National Journal of Chemistry,2008, Volume 30,330-337 المجلة القطرية للكيمياء-2008 المجلد الثلاثون

Preparation of Some Nickel (II) Complexes Containing Mixed Ligands (Salicylaldehyde Semicarbazone and Carboxylic Acids)

Z. F. Dawood and M. W. Ibrahim
Chemistry Department , Education College , Mosul University, Mosul-Iraq

(NJC)

(Received on 9/9/2007) **(Accepted for publication 24/3/2008)**

Abstract

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

الخلاصة

يتضمن البحث تحضير وتشخيص عددا من معقدات النيكل (II) الجديدة مع مزيج من الليكندات: ساليسالديهايد سميكاربازون - SCH_2 وبعض الأحماض الكاربوكسيلية (حامض السالساليك – SH_2 أو حامض الأنثرانيليك – AnH_2 أو حامض الفثاليك – PH_2). شخصت المعقدات الناتجة باستخدام طرق فيزيائية-كيميائية مختلفة. عززت النتائج أن المعقدات تكون ثنائية النوى وذات شكل ثماني السطوح منحرف.

Introduction

Nickel complexes occurred in several nickel containing enzymes and have been proposed to be involved in catalytic reaction. Nickel complexes with some macrocyclic ligands have been studied and some of them forming poly-nuclear complexes(1-3).

Agood deal of work has been reported on the preparation, spectral and structural investigation of semicarbazones and their complexes, due to their capability of acting as polydentate donor with the formation of either mono- or bi- or poly-nuclear complexes(4-8).In addition to their interesting ligational properties, semicarbazones and their complexes have important biological activities(9,10). Awide studies have been done on the substituted benzoic acids due to their interesting ligational properties(11-16).

There has been growing interest in the formation of mixed ligand chelates involving ligands containing different functional groups and transition metals of different oxidation states which can formed chelates with ligands containing different donation sites(17). On the other hand, coordination compounds with mixed ligands are of considerable importance in the field of metalloenzymes and other biological activities, hence a large body of the coordination chemistry of mixed ligands with transition and non-transition metal ions have been reported recently(18-20). Due to the importance of mixed ligand complexes, we took a humble part in the chemistry of mixed ligands containing semicarbazones and some articles have been published on their coordination chemistry with transition and non-transition metal ions(21-24).

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

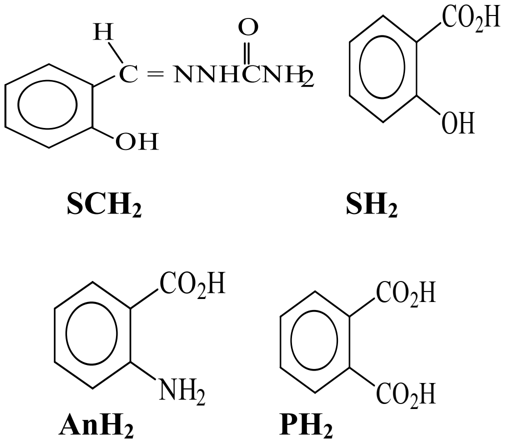


Figure 1 : Structures of the ligands

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(25) with concentrated nitric acid .

Conductivity measurements have been carried out with an electrolytic conductivity measuring set LF-42 and Multiline f / SET-2WTW Wissenschaf 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 cm^{-1} using KBr pellets. Electronic spectra has been recorded on Shimadzu UV-Vissible Recording Spectrophotometer UV 160 for 10^{-4} M solutions of the ligands and their complexes in dimethylformamide at 25 ^{o}C, using a 1cm seleca cell. Magnetic suscepibility of some complexes have been measured by Bruker-BM6 . The molecular weights of the complexes have been determined cryoscopically(26).

