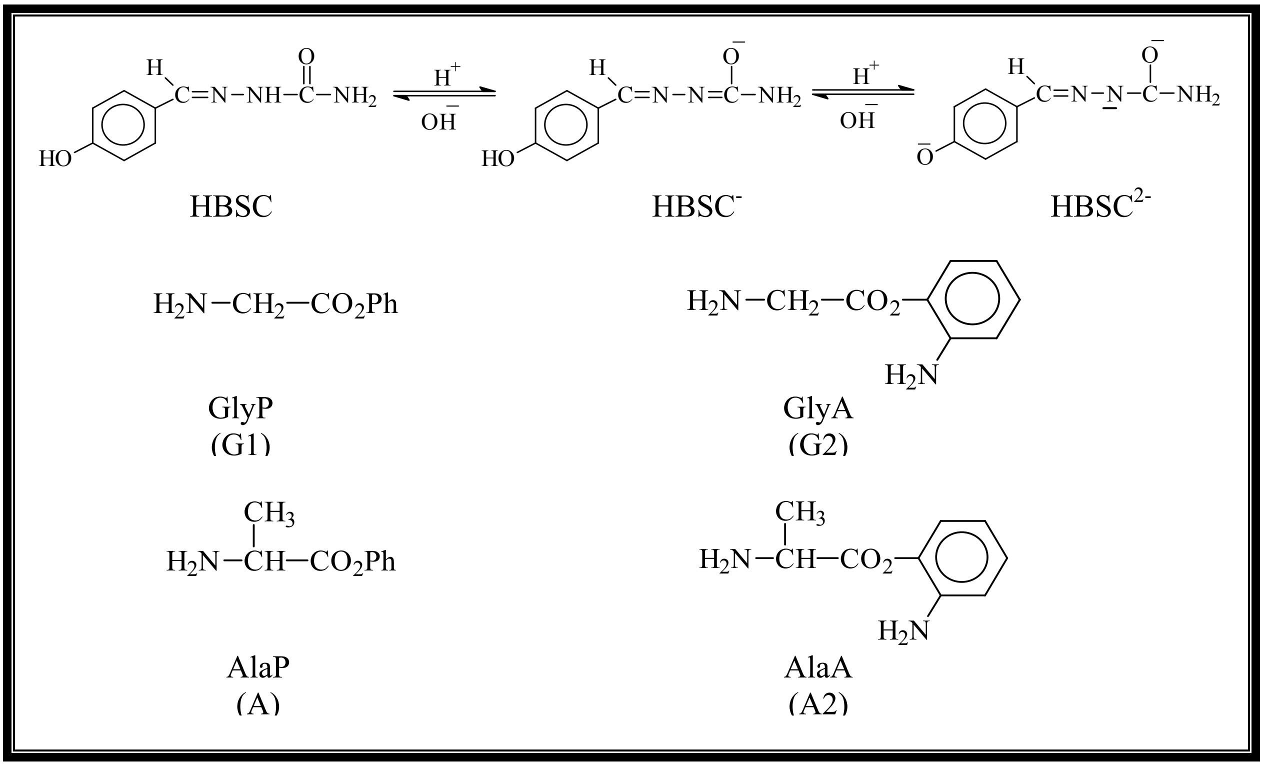


Figure 2: Structures of the ligands

EXPERIMENTAL

1. Synthetic methods

4-Hydroxybenzaldehyde semicarbazone (HBSCH) has been prepared according to the standard method [37]. Amino acid esters have been prepared according to the previous method [37].

A general procedure has been adopted for the preparation of the complexes in neutral and basic medium.

I. In neutral medium

A solution of 0.5 g (1.72 mmole) of cobalt (II) nitrate in 5 ml distilled water has been added to the solution of 1.72 or 3.44 mmole 4-hydroxybenzaldehyde semicarbazone in 20 ml hot ethanol and 3.44 or 1.72 mmole of amino acid ester in 25 ml hot ethanol (the amounts in grams have been listed in Table 1). The mixtures have been refluxed for two hours followed by evaporation to about half their volumes then cooled. The products were filtered off, washed with diethylether and dried.

