

SOME COMPLEXES OF Ni(II) CONTAINING MIXES LIGANDS

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Abstract

Nickel (II) Complexes containing mixed ligands : semicarbazone (benzaldehyde semicarbazone-BSCH; 2-fluorobenzaldehyde semicarbazone-FSCH) and substituted pyridine {2-aminopyridine (p₁); 4-aminopyridine (p₂); 2,3-dicarboxypyridine (p₃); 2-amino-3-hydroxypyridine (p₄); 2-amino-4-methylpyridine (p₅) and 3,4-dicarboxypyridine (p₆) have been prepared. The resulted complexes have been characterized by elemental analysis, molar conductance values, magnetic moment, infrared and electronic spectral data. Complexes of the type [Ni₂(SCH)₂(P)₄(NO₃)₂](NO₃)₂ and [Ni₂(SCH)₂(P)₄(NO₃)₃]NO₃ (where SCH= BSCH or FSCH, P= substituted pyridine ligands) have been proposed.

Key words: Ligands, semicarbazone, substituted pyridine, nickel.

Résumé

Des complexes de Nickel (II) Complexes contenant un mélange de ligands : semicarbazone (benzaldehyde semicarbazone-BSCH; 2-fluorobenzaldehyde semicarbazone-FSCH) and de la pyridine substituée {2-aminopyridine (p₁); 4-aminopyridine (p₂); 2,3-dicarboxypyridine (p₃); 2-amino-3-hydroxypyridine (p₄); 2-amino-4-methylpyridine (p₅) and 3,4-dicarboxypyridine (p₆) ont été préparés, puis caractérisés par différentes méthodes: analyse élémentaire, conductance molaire, moment magnétique, spectroscopies infra-rouge et électronique. Des complexes de type [Ni₂(SCH)₂(P)₄(NO₃)₂](NO₃)₂ et [Ni₂(SCH)₂(P)₄(NO₃)₃]NO₃ (où SCH= BSCH or FSCH, P = ligands pyridine substitués) ont été proposés.

Key words: Ligands, semicarbazone, pyridine substitué, nickel.

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ملخص

تم دراسة تكوين بعض معقدات النيكل (II) الحاوية على مزيج من ليكاندات السميكاربازونات (تشمل بنزالديهيد سميكاربازون-BSCH أو 2-فلوروبنزالديهيد سميكاربازون-FSCH) وليكاندات البريدينا المعوض (تشمل 2-أمينوبريدين P1 أو 4-أمينوبريدين P2 أو 3,2-ثنائي كربوكسي بريدين P3 أو 2-أمينو-3-هيدروكسي بريدين P4 أو 2-أمينو-4-ميثيل بريدين P5 أو 3,4-ثنائي كربوكسي بريدين P6). شخصت المعقدات الناتجة باستخدام الأشعة تحت الحمراء وفوق البنفسجية والتحليل الدقيق للعناصر وقياس التوصيلية الكهربائية والقياسات المغناطيسية، ولقد اقترحت الصيغ التالية للمعقدات [Ni₂(SCH)₂(P)₄(NO₃)₂](NO₃)₂ و [Ni₂(SCH)₂(P)₄(NO₃)₃]NO₃ حيث SCH = بنز الديهايسميكاربازون أو 2-فلوروبنزالديهيد سميكاربازون و P = ليكاندات البريدين المعوضة.

الكلمات المفتاحية: سميكاربازون، معقدات النيكل، ليكاندات البريدين.

Semicarbazones are ligands bonding through the nitrogen and oxygen atoms to the central metal ion forming an important class of biologically active ligands and provide models for metal-ligand bonding sites in several enzymes [1]. Semicarbazone complexes of some transition and non transition elements have been reported [2-5].

