



## STUDIES ON SOME NICKEL (II) COMPLEXES CONTAINING MIXED LIGANDS

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### ABSTRACT

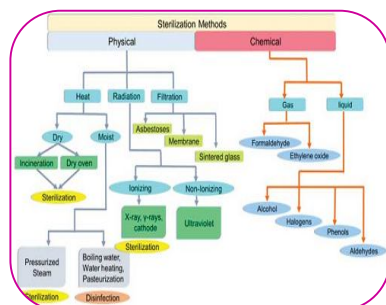
This study concerns with the preparation and characterization of some new complexes of nickel (II) with mixed ligands : salicylaldehyde semicarbazone  $-SCH_2$  and a few acid (salicylic acid  $-SH_2$  or anthranilic acid  $-AnH_2$  or phthalic acid-  $PH_2$ ). The complexes are characterized using different physico-chemical methods. The study supports that the complexes are binuclear with distorted octahedral geometries

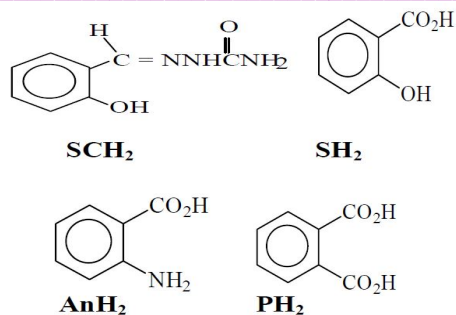
**KEY WORD:** preparation and characterization , physico-chemical methods.

### INTRODUCTION

Nickel complexes occurred in several nickel containing enzymes and are proposed to be involved in catalytic reaction. Nickel complexes with some macrocyclic ligands are studied and a few of them forming polynuclear complexes. A good deal of labor has been reported on the preparation, spectral and structural investigation of semicarbazones and their complexes, because of their capability of acting as polydentate donor with the formation of either mono- or bi- or polynuclear complexes. In addition to their interesting ligational properties, semicarbazones and their complexes have important biological activities. A wide studies are done on the substituted benzoic acids thanks to their interesting ligational properties. There has been growing interest within the formation of mixed ligand chelates involving ligands containing different functional groups and transition metals of various oxidation states which may formed chelates with ligands containing different donation sites. On the opposite hand, coordination compounds with mixed ligands are of considerable importance within the field of metalloenzymes and other biological activities, hence an outsized body of the coordination chemistry of mixed ligands with transition and non-transition metal ions are reported recently. thanks to the importance of mixed ligand complexes, we took a humble part within the chemistry of mixed ligands containing semicarbazones and a few articles are published on their coordination chemistry with transition and non-transition metal ions

In the present work, nickel (II) complexes with mixed ligands {salicylaldehyde semicarbazone and substituted benzoic acids (Figure -1)} have been synthesized and characterized physicochemically





**Figure 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 Department of Chemistry, College of Science, University of Mosul. Nickel contents have been determined by applying precipitation method after the decomposition of the complexes<sup>(25)</sup> with concentrated nitric acid<sup>(1-14)</sup>

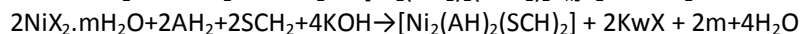
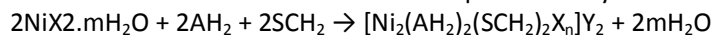
Conductivity measurements have been carried out with an electrolytic conductivity measuring set LF-42 and Multiline f / SET-2WTW Wissenschaft using  $10^{-3}$  M dimethylformamide solution at room temperature . The infrared spectra has been recorded on a Pye-Unicam 1100 Infrared Spectrophotometer in the region 400-4000  $\text{cm}^{-1}$  using KBr pellets. Electronic spectra has been recorded on Shimadzu UVVisible Recording Spectrophotometer UV 160 for  $10^{-4}$  M solutions of the ligands and their complexes in dimethylformamide at  $25^\circ\text{C}$ , using a 1cm selea cell. Magnetic susceptibility of some complexes have been measured by Bruker-BM6 . The molecular weights of the complexes have been determined cryoscopically<sup>(15-26)</sup>