II. In basic medium

Complexes of the types [Co(HBSC)(A)$_2$] and [Co(HBSC)$_2$(A)] have been prepared by applying same amounts used in neutral medium, after mixing the metal salts with the ligands solutions and on heating on a water bath, potassium hydroxide solution 1M has been added dropwise until complete precipitation (pH ≈ 8-9). The mixtures have been heated on a water bath for half an hour then allowed to stand then cooled. The products were filtered off, washed with diethylether and dried.

2. Analytical and physical measurements

Cobalt contents have been determined by applying gravimetric method [38]. Relative molecular weights of the ligands and their complexes have been determined cryoscopically [39]. Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring set LF-42 using 10^{-3} M dimethylformamide solution at room temperature. Infrared spectra has been recorded on FT-IR Bruker type Tensor 27 in the range 400-4000 cm^{-1} using KBr pellets. Electronic spectra has been recorded by Shimadzu UV-1601 Spectrophotometer for 10^{-3} M or 10^{-4} M solution of the ligands and their complexes in dimethylformamide at 25 °C. Magnetic susceptibilities of the complexes have been measured by Bruker B.M6.

RESULTS AND DISCUSSION

The reaction of cobalt (II) nitrate with 4-hydroxybenzaldehyde semicarbazone and amino acid esters in both neutral and basic medium can be represented by the following reactions:

$Co(NO_3)_2.6H_2O + HBSCH + 2A \longrightarrow [Co(HBSCH)(A)_2(NO_3)]NO_3 + 6H_2O$
$Co(NO_3)_2.6H_2O + HBSCH + 2G_2 \longrightarrow [Co(HBSCH)(G_2)_2(NO_3)_2] + 6H_2O$
$Co(NO_3)_2.6H_2O + 2HBSCH + A \longrightarrow [Co(HBSC)_2(A)(NO_3)]NO_3 + 6H_2O$
$Co(NO_3)_2.6H_2O + 2HBSCH + A^{-} \longrightarrow [Co(HBSCH)_2(A^{-})(NO_3)_2] + 6H_2O$
$Co(NO_3)_2.6H_2O + HBSCH + 2A + 2KOH \longrightarrow [Co(HBSC)(A)_2] + 2KNO_3 + 8H_2O$
$Co(NO_3)_2.6H_2O + 2HBSCH + A + 2KOH \longrightarrow [Co(HBSC)_2(A)] + 2KNO_3 + 8H_2O$
(where $A^{-} = G_1$ or A_2)

The complexes under investigation were colored, solid, soluble in dimethylformamide and dimethylsulphoxide. Cobalt contents and relative molecular weights (Table 2) revealed that the complexes had the general formulaes [Co(HBSCH)(A)$_2$(NO$_3$)]NO$_3$, [Co(HBSCH)(G$_2$)$_2$(NO$_3$)$_2$], [Co(HBSCH)$_2$(A)(NO$_3$)]NO$_3$ or [Co(HBSCH)$_2$(A`)(NO$_3$)$_2$] and [Co(HBSC)(A)$_2$] or [Co(HBSC)$_2$(A)] respectively. The values of the molar conductivities (Λ_M) shown in Table (2) approached those expected for 1:1 and non-electrolytes [40] for complexes prepared in neutral medium, and non-electrolytes for complexes prepared in basic medium. The room temperature magnetic moments ($\mu_{eff.}$) of cobalt (II) complexes were in the range of 3.83-3.97 B.M (Table 2) indicating the presence of three unpaired electron and assigned to high spin monomeric structures having octahedral geometries [32,41].

