

New nickel (II) complexes with benzilbis (semicarbazone) and dithiocarbamate ligands

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Abstract

The preparation of new nickel (II) complexes with mixed ligands including benzilbis- (semicarbazone) - SCH₂ and one of dithiocarbamate ligands (ammonium pyrrolidenedithio- carbamate - Pyrdtc or ammonium indolinedithiocarbamate - Indtc) have been carried out in both neutral and basic medium. The resulted complexes have been characterized using elemental analysis by atomic absorption spectroscopy and by precipitation method, molar conductance measurements, refraction measurements, magnetic susceptibilities, infrared and electronic spectra. The study suggested that the above ligands formed neutral complexes having general formula [Ni(SCH₂)(L)X] or [Ni₂(SCH₂)₂(L)₂X_n] in neutral medium and [Ni(SCH)(L)] or [Ni₂(SCH)₂(L)₂] in basic medium (where SCH=deprotonated (-1H) from SCH₂ ligand; L= the ligand Pyrdtc or Indtc; X= Cl⁻ or NO₃⁻ or CH₃COO⁻ or SO₄⁻², n= 1 or 2). Hexacoordinated mononuclear (monomer) complexes or dimeric complexes have been investigated by this study, having octahedral geometries.

Keywords: Mixed ligands, Benzilbis(semicarbazone), Dithiocarbamate, Nickel(II) complexes.

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معقدات جديدة للنیکل (II) مع لیکندی بنزل بس (سمیکاربازون) وثنائي ثايوكارباميت

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الخلاصة

حضرت معقدات جديدة للنیکل (II) مع مزيج من لیکندی بنزل بس (سمیکاربازون) - SCH₂ وأحد لیکندات الثايوكارباميت (امونيوم بايرولدين ثنائي ثايوكارباميت - Pyrdtc او امونيوم اندولين ثنائي ثايوكارباميت - Pyrdts Indtc). شخصت المعقدات الناتجة باستخدام التحليل العنصري بجهاز طيف الامتصاص الذري والطريقة الترسيبية وقياس التوصيلية الكهربائية ومعامل الانكسار والمغناطيسية وأطياف الأشعة تحت الحمراء والالكترونية. واستنتج ان الليکندات تعطي معقدات متعادلة ذات صيغ عامة [Ni(SCH₂)(L)X] أو [Ni₂(SCH₂)₂(L)₂X_n] في الوسط المتعادل و [Ni(SCH)(L)] أو [Ni₂(SCH)₂(L)₂] في الوسط القاعدي (حيث SCH = الليکند SCH₂ مزال منه بروتون، L = الليکند Pyrdtc او Indtc ، X = Cl⁻ او NO₃⁻ او CH₃COO⁻ او SO₄⁻² ، n = 1 أو 2). اثبتت الدراسة ان المعقدات تكون سداسية التناسق ذات أشكال ثمانية السطوح وتكون بعض المعقدات احادية النواة وبعضها الآخر ثنائية النواة (دايمر).

Introduction

Nickel complexes occurred in several nickel-containing enzymes have been proposed to be involved in catalytic reaction (1).

A good deal of work has been reported on the preparation and structural investigation of semicarbazone

and their complexes (2,3). This is due partially to their capability of acting as multidentate, NO, NNO and ONNO donors with the formation of either mono- or bi- or polynuclear complexes (4,5). In addition to their interesting ligational properties, semi carbazones and their complexes have important biological applications (6).

Dithiocarbamate formed an important class of biologically active ligands (7). An extremely large number of dithiocarbamate complexes with transition and non transition metal ions have been known (8,9).

There has been growing interest in the formation of mixed ligands chelates involving ligands containing different functional groups and transition metals of different oxidation states which can form chelates with ligands containing different donation sites (10,11). On the other hand, coordination compounds with mixed ligands are of considerable importance in the field of metalloenzymes and other biological activities (12). Hence a large body of the coordination chemistry of mixed ligands with transition and non-transition metal ions have been reported recently (13,14). Due to the importance of semicarbazone ligands, we took a modest part in the chemistry of mixed ligands containing semicarbazones and their complexes, and some articles have been published so far on their coordination chemistry with transition and non-transition metal ions (15,16).

In the present work, nickel (II) complexes with mixed ligands {benzilbis-(semicarbazone) - SCH₂ and ammonium pyrrolidenedithiocarbamate - Pyrdtc or ammonium indolenedithiocarbamate - Indtc} have been prepared and characterized physicochemically. The structures of the ligands are shown in Figure (1).

