

have been studied very widely with different metal ions (Petrovic and Petrovic, 1982) (Al-Abaydi et al., 2002) (Afrasiabi et al., 2003). Thiosemicarbazone complexes of some transition and non transition elements have been reported (Kanoongo et al., 1987) (Wilkinson et al., 1987) (Sartorelli et al., 1971) (Agrawal et al., 1972) (Mahto, 1980, 1881).

Carboxylic acids bonded through the oxygen atoms to the central metal ion and formed chelating complexes with 3d transition elements and non transition elements. A wide studies have been done on salicylic acid complexes, anthranilic acid complexes and phthalic acid complexes with different transition metal ions (Wieghardt et al., 1973) (Palaskar et al., 1975) (Mahapatra and Panda, 1986).

In recent years, there has been a considerable interest in the study of mixed ligands complexes of transition and non-transition metals due to their important role in biological processes (El-ajaily and Maihub, 2003) (Dawood et al., 2004) (Hassan, 2005).

In view of this, and since mixed ligand complexes with nickel (II) ion of such ligands have not yet been reported, it is a matter of interest to determine the extent to which the biological properties of these ligands would be affected by incorporating nickel (II) ion. This information can be gained by biological examination of the various complexes derived from the carboxylic acids and salicylaldehyde thiosemicarbazone which would be synthesized.

In the present work, new nickel (II) complexes with mixed ligand {salicylaldehyde thiosemicarbazone and substituted carboxylic acids (Figure -1)} have been synthesized and characterized physico-chemically.

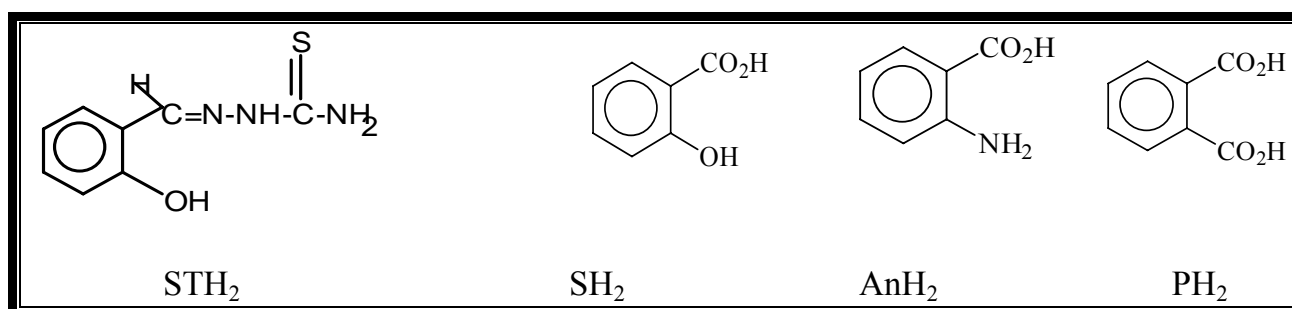


Fig. 1: Structures of the ligands

EXPERIMENTAL

1-Analytical and Physical Measurements :

Carbon, hydrogen and nitrogen have been estimated for some complexes using CHN microanalyser type 1106 (Carlo-Erba) at Chemistry Department, Science College, Mosul University. Nickel content has been determined gravimetrically (Vogel, 1981) after the decomposition of the complexes with concentrated nitric acid (Singh and Misra, 1986).

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 dimethylformamide solution at room temperature. The infra red spectra was recorded on a Pye-Unicam 1100 Infrared Spectrophotometer in the $400-4000\text{ cm}^{-1}$ range using KBr pellets. Electronic spectra has been recorded on Shimadzu UV-Visible Recording

Spectrophotometer UV 160 and Shimadzu Double-Beam Spectrophotometer UV 210A for 10^{-4} M solutions of the ligands and their complexes in dimethylformamide at 25°C , using a 1cm cell. Magnetic susceptibility of the complexes have been measured by Bruker B.M6. Molecular weights of some complexes have been determined cryoscopically (Danials,1962).