2- Synthetic Methods :

Salicylaldehyde semicarbazone has been prepared according to previous method(27). 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 nickel nitrate or acetate or carbonate, respectively in 5 ml water has been added to the solution of salicylaldehyde semicarbazone (0.003, 0.004, 0.008 mole) and one of the carboxylic 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 have been refluxed for three hours followed by evaporation to half their volumes then cooled. The products are separated by filteration, washed with petroleum ether and dried. In basic medium, complexes have been prepared by applying the same amounts used for neutral medium, and after mixing the metal salts with the ligands and heating on a waterbath, potassium hydroxide solution (1M) was added until pH of the solutions have been adjusted to about 8-9. The mixtures have been heated on a waterbath for half an hour, allowed to stand 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 :

$$2NiX_2.mH_2O + 2AH_2 + 2SCH_2 \rightarrow [Ni_2(AH_2)_2(SCH_2)_2X_n]Y_2 + 2mH_2O$$

$$2NiX_2.mH_2O + 2AH_2 + 2SCH_2 + 4KOH \rightarrow [Ni_2(AH)_2(SCH)_2] + 2K_wX + {}_{2m+4}H_2O$$

where X=NO_3^- or CH_3COO^- or CO_3^{-2} ; Y= NO_3^- or nothing ; n=2 or 4 or 1 ; m= 6 or 4 or 0 ; w=1 or 2 ; AH_2 = SH_2 or AnH_2 or 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 $[Ni_2(AH_2)_2(SCH_2)_2(NO_3)_2](NO_3)_2$, $[Ni_2(AH_2)_2(SCH_2)_2X_n]$ and $[Ni_2(AH)_2(SCH)_2]$ 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(28) 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 six-coordinate high-spin octahedral complexes possibly attributed to the ligand participation(29,30) .

The infrared spectra of SCH_2 ligand (Table 2) shows a strong band at 1600 cm^{-1} attributed to C=N group shifts towards a lower frequency on coordination due to the decrease of the bond order as a result of metal nitrogen bond formation(31). The next strong band at 1700 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 the metal ion(32,33). Meanwhile, in basic medium , this band is disappeared in the complexes and a new band has been observed at 1400 cm^{-1} due to bending enolic OH thereby establishing coordination of the ligand through the enolic oxygen atom(2). The appearance of strong bands at 1630-1635 cm^{-1} and 1570-1580 cm^{-1} attributed to $\upsilon_{(C=N)} + {}_{(O-C=N)}$ and azine chromophore $\upsilon_{(C=N-N=C)}$, respect - tively, support the formation of enolic structure in basic medium(9). The position band of the ligand in the range 3200-3300 cm^{-1} is assigned to υ_{NH} remains unaltered in the complexes prepared in neutral medium indicating that there is no coordination through the NH group. whereas in basic medium, this band is disappeared in basic medium(22) due to the enolic form. The other strong bands at 3390, 3410 cm^{-1} and 1450 cm^{-1} are assigned to υ_{NH2}(12,33) . These bands remain unaltered on complexation indicating that there is no coordination through this group and metal ion . Moreover the other wide band observes at 3500-3600 cm^{-1} is attributed to stretching vibration of phenolic hydroxyl shifts to lower frequency on complexation .The band at 1290-1310 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 appearance of a band at 1170 cm^{-1} which belongs to $\upsilon_{(C-O)}$ is shifted to higher frequency 1330 cm^{-1} on complexation indicating the coordination of oxygen atom(31,33) .

The spectra of substituted benzoic acids (SH_2 , AnH_2 , PH_2) show a wide bands in the regions 3500-3600 , 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 is due either to the inter or intra molecular hydrogen bonding. In the spectra of the complexes it is 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 is shifted to higher frequency . Whereas for complexes prepared in basic medium it is very difficult to observe the disappearance of this band, but it is well known that this band is disappeared due to the deprotonation of the acid and the formation of ionic form (16,31) . The other two bands observed at 1370-1390 cm^{-1} and 1550-1570 cm^{-1} are due to the symmetric and asymmetric stretching frequency of carboxylic group, respectively. On complexation these bands are shifted to 1350-1420 cm^{-1} and 1500-1575 cm^{-1}, respecttively(32,33). The difference between the symmetry and asymmetry stretching vibration for COO^- group ($\Delta\upsilon$ =150-180 cm^{-1}) gives indication about the manner of coordination of carboxylic group, this value shows that the carboxylic acid coordinate through COO$^-$ group which act as monodentate. The complexes in neutral medium which contain nitrato group show two kind of bonding, because the appearance of the bands at 1380-1385 cm^{-1}, 1400-1480 cm^{-1} , 1285-1365 cm^{-1} 945-1010 cm^{-1} due to the ionic bonding , υ_{sNO3} , υ_{asNO3} and υ_{NO} (υ_2 , υ_1 , υ_5), respecttively(11,31). The difference between υ_1–υ_5 equel to 115 cm^{-1} which supports the bonding of nitrato group as monodentate ligand through the oxygen atom . Whereas, the complexes prepared in basic medium do not show any of these bands indicating the absence of NO_3^- group in these complexes .