Infrared spectra of semicarbazone ligand (Table 3) showed a strong band at 1656 cm^{-1} which was attributed to $\upsilon_{C=O}$. This value shifted towards a lower frequency (1613-1617 cm^{-1}) on coordination, in neutral medium, indicating a coordination of the oxygen atom of C=O group to the metal ion [32,42]. Whereas, the infrared spectra of the complexes 9 and 15 showed two bands at 1656 and 1614 cm^{-1}, this splitting may be due to the coordination of only one C=O group to the metal ion [7,42]. In basic medium, this band was disappeared in the infrared spectra of the complexes and a new band was observed at 1107-1138 cm^{-1} due to bonding enolic C-O thereby establishing coordination of the ligand through the enolic oxygen atom [5,42]. The appearance of strong bands at 1636-1640 cm^{-1} and 1575-1581 cm^{-1} which were attributed to $\upsilon_{C=N}$ + $\upsilon_{O-C=N}$ and azine chromophore C=N-N=C, respectively, supported the formation of enolic structure in a basic medium [5,7]. The strong band at 1608 cm^{-1} attributed to $\upsilon_{C=N}$ has been shifted towards a lower frequency on coordination due to the decrease of the bond order as a result of metal nitrogen bond formation [5.32]. The band in the region 3187 cm^{-1} was attributed to υ_{NH} , the broadening of this band was due to the hydrogen bonding phenomenon. By complexation, this phenomenon becomes more complicated due to different factors such as the effect of hydrogen bonding and the presence of other group (NH_2) situated at the same position [2,6]. The υ_{NH} band remained unaltered in the spectra of the complexes prepared in neutral medium indicating that NH group was uncoordinated. Whereas in a basic medium, it is more difficult to notice the absence of NH group due to the presence of hydrogen bonding and other functional groups (OH, NH_2), but it is well known that this band has been disappeared [2,5] due to the enolic form. The strong bands appeared at 3440-3447 cm^{-1} and 1450-1456 cm^{-1} due to υ_{NH_2} and δ_{NH_2} , respectively, remained unchanged on complexation indicated the uncoordination of this group with the metal ion [2,5].

Infrared spectra of amino acid esters (Table 3) showed two bands at 1593-1605 cm^{-1} and 1354-1403 cm^{-1} assigned to the symmetric and asymmetric stretching frequency of COO group, respectively. On complexation these bands were shifted to 1485-1511 cm^{-1} and 1308-1338 cm^{-1}, respectively. The difference between these bands ($\Delta\upsilon$ = 170-178 cm^{-1}) indicated that COO group coordinated to the central metal ion in a monodentate manner [16,42]. The next wide bands 3088-3105 cm^{-1} and 3376-3424 cm^{-1} were attributed to $\upsilon_{NH_2\ (amino\ acid)}$ and $\upsilon_{NH_2\ (Ph)}$, respectively. In the spectra of the complexes, prepared in neutral medium, these bands remained unaltered indicating the uncoordination of these groups to the metal ion [14,16,42]. Whereas the spectra of the complexes prepared in basic medium showed that the first band only was shifted to lower frequency indicating the coordination of the nitrogen atom of amino acid group forming 5-membered ring, giving more stable complexes [14,16].

The spectra of all the complexes prepared in neutral medium showed bands at 1374-1421, 1259-1305 and 957-958 cm^{-1} due to ν_{sNO3}, ν_{asNO3} and ν_{NO} respectively. The difference between υ_{sNO3} and υ_{asNO_3} ($\Delta\nu = 115\ cm^{-1}$) supported the bonding of nitrato group as monodentate ligand through the oxygen atom [33,41,42]. Moreover, complexes 1,3,7,11 and 13 showed band at 1385-1386 cm^{-1} due to ionic bonding of NO_3^- group [42]. Whereas the spectra of the complexes prepared in basic medium did not show any of these bands indicating the non presence of nitrato group. The spectra of all the complexes showed new bands at 524-539 cm^{-1} and 607-628 cm^{-1} due to $\upsilon_{Co\text{-}N}$ and $\upsilon_{Co\text{-}O}$, respectively. The presence of these bands supported the formation of the complexes under investigation [41,32].