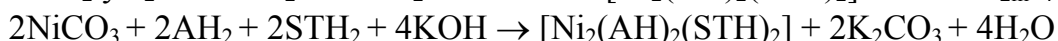
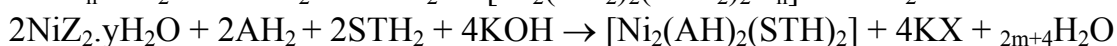
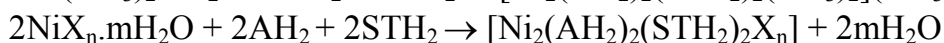
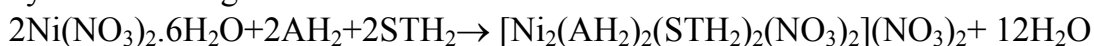
2- Synthetic Methods :

Salicylaldehyde thiosemicarbazone (STH₂) has been prepared according to previous method (Mahto, 1980).

A general procedure has been adopted for the preparation of complexes in neutral and basic medium. In neutral medium, a solution of 0.003,0.004, 0.008 mole(1 gm) of nickel nitrate or acetate or carbonate in 5 ml of water has been added to the solution of salicylaldehyde thiosemicarbazone {0.003 mole (0.67g) ; 0.004 mole (0.70g) ; 0.008 mole (1.60g)} and one of the carboxylic acid {salicylic or anthranilic or phthalic "0.003 mole(0.47g , 0.41g , 0.57g)" ; "0.004 mole (0.50g , 0.40 g , 0.60 g)" or "0.008 mole (1.10g , 1.00 g , 1.30 g)" } in 15 ml hot ethanol, respectively. The mixtures have been refluxed for three hours followed by evaporation to half then cooled. The products are isolated by filtration, washed with petroleum ether and dried. In basic medium, complexes have been prepared by applying the 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 of the solutions were 8-9. The mixtures were heated on a waterbath for half hour then allowed to stand then cooled. The products were filtered off, washed with petroleum ether and dried.

RESULTS AND DISCUSSION

The reaction of nickel (II) salts, salicylaldehyde thiosemicarbazone and the carboxylic acids in 2:2:2 molar ratio in both neutral and basic medium can be represented by the following reactions :



where $\text{X} = \text{CO}_3^{-2}$ or CH_3COO^- , $n=1$ or 2 , $m=0$ or 4 , $\text{Z} = \text{NO}_3^-$ or CH_3COO^- , $y = 6$ or 4 , $\text{AH}_2 = \text{ligand SH}_2$ or AnH_2 or PH_2 .

The elemental analyses and molecular weights determinations revealed that the complexes have the compositions $[\text{Ni}_2(\text{AH}_2)_2(\text{STH}_2)_2(\text{NO}_3)_2](\text{NO}_3)_2$, $[\text{Ni}_2(\text{AH}_2)_2(\text{STH}_2)_2\text{X}_n]$, and $[\text{Ni}_2(\text{AH})_2(\text{STH})_2]$ in neutral and basic medium, respectively (Table 1). The molar conductivities values in 10^{-3} M dimethylformamide (Table 1) approached those expected for 1:2 and non electrolytes ($120-160$ and $3-30 \Omega^{-1}\text{cm}^2 \text{mol}^{-1}$) for complexes prepared in neutral medium and non electrolytes ($0-17 \Omega^{-1}\text{cm}^2 \text{mol}^{-1}$) for complexes prepared in basic medium (Geary, 1971).

The room temperature magnetic moments of complexes 4 and 5 (2.78 and 3.05 for each ion, respectively) compared to the expected value for octahedral high spin d^8 complexes (2.8 B.M.) could be attributed to the participation of the ligand molecules, where as the values of the magnetic moments for the other nickel (II) complexes were in the range of 1.14-2.06 B.M. (Table 1) for each ion. The values indicated the presence of

some coupling interaction by super-exchange through the binding atoms arising from dimerisation in the solid state (Al-Tayy, 1996).