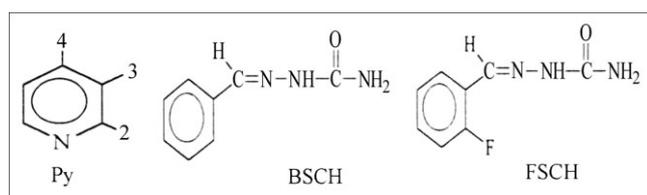
Pyridine is the best known heterocyclic nitrogen ligand and its coordination chemistry has been studied in great details. The metal-nitrogen distances, as observed in a very large number of crystal structure determinations, are almost the same as those observed for the nitrogen ligands. Comparing pyridine with substituted ligands, it is observed that substituents at position 2 (and 6) next to the donor atom have a dramatic effect upon the stoichiometry and properties of the compounds formed [6]. The majority of pyridine compounds use the free electron pair to bind to metal ions in monodentate fashion, bridging coordination using the nitrogen atom is also possible. Usually, coordinated pyridine ligands are rather stable towards substitution [6]. Upon complex formation the pyridine vibrations in the high-frequency region are not shifted appreciably, whereas those at 604 (inplane ring deformation) and at 405 cm (out-of-plane ring deformation) are shifts to higher frequencies [7]. An extensive review on infrared spectra of metal pyridine complexes has been reported [8-10].

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 [11-16].

Nickel complexes occur in several nickel-containing enzymes [17] and have been proposed to be involved in catalytic reaction [18]. Nickel complexes with macrocyclic ligands have been prepared, six-coordinate nickel complexes resulted having magnetic moment ranging from 1.88-2.29 B.M. [19]. Nickel (II) complexes of macrocyclic ligands have been prepared forming a coordination polymer [20].

In view of this, and since mixed ligands complexes of semicarbazones and amines with nickel (II) ion 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 the nickel (II) ion. This information can be gained by biological examination of the various complexes derived from semicarbazone and substituted pyridine which would be prepared.

In the present work, nickel (II) complexes with mixed ligands (semicarbazones and substituted pyridines) have been prepared and characterized physicochemically. The structures of the ligands are shown in **figure 1**.



Py	2	3	4
P ₁	NH ₂	H	H
P ₂	H	H	NH ₂
P ₃	COOH	COOH	H
P ₄	NH ₂	OH	H
P ₅	NH ₂	H	CH ₃
P ₆	H	COOH	COOH

Figure 1: Model structure of the ligands.

EXPERIMENTS

Chemicals

Nickel (II) nitrate, 2-fluorobenzaldehyde, semicarbazide hydrochloride, substituted pyridine ligands (Fluka) have been used as supplied, whereas benzaldehyde (Fluka) has been used after purification by distillation.

Preparation of the ligands

Semicarbazone ligands have been prepared according to the standard methods [21]: 0.0890 mole of semicarbazide hydrochloride and 0.0163 mole sodium acetate dissolved in 10 ml water have been mixed with 0.0940 mole of the appropriate aldehyde. The mixtures were shaken and heated on a water bath for few minutes. On cooling, the solid products were separated, filtered off, washed with water, recrystallized from ethanol and dried. White crystals were obtained (m.p. of BSCH=200°C, FSCH= 240°C).

Preparation of the complexes

The complexes have been prepared by the reaction of aqueous solution of nickel (II) nitrate with ethanolic solution of semicarbazones (BSCH or FSCH) and substituted pyridine ligands (p₁ – p₆) in 1:1:2 molar ratio at pH 6-7. The mixtures have been refluxed for 3 hrs., evaporated to about half their volumes and cooled. The resulting products were filtered, washed with diethylether and dried.

Analytical and physical measurements

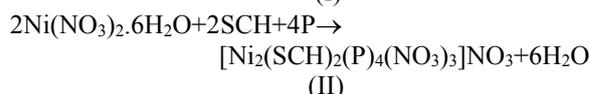
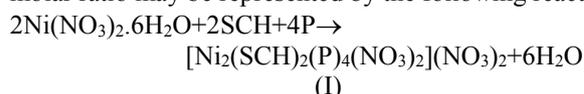
Elemental analyses for the complexes have carried out on a CHN analyzer, type 1106 (Carlo-Erba) at the Chemistry Department, Science College, Mosul University. The metal contents have been determined by a standard precipitation method [22].

Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring set LF-42 using 10⁻³ M absolute ethanol at room temperature. Magnetic susceptibilities of the complexes have been measured by Bruker-B-MNC₄.

IR spectra of the ligands and their complexes have been recorded on a Pye- Unicam 1100 spectrophotometer in the 400-4000 cm⁻¹ range using KBr pellets. UV/Visible spectra have been recorded on Shimadzu- 160 spectrophotometer for 10⁻³ M solution of the ligands and their complexes in absolute ethanol at 25°C using a 1 cm cell.

RESULTS & DISCUSSION

The reaction of nickel (II) nitrate with the semicarbazone and substituted pyridine ligands in 1:1:2 molar ratio may be represented by the following reactions:



The resulted complexes are colored solid, moderately soluble in ethanol, soluble in dimethylformamide and dimethylsulfoxide. The elemental analyses reveals that the complexes have the composition [Ni₂(SCH)₂(P)₄(NO₃)₂](NO₃)₂ and [Ni₂(SCH)₂(P)₄(NO₃)₃]_{NO₃}. The molar conductivities of the complexes in 10⁻³M absolute ethanol are determined, the values shown in **Table 1** approach those expected for 1:2 and 1:1 electrolytes [23] for the complexes of thype (I) and (II), respectively.

According to the analytical and physical data of the metal complexes, the central metal atoms are probably hexa-coordinated leading to binuclear complexes.

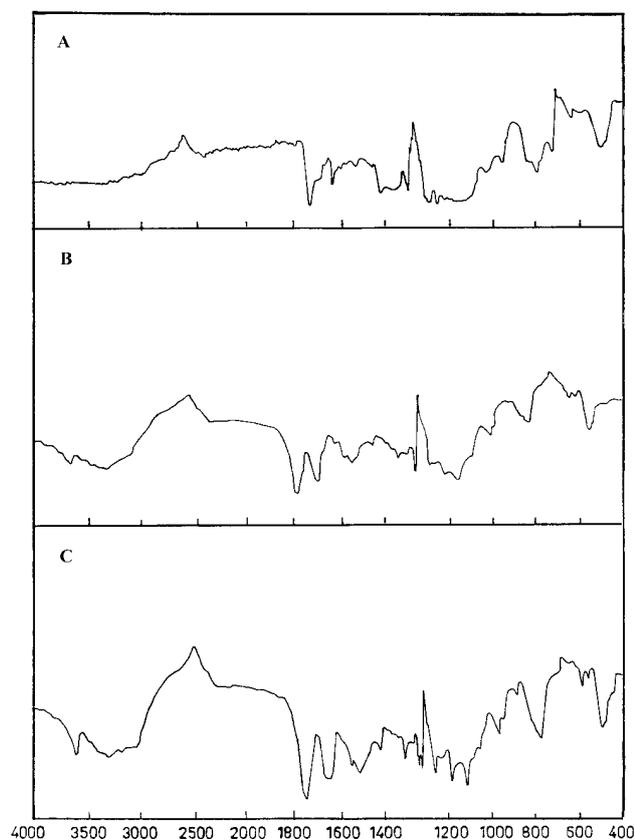
The magnetic moments of the complexes calculated from the corrected magnetic susceptibilities determined at room temperature are shown in Table 1. The μ_{eff} values reported for the complexes supported the dimeric structures (binuclear complexes) where a kind of antiferromagnetic superexchange happened and indicating octahedral geometry around the metal ions [24-25].