The spectra of the complexes prepared in neutral medium show stretching vibration for carbonyl CO_3^{-2} group at 1480 and 1550 cm^{-1} which indicate that the carbonato group act as monodentate ligand bonding to the metal ion through the oxygen atom(11,31). 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 cm^{-1} indicating that the $CH_3CO_2^-$ group joint to the metal ion through the oxygen atom and act as monodentate ligand(11,31). Meanwhile there is no band observed in the spectra of the complexes prepared in basic medium indicating the absence of this group .

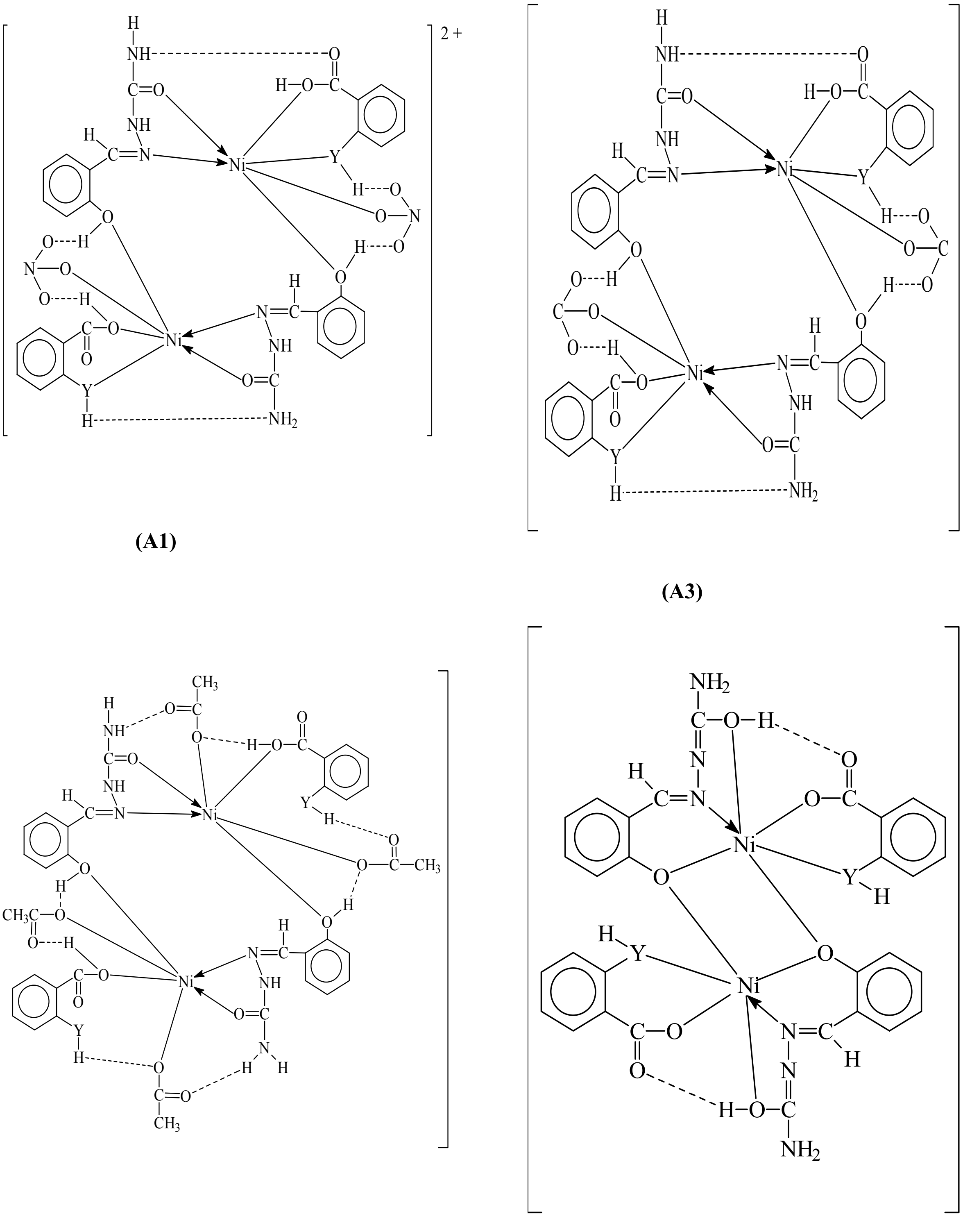
On the other hand the spectra of all the complexes show new bands around 450-675 cm^{-1} , 550-750 cm^{-1}, and 750-770 cm^{-1} due to $\upsilon_{M\text{-}N}$, $\upsilon_{M\text{-}O}$ and $\upsilon_{M\text{-}O\text{-}M}$, respecttively(21,31,32). The presence of these bands support the formation of the complexes under investigation and the formation of dimer due to the presence of $\upsilon_{M\text{-}O\text{-}M}$ 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 7196-10193 cm^{-1}, 10152-18348 cm^{-1} and 24390-25641 cm^{-1} due to υ_1 , υ_2 and υ_3 {attributed to the transitions ^3A_2g (F)→^3T_2g (F), ^3A_2g (F)→ ^3T_1g (F) and ^3A_2g(F)→^3T_1g (P)}, respectively, are expected for d^8 system in octahedral field (23) . The ligand field parameter B and the ligand field splitting energy (10Dq) in case of nickel (II) complexes have been calculated(35). The values of β of the complexes are between 0.72-0.84 clearly indicate the covalent character of the bond concerned. However, the electronic spectral data suggest distorted octahedral geometry for all the complexes(34,35).