Materials and methods

Starting Materials

All the chemicals used were supplied from Fluka, BDH and Aldrich.

Table 1: Amounts of ligands and medium of reaction.

No.	Complexes	Wt of SCH ₂	Wt of Pyrdtc or Indtc	Wt of salt	Medium
1	[Ni(SCH ₂)(Pyrdtc)Cl]	0.682	0.345	0.5	Neutral
2	[Ni ₂ (SCH ₂) ₂ (Pyrdtc) ₂]	0.682	0.345	0.5	Basic
3	[Ni(SCH ₂)(Indtc)Cl]	0.682	0.446	0.5	Neutral
4	[Ni(SCH)(Indtc)]	0.682	0.446	0.5	Basic
5	[Ni(SCH ₂)(Pyrdtc)NO ₃]	0.558	0.282	0.5	Neutral
6	[Ni ₂ (SCH ₂) ₂ (Pyrdtc) ₂]	0.558	0.282	0.5	Basic
7	[Ni(SCH ₂)(Indtc)NO ₃]	0.558	0.365	0.5	Neutral
8	[Ni ₂ (SCH ₂) ₂ (Indtc) ₂]	0.558	0.365	0.5	Basic
9	[Ni ₂ (SCH ₂) ₂ (Pyrdtc) ₂ SO ₄]	0.577	0.292	0.5	Neutral
10	[Ni(SCH)(Pyrdtc)]	0.577	0.292	0.5	Basic
11	[Ni ₂ (SCH ₂) ₂ (Indtc) ₂ SO ₄]	0.577	0.378	0.5	Neutral
12	[Ni(SCH)(Indtc)]	0.577	0.378	0.5	Basic
13	[Ni ₂ (SCH ₂) ₂ (Pyrdtc) ₂ (Ac) ₂]	0.652	0.330	0.5	Neutral
14	[Ni(SCH)(Pyrdtc)]	0.652	0.330	0.5	Basic
15	[Ni(SCH ₂)(Indtc)Ac]	0.652	0.426	0.5	Neutral
16	[Ni(SCH)(Indtc)]	0.652	0.426	0.5	Basic

Preparative methods

Semicarbazone ligands have been prepared according to literature method (17). Dithiocarbamate ligands have been prepared according to literature method (18).

A general procedure has been adopted for the preparation of the complexes in neutral and basic medium.

In neutral medium

A solution of 0.5 gm (2×10^{-3} mole) of NiCl₂.6H₂O in 5 ml water has been added to the solution of gm SCH₂ (2×10^{-3}) and 2×10^{-3} mole of one of the dithiocarbamate ligands in a small amount of ethanol and water with heating until a clear solution has been resulted (the amounts in grams were listed in Table 1). The mixtures have been refluxed for three hours followed by evaporation to half their volumes then cooled. The products were separated by filtration, washed with petroleum ether and dried. The complexes of the other salts Ni(CH₃COO)₂.4H₂O or (Ni(NO₃)₂.6H₂O or NiSO₄.7H₂O) have been prepared by applying same procedure.

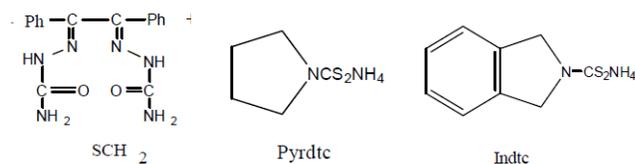


Figure (1): Structures of the ligands.

In basic medium

The complexes have been prepared by applying the same amounts used for neutral medium, and after mixing the metal salts with the ligands and heating, sodium hydroxide solution (1M) has been added until pH of the solutions have been adjusted to about 9-10. The mixtures have been allowed to stand, then the products were filtered off and washed with petroleum ether and dried.