The infrared spectra of STH_2 ligand (Table 2) showed a strong band at 1600 cm^{-1} which was attributed to C=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 (Singh et al., 1981). The next bands at 1430 cm^{-1} and $1200\text{-}1300\text{ cm}^{-1}$ were attributed to the stretching and bending frequencies of C=S group. The first value shifted towards a lower frequency on coordination, in neutral medium, indicating the formation of chelation between the sulfur of the C=S group and the metal ion (Singh et al., 1981) (Shrivastava and Bana, 1974). Meanwhile, in basic medium, this band was disappeared and a 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 C-S and SH, respectively, thereby establishing coordination of the ligand through the thiolic sulfur atom (Shrivastava and Bana, 1974). The position of the ligand in the range $3200\text{-}3300\text{ cm}^{-1}$ was due to ν_{NH} , the broadening of this band was a consequence of hydrogen bonding phenomenon. On complexation, this phenomenon was more complicated due to different factors (Shrivastava and Bana, 1974) such as the effect of hydrogen bonding and the effect of coordination and also the presence of other groups (NH_2 , OH) appeared in the same position. This band, however was remained unaltered in the complexes prepared in neutral medium indicating that there is no coordination through the NH group. Meanwhile in basic medium, because of the presence of hydrogen bonding it was more difficult to notice the absence of NH group, but it was well known that this band was disappeared in basic medium (Kanoongo et al., 1987) due to the thiolic form. The other strong bands at 3390 , 3410 cm^{-1} and 1450 cm^{-1} were due to ν_{NH_2} (Petrovic and Petrovic, 1982) (Dawood, 2002). These bands remained unaltered on complexation indicated that there is no coordination through this group and metal ion. Moreover the other wide band observed at $3500\text{-}3600\text{ cm}^{-1}$ due to stretching vibration of phenolic hydroxyl (Nakamoto, 1976), this wide band was 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 (Nakamoto, 1976) shifted to lower frequency on complexation indicating the coordination of this group with the metal ion. Moreover the appearance of a band at 1170 cm^{-1} which belongs to $\nu_{\text{C-O}}$ has been shifted to higher frequency ($1270\text{-}1330\text{ cm}^{-1}$) on complexation indicating the coordination of oxygen atom to the metal ion (Nakamoto, 1976).

The spectra of carboxylic acids (SH_2 , AnH_2 , PH_2 – Table 2) showed a 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 higher 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 was disappeared due to the deprotonation of the acid and the formation of ionic form (Palaskar et al., 1975) (Wiegardt et al., 1973) (Nakamoto, 1976). The other two bands observed at $1370\text{-}1390\text{ cm}^{-1}$ 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 $1370-1400\text{ cm}^{-1}$ and $1550-1560\text{ cm}^{-1}$, respectively ((Palaskar et al., 1975). The difference between the asymmetry and symmetry stretching vibration for COO^- group ($\Delta\nu = \nu_{\text{asCOO}} - \nu_{\text{s COO}}$ which equal to $150-180\text{ cm}^{-1}$) gave indication about the manner of coordination of carboxylic group, this value showed that the carboxylic acid coordinate through COO^- group which acted as monodentate. The complexes in neutral medium which contained nitrate group showed two kind of bonding, because the appearance of the bands at $1380-1385\text{ cm}^{-1}$, 1400 cm^{-1} , 1285 cm^{-1} 945 cm^{-1} due to the ionic bonding, $\nu_{\text{s NO}_3}$, $\nu_{\text{as NO}_3}$ and ν_{NO} (ν_2 , ν_1 , ν_5), respectively (Nakamoto, 1976). 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. Whereas, the complexes prepared in basic medium did not showed any of these bands indicating the absence of NO_3^- group.

The spectra of the complexes prepared in neutral medium showed stretching vibration for carbonate group at 1400 and 1550 cm^{-1} which indicated that the carbonate group acted as monodentate ligand bonding to the metal ion through the oxygen atom (Nakamoto, 1976). Where as the complexes prepared in basic medium did not showed any band indicating the absence of carbonate group.

The spectra of the other complexes prepared in neutral medium showed two stretching vibration of symmetric and asymmetric acetate group at 1370 and 1540 cm^{-1} indicating that the CH_3CO_2^- group joint to the metal ion through oxygen atom and acted as monodentate ligand (Nakamoto, 1976). Meanwhile there was no band observed in the spectra of the complexes prepared in basic medium indicating the absence of this group.