Conclusion:

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

1. 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.
2. Substituted benzoic acids acted as either monodentate or bidentate chelating ligands.
3. 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.
4. Carbonato and acetate groups acted as monodentate ligands.
5. Binuclear complexes(36,38) have been suggested with distorted octahedral geometries (Figure 2).



(A1)

(A3)

(A2)

(B)

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_2 gm	A* AH_2 gm	Colour	M. Wt. Calc./ Obs.	^M **	M.P ^0C	μ_{eff} ***	% analysis calc./ obs.			
									C	H	N	Ni
1	$[Ni_2(SH_2)_2(SCH_2)_2(NO_3)_2]\ (NO_3)_2$	0.61	0.46	Pale green	996 980	161	150d	2.21	36.19 35.88	3.01 2.95	14.06 13.29	11.79 10.71
2	$[Ni_2(AnH_2)_2(SCH_2)_2(NO_3)_2](NO_3)_2$	0.61	0.41	Green	966 950	129	180d	1.95	37.28 36.89	3.31 3.18	17.40 17.22	12.16 11.63
3	$[Ni_2(PH_2)_2(SCH_2)_2(NO_3)_2]\ (NO_3)_2$	0.61	0.57	Dark green	1056 1041	105	275d	1.93	36.38 35.96	2.84 3.00	13.26 12.98	11.12 11.61
4	$[Ni_2(SH)_2(SCH)_2]$	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	$[Ni_2(AnH)_2(SCH)_2]$	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	$[Ni_2(PH)_2(SCH)_2]$	0.61	0.57	Pale green	804 780	0	260d	2.16	47.79	3.23	10.22	14.12 14.61
7	$[Ni_2(SH_2)_2(SCH_2)_2(Ac)_4]$	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	$[Ni_2(AnH_2)_2(SCH_2)_2(Ac)_4]$	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	$[Ni_2(PH_2)_2(SCH_2)_2(Ac)_4]$	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	$[Ni_2(SH)_2(SCH)_2]$	0.71	0.54	Pale green	744 730	18	280d	2.04	48.42	3.49	11.29	15.79 15.02
11	$[Ni_2(AnH)_2(SCH)_2]$	0.71	0.48	Pale green	714 685	0	290d	-	50.46 49.95	3.92 4.35	15.69 15.22	16.45 16.48
12	$[Ni_2(PH)_2(SCH)_2]$	0.71	0.66	Pale green	804 781	12	295d	2.04	47.79	3.23	10.45	14.61 13.52
13	$[Ni_2(SH_2)_2(SCH_2)_2(CO_3)_2]$	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	$[Ni_2(AnH_2)_2(SCH_2)_2(CO_3)_2]$	1.50	1.02	Pale green	838 825	5	285d	1.36	45.85 45.55	3.82 4.02	13.37 14.45	14.02 13.75
15	$[Ni_2(PH_2)_2(SCH_2)_2(CO_3)_2]$	1.50	1.39	Pale green	927 915	16	290d	1.93	43.99 43.59	3.23 3.11	9.05 8.86	12.66 12.37
16	$[Ni_2(SH)_2(SCH)_2]$	1.50	1.14	Pale green	744 730	12	220d	-	48.42	3.49	11.24	14.61 14.06
17	$[Ni_2(AnH)_2(SCH)_2]$	1.50	1.02	Pale green	745 730	10	288d	2.29	53.97	3.65	11.80	16.45 16.04
18	$[Ni_2(PH)_2(SCH)_2]$	1.50	1.39	Green	804 779	9	284d	2.18	47.79	4.23	10.45	14.61 15.31