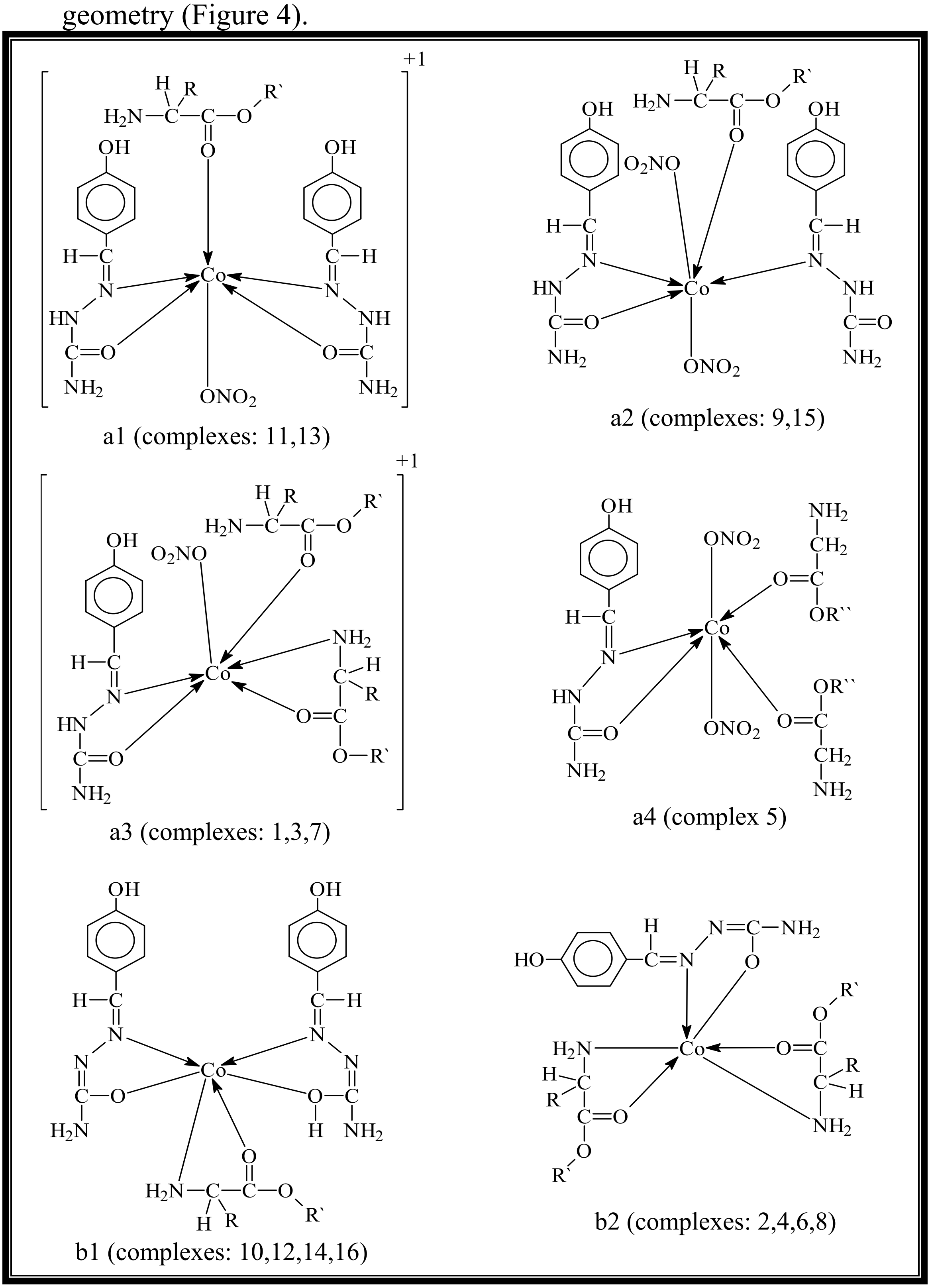
The electronic spectra of the complexes in dimethylformamide solution have been recorded giving d-d spectra and charge transfer spectra (Table 4). Cobalt (II) complexes showed absorption bands at 15013-17594 and 18001-22124 cm^{-1} due to υ_2 and υ_3 (attributed to the transitions $^4T_1g(F) \rightarrow {}^4A_2g(F)$ and $^4T_1g(F) \rightarrow {}^4T_1g(P)$) respectively. υ_1 {7184-8928 cm^{-1} attributed to the transition $^4T_1g\ (F) \rightarrow {}^4T_2g\ (F)$} has been not observed due to instrumental limitation, it was calculated by the literature method [43]. The ligand field parameter B and the ligand field splitting energy (10Dq) have been calculated [43]. The values of β of the complexes were 0.72 clearly indicated the covalent character of the bond concerned. The values of Dq/B which were in the range 1.45-1.50 suggested octahedral geometry for all the complexes [32,43]. The values of the C.F.S.E have been also determined which were in the range 8178-8508 cm^{-1}.