On the other hand the spectra of all the complexes (Table 2) showed new bands around $450-675\text{ cm}^{-1}$, $550-750\text{ cm}^{-1}$, and $750-770\text{ cm}^{-1}$ due to $\nu_{\text{M-N}}$, $\nu_{\text{M-S}}$ and $\nu_{\text{M-O-M}}$, respectively (Lin et al., 1972) (Nakamoto, 1976). The presence of these bands strongly 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 of the prepared complexes in basic medium.

The electronic spectra of the ligand and some of their complexes in DMF solution have been recorded giving d-d spectra and charge transfer spectra (Table 3).

Nickel (II) complexes showed absorption bands at $7178 - 10183\text{ cm}^{-1}$, $11049 - 12920\text{ cm}^{-1}$ and $23040 - 23585\text{ cm}^{-1}$ due to ν_1 , ν_2 and ν_3 which were attributed to the transitions $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{2g}(\text{F})$, $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{F})$ and $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{P})$ respectively, expected for d^8 system having high spin octahedral geometry (Lever, 1968). The ligand field parameter B and the ligand field splitting energy (10Dq) in case of nickel (II) complexes have been calculated (Mahto, 1981) (Lever, 1968). The values of β of the complexes are between $0.40-0.92$ clearly indicated the covalent character of the bond concerned. The values of Dq/B which are in the range $0.71-2.35$ suggested octahedral geometry for all the complexes (Lever, 1968). The values of C.F.S.E. have been also determined which were in the range $8614-12220\text{ cm}^{-1}$.

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 $[\text{Ni}_2(\text{AH}_2)_2(\text{STH}_2)_2(\text{NO}_3)_2](\text{NO}_3)_2$ or $[\text{Ni}_2(\text{AH}_2)_2(\text{STH}_2)_2\text{Xn}]$ where $\text{X} = \text{CO}_3^{2-}$ or CH_3CO_2^- , $n = 2$ or 4 , $\text{AH}_2 =$ any of the carboxylic acid. Whereas in basic medium, the resulted complexes had the formula $[\text{Ni}_2(\text{AH})_2(\text{STH})_2]$ {where $\text{AH} =$ any deprotonated carboxylic acid, $\text{STH} =$ deprotonated salicylaldehyde thiosemicarbazone}. The study

supported that the metal ion in all the complexes had hexa-coordinated and the complexes had an octahedral geometries. The proposed structures of the prepared complexes in neutral and basic medium are shown in figure (2).