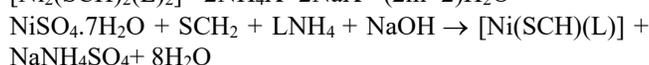
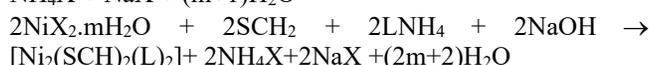
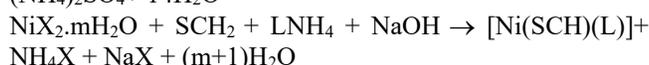
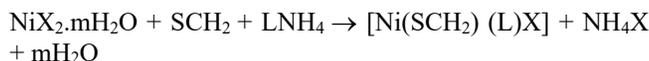
Analytical and physical measurements

Nickel contents have been determined by applying precipitation method after the decomposition of the complexes with concentrated nitric acid and also determined by atomic absorption spectroscopy (19). Refraction measurements have been carried out with Atago Illumination, Atago Co-LTD, Japan using 10⁻³ M dimethylformamide solution. Conductivity measurements have been carried out with an electrolytic conductivity measuring set LF-42 (apparatus A) and Multiline f/SET-2WTW Wissenschaft Technische Werkstatt 82362 Weiheim (apparatus B) using 10⁻³ M dimethylformamide solution at 25 °C. The infrared spectra has been recorded on FT-IR Bruker type Tensor 27 in the range 400-4000 and 200-4000 cm⁻¹ using KBr pellets. Electronic spectra has been recorded on Shimadzu UV-1650 PC UV-Visible Spectrophotometer for 10⁻³ 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-BM6.

Results and discussion

The reaction of nickel(II) salts, benzilbis (semicarbazone) and dithiocarbamate ligands in 1:1:1 and 2:2:2 molar ratio in both neutral and basic medium may be represented by the following equations:



(where X = Cl⁻ or NO₃⁻ or CH₃COO⁻; LNH₄ = Pyrdtc or Indtc ligands; SCH = deprotonated SCH₂ ligand; m = 4 or 6).

Table 2: Analytical and physical properties of the complexes.

No.	Color	M.P or d °c	* ^Λ _M		**M _{eff}	Ni% Calc. (Obs.)	Theo. M. Wt.	Ref x10 ⁻³ .
			app.A	app.B				
SCH ₂	White	212	—	—	—	—	324.38	-3.010
Pydtc	Pale yellow	150*	—	—	—	—	164.17	-3.010
Indtc	Pale yellow	216	—	—	—	—	212.21	+0.005
1	Pale green	190*	04.36	04.36	2.600	10.395 (11.640)	0564.76	-4.015
2	Yellowish green	280*	07.99	07.99	1.190	11.112 (11.050)	1056.52	-4.015
3	Yellowish orange	165*	14.54	13.81	2.411	09.581 (09.571)	0612.80	-4.015
4	Yellowish green	210*	22.53	21.80	2.343	10.189 (10.180)	0576.23	-4.015
5	Pale green	170*	19.62	18.90	2.392	08.788 (08.781)	0591.26	-5.020
6	Pale green	280*	14.54	14.54	1.031	11.112 (11.710)	1056.52	-4.015
7	Yellowish green	235*	10.90	11.63	2.880	09.183 (09.140)	0639.30	-2.005
8	Yellowish orange	210*	27.62	29.07	1.855	10.188 (09.710)	1152.46	-5.020
9	Bage	205*	18.17	08.72	2.707	09.387 (09.389)	1154.47	-4.015
10	Bage	220*	05.81	02.91	2.611	11.112 (09.910)	0528.26	-3.010
11	Bage	260*	12.36	13.81	1.982	09.581 (09.571)	1250.55	-4.015
12	Bage	225*	05.09	05.81	2.542	10.189 (10.180)	0576.23	-3.010
13	Pale green	200*	13.08	06.54	1.812	09.980 (10.440)	1176.52	-3.010
14	Yellowish green	220*	10.90	03.27	2.049	11.112 (09.950)	0528.26	+4.015
15	Bage	250*	03.63	04.51	2.982	09.226 (08.420)	0636.30	-4.015
16	Bage	205*	09.47	09.47	2.669	10.189 (10.175)	0576.23	-4.015

Λ_M: Molar conductivities in Ω⁻¹ cm² mol⁻¹; **μ_{eff}: Magnetic moment in Bohr Magnetons; d=decomposition points; app=apparatus.

The resulted complexes were color-ed solid, moderately soluble in ethanol, soluble in dimethylformamide and dimethylsulfoxide. Elemental analyses revealed that the complexes have the compositions $[\text{Ni}(\text{SCH})(\text{L})_n\text{X}_n]$ and $[\text{Ni}_n(\text{SCH})_n(\text{L})_n]$. The molar conductivities (\wedge_M) of the complexes in 10^{-3} M dimethylformamide are determined, the values shown in Table-2 approached those expected for non electrolytes (20). The magnetic moments of the complexes calculated from the corrected magnetic susceptibilities determined at room temperature are shown in Table-2. The μ_{eff} values reported for the complexes (1.031-1.982 and 2.049-2.982 B.M.) supported the monomeric or dimeric structures indicating octahedral geometry around the metal ions (21). Refraction measurement (Table 2) of the complexes were found to be either positive or negative values (22). The molar refraction is an additive and constitutive property. It has been used to construct the correct structure of the compound (23).