### 2- Synthetic Methods :

Salicylaldehyde semicarbazone has been prepared consistent with previous method. A general procedure has been adopted for the preparation of complexes in neutral and basic medium . In neutral medium, an answer of 1 gm (0.003,0.004 0.008 mole) of nickel nitrate or acetate or carbonate, respectively in 5 ml water has been added to the answer of salicylaldehyde semicarbazone (0.003, 0.004, 0.008 mole) and one among the acid (salicylic or anthranilic or phthalic (0.003, 0.004, 0.008 mole) in 15 ml hot ethanol (the amounts in grams are listed in Table 1). The mixtures are refluxed for 3 hours followed by evaporation to half their volumes then cooled. The products are separated by filtration, washed with petroleum ether and dried. In basic medium, complexes are prepared by applying the identical amounts used for neutral medium, and after mixing the metal salts with the ligands and heating on a waterbath, caustic potash solution (1M) was added until pH of the solutions are adjusted to about 8-9. The mixtures are heated on a waterbath for half an hour, allowed to square then cooled. The products are filtered off and washed with petroleum ether and dried .

## RESULTS AND DISCUSSION

The reaction of nickel (II) salts, salicylaldehyde semicarbazone and the carboxylic acids in 1:1:1 molar ratio in both neutral and basic medium can be represented by the following equations :



where  $\text{X} = \text{NO}_3^-$  or  $\text{CH}_3\text{COO}^-$  or  $\text{CO}_3^{2-}$  ;  $\text{Y} = \text{NO}_3^-$  or nothing ;  $n=2$  or  $4$  or  $1$  ;  $m=6$  or  $4$  or  $0$  ;  $w=1$  or  $2$  ;  $\text{AH}_2 = \text{SH}_2$  or  $\text{AnH}_2$  or  $\text{PH}_2$  .

The resulting complexes are colored solid, soluble in dimethylformamide and dimethylsulphoxide. The elemental analyses and molecular weight determinations reveal that the complexes have the compositions  $[\text{Ni}_2(\text{AH}_2)_2(\text{SCH}_2)_2(\text{NO}_3)_2](\text{NO}_3)_2$ ,  $[\text{Ni}_2(\text{AH}_2)_2(\text{SCH}_2)_2\text{Xn}]$  and  $[\text{Ni}_2(\text{AH})_2(\text{SCH}_2)_2]$  in neutral and basic medium, respectively (Table 1). The molar conductivities of the complexes in  $10^{-3}$  M dimethylformamide are determined, the values shown in Table 1 approach those expected for 1:2 and non electrolytes for complexes prepared in neutral medium and non electrolytes for complexes prepared in basic medium.

The room temperature magnetic moments of Ni (II) complexes are in the range of 1.36 - 2.29 B.M. per nickel atom (Table 1). The low magnetic values compared to the expected values for sixcoordinate high-spin octahedral complexes possibly attributed to the ligand participation.