The infrared spectra of semicarbazone ligands showed a strong band at about 1675 cm⁻¹ which was attributed to the C=O group [2-5]. This value shifted towards a lower frequency on coordination indicating the formation of a chelation between the oxygen of the carbonyl group and the metal ion [4]. The next strong band at 1580 cm⁻¹ which was and the metal ion attributed to C=N group [14-16] shifted towards a lower frequency on coordination [2,14-16] which was due to the decrease of the bond order as a result of metal nitrogen bond formation [14-16]. The position of the ligand in the range 3300-3500 cm⁻¹ remained unaltered in the complexes indicating that there was no coordination

N°	Compounds	Colors	M.P. °C	*	**	%Analysis (calc./obs.)			
						C	H	N	Ni
1	[Ni ₂ (FSCH) ₂ (P ₁) ₄ (NO ₃) ₂](NO ₃) ₂	Olive	189- 190	82.3	4.1	39.18	3.65	22.84	10.63
						38.91	3.55	22.66	10.42
2	[Ni ₂ (FSCH) ₂ (P ₂) ₄ (NO ₃) ₃](NO ₃)	Green	184- 186	45.9	4.5	39.18	3.65	22.84	10.63
						38.88	3.49	22.59	10.38
3	[Ni ₂ (FSCH) ₂ (P ₃) ₄ (NO ₃) ₃](NO ₃)	Green	160- 162	38.9	4.7	37.87	2.60	14.05	8.41
						37.44	2.48	13.85	8.25
4	[Ni ₂ (FSCH) ₂ (P ₄) ₄ (NO ₃) ₃](NO ₃)	Brown	128- 130	39.2	5.5	37.03	3.45	21.59	10.05
						36.69	3.35	21.38	9.8
5	[Ni ₂ (FSCH)(P ₅) ₄ (NO ₃) ₂](NO ₃) ₂	Green	185- 187	76.7	4.3	41.43	4.17	21.74	10.12
						41.22	4.08	21.55	9.93
6	[Ni ₂ (FSCH) ₂ (P ₆) ₄ (NO ₃) ₂](NO ₃) ₂	Olive	166- 168	86.5	4.6	37.87	2.60	14.05	8.41
						37.60	2.46	13.86	8.25
7	[Ni ₂ (BSCH) ₂ (P ₁) ₄ (NO ₃) ₂](NO ₃) ₂	Green	150- 152	82.3	3.8	40.50	3.96	23.62	10.99
						40.09	4.04	23.44	10.60
8	[Ni ₂ (BSCH) ₂ (P ₂) ₄ (NO ₃) ₃](NO ₃)	Olive	158- 160	42.7	4.0	40.50	3.96	23.62	10.99
						40.15	3.88	23.50	10.83
9	[Ni ₂ (BSCH) ₂ (P ₃) ₄ (NO ₃) ₃](NO ₃)	Olive	146- 148	43.6	3.7	38.87	2.81	14.42	10.37
						38.59	2.66	14.30	10.11
10	[Ni ₂ (BSCH) ₂ (P ₄) ₄ (NO ₃) ₃](NO ₃)	Green	173- 174	47.1	3.9	38.87	2.81	14.42	10.45
						38.59	2.68	14.29	10.14
11	[Ni ₂ (BSCH) ₂ (P ₅) ₄ (NO ₃) ₂](NO ₃) ₂	Green	181	74.1	3.7	38.21	3.74	22.28	10.87
						37.89	3.60	22.09	10.58
12	[Ni ₂ (BSCH) ₂ (P ₆) ₄ (NO ₃) ₂](NO ₃) ₂	Olive	212	80.0	3.5	42.76	4.48	22.44	8.63
						42.43	4.37	22.30	8.50

Table 1: Analytical data and physical properties of the complexes.* Values in $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$

** Values in Bohr magneton (B.M.)

**Figure 2:** Infrared spectra of some complexes (values in cm^{-1}).

A : IR spectra of complex n°12,

B : IR spectra of complex n°19,

C : IR spectra of complex n°3.

