

and non-transition metals due to their important role in biological processes⁽¹⁶⁻²²⁾.

In view of this, and since mixed ligand complexes with cobalt (II) ion of such ligands have not yet been reported,

therefore new cobalt (II) complexes with mixed ligand {salicylaldehyde thiosemicarbazone and substituted carboxylic acids (Figure 1)} have been synthesized and characterized physico-chemically.

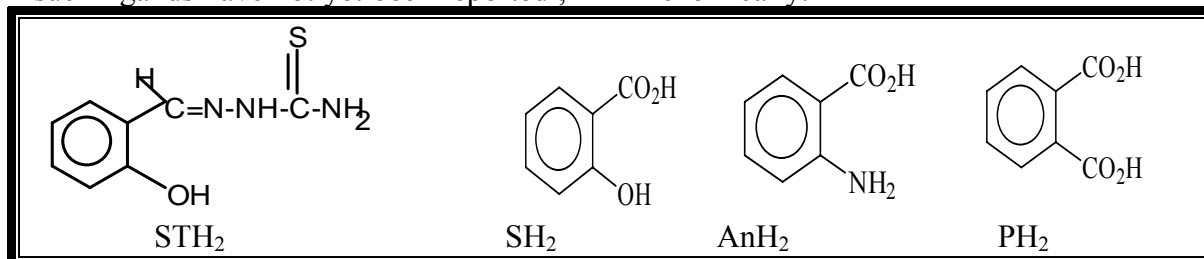


Figure 1 : Structures of the ligands

Experimental

Analytical and Physical Measurements

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Carbon, hydrogen and nitrogen have been estimated for some complexes using CHN microanalyser type 1106 (Carlo-Erba) at Chemistry Department, Science College, Mosul University. Cobalt content has been determined by applying precipitation method after the decomposition of the complexes with concentrated nitric acid⁽²³⁾.

Conductivity measurements have been carried out with an electrolytic conductivity measuring set LF-42 and Multiline f / SET-2 WTW Wissenschaft using 10^{-3} M DMF solution at 25 °C at Chemistry Department, Education College, Mosul University. The infrared spectra has been recorded on a Pye-Unicam 1100 Infrared Spectrophotometer in the 400-4000 cm^{-1} range using KBr pellets. Electronic spectra has been recorded on Shimadzu UV - Visible Recording Spectrophotometer (UV 160) for 10^{-4} M solutions of the ligands and their complexes in DMF at 25 °C, using a 1cm cell. Magnetic susceptibility of the complexes have been measured by Bruker B. M6 instrument at Chemistry Department, Science College, Mosul University.

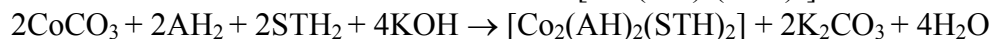
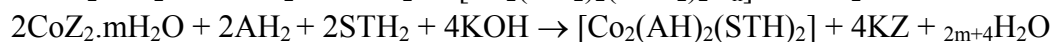
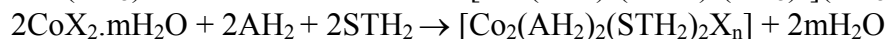
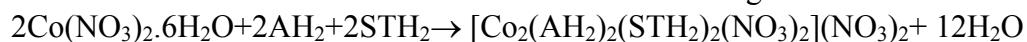
Synthetic Methods:

Salicylaldehyde thiosemicarbazone (STH₂) has been prepared according to the published method⁽⁹⁾.

A general procedure has been adopted for the preparation of complexes in neutral and basic medium. In neutral medium, a solution of 1 gm (0.003, 0.004, 0.008 mole) of cobalt nitrate or acetate or carbonate, respectively, in 5 ml water has been added to the solution of salicylaldehyde thiosemicarbazone (0.003, 0.004, 0.008 mole) and one of the carboxylic acid {salicylic or anthranilic or phthalic acid (0.003, 0.004, 0.008 mole)} in 15 ml hot ethanol (the amounts in grams are listed in Table 1). The mixtures have been refluxed for three hours followed by evaporation to half their volumes then cooled. The residues were separated by filtration, washed with petroleum ether and dried. In basic medium, complexes have been prepared by applying same amounts used in neutral medium, and after mixing the metal salts with the ligands and heating on a waterbath, potassium hydroxide solution (1M) has been added until pH=8-9 of the solutions. The mixtures were heated on a waterbath for half an hour then allowed to stand then cooled. The products were filtered off, washed with petroleum ether and dried.