CONCLUSION

According to the analytical, physical and spectral data, some observations have been achieved that lead to establish the following points:

1. HBSCH ligand acts either as bidentate chelating ligand connected to cobalt (II) ion through the azomethine nitrogen and carbonyl oxygen or as monodentate ligand connected to cobalt (II) ion through the azomethine nitrogen (complex 9 and 15). $HBSC^-$ or $HBSC^{-2}$ (Figure 2) acts as bidentate chelating ligand joints to cobalt (II) ion through the azomethine nitrogen and enolic oxygen.
2. Amino acid esters act either as monodentate ligand joint to Co(II) ion through the carboxylate oxygen (in the neutral medium), or as bidentate chelating ligand connected to Co(II) ion through the carboxylate oxygen and amino nitrogen (in the basic medium).
3. NO_3^- connected to Co(II) ion in two manners, as monodentate ligand through the oxygen atom and in an ionic manner.

4. Cobalt (II) ion is probably hexacoordinated, leading to octahedral geometry (Figure 4).



a1 (complexes: 11,13)

a2 (complexes: 9,15)

a3 (complexes: 1,3,7)

a4 (complex 5)

b1 (complexes: 10,12,14,16)

b2 (complexes: 2,4,6,8)

Figure 4: Proposed structure of the complexes a1-a4 complexes in neutral medium, b_1 and b_2 complexes in basic medium, R` = Ph or 2-amino phenyl, R = H or CH_3,

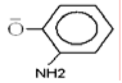
R"= 

Table 1: Medium, amounts used in the preparation of the complexes

No.	**Complex**	**Medium**	**Molar ration $M:L_1:L_2$**	**Wt. of HBSCH**	**Wt. of ester**	**Yield %**
1	$[Co(HBSCH)(G_1)_2(NO_3)]NO_3$	Neutral	1:1:2	0.31	0.52	82
2	$[Co(HBSC)(G_1)_2]$	Basic	1:1:2	0.31	0.52	67
3	$[Co(HBSCH)(A_1)_2(NO_3)]NO_3$	Neutral	1:1:2	0.31	0.57	55
4	$[Co(HBSC)(A_1)_2]$	Basic	1:1:2	0.31	0.57	76
5	$[Co(HBSCH)(G_2)_2(NO_3)_2]$	Neutral	1:1:2	0.31	0.57	52
6	$[Co(HBSC)(G_2)_2]$	Basic	1:1:2	0.31	0.57	70
7	$[Co(HBSCH)(A_2)_2(NO_3)]NO_3$	Neutral	1:1:2	0.31	0.62	50
8	$[Co(HBSC)(A_2)_2]$	Basic	1:1:2	0.31	0.62	59
9	$[Co(HBSCH)_2(G_1)(NO_3)_2]$	Neutral	1:2:1	0.615	0.26	56
10	$[Co(HBSC)_2(G_1)]$	Basic	1:2:1	0.615	0.26	52
11	$[Co(HBSCH)_2(A_1)(NO_3)]NO_3$	Neutral	1:2:1	0.615	0.284	58
12	$[Co(HBSC)_2(A_1)]$	Basic	1:2:1	0.615	0.284	66
13	$[Co(HBSCH)_2(G_2)(NO_3)]NO_3$	Neutral	1:2:1	0.615	0.285	82
14	$[Co(HBSC)_2(G_2)]$	Basic	1:2:1	0.615	0.285	62
15	$[Co(HBSCH)_2(A_2)(NO_3)_2]$	Neutral	1:2:1	0.615	0.31	74
16	$[Co(HBSC)_2(A_2)]$	Basic	1:2:1	0.615	0.31	80