The infrared spectra of SCH<sub>2</sub> ligand (Table 2) shows a powerful band at 1600  $\text{cm}^{-1}$  attributed to C=N group shifts towards a lower frequency on coordination thanks to the decrease of the bond order as a results of metal nitrogen bond formation. the subsequent strong band at 1700  $\text{cm}^{-1}$  is attributed to C=O group . This value shifts towards a lower frequency on coordination in neutral medium, indicating the formation of chelation between the oxygen of the C=O group and therefore the metal ion. Meanwhile, in basic medium , this band is disappeared within the complexes and a replacement band has been observed at 1400  $\text{cm}^{-1}$  because of bending enolic OH thereby establishing coordination of the ligand through the enolic oxygen atom(2). the looks of strong bands at 1630-1635  $\text{cm}^{-1}$  and 1570- 1580  $\text{cm}^{-1}$  attributed to  $\nu(\text{C}=\text{N}) + (\text{O}-\text{C}=\text{N})$  and azine chromophore  $\nu(\text{C}=\text{N}-\text{N}=\text{C})$  , respect–tively, support the formation of enolic structure in basic medium. The position band of the ligand within the range 3200-3300  $\text{cm}^{-1}$  is assigned to  $\nu\text{NH}$  remains unaltered within the complexes prepared in neutral medium indicating that there's no coordination through the NH group. Whereas in basic medium, this band is disappeared in basic medium because of the enolic form. The opposite strong bands at 3390, 3410  $\text{cm}^{-1}$  and 1450  $\text{cm}^{-1}$  are assigned to  $\nu\text{NH}_2$  . These bands remain unaltered on complexation indicating that there's no coordination through this group and metal ion . Moreover the opposite wide band observes at 3500-3600  $\text{cm}^{-1}$  is attributed to stretching vibration of phenolic hydroxyl shifts to lower frequency on complexation .The band at 1290-1310  $\text{cm}^{-1}$  is attributed to the bending vibration of phenolic OH(31) shifts to lower frequency on complexation indicating the coordination of this group with the metal ion. Moreover the looks of a band at 1170  $\text{cm}^{-1}$  which belongs to  $\nu(\text{C}-\text{O})$  is shifted to higher frequency 1330  $\text{cm}^{-1}$  on complexation indicating the coordination of oxygen atom. The spectra of substituted benzoic acids ( $\text{SH}_2$  ,  $\text{AnH}=\text{}$  ,  $\text{PH}_2$ ) show a good bands within the regions 3500-3600 , 2900 and 3400  $\text{cm}^{-1}$  thanks to the stretching vibration of carboxylic OH, phenolic OH in  $\text{SH}_2$  and  $\text{NH}_2$  group in  $\text{AnH}_2$ , respectively, this wide selection is due either to the inter or intra molecular hydrogen bonding. Within the spectra of the complexes it's tougher to watch the coordination because of the presence of various groups and hydrogen bonding. Whatever, within the complexes prepared in neutral medium this wide band is shifted to higher frequency. Whereas for complexes prepared in basic medium it's very difficult to watch the disappearance of this band, but it's well-known that this band is disappeared thanks to the deprotonation of the acid and therefore the formation of ionic form. The opposite two bands observed at 1370-1390  $\text{cm}^{-1}$  and 1550-1570  $\text{cm}^{-1}$  are thanks to the symmetric and asymmetric stretching frequency of carboxylic group, respectively. On complexation these bands are shifted to 1350- 1420  $\text{cm}^{-1}$  and 1500-1575  $\text{cm}^{-1}$ , respectively. The difference between the symmetry and asymmetry stretching vibration for  $\text{COO}^-$  group ( $\Delta\nu = 150-180 \text{ cm}^{-1}$ ) gives indication about the way of coordination of carboxylic group, this value shows that the acid coordinate through  $\text{COO}^-$  group which act as monodentate. The complexes in neutral medium which contain nitrate group show two reasonably bonding, because the looks of the bands at 1380-1385  $\text{cm}^{-1}$ , 1400-1480  $\text{cm}^{-1}$  , 1285-1365  $\text{cm}^{-1}$  945- 1010  $\text{cm}^{-1}$  because of the ionic bonding ,  $\nu\text{NO}_3$ ,  $\nu\text{asNO}_3$  and  $\nu\text{NO}$  ( $\nu_2$ ,  $\nu_1$  ,  $\nu_5$ ), respectively. The difference between  $\nu_1-\nu_5$  equal to 115  $\text{cm}^{-1}$  which supports the bonding of nitrate group as monodentate ligand through the oxygen atom . Whereas, the complexes prepared in basic medium don't show any of those bands indicating the absence of  $\text{NO}_3^-$  group in these complexes .

The spectra of the complexes prepared in neutral medium show stretching vibration for carbonyl  $\text{CO}_3^{-2}$  group at  $1480$  and  $1550 \text{ cm}^{-1}$  which indicate that the carbonato group act as monodentate ligand bonding to the metal ion through the oxygen atom<sup>(11)</sup>. Whereas the complexes prepared in basic medium do not show any band indicating the absence of carbonato group .

The spectra of the other complexes prepared in neutral medium show two stretching vibration of symmetric and asymmetric acetate group at  $1350$  and  $1400 \text{ cm}^{-1}$  indicating that the  $\text{CH}_3\text{CO}_2^-$  group joint to the metal ion through the oxygen atom and act as monodentate ligand<sup>(11)</sup>. Meanwhile there is no band observed in the spectra of the complexes prepared in basic medium indicating the absence of this group.