Results and Discussions

The reaction of cobalt (II) salts, salicylaldehyde thiosemicarbazone and the carboxylic acids in 2:2:2 medium can be represented by the following reactions:



where $\text{X} = \text{CO}_3^{2-}$ or CH_3COO^- ; $\text{Z} = \text{NO}_3^-$ or CH_3COO^- ; $n = 2$ or 4 , $m = 0, 4$ or 6

The resulted complexes are colored solid, soluble in DMF and DMSO. The elemental analyses revealed that the complexes had the composition $[\text{Co}_2(\text{AH}_2)_2(\text{STH}_2)_2(\text{NO}_3)_2](\text{NO}_3)_2$, $[\text{Co}_2(\text{AH}_2)_2(\text{STH}_2)_2\text{X}_n]$, and $[\text{Co}_2(\text{AH}_2)_2(\text{STH}_2)_2]$ in neutral and basic medium, respectively (Table 1). The molar conductivities of the complexes in 10^{-3}M dimethylformamide were determined, the values shown in Table 1 approached those expected for 1:2 and non electrolytes for complexes prepared in neutral medium and non electrolytes for complexes prepared in basic medium⁽²⁴⁾.

The room temperature magnetic moments of cobalt (II) complexes were in the range of 1.63-2.74 B.M. (Table 1) for each ion. This subnormal values indicated the presence of some coupling interaction by super-exchange through the binding atoms and thus this low values may be assigned to a dimeric structure^(9,25).

The infrared spectra of STH_2 ligand (Table 2) showed a strong band at 1600 cm^{-1} attributed to the stretching vibration of $\text{C}=\text{N}$ group shifted towards a lower frequency on coordination due to the decrease of the bond order as a result of metal nitrogen bond formation⁽²⁶⁾. The next bands at 1430 cm^{-1} and $1200\text{--}1300\text{ cm}^{-1}$ attributed to stretching and bending frequencies of $\text{C}=\text{S}$ group, respectively. The first value shifted towards a lower frequency on coordination, in neutral medium, indicating the formation of chelation

between the sulfur of the $\text{C}=\text{S}$ group and the metal ion^(26,27). Meanwhile, in basic medium, these bands were disappeared in the complexes and new bands have been observed at $700\text{--}875\text{ cm}^{-1}$ and $2200\text{--}2300\text{ cm}^{-1}$ due to the stretching frequencies of $\text{C}-\text{S}$ and SH , respectively, thereby establishing coordination of the ligand through the thiolic sulfur atom⁽²⁷⁾. The position of the ligand in the range $3200\text{--}3300\text{ cm}^{-1}$ due to the stretching vibration of NH group. This band was remained unaltered in the complexes prepared in neutral medium indicating that there is no coordination through the NH group. Meanwhile in basic medium, this band has been disappeared due to the thiolic form⁽⁹⁾. The other strong bands at $3390, 3410\text{ cm}^{-1}$ and 1450 cm^{-1} were due to ν_{NH_2} ⁽⁶⁾. These bands remained unaltered on complexation indicated that there were no coordination through the NH_2 group and the metal ion. Moreover the other wide band observed at $3500\text{--}3600\text{ cm}^{-1}$ due to stretching vibration of phenolic hydroxyl⁽²⁸⁾, this wide band due to the presence of hydrogen bonding and presence of other groups appeared in the same region (NH_2, NH), it was more difficult to observe the shift of this band in the spectra of the complexes. The band at $1290\text{--}1310\text{ cm}^{-1}$ was due to the bending vibration of phenolic OH ⁽²⁸⁾ shifted towards lower frequency on complexation indicating the coordination of this group with the metal ion. Moreover the appearance of a band at 1270 cm^{-1} which belongs to the stretching vibration of the phenolic $\text{C}-\text{O}$ group has been shifted to higher

frequency (1330 cm^{-1}) on complexation indicating the coordination of phenolic oxygen atom⁽²⁸⁾.