Table 2: Analytical data and physical properties of the complexes

No.	**Color**	**M.P. °C**	Λ_M	$\mu_{eff.}$	**Co% Calc.(obs.)**	**M.Wt. Calc.(obs.)**
1	Greenish blue	206	77	3.83	9.10 (8.50)	648 (644)
2	Dark brown	120 d	29	3.81	10.09 (9.80)	585 (582)
3	Yellow	224	76	3.87	8.73 (7.80)	676 (680)
4	Dark brown	130	27.5	3.93	9.62 (9.30)	613 (582)
5	Dark brown	206	22	3.97	8.70 (7.80)	678 (680)
6	Brown	182 d	16	3.87	9.59 (9.10)	615 (582)
7	Black	230	50	3.94	8.36 (8.10)	706 (680)
8	Brown	180 d	17	3.91	9.18 (9.00)	643 (610)
9	Pale yellow	250	14	3.92	8.94 (8.70)	660 (680)
10	Pale yellow	260	12	3.92	11.05 (9.30)	534 (532)
11	Pale yellow	236	52	3.89	8.75 (7.90)	674 (680)
12	Dark pink	266 d	24.5	3.95	10.77 (9.30)	548 (556)
13	Black	230	60	3.85	8.59 (7.30)	687 (680)
14	Brown	182 d	28	3.85	10.52 (9.00)	561 (556)
15	Dark brown	256	35	3.90	8.56 (8.50)	689 (680)
16	Brown	174 d	25	3.95	10.48 (8.80)	563 (556)

Table 3: IR spectral data of the ligands and their complexes

No.	$\upsilon_{C=N}$ (semi)	$\upsilon_{C=O}$ (semi)	υ_{C-O} (semi)	υ_{asCO2} (ester)	υ_{sCO2} (ester)	$\Delta\upsilon$ (ester)	υ_{NH2} (ester)	υ_{sNO2}	υ_{asNO2}	$\Delta\upsilon$	υ_{NO3}	υ_{Co-N}	υ_{Co-O}	Other bands
HBSCH	1608 s	1656 s	-	-	-	-	-	-	-	-	-	-	-	υ_{OH} 3440 ω
G_1	-	-	-	1596 s	1395 s	201	3105 m	-	-	-	-	-	-	-
G_2	-	-	-	1605 s	1403 s	202	3305 m 3376 m	-	-	-	-	-	-	-
A_1	-	-	-	1593 s	1354 s	239	3088 m 3424 m	-	-	-	-	-	-	-
A_2	-	-	-	1604 s	1402 s	202	3305 m 3376 m	-	-	-	-	-	-	-
1	1542 s	1616 s	-	1508 s	1338 s	170	3444 m	1374 m	1259 m	115	1385	526 m 528 m	609 m 626 m	υ_{OH} 3440 ω
2	1541 s	-	1125 m	1507 s	1335 s	172	3636 m	-	-	-	-	529 m	609 m	-
3	1585 s	1615 s	-	1509 s	1335 s	174	3280 m	1374 m	1259 m	115	1385	524 m	621 m	υ_{OH} 3440 ω
4	1541 s	-	1115 m	1507 s	1335 s	172	3632 m	-	-	-	-	530 m	616 m	-
5	1558 s	1617 s	-	1508 s	1335 s	173	3276 m	1420 m	1305 m	115	-	539 m	607 m	υ_{OH} 3440 ω
6	1550 s	-	1107 m	1486 s	1308 s	178	3257 m 3322 m	-	-	-	-	539 m	628 m	-
7	1586 s	1613 s	-	1508 s	1335 s	173	3276 m	1374 m	1259 m	115	1386	524 m	620 m	υ_{OH} 3440 ω
8	1590 s	-	1138 m	1485 s	1315 s	170	3276 m	-	-	-	-	539 m	607 m	-
9	1584 s	1614 s 1656 s	-	1508 s	1335 s	173	3263 m	1420 m	1305 m	115	-	524 m	621 m	υ_{OH} 3440 ω
10	1585 s	-	1128 m	1508 s	1335 s	173	3266 m	-	-	-	-	524 m	620 m	υ_{OH} 3350 ω
11	1585 s	1614 s	-	1511 s	1334 s	177	3244 m	1420 m	1305 m	115	1385	524 m	620 m	υ_{OH} 3440 ω
12	1542 s	-	1121 m	1508 s	1335 s	173	3264 m	-	-	-	-	524 m	618 m	υ_{OH} 3350 ω
13	1585 s	1615 s	-	1485 s	1314 s	171	3276 m	1374 m	1259 m	115	1386	525 m	618 m	υ_{OH} 3440 ω
14	1585 s	-	1138 m	1487 s	1315 s	172	3257 m 3222 m	-	-	-	-	539 m	648 m	υ_{OH} 3350 ω
15	1586 s	1614 s 1656 s	-	1485 s	1315 s	170	3276 m 3413 m	1420 m	1305 m	115	-	525 m	618 m	υ_{OH} 3440 ω
16	1587 s	-	1138 m	1487 s	1315 s	172	3221 m	-	-	-	-	524 m	619 m	υ_{OH} 3350 ω