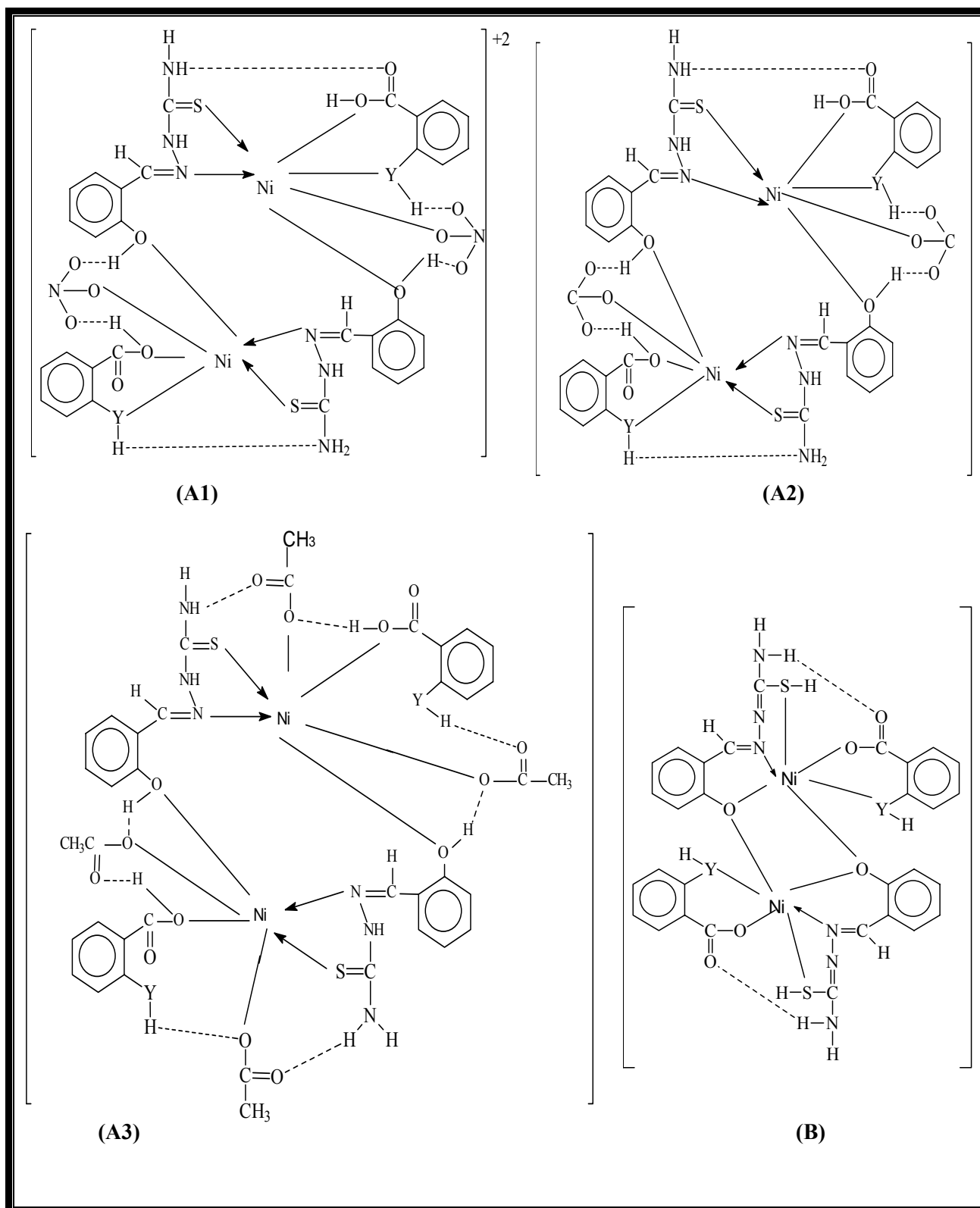


Fig. 2: Proposed structures of the complexes (A1,A2,A3) Complexes in neutral medium ; (B) complexes in basic medium.

Table 1 : Proposed formula, analytical and physical properties of some complexes.