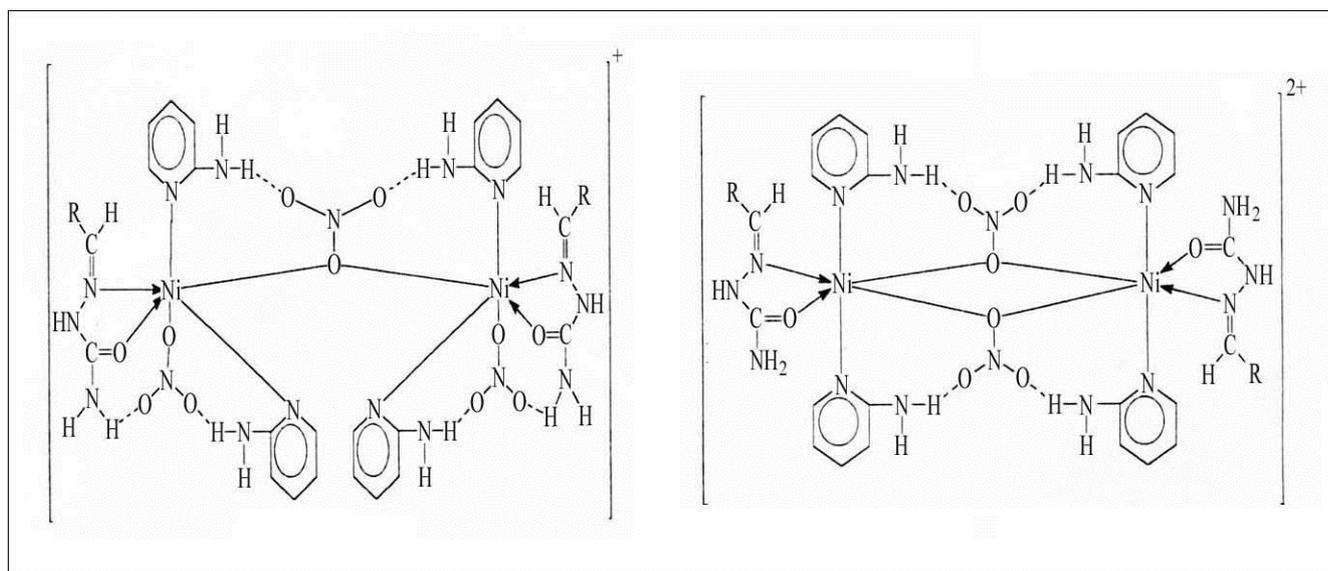
through the NH group [2-4].

The infrared spectra of substituted pyridine ligands showed a band at $1595\text{--}1600\text{ cm}^{-1}$ which was due to the pyridine ring deformation, upon complexation this band was not shifted. The two bands at $604\text{--}608$ and $405\text{--}408\text{ cm}^{-1}$ which were due to the in-plane ring deformation and out-of-plane ring deformation, were shifted to higher frequencies (Table 2, Fig. 2) upon complexation. The upward shift in these vibrations of the pyridine ring indicated coordination with the metal atom [7,26].

On the other hand, the spectra of all complexes showed new bands at $1380\text{--}1385$, $1400\text{--}1480$, $1250\text{--}1330$ and $1000\text{--}1010\text{ cm}^{-1}$ as due to ionic nature of nitrate group, $\nu_{(\text{sym.})}\text{NO}_2$, $\nu_{(\text{asym.})}\text{NO}_2$ and ν_{NO} , respectively. These observations suggested that the nitrate ion joint to the metal ion in two manners as ionic and bridging monodentate ligands [6,7,27]. In addition, new bands were observed in the spectra of the complexes at $500\text{--}520$ and $550\text{--}580\text{ cm}^{-1}$ as due to $\nu_{\text{Ni-N}}$ and $\nu_{\text{Ni-O}}$, respectively. The presence of these bands strongly support the coordination of the ligand to the metal ion.