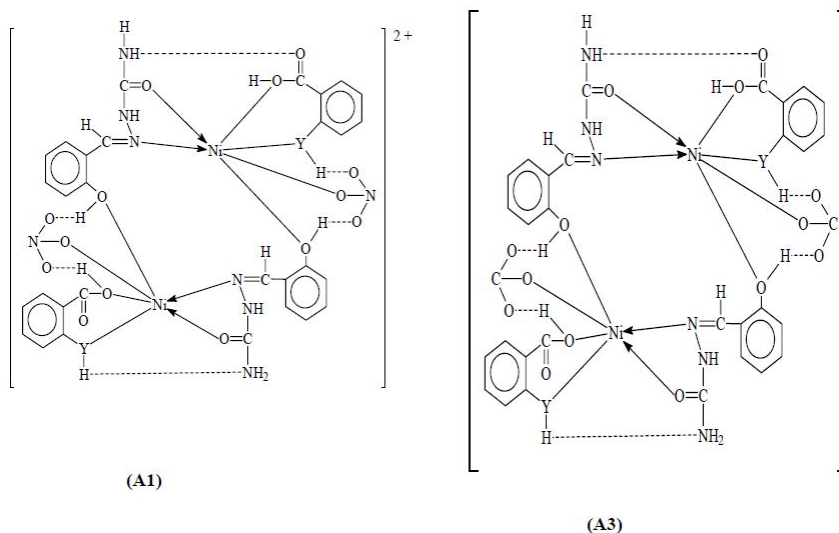
On the other hand the spectra of all the complexes show new bands around  $450\text{-}675 \text{ cm}^{-1}$ ,  $550\text{-}750 \text{ cm}^{-1}$ , and  $750\text{-}770 \text{ cm}^{-1}$  due to  $\nu_{\text{M-N}}$ ,  $\nu_{\text{M-O}}$  and  $\nu_{\text{M-O-M}}$ , respectively. The presence of these bands support 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 some complexes in dimethylformamide solution have been recorded giving d-d transitions and charge transfer spectra (Table-3) . Nickel (II) complexes show absorption bands at  $7196\text{-}10193 \text{ cm}^{-1}$ ,  $10152\text{-}18348 \text{ cm}^{-1}$  and  $24390\text{-}25641 \text{ cm}^{-1}$  due to  $u_1$ ,  $u_2$  and  $u_3$  {attributed to the transitions  ${}^3\text{A}_2\text{g}(\text{F}) \rightarrow {}^3\text{T}_2\text{g}(\text{F})$ ,  ${}^3\text{A}_2\text{g}(\text{F}) \rightarrow {}^3\text{T}_1\text{g}(\text{F})$  and  ${}^3\text{A}_2\text{g}(\text{F}) \rightarrow {}^3\text{T}_1\text{g}(\text{P})$ }, respectively, are expected for  $d^8$  system in octahedral field<sup>(23)</sup>. The ligand field parameter B and the ligand field splitting energy ( $10\text{Dq}$ ) in case of nickel (II) complexes have been calculated<sup>(3)</sup>. The values of  $\beta$  of the complexes are between  $0.72\text{-}0.84$  clearly indicate the covalent character of the bond concerned. However, the electronic spectral data suggest distorted octahedral geometry for all the complexes

## CONCLUSION:

Salicylaldehyde semicarbazone acted as tridentate chelating ligand on coordination with nickel (II) ion through the azomethine nitrogen and the two oxygen atoms of the carbonyl and phenol groups.

Substituted benzoic acids acted as either monodentate or bidentate chelating ligands.  $\text{NO}_3^-$  ion acted in two manars in the complexes, two group acted as monodentate ligand joint to the metal ion through the oxygen atom and the two others acted as counter ions. Carbonato and acetate groups acted as monodentate ligands. Binuclear complexes have been suggested with distorted octahedral geometries (Figure 2).



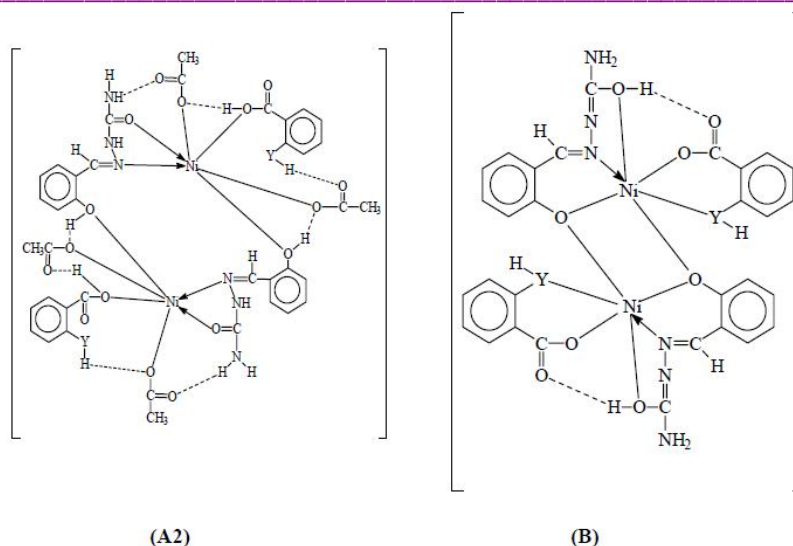


Figure 2 : Model structures of the complexes

(A1,A2,A3) Complexes in neutral medium ; (B) complexes in basic medium Y= O or NH or COO