No.	Complexes	Colour	M. Wt. Calc. / (Obs.)	Λ_M^*	M.P °C	μ_{eff}^{**}	% analysis calc./ (obs.)			
							C	H	N	Ni
1	$[\text{Ni}_2(\text{SH}_2)_2(\text{STH}_2)_2(\text{NO}_3)_2](\text{NO}_3)_2$	Pale green	1031.42 (1000.50)	120	165 d	1.87	35.03	2.91	13.62	11.42 12.63
2	$[\text{Ni}_2(\text{AnH}_2)_2(\text{STH}_2)_2(\text{NO}_3)_2](\text{NO}_3)_2$	Olivy green	1029.42 (1015.30)	130	143 d	1.78	36.09	3.20	16.84	11.77 (12.01)
3	$[\text{Ni}_2(\text{PH}_2)_2(\text{STH}_2)_2(\text{NO}_3)_2](\text{NO}_3)_2$	Green	1087.42 (1075.50)	160	185 d	1.90	35.31	2.75	12.87	10.79 (12.60)
4	$[\text{Ni}_2(\text{SH})_2(\text{STH})_2]$	Brown	779.42 (760.00)	10	260 d	2.78	46.42	3.35	10.83	15.14 (13.75)
5	$[\text{Ni}_2(\text{AnH})_2(\text{STH})_2]$	Brown	777.42 (750.50)	17	270 d	3.05	48.29	3.75	15.02	15.75 (14.12)
6	$[\text{Ni}_2(\text{PH})_2(\text{STH})_2]$	Dark brown	835.42	10	260 d	1.50	45.96	3.11	10.05	14.05 (12.37)
7	$[\text{Ni}_2(\text{SH}_2)_2(\text{STH}_2)_2(\text{Ac})_4]$	Pale green	1019.42 (1000.00)	36	260 d	1.92	43.79 (44.90)	4.06 (4.13)	8.11 (8.27)	11.56 (12.06)
8	$[\text{Ni}_2(\text{AnH}_2)_2(\text{STH}_2)_2(\text{Ac})_4]$	Green	1017.42 (999.00)	3	256	1.52	45.95 (46.27)	4.33 (4.46)	11.12 (11.25)	11.79 (11.36)
9	$[\text{Ni}_2(\text{PH}_2)_2(\text{STH}_2)_2(\text{Ac})_4]$	Redish brown	1075.42 (1050.30)	4	252	1.95	44.28 (44.63)	4.02 (3.90)	7.66 (7.81)	10.91 (11.15)
10	$[\text{Ni}_2(\text{SH})_2(\text{STH})_2]$	Brown	779.42	3	260 d	1.14	45.99 (46.42)	3.26 (3.35)	10.59 (10.83)	15.14 (14.05)
11	$[\text{Ni}_2(\text{AnH})_2(\text{STH})_2]$	Brown	777.42	0	270 d	2.05	47.88 (48.29)	3.66 (3.75)	14.85 (15.02)	15.75 (14.61)
12	$[\text{Ni}_2(\text{PH})_2(\text{STH})_2]$	Dark brown	835.42	2	260 d	2.05	47.68 (45.96)	3.03 (3.11)	9.88 (10.05)	14.05 (13.03)
13	$[\text{Ni}_2(\text{SH}_2)_2(\text{STH}_2)_2(\text{CO}_3)_2]$	Green	903.42 (889.50)	11	260 d	1.50	42.69	3.33	9.33	13.05 (13.82)
14	$[\text{Ni}_2(\text{AnH}_2)_2(\text{STH}_2)_2(\text{CO}_3)_2]$	Pale green	901.42 (890.00)	24	264 d	1.16	44.16	3.68	12.88	13.50 (14.45)
15	$[\text{Ni}_2(\text{PH}_2)_2(\text{STH}_2)_2(\text{CO}_3)_2]$	Pale green	959.42 (940.00)	24	Not melt	1.36	42.52	3.12	8.75	12.23 (11.65)
16	$[\text{Ni}_2(\text{SH})_2(\text{STH})_2]$	Brown	779.42	7	256 d	2.01	46.42	3.35	10.83	15.14 (14.07)
17	$[\text{Ni}_2(\text{AnH})_2(\text{STH})_2]$	Brown	777.42	2	270 d	2.05	48.29	3.75	15.02	15.75 (16.25)
18	$[\text{Ni}_2(\text{PH})_2(\text{STH})_2]$	Brown	835.42	5	260 d	2.06	45.65	3.49	11.24	15.79 (16.50)

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

d=decomposition point

M. Wt = Molecular weight

Table 2 : IR spectra of complexes (values in cm^{-1}).