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

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

No.	$\upsilon_{C=N}$	$\upsilon_{C=O}$ semi	υ_{C-O} semi	υ_{C-O} phen	$\upsilon_{s\ Coo}$ acid	υ_{sCoo} acid	υNO_3 υAc^- υCO_3^{-2}	υ_{M-O-M}	υM-N	υM-O
SCH_2	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	450,500	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, 500	700, 750
18	1550	-	1350	1250	1370	1500	-	770	550	650, 750

Table 3 : Electronic spectral data of some complexes

No.	υ_1 cm^{-1}	υ_2 cm^{-1}	υ_3 cm^{-1}	Charge transfer cm^{-1}	B cm^{-1}	10Dq cm^{-1}	Dq/B	υ_3 / ν_1	β	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

References

1- G. Eichhorn and L. Marzilli; Advances in inorganic biochemistry; Elsevier Sci. Pub. Company, Inc., New York, 1982, 87,134,152,172, 176, 191.

2- Q. Zhang, J.J. Zhai, Y.R. Zhang, Y.M. Lin, L.F. Wang, S.B. Li, D.E. Liao and G.***Transit. Met. Chem.*****;** 2000, **25**(1), 93.

3- M. Joudadel, X.D. Thanh, G. Bonet, S. Bonneau and M.A.Khan; ***Anticancer Res.*****;** 2002, **22**(3), 1713.

4- B. Singh, P.L. Manrya and B.V. Agarwala**;** ***J. Indian Chem. Soc.*****;** 1982, **6**, 1130.

5- M. Campbell, C. Elizabeth and N.R. Verno; ***Polyhedron*** ; 1988, **7**(18),1719 .

6- D.D. Yin, Z.W. Wang and L. Shan; Chinese ***J. Chem.***; 2000, **18(3)**, 364.

7- A. Seyam, A. Jarrar and F. Khalili; ***J. Abhath Al-Yarmouk Basic Sci.***; 2001, **2A**, 243.

8- N. Kanoongo, R.V. Singh and J.P. Tandon ; ***J. Synth. React. Inorg. Met-Org. Chem.***; 1987, **17**(8), 837.

9- N.C. Kasuga, K. Sekino, C. Koumo, N. Shimada and I.M. Normiya; ***J. Inorg. Biochem.***; 2001, **84**(1-2), 55.

10- J. Patole, S. Dutta, S. Padhye and E. Sinn; ***Inorg. Chim. Acta***; **318**, 207.