Table 1: Amounts, analytical and physical properties of some complexes

No.	Complexes	A* SCH <sub>2</sub> gm	A* AH <sub>2</sub> gm	Colour	M. Wt. Calc./ Obs.	^M **	M.P °C	μ <sub>eff</sub> ***	% analysis calc./ obs.			
									C	H	N	Ni
1.	[Ni <sub>2</sub> (SH <sub>2</sub> ) <sub>2</sub> (SCH <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	0.61	0.46	Pale green	996 980	16 1	150d	2.21	36.19 35.88	3.01 2.95	14.06 13.29	11.79 10.71
2.	[Ni <sub>2</sub> (AnH <sub>2</sub> ) <sub>2</sub> (SCH <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	0.61	0.41	Green	966 950	12 9	180d	1.95	37.28 36.89	3.31 3.18	17.40 17.22	12.16 11.63
3.	[Ni <sub>2</sub> (PH <sub>2</sub> ) <sub>2</sub> (SCH <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	0.61	0.57	Dark green	1056 1041	10 5	275d	1.93	36.38 35.96	2.84 3.00	13.26 12.98	11.12 11.61
4.	[Ni <sub>2</sub> (SH) <sub>2</sub> (SCH) <sub>2</sub> ]	0.61	0.46	Pale green	744 725	0	275d	2.16	48.12 47.98	3.49 3.29	11.20 10.89	15.79 15.54
5.	[Ni <sub>2</sub> (AnH) <sub>2</sub> (SCH) <sub>2</sub> ]	0.61	0.41	Pale green	714 700	10	290d	1.80	50.46 49.98	3.92 4.06	15.69 15.32	16.45 16.86
6.	[Ni <sub>2</sub> (PH) <sub>2</sub> (SCH) <sub>2</sub> ]	0.61	0.57	Pale green	804 780	0	260d	2.16	47.79	3.23	10.22	14.12 14.61
7.	[Ni <sub>2</sub> (SH <sub>2</sub> ) <sub>2</sub> (SCH <sub>2</sub> ) <sub>2</sub> (Ac) <sub>4</sub> ]	0.71	0.54	Green	984 969	30	245d	2.04	46.36 45.97	4.27 4.09	8.54 8.36	11.93 11.24
8.	[Ni <sub>2</sub> (AnH <sub>2</sub> ) <sub>2</sub> (SCH <sub>2</sub> ) <sub>2</sub> (Ac) <sub>4</sub> ]	0.71	0.48	Pale green	954 935	5	290d	2.18	47.82 47.55	4.61 4.49	11.74 11.55	12.31 11.25
9.	[Ni <sub>2</sub> (PH <sub>2</sub> ) <sub>2</sub> (SCH <sub>2</sub> ) <sub>2</sub> (Ac) <sub>4</sub> ]	0.71	0.66	Pale green	1044 1021	23	260d	2.04	46.00 46.10	4.25 4.00	8.05 8.00	11.25 10.21
10.	[Ni <sub>2</sub> (SH) <sub>2</sub> (SCH) <sub>2</sub> ]	0.71	0.54	Pale green	744 730	18	280d	2.04	48.42	3.49	11.29	15.79 15.02
11.	[Ni <sub>2</sub> (AnH) <sub>2</sub> (SCH) <sub>2</sub> ]	0.71	0.48	Pale green	714 685	0	290d	—	5.46 49.95	3.92 4.35	15.69 15.22	16.45 16.48
12.	[Ni <sub>2</sub> (PH) <sub>2</sub> (SCH) <sub>2</sub> ]	0.71	0.66	Pale green	804 781	12	295d	2.04	47.79	3.23	10.45	14.61 13.52
13.	[Ni <sub>2</sub> (SH <sub>2</sub> ) <sub>2</sub> (SCH <sub>2</sub> ) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> ]	1.50	1.14	Pale green	879 855	27	270d	1.89	44.26 43.88	3.45 3.29	9.68 9.45	13.35 13.00
14.	[Ni <sub>2</sub> (AnH <sub>2</sub> ) <sub>2</sub> (SCH <sub>2</sub> ) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> ]	1.50	1.05	Pale green	838 825	5	285d	1.36	45.85 45.555	3.82 4.02	13.37 14.45	14.02 13.75
15.	[Ni <sub>2</sub> (PH <sub>2</sub> ) <sub>2</sub> (SCH <sub>2</sub> ) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> ]	1.50	1.39	Pale	927	16	290d	1.93	43.99	3.23	9.05	12.66