No.	$\nu_{\text{C=N}}$	ν_{NH_2} semi	ν_{NH} $\nu_{\text{OH alc}}$ ν_{OH} acid.	$\nu_{\text{C=S}}$ semi	$\nu_{\text{C-S}}$ semi	$\nu_{\text{C-O}}$ phen	ν_{asCoo} acid	$\nu_{\text{s Coo}}$ acid	$\Delta\nu$	ν_{SH}	$\nu_{\text{M-S}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$
STH ₂	1600	1450 3390-3410	3200- 3300	1200 1300 - 1430	-	1170	-	-	-	-	-	-	-
1	1575	1450 3390-3400	3200- 3300 3500- 3600	1100 1400	-	1300	1500	1350	150	-	500	600	625, 650
2	1540	1450 3390-3400	3200- 3300 3500- 3600	1120 1400	-	1300	1540	1370	170	-	500	600, 450	700, 750
3	1550	1450 3390-3400	3200- 3300 3500- 3600	1150 1395	-	1270	1530	1380	150	-	500	550	700, 750
4	1550	1450 3390-3400	3500- 3600	-	700	1270	1550	1375	175	2200- 2300	500	600	700, 750
5	1550	1450 3390-3400	3500- 3600	-	700	1270	1550	1370	180	2200- 2300	600	650, 500	700, 750
6	1550	1440 3390-3400	3500- 3600	-	750	1280	1550	1370	180	2200- 2300	600	650	700, 775
7	1550	1450 3390-3400	3200- 3300 3500- 3600	1100 1395	-	1300	1600	1420	180	-	500	600	700, 750
8	1575	1450 3390-3400	3200- 3300 3500- 3600	1250 1400	-	1300	1600	1450	150	-	500	575, 430	600, 700
9	1540	1450 3390-3400	3200- 3300 3500- 3600	1225 1400	-	1275	1550	1370	180	-	500	600	700, 750
10	1575	1450 3390-3400	3500- 3600	-	800	1300	1550	1375	175	2200- 2300	550	600	650, 750
11	1550	1450 3390-3400	3500- 3600	-	850	1300	1500	1330	170	2200- 2300	500	550	700, 750
12	1550	1450 3390-3400	3500- 3600	-	850	1300	1550	1390	160	2200- 2300	550	500 , 600	700, 750
13	1550	1450 3390-3400	3200- 3300 3500- 3600	1175 1400	-	1300	1550	1375	175	-	575	600	700, 775
14	1550	1450 3390-3400	3200- 3300 3500- 3600	1175 1400	-	1300	1575	1395	180	-	550	650	675, 750
15	1550	1450 3390-3400	3200- 3300 3500- 3600	1200 1400	-	1300	1550	1375	175	-	550	600	650, 700
16	1550	1450 3390-3400	3500- 3600	-	900	1300	1550	1375	175	2200- 2300	550	600	700, 750
17	1580	1450 3390-3400	3500- 3600	-	875	1300	1550	1375	175	2200- 2300	550	600, 430	700, 750
18	1550	1450 3390-3400	3500- 3600	-	875	1300	1575	1400	170	2200- 2300	550	600	650, 750

Table 3 : Electronic spectral data of the complexes.

No.	ν_1 cm ⁻¹ *	ν_2 cm ⁻¹	ν_3 cm ⁻¹	C.T cm ⁻¹	B cm ⁻¹	10Dq	Dq/B	ν_2/ν_1	β	C.F.S.E
1	10183	11833	23585	28571	721	10183	1.41	1.16	0.66	12220
2	7640	11550	23120	28500	783	7640	0.98	1.51	0.72	9168
3	8600	11075	23050	25700	752	8600	1.14	1.29	0.70	10320
4	9460	11049	23364	28653	402	9460	2.35	1.16	0.40	11352
5	7178	12920	23585	28571	998	7178	0.71	1.80	0.92	8614
6	7250	11833	23200	28750	885	7250	0.82	1.63	0.82	8700
7	7750	11750	23200	28800	780	7750	0.99	1.52	0.72	9300
8	8600	11675	23300	28560	612	8600	1.41	1.36	0.57	10320
9	7200	11780	23580	28570	917	7200	0.79	1.64	0.85	8640
10	9040	11830	23040	28890	517	9040	1.75	1.31	0.48	10848
11	9560	11525	23250	28850	406	9560	2.35	1.21	0.40	11472
12	9560	11525	23250	28750	406	9560	2.35	1.21	0.40	11472
13	9450	11500	23260	28755	427	9450	2.21	1.22	0.40	11340
14	9450	11625	23575	28855	457	9450	2.07	1.23	0.42	11340
15	9560	11525	23250	28850	406	9560	2.35	1.21	0.40	11472
16	9015	11670	23585	28575	547	9015	1.65	1.29	0.51	10818
17	9400	11833	23580	28660	481	9400	1.95	1.26	0.44	11280
18	9120	11833	23585	28750	537	9120	1.70	1.30	0.50	10944

* calculated

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