The electronic spectra of the ligands and their complexes in absolute ethanol solution have been recorded. The maximum at about ~ 288 , $260\text{--}280\text{ nm}$ in case of the ligands may be assigned to $\pi \rightarrow \pi^*$ transition of NH_2 chromophore and $\pi \rightarrow \pi^*$ (benzenoid) electronic transition [2], respectively. These bands are almost unchanged in the complexes. Moreover, the spectra of the ligands showed two bands at ~ 318 and $335\text{--}350\text{ nm}$ which may due to $\pi \rightarrow \pi^*$ transition of $\text{C}=\text{N}$ chromophore [28] and $n \rightarrow \pi^*$ transition within the $\text{C}=\text{N}$ chromophore, respectively. On

Comp.	VC=N	VNH	VC=O	VNH2	Vpy(in plane)	Vpy(out of plane)	VNI -O	VNI -N	Other bands
FSCH& P ₁	1580	3200-3500	1675	1450	604	405			
1	1550	3200-3500	1650	1450	640	430	550	500	
FSCH& P ₂	1580	3200-3500	1675	1450	605	405			
2	1545	3200-3500	1650	1450	640	435	550	500	
FSCH& P ₃	1580	3200-3500	1675	1450	602	408			V _S COO 1730 V _{AS} COO 1240
3	1540	3200-3500	1645	1450	640	445	570	505	V _S COO 1730 V _{AS} COO 1240
FSCH& P ₄	1580	3200-3500	1675	1450	602	408			V _{OH} 3100-3200
4	1550	3200-3500	1650	1450	645	445	550	505	V _{OH} 3100-3200
FSCH& P ₅	1580	3200-3500	1675	1450	605	410			
5	1545	3200-3500	1650	1450	635	450	580	515	
FSCH& P ₆	1580	3200-3500	1675	1450	605	405			V _S COO 1730 V _{AS} COO 1240
6	1545	3200-3500	1650	1450	640	440	580	510	V _S COO 1730 V _{AS} COO 1240
BSCH& P ₁	1580	3200-3500	1675	1450	608	410			
7	1550	3200-3500	1650	1450	645	450	570	520	
BSCH& P ₂	1580	3200-3500	1675	1450	608	445			
8	1545	3200-3500	1645	1450	640	445	580	520	
BSCH& P ₃	1580	3200-3500	1675	1450	605	405			V _S COO 1730 V _{AS} COO 1240
9	1545	3200-3500	1650	1450	640	435	560	510	V _S COO 1730 V _{AS} COO 1240
BSCH& P ₄	1580	3200-3500	1675	1450	605	408			V _{OH} 3100-3200
10	1545	3200-3500	1645	1450	640	440	560	500	V _{OH} 3100-3200
BSCH& P ₅	1580	3200-3500	1675	1450	605	405			
11	1540	3200-3500	1645	1450	635	450	570	510	
BSCH& P ₆	1580	3200-3500	1675	1450	605	408			V _S COO 1730 V _{AS} COO 1240
12	1545	3200-3500	1650	1450	640	445	570	510	V _S COO 1730 V _{AS} COO 1240

Table 2: IR spectral data of the ligands and their complexes (values in cm⁻¹).**Figure 3:** Model structures of the complexes.

complexation a blue shift was observed due to the polarization in the C=N bond caused by the metal ligand electron interaction during the chelation [2]. This shift is due to the donation of nitrogen lone pair of the azomethine group to nickel atom [29]. However in the visible region at about 410 nm a band observed which can be related to a charge transfer from ligand to metal orbitals. This ligand to metal transfer absorption band is possibly the band responsible for the colours of these complexes [13].

From the present study we can conclude that the complexes having the formula $[\text{Ni}_2(\text{SCH})_2(\text{P})_4(\text{NO}_3)_2](\text{NO}_3)_2$ and $[\text{Ni}_2(\text{SCH})_2(\text{P})_4(\text{NO}_3)_3]\text{NO}_3$ having the following proposed geometry (Fig.3).

CONCLUSION

This work in fact is a continue of our studies [13-16] including mixed ligand complexes. In this work some observations have been achieved that lead to establish the following points:

- 1/ Substituted pyridines act as monodentate ligand joint to nickel (II) ion through the pyridine-nitrogen atom.
- 2/ Semicarbazones act as bidentate chelating ligands joint to nickel (II) ion through the carbonyl-oxygen and azomethane-nitrogen atoms.
- 3/ Nitrate ion joint in two manners as ionic and bridging monodentate ligand.
- 4/ Nickel (II) ions are probably hexa-coordinated, leading to binuclear complexes (dimer).