The infrared spectra of semicarba- zone ligands (Table 3) showed a strong band at 1688 cm^{-1} attributed to the C=O group (2,16,24) shifted towards a lower frequency on coordination in neutral medium, indicating the formation of a chelation between the oxygen of the C=O group and the metal ion (2,24). Mean- while, in basic medium, this band was disappeared in the complexes and a new band has been observed at $1217\text{-}1251 \text{ cm}^{-1}$ due to C-O group, thereby establishing coordination of the ligand through the enolic oxygen atom (3,24). The next strong band at 1575 cm^{-1} attributed to C=N group (24) shifted towards a lower frequency on coordination due to the decrease of the bond order as a result of metal nitrogen bond formation (3,24). The appearance of strong bands at $1630\text{-}1635 \text{ cm}^{-1}$ and $1580\text{-}1585 \text{ cm}^{-1}$ attributed to $\nu_{(\text{C}=\text{N})} + \nu_{(\text{O}-\text{C}=\text{N})}$ and azine chromophore $\nu_{(\text{C}=\text{N}-\text{N}=\text{C})}$, respectively, supported the formation of enolic structure in basic medium (2,3,24). The other band at 3473 cm^{-1} due to NH group remained unaltered in the complexes prepared in neutral medium indicating that there is no coordination through the NH group (3,24). Whereas in basic medium, this band was disappeared due to the enolic form. The other bands at 1450.00 cm^{-1} attributed to δ_{NH_2} (2,24) remained unaltered on complexation indicating that there is no coordination through this group and the metal ion (2,3,24).

The infrared spectra of dithiocar- bamate ligands (Table 3) showed band at $1322\text{-}1325 \text{ cm}^{-1}$ assigned to C=S group shifted towards a lower frequency on coordination (24,25). The other band observed at $1212\text{-}1217 \text{ cm}^{-1}$ due to C-S group shifted towards a lower frequency on complexation indicating the formation of a chelation between the sulfur atom and the metal ion (24,25).

On the other hand the spectra of the complexes 5 and 7 showed bands at $1450\text{-}1486 \text{ cm}^{-1}$, $1355\text{-}1371 \text{ cm}^{-1}$ and 946 cm^{-1} due to $\nu_{\text{S}(\text{NO}_3)}$, $\nu_{\text{as}(\text{NO}_3)}$ and ν_{NO} (ν_2 , ν_1 , ν_5), respectively (24). The difference between ν_1, ν_5 equal to 115 cm^{-1} which

supported the bonding of nitrate group as mono- dentate ligand through the oxygen atom. The spectra of the complexes 1 and 3 showed bands at $290\text{-}300 \text{ cm}^{-1}$ due to $\nu_{\text{M}-\text{Cl}}$. The spectra of the complexes 9 and 11 showed bands at $1125\text{-}1180 \text{ cm}^{-1}$, $1068\text{-}1077 \text{ cm}^{-1}$, $1005\text{-}1025 \text{ cm}^{-1}$ and 946 cm^{-1} due to ν_{SO_4} indicating the monodentate coordination of sulfate group to the metal ion^[28]. The spectra of the complexes 13 and 15 showed two bands at $1535\text{-}1540 \text{ cm}^{-1}$ and $1365\text{-}1370 \text{ cm}^{-1}$ attributed to $\nu_{\text{COO}(\text{s})}$ and $\nu_{\text{COO}(\text{as})}$, respectively. The presence of these two bands supported the coordination of the acetate group to the metal ion through one oxygen atom {i.e. the acetate group act as monodentate ligand} (24). Moreover the spectra of all the complexes showed new bands at $450\text{-}500 \text{ cm}^{-1}$, $417\text{-}420$ and $525\text{-}579 \text{ cm}^{-1}$ due to $\nu_{\text{M}-\text{N}}$, $\nu_{\text{M}-\text{S}}$ and $\nu_{\text{M}-\text{O}}$, respectively (24,25). The presence of these bands supported the formation of the complexes under inves- tigation.