The spectra of carboxylic acids (SH_2 , AnH_2 , PH_2 – Table 2) showed wide bands in the regions $3500\text{--}3600$, 2900 and 3400 cm^{-1} due to the stretching vibration of carboxylic OH, phenolic OH in SH_2 and NH_2 group in AnH_2 , respectively, this wide range was due to the hydrogen bonding. In the spectra of the complexes it was more difficult to observe the coordination due to the presence of different groups and hydrogen bonding. Whatever, in the complexes prepared in neutral medium this wide band was shifted to lower frequency. Whereas for complexes prepared in basic medium it was very difficult to observe the disappearance of this band, but it was well known that this band has been disappeared due to the deprotonation of the acid and the formation of ionic form^(13,15,28). The other two bands observed at $1390\text{--}1370\text{ cm}^{-1}$ and $1575\text{--}1600\text{ cm}^{-1}$ were due to the symmetric and asymmetric stretching frequency of carboxylic group, respectively. On complexation these bands were shifted to lower frequencies^(14,15). The difference between the symmetry and asymmetry stretching vibration for COO^- group ($\Delta\nu = 150\text{--}180\text{ cm}^{-1}$) gave indication about the manner of coordination of carboxylic group, this value showed that the carboxylic acid coordinate through COO^- group which was acted as monodentate. The complexes (1, 2, 3) showed two kind of bonding for NO_3^- group due to the appearance of the bands at $1380\text{--}1385\text{ cm}^{-1}$, 1400 cm^{-1} , 1285 cm^{-1} and 945 cm^{-1} due to the ionic bonding, ν_{sNO_3} , ν_{asNO_3} and ν_{NO} (ν_2 , ν_1 , ν_5), respectively⁽²⁸⁾. The difference between $\nu_1 - \nu_5$ equal to 115 cm^{-1} which supported the bonding of nitrate group as monodentate ligand through the oxygen atom. i.e., there were two NO_3^- group bonded in ionic form and the other two NO_3^- acted as

monodentate ligand. Whereas, the complexes (4, 5, 6) did not show any of these bands indicating the absence of NO_3^- group in these complexes.

The spectra of the complexes (7, 8, 9) showed stretching vibration for the carbonato group at 1400 and 1550 cm^{-1} indicating that the carbonato group acted as monodentate ligand bonding to the metal ion through the oxygen atom⁽²⁸⁾. Whereas the complexes (10, 11, 12) did not show any band indicating the absence of carbonato group in these complexes. The spectra of the complexes (13,14,15) showed two stretching vibration of symmetric and asymmetric acetato group at 1370 and 1540 cm^{-1} indicating that the CH_3CO_2^- group joint to the metal ion through the oxygen atom and acted as monodentate ligand⁽²⁸⁾. Meanwhile there were no band observed in the spectra of the complexes (16, 17, 18) indicating the absence of this group in these complexes.

On the other hand the spectra of all the complexes showed new bands around $430\text{--}600\text{ cm}^{-1}$, $475\text{--}550\text{ cm}^{-1}$, and $600\text{--}780\text{ cm}^{-1}$ due to $\nu_{\text{M-N}}$, $\nu_{\text{M-S}}$ and $\nu_{\text{M-O-M}}$, respectively^(8,12,15). The presence of these bands supported the formation of the complexes under investigation and the formation of dimer due to the presence of $\nu_{\text{M-O-M}}$ in the spectra.