REFERENCES

- [1]- Wayland B.B., Abid-Elmageed M.F. and Mohns L.P., *Inorg. Chem.*, 4, (1975), p.1456
- [2]- Kanoongo N., Singh R.V. and Tondon J.P., *Synth. React. Inorg. Met.-Org. Chem.*, 17, (1987), p.837.
- [3]- Karampurwala A.M., Patel R. P. and Ray A., *Synth. React. Inorg. Met.-Org. Chem.*, 19, (1989), p.219.
- [4]- Kumar Y. and Tolami S.P., *Croat. Chem. Acta*, 62, (1989), p.73.
- [5]- Buker R.A. and Dawood Z.F., *Dirasat, Nat. & Eng. Sci.*, 24(3), (1997), p.550.
- [6]- Wilkinson G., Gillard R.D. and McCleverty J.A., "Comprehensive coordination chemistry", Pergamon Press, Ltd, Great Britain, Vol.II, (1987), p.79-80.
- [7]- Nakamoto K., "Infrared and Raman spectra of inorganic and coordination compound", Part B, John Wiley and sons, Inc., 5th Ed., (1997), p.23.
- [8]- Choca M., Ferraro J.R. and Nakamoto K., *J. Chem. Soc. Dalton Trans.*, (1972), p.2297.
- [9]- Allan J.R., Brown D.H., Nuttall R. H. and Sharp D.W.A., *J. Inorg. Nucl. Chem.*, 27, (1965), p.1305.
- [10]- Farha F. and Iwamoto R.T., *Inorg. Chem.*, 4 (1965), p.844.
- [11]- Bajpal S. and Saxena R.C., *J. Indian Chem. Soc.*, 65, (1988), p.677.
- [12]- Sharma C.L. and Islam M.S., *J. Indian Chem. Soc.*, 64, (1987), p.246.
- [13]- Dawood Z.F., *Sci. & Tech.*, 4, (2000), p.47.
- [14]- Dawood Z.F. and Sheet A.Z.M., *Sci. J. Tekreet Univ.*, 7(3), (2001), p.37.
- [15]- Dawood Z.F., *Sci. J. Tekreet Univ.*, 7(2), (2001), p.33.
- [16]- Dawood Z.F., *Sci. & Tech.*, 17, (2002), p.35.
- [17]- Cammack R., *Adv. Inorg. Chem.*, 32, (1988), p.297.
- [18]- Yoon H., Wagler T.R., O'Connor K.J. and Buroows C.I., *J. Am. Chem. Soc.*, 112, (1990), p.4568.
- [19]- Suh M.P., Lee E.Y. and Shim B.Y., *Inorg. Chim. Acta*, 269, (1998), p.337.
- [20]- Suh M.P., Shim B.Y. and Yoom T.S., *Inorg. Chem.*, 33, (1994), p.5509.
- [21]- Vogel A.I., "Textbook of practical organic chemistry", Longmans Green, London, 3th ed. (1964), p.344.
- [22]- Vogel A.I., "Textbook of quantitative inorganic analysis", Longmans 4th ed. (1981), p.447.
- [23]- Geary W.J., *Coord. Chem. Rev.*, 7, (1971), p.81.
- [24]- Guerriero P., Ajo D., Vigato P.A., Casellato U. and Tamburini S., *Inorg. Chim. Acta*, 120, (1986), p.19.
- [25]- Arora D.L., Lal K., Gupta S.P. and Sahli S.K., *Polyhedron*, 5(10), (1986), p.1499.
- [26]- Agarwal R.C. and Rao T.R., *Transition Met. Chem.*, 2, (1977), p.201.
- [27]- Addison C. and Gatehouse B.N., *J. Chem. Soc.*, (1960), p.613.
- [28]- Varshney A. and Tandon J.P., *Polyhedron*, 5(2), (1986), p.739.
- [29]- Kanoongo N., Singh R. and Tandon J.P., *Transition Met. Chem.*, 12, (1978), p.271. □