The electronic spectra of the Ni (II) complexes (Table 4) showed absorption bands at $7212.72\text{-}9608.28 \text{ cm}^{-1}$ (ν_1 calculated (26)), $15625.00\text{-}18867.92 \text{ cm}^{-1}$ (ν_2) and $21097.04\text{-}27247.95 \text{ cm}^{-1}$ (ν_3) attributed to the three 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, which were expected for d^8 system having high spin octahedral geometries (26). The ligand field parameter B {Racah parameter (interelectronic repul- sion)}, the crystal field parameter Dq and the ligand field splitting energy (10Dq) have been calculated (26). The values of β {nephelauxetic ratio ($\beta=B'/B$)} has been determined. The apparent value of B' was always smaller than that of the free ion (B of free nickel ion=1084). The phenomenon is known as the nephelauxetic effect and was attributed to delocalization of the metal electrons over molecular orbitals that encompass not only the metal but the ligands as well. As a result of this delocalization or (cloud expanding) the average interelectronic repulsion was reduced and B' was smaller. The values of β values of the complexes were between 0.791-1.001 indicating the covalent character of the bond concerned. The values of Dq/B indicated that the complexes had octahedral geometries of all the complexes (26).

Conclusions

This work in fact is a continuation of our studies including mixed ligand complexes. In this work some observations have been achieved that lead to establish the SCH₂ ligand acted as tetradentate or tridentate chelating ligands joint to nickel (II) ion through the nitrogen and oxygen atoms. This ligand acted as neutral molecule in the complexes prepared in neutral medium, whereas in basic medium it acted as anion (-I, or -2) due to the deprotonation process that took place in enol form of this ligand. The ligands Pyrdtc and Indtc acted as anion (-1) joint to metal ion through sulfur atom, they acted as either monodentate

or bidentate chelating ligands. Chloride ion, nitrate ion, acetate ion and sulfate ion acted as mono-dentate ligands in the complexes prepared in neutral medium. Nickel (II) ion

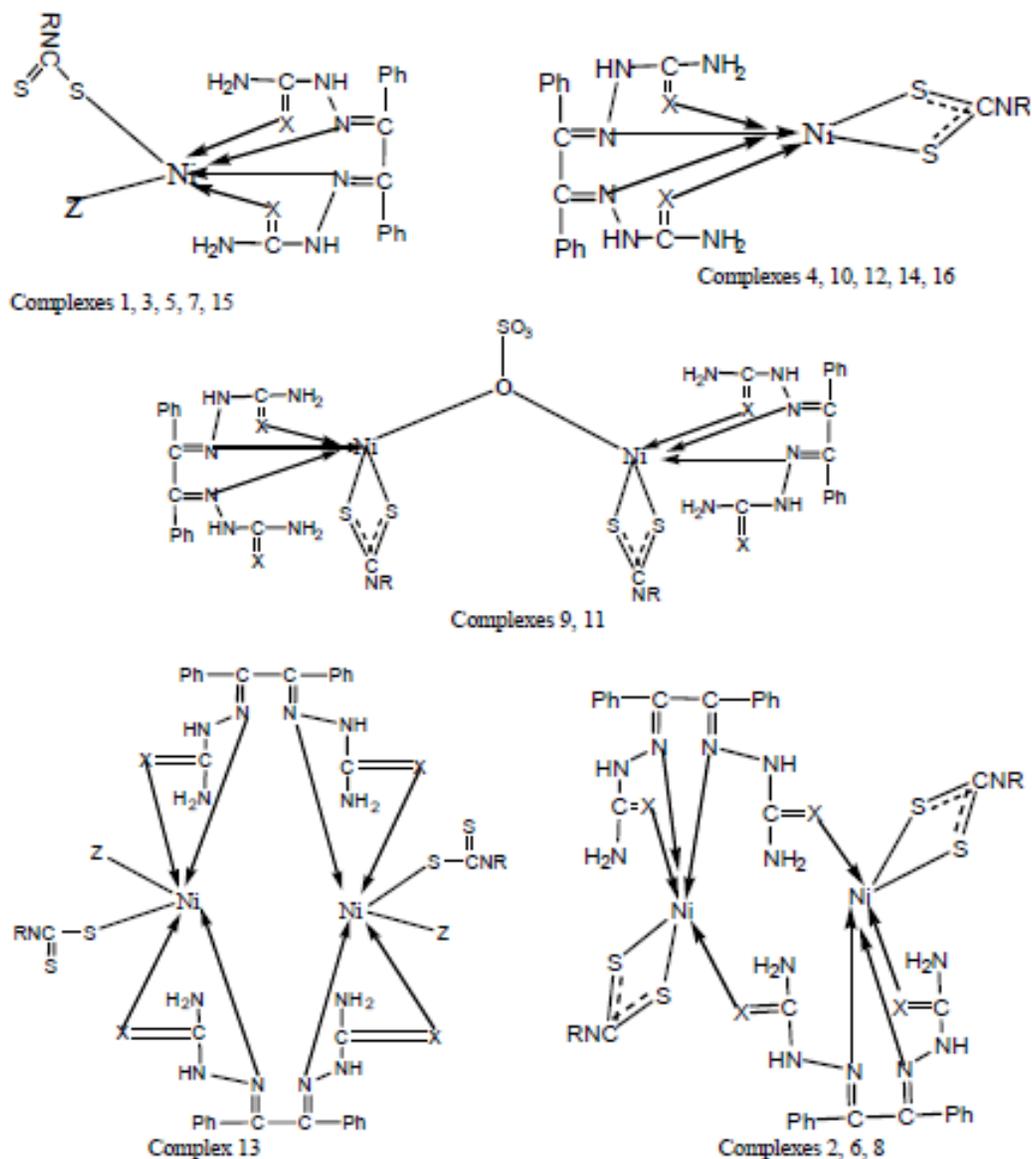
had probably hexa-coordinated, leading to high spin octahedral geometry (Figure 2).