The electronic spectra of the complexes in dimethylformamide solution (Table 3) have been recorded giving d-d spectra and charge transfer spectra. Cobalt (II) complexes showed absorption bands at $9407\text{--}9460\text{ cm}^{-1}$ and $18814\text{--}18920\text{ cm}^{-1}$ due to ν_1 and ν_3 {attributed to the transitions ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ }, respectively, expected for d^7 system in octahedral field. ν_2 (attributed to the transition ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$) has been not observed due to instrumental limitation, it was calculated by the literature method^(9,29,30). The ligand field parameter B and the ligand field splitting energy (10Dq) in case of cobalt (II)

complexes have been calculated^(9,29). The values of β of the complexes were 0.72-0.73 clearly indicated the covalent character of the bond concerned. The values of Dq/B which were in the range 1.49-1.50 suggested octahedral geometry for all the complexes^(9,29,30). The values of C.F.S.E. have been also determined which were in the range 8424-8464 cm^{-1} .

Conclusion

According to the analytical, physical and spectral studies, the resulted complexes prepared in neutral medium have been either cationic or neutral complexes having the formula

$[\text{Co}_2(\text{AH}_2)_2(\text{STH}_2)_2(\text{NO}_3)_2](\text{NO}_3)_2$ or $[\text{Co}_2(\text{AH}_2)_2(\text{STH}_2)_2\text{X}_n]$ (where $\text{X} = \text{CO}_3^{2-}$ or CH_3CO_2^- , $n = 2$ or 4). Whereas in basic medium, the resulted complexes had the formula $[\text{Co}_2(\text{AH})_2(\text{STH})_2]$ {where $\text{AH} =$ any deprotonated carboxylic acid, $\text{STH} =$ deprotonated salicylaldehyde thio-semicarbazone}. The study supported that the metal ion in all the complexes have hexa-coordinated and the complexes had distorted octahedral geometries. The proposed structures of the prepared complexes in neutral and basic medium are shown in Figure 2.