				green	915				43.59	3.11	8.86	12.37
16.	[Ni <sub>2</sub> (SH) <sub>2</sub> (SCH) <sub>2</sub> ]	1.50	1.14	Pale green	744 730	12	220d	–	48.42	3.49	11.24	14.61 14.06
17.	[Ni <sub>2</sub> (AnH) <sub>2</sub> (SCH) <sub>2</sub> ]	1.50	1.02	Pale green	745 730	10	288d	2.29	53.97	3.65	11.80	16.45 16.04
18.	[Ni <sub>2</sub> (PH) <sub>2</sub> (SCH) <sub>2</sub> ]	1.50	1.39	Green	804 779	9	284d	2.18	47.79	4.23	10.45	14.61 15.31

\*A : Amounts ; \*\*  $\Lambda_M$  : Molar conductivities in  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  ; \*\*\*  $\mu_{\text{eff}}$  : Magnetic moment in Bohr Magneton ; d=decomposition point ; M. Wt. = Molecular weight

**Table 2 : IR spectra of complexes ( values in  $\text{cm}^{-1}$  )**

No.	$\nu_{\text{C=N}}$	$\nu_{\text{C=O}}$ semi	$\nu_{\text{C-O}}$ semi	$\nu_{\text{C-O}}$ phen	$\nu_{\text{S}_{\text{Coo}}}$ acid	$\nu_{\text{S}_{\text{Coo}}}$ acid	$\nu_{\text{NO}_3}$ $\nu_{\text{Ac}^-}$ $\nu_{\text{CO}_3}^{-2}$	$\nu_{\text{M-O-M}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$
SCH <sub>2</sub>	1600	1700	-	-	-	-	-	-	-	-
1	1500	1650	-	1250			1385	-	600	650, 700
2	1500	1620	-	1230			1385	-	600, 675	700, 800
3	1575	1620	-	1230			1385	-	600	700, 750
4	1520	-	1360	1250			-	750	500	550, 600
5	1580	-	1350	1240	1350	1500	-	770	450,50 0	650, 750
6	1590	-	1345	1275			-	770	550	600, 675
7	1570	1640	-	1200	1370	1550	1350	-	650	675, 750
8	1555	1630	-	1200	1375	1550	1350	-	500, 550	650, 725
9	1575	1650	-	1200	1360	1540	1400	-	575	600, 700
10	1570	-	1360	1200	1375	1550	-	760	500	550, 600
11	1570	-	1350	1200	1375	1550	-	760	550, 450	575, 600
12	1570	-	1350	1200	1400	1550	-	770	500	600, 675
13	1550	1650	-	1250	1360	1550	1480	-	550	600, 650
14	1550	1650	-	1250	1390	1540	1500	-	575, 500	650, 700
15	1540	1650	-	1250	1375	1550	1550	-	575	675, 720
16	1540	-	1340	1250	1375	1500	-	770	550	650, 700
17	1550	-	1350	1250	1360	1500	-	770	600,	700,

									500	750
18	1550	-	1350	1250	1370	1500	-	770	550	650, 750

Table 3 : Electronic spectral data of some complexes

No.	$u^1$ $cm^{-1}$	$u^2$ $cm^{-1}$	$u^3$ $cm^{-1}$	Charge transfer $cm^{-1}$	B $cm^{-1}$	10Dq $cm^{-1}$	Dq/B	$u_3 / v_1$	$\beta$	C.F.S.E. $cm^{-1}$
1	9569	10152	25062	29154	434	9569	2.20	1.06	0.40	11483
3	10183	18330	24813	3333	839	10183	1.21	1.80	0.77	12220
6	7196	12953	24692	28571	1070	7196	0.67	1.80	0.90	8636
7	10194	18349	25124	8571	859	10194	1.19	1.80	0.79	12232
12	10066	18119	24390	28653	821	10066	1.22	1.80	0.75	12079
13	9451	13037	25641	28653	688	9451	1.37	1.37	0.63	11341
16	-	-	24510	28653	-	-	-	-	-	-
18	13228	13228	24390	28571	1038	13227	0.70	1.80	0.95	8818

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