11- G.A. Wilkinson, R.D. Gillard and J.A. McCleverty; Comprehensive Coordination Chemistry; Pergamon Press Oxford, England, 1987, **2**, 1st ed., 355, 357, 437-439, 715.

12- K. Wieghardt, H. Siebert and G. Tremmel; ***J.C.S. Dalton Transfer;*** 1973**, 23**, 2548.

13- S. Jagner, R.G. Hazell and K.P.Larsen; ***Acta Cryst.***, 1976, **B 32**, 548.

14- D.A. dʾAvignon and T. L. Brown; ***Inorg. Chem.***; 1982, **21**, 3041.

15- N.G. Palaskar, D.V. Jahagirdar and D.D. Khanolkar; ***J. Indian Chem. Soc.***; 1975**, 14**, 134.

16- I.R. Desai and V.S.K. Nair ; ***J.C.S. Dalton Trans.***; 1962, **22**, 2360.

17- Z. Afrasiabi, E. Sinn, W. Lin, Y. Ma, Ch. Campana and S. Padhye; **J. *Inorg. Biochem.***; 2005, 00, 0000.

18- Js Casas, A. Castineira, A.M. Rodrigues, A.Sanchez , J. Sordo ,A. Vazquez-Lopez, S. Pinelli, P. Lungli, P. Ciancianaini, A. Bonati, P.D. Aglio and P. Albertini; ***J. Inorg. Biochem.;*** 1999**, 76** (3-4), 277.

19- P. Bindu, M. R. P. Kurup and T. R. Satyakeerthy; ***Polyhedron;*** 1998, **18**, 321.

20- R. Ramesh and M. Sivamasundari; ***Synth. React. Inorg. Met-Org. Chem.***; 2003, **33**(5), 899.

21- Z.F. Dawood, S.H. Hessein and M.A. Al-Shamaʾa; ***Sci. & Tech.A;*** 2004**, 12**, 71.

22- Z.F. Dawood and Y.T. Mahmood; ***Raf. Jour. Sci.***; 2006, **17**(4), 1.

23- Z.F. Dawood and A.A.Mohamad; Al-Taqani; 2006, **19**(2),100-108.

24- Z.F. Dawood, and Y.T. Mahmood; ***National J. Chem.***; Accepted in 2007

25- A. I. Vogel; Textbook of Quantitative Inorganic Analysis; Longman Inc., New York, 1981, 4th ed., 457, 461, 463, 470, 477, 489 .

26- J.W. Danials; Experimental physical chemistry ; McGraw-Hill , 1962, 6th ed., 81.

27- A.I. Vogel; Textbook of Practical Organic Chemistry; Longman Green, London, 1964, 3rd ed., 344.

28- W.J. Geary; ***Coord. Chem. Rev.***; 1971, **7**, 81 .

29- F.B. Hokins, R. Robson and H. Schaap; ***J. Inorg. Nucl. Chem. Letters;*** 1972, **8**, 25.

30- D.L. Arora, K. Lal, S.P. Gupta and S.K. Sahni; ***Polyhedron***; 1986**, 5**(10), 1499.

31- K. Nakamoto; Infrared and Raman Spectra of Inorganic and Coordination Compounds; John Wiley and Sons, New York, 1976, 3rd ed.

32. Y. Kumar and S.P. Tolani; ***Croat. Chem. Acta***; 1989**, 62**, 73.

33- Z.F. Dawood; ***Sci. & Tech.***; 2002**, 17**, 35.

34- A.B.P. Lever; ***J. Chem. Edu.***; 1968**, 45**, 711.

35- D. Nicholls; The Chemistry of Iron, Cobalt and Nickel; Pergamon Press, Oxford, England; 1973, 1st ed., 1048, 1049, 1087, 1090, 1091, 1151, 1152, 1155.

36- Z.F. Dawood and M.W. Ibrahim, Accepted in ***J. Univ. Thi-Qar***, 2006.

37- Z.F. Dawood and M.W. Ibrahim, ***Raf. Jour. Sci.***, 2006, **17**(2), 8.

38- Z.F. Dawood and M.W. Ibrahim, **National J. Chem.**, 2006, **21**, 24.