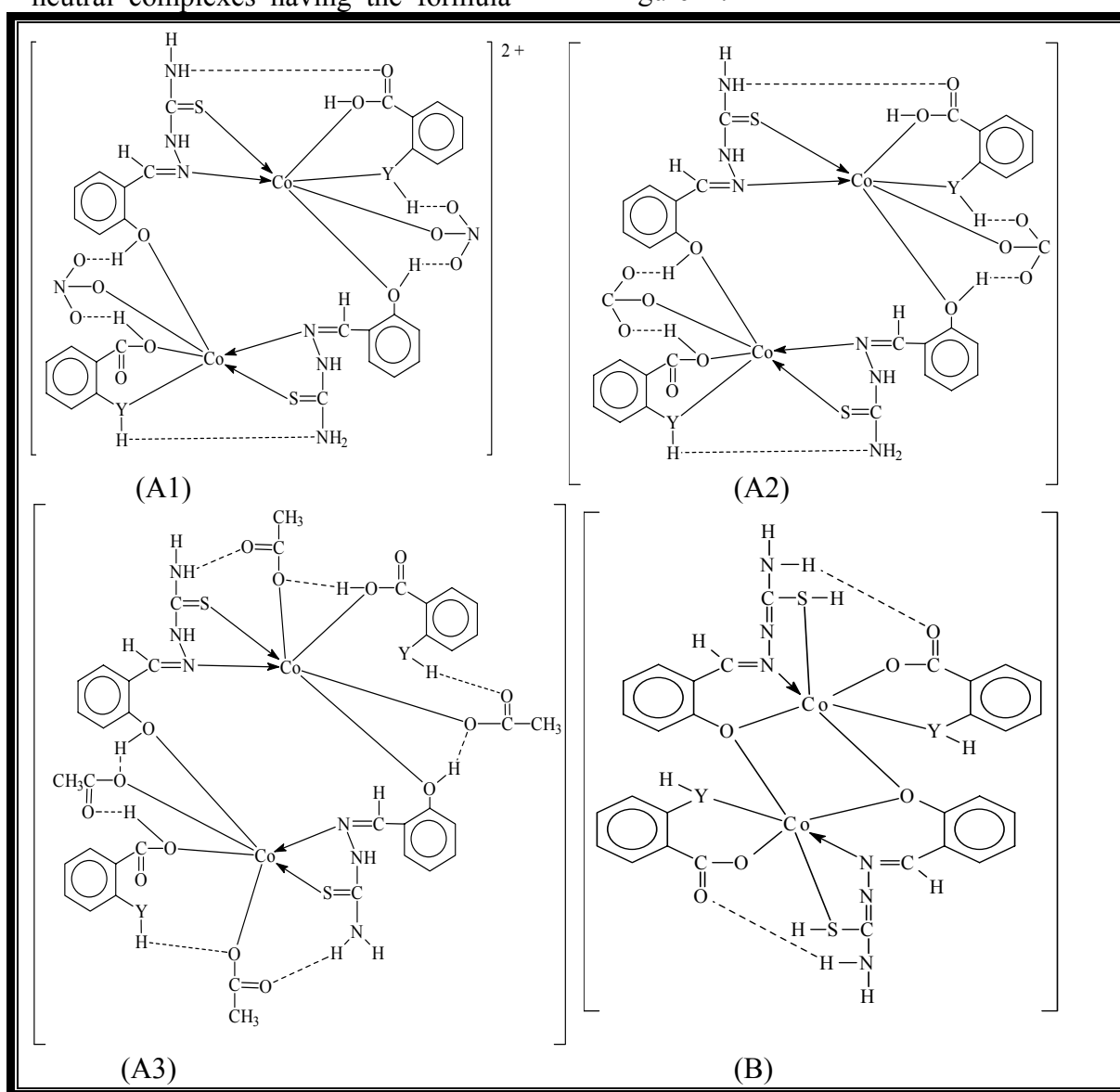


Figure 2 : Proposed structures of the complexes (A1,A2,A3) Complexes in neutral medium, (B) complexes in basic medium.

Table –1 : Amounts, Analytical and Physical Properties of Some Complexes

No.	Complexes	A* STH ₂ gm	A* AH ₂ gm	Colour	Λ_M **	M.P °C	μ_{eff} ***	% analysis calc./ obs.			
1	[Co ₂ (SH ₂) ₂ (STH ₂) ₂ (NO ₃) ₂] (NO ₃) ₂	0.67	0.46	Brown	122	176 sh	2.74	35.01 ---	2.91 ---	13.62 ---	11.47 12.05
2	[Co ₂ (AnH ₂) ₂ (STH ₂) ₂ (NO ₃) ₂] (NO ₃) ₂	0.67	0.41	Dark brown	132	175 sh	2.03	36.07 ---	3.20 ---	16.84 ---	11.80 12.59
3	[Co ₂ (PH ₂) ₂ (STH ₂) ₂ (NO ₃) ₂] (NO ₃) ₂	0.67	0.90	Dark brown	122	200	1.63	35.29 ---	2.75 ---	12.87 ---	10.48 11.87
4	[Co ₂ (SH) ₂ (STH) ₂]	0.67	0.46	Brown	1	285d	2.31	46.39 45.89	3.35 3.19	10.82 10.68	14.50 14.50
5	[Co ₂ (AnH) ₂ (STH) ₂]	0.67	0.41	Redish brown	0	290d	2.12	48.25 47.95	3.75 3.13	15.01 14.88	15.18 15.57
6	[Co ₂ (PH) ₂ (STH) ₂]	0.67	0.90	Dark brown	0	290d	2.31	39.46 39.45	3.35 3.19	10.04 9.94	14.43 13.67
7	[Co ₂ (SH ₂) ₂ (STH ₂) ₂ (Ac) ₄]	0.70	0.50	Gray	20	258d	2.74	44.88 44.59	4.13 4.05	8.26 8.09	11.60 12.40
8	[Co ₂ (AnH ₂) ₂ (STH ₂) ₂ (Ac) ₄]	0.70	0.40	Gray	26	234d	2.03	46.24 45.93	4.46 4.35	11.35 11.19	11.90 12.00
9	[Co ₂ (PH ₂) ₂ (STH ₂) ₂ (Ac) ₄]	0.70	0.60	Gray	20	260d	2.31	44.61 44.45	3.90 3.80	7.80 6.57	10.90 11.50
10	[Co ₂ (SH) ₂ (STH) ₂]	0.70	0.50	Brown	16	286d	2.03	46.39 45.96	3.35 3.23	10.82 10.65	15.20 14.60
11	[Co ₂ (AnH) ₂ (STH) ₂]	0.70	0.40	Dark brown	0	230d	2.12	48.25 48.55	3.75 3.62	15.01 14.90	15.80 14.70
12	[Co ₂ (PH) ₂ (STH) ₂]	0.70	0.60	Dark brown	0	246d	2.31	45.93 45.66	3.11 3.05	9.19 9.06	14.11 13.80
13	[Co ₂ (SH ₂) ₂ (STH ₂) ₂ (CO ₃) ₂]	1.60	1.10	Gray	10	260d	1.74	40.00 ---	3.33 ---	9.33 ---	13.10 12.60
14	[Co ₂ (AnH ₂) ₂ (STH ₂) ₂ (CO ₃) ₂]	1.60	1.00	Gray	8	262d	2.03	41.37 ---	3.67 ---	12.87 ---	13.50 13.00
15	[Co ₂ (PH ₂) ₂ (STH ₂) ₂ (CO ₃) ₂]	1.60	1.30	Black	22	266d	2.31	42.50 ---	3.12 ---	8.75 ---	12.29 12.33
16	[Co ₂ (SH) ₂ (STH) ₂]	1.60	1.10	Brown	8	260	2.03	46.38 ---	3.35 ---	10.82 ---	15.20 14.40
17	[Co ₂ (AnH) ₂ (STH) ₂]	1.60	1.00	Brown	18	224d	2.12	48.25 ---	3.75 ---	15.01 ---	15.81 14.55
18	[Co ₂ (PH) ₂ (STH) ₂]	1.60	1.30	Brown	1	220 sh	2.31	45.93 ---	3.11 ---	10.04 ---	14.11 13.62