Table 4: Electronic spectral data of the complexes

No.	υ_1*	υ_2	υ_3	υ_3/υ_2	υ_3/υ_1	υ_2/υ_1	υ_3/B	B	Dq	Dq/B	10Dq	β	C.F.S.E	C.T
1	7197	15490	19920	1.286	2.768	2.152	28.10	709	1063.50	1.50	10635	0.72	8508	29240
2	7366	15856	20390	1.286	2.768	2.152	28.84	707	1060.50	1.50	10605	0.72	8484	31847
3	7184	15427	19144	1.241	2.665	2.147	27.16	705	1057.50	1.50	10575	0.72	8460	30120
4	7838	16871	21697	1.286	2.768	2.152	30.78	705	1022.25	1.45	10223	0.72	8178	34014
5	8193	17594	21834	1.241	2.665	2.147	30.98	706	1023.70	1.45	10237	0.72	8190	30120
6	7993	17204	22124	1.286	2.768	2.152	31.25	708	1062.00	1.50	10620	0.72	8496	29240
7	7689	16512	20492	1.241	2.665	2.147	28.94	708	1062.00	1.50	10620	0.72	8496	29240
8	8193	17594	21834	1.241	2.665	2.147	30.84	708	1026.60	1.45	10266	0.72	8248	27778
9	7457	15013	18001	1.199	2.414	2.013	25.53	705	1022.25	1.45	10223	0.72	8178	30488
10	7453	16005	19862	1.241	2.665	2.147	28.21	704	1056.00	1.50	10560	0.72	8448	30303
11	7730	16582	19881	1.199	2.572	2.145	28.16	706	1059.00	1.50	10590	0.72	8472	29940
12	7985	17074	19276	1.129	2.414	2.138	27.23	708	1062.00	1.50	10620	0.72	8496	31847
13	8928	16759	21552	1.286	2.414	1.877	30.44	708	1026.60	1.45	10266	0.72	8213	29069
14	7785	16718	20747	1.241	2.665	2.147	29.43	705	1022.25	1.45	10223	0.72	8178	31847
15	8852	16615	21368	1.286	2.414	1.877	30.31	705	1057.50	1.50	10575	0.72	8460	32810
16	8193	17594	21834	1.241	2.665	2.147	30.80	709	1063.50	1.50	10635	0.72	8508	28249

* calculated

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