* A : Amounts

** Λ_M : Molar conductivities in $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ *** μ_{eff} : Magnetic moment in Bohr Magneton

d=decomposition point

sh = sharp

Table -2 : IR Spectra of Complexes (Values in cm^{-1})

Compd.	$\nu_{\text{C=N}}$	ν_{NH} $\nu_{\text{OH alc}}$ $\nu_{\text{OH acid}}$	$\nu_{\text{C-S}}$	$\nu_{\text{C-S}}$	$\nu_{\text{C-O}}$ phen	ν_{SH}	$\Delta\nu$ *	ν_{NO_3} ν_{Ac} ν_{CO_3}	$\nu_{\text{M-N}}$	$\nu_{\text{M-S}}$	$\nu_{\text{M-O-M}}$
STH ₂	1600	3200-3300	1200-1300 1430	-	1170	-	-	-	-	-	-
[Co ₂ (SH ₂) ₂ (STH ₂) ₂ (NO ₃) ₂]	1575	3200-3300 3500-3600	1180 1400	-	1270	-	160	1385	550	500	600, 650
[Co ₂ (AnH ₂) ₂ (STH ₂) ₂ (NO ₃) ₂]	1575	3200-3300 3500-3600	1100 1400	-	1300	-	160	1380	430	500	550, 600
[Co ₂ (PH ₂) ₂ (STH ₂) ₂ (NO ₃) ₂]	1575	3200-3300 3500-3600	1130 1395	-	1300	-	170	1380	550	500	600, 650
[Co ₂ (SH) ₂ (STH) ₂]	1575	3500-3600	-	725	1280	2200-2300	175	-	550	500	650, 700
[Co ₂ (AnH) ₂ (STH) ₂]	1550	3500-3600	-	725	1270	2200-2300	175	-	550	500	700, 750
[Co ₂ (PH) ₂ (STH) ₂]	1550	3500-3600	-	700	1270	2200-2300	180	-	600	550	670, 700
[Co ₂ (SH ₂) ₂ (STH ₂) ₂ (Ac) ₄]	1570	3200-3300 3500-3600	1150 1395	-	1270	-	175	1400 1550	600	550	700, 780
[Co ₂ (AnH ₂) ₂ (STH ₂) ₂ (Ac) ₄]	1575	3200-3300 3500-3600	1175 1400	-	1290	-	175	1400 1550	600	550	700, 750
[Co ₂ (PH ₂) ₂ (STH ₂) ₂ (Ac) ₄]	1550	3200-3300 3500-3600	1100 1400	-	1290	-	150	1400 1550	550	500	650, 750
[Co ₂ (SH) ₂ (STH) ₂]	1550	3500-3600	-	740	1300	2200-2300	150	-	575	550	650, 750
[Co ₂ (AnH) ₂ (STH) ₂]	1540	3500-3600	-	750	1300	2200-2300	175	-	600	550	700, 750
[Co ₂ (PH) ₂ (STH) ₂]	1540	3500-3600	-	740	1300	2200-2300	170	-	575	500	675, 750
[Co ₂ (SH ₂) ₂ (STH ₂) ₂ (CO ₃) ₂]	1550	3200-3300 3500-3600	1100 1400	-	1300	-	175	1540 1370	550	500	700, 750
[Co ₂ (AnH ₂) ₂ (STH ₂) ₂ (CO ₃) ₂]	1550	3200-3300 3500-3600	1240 1400	-	1300	-	175	1540 1370	600	550	700, 750
[Co ₂ (PH ₂) ₂ (STH ₂) ₂ (CO ₃) ₂]	1540	3200-3300 3500-3600	1225 1400	-	1300	-	175	1540 1370	550	500	650, 760
[Co ₂ (SH) ₂ (STH) ₂]	1580	3500-3600	-	875	1300	2200-2300	175	=	550	475	600, 650
[Co ₂ (AnH) ₂ (STH) ₂]	1560	3500-3600	-	775	1300	2200-2300	175	-	500	475	650, 700
[Co ₂ (PH) ₂ (STH) ₂]	1550	3500-3600	-	750	1275	2200-2300	180	-	550	500	600, 675

* $\Delta\nu = \nu_{\text{sym COO}}(\text{acid}) - \nu_{\text{asym COO}}(\text{acid})$ **Table 3 : Electronic spectral data of the complexes in 10^{-4} M DMF solution**

No.	ν_1 cm^{-1}	ν_2 cm^{-1} *	ν_3 cm^{-1}	Charge transfer cm^{-1}	B cm^{-1}	Dq cm^{-1}	Dq/B	ν_3 / ν_1	ν_3 / ν_2	β	C.F.S.E cm^{-1}
1	9460	16171	18920	32362	701	1045	1.49	2.00	1.17	0.72	8360
2	9420	16103	18840	29950	704	1049	1.49	2.00	1.17	0.73	8392
3	9416	15961	18834	29154	708	1055	1.49	2.00	1.18	0.73	8440
4	9460	16171	18920	32362	701	1045	1.49	2.00	1.17	0.72	8360
5	9407	15810	18814	32362	705	1058	1.50	2.00	1.19	0.73	8464
6	9407	15944	18814	32362	705	1058	1.50	2.00	1.18	0.73	8464
7	9425	15975	18850	31350	707	1053	1.49	2.00	1.18	0.73	8424
8	9433	16126	18868	28571	705	1055	1.49	2.00	1.17	0.72	8440
9	9460	15899	18920	32362	701	1045	1.49	2.00	1.19	0.72	8360
10	9455	16162	18910	29500	702	1045	1.49	2.00	1.17	0.72	8360
11	9416	15827	18834	29154	708	1055	1.49	2.00	1.19	0.73	8440
12	9433	15990	18868	28571	703	1055	1.49	2.00	1.18	0.72	8440
13	9460	15899	18920	32362	701	1045	1.49	2.00	1.19	0.72	8360
14	9460	15827	18834	32362	701	1045	1.49	2.00	1.19	0.72	8360
15	9407	16080	18814	32362	705	1058	1.50	2.00	1.17	0.73	8464
16	9416	15961	18834	29154	708	1055	1.49	2.00	1.18	0.73	8440
17	9407	16080	18814	28350	705	1058	1.50	2.00	1.17	0.73	8464
18	9433	15855	18868	28571	703	1055	1.49	2.00	1.19	0.72	8440

• calculated

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