Table 3: IR spectra of complexes (values in cm^{-1}).

No.	$\nu_{\text{C=N}}$	$\nu_{\text{C=S}}$	$\nu_{\text{C-S}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C-O}}$	ν_{OH}	$\nu_{\text{M-N}}$	$\nu_{\text{M-S}}$	$\nu_{\text{M-O}}$	Other bands
SCH ₂	1575	—	—	1688	—	3213	—	—	—	—
Pyrdtc	—	1325	1211	—	—	—	—	—	—	—
Indtc	—	1322	1217	—	—	—	—	—	—	—
1	1509	1164, 1002	946	1565	—	—	500	417	550	$\nu_{\text{M-Cl}}$ 290
2	1510	1060, 1010	945	—	1217	3200	450	418	550	—
3	1510	1078, 1024	933	1560	—	—	454	420	549	$\nu_{\text{M-Cl}}$ 300
4	1509	1138, 1025	934	—	1218	3250	454	420	538	—
5	1509	1164, 1025	911	1561	—	—	450	417	526	ν_{NO} 1450, 1335, 946
6	1508	1074, 998	945	—	1250	3220	454	417	540	—
7	1509	1155, 1020	934	1561	—	—	454	418	540	ν_{NO} 1486, 1371
8	1509	1079, 1020	934	—	1250	3200	450	420	530	—
9	1509	1163, 1025	914	1560	—	—	456	420	525	ν_{SO_4} 1180, 1077, 1025, 946
10	1510	1074	945	—	1250	3220	450	418	543	—
11	1510	1079, 1020	999	1565	—	—	450	420	540	ν_{SO_4} 1125, 1068, 1005
12	1510	1104, 1015	915	—	1250	3200	454	420	540	—
13	1510	1163, 1020	1000	1559	—	—	456	418	579	ν_{Ac} 1370, 1540
14	1509	1075, 1026	945	—	1251	3286	451	420	537	—
15	1514	1079, 1020	910	1565	—	—	500	420	550	ν_{Ac} 1365, 1535
16	510	137, 025	933	—	1218	3200	454	420	539	—

Table 4: Electronic spectral data of some complexes.

No.	$\nu_1 \text{ cm}^{-1}$	$\nu_2 \text{ cm}^{-1}$	$\nu_3 \text{ cm}^{-1}$	C.T cm^{-1}	B	10Dq	Dq/B	β	C.F.S.E
1	7226.27	15723.27	20833.33	30674.84	903.28	7226.30	0.80	0.833	8671.524
2	7212.72	15723.27	21739.13	31055.90	901.59	7212.72	0.80	0.832	8655.264
3	9187.31	16077.17	22935.77	29940.11	1080.9	9187.31	0.85	0.997	11024.77
4	8286.04	18867.92	22935.77	29940.11	920.67	8286.04	0.90	0.849	9943.248
5	9225.02	15625.00	26595.74	30120.48	1085.3	9225.02	0.85	1.001	11070.24
6	9608.29	15723.27	26595.74	31055.90	1011.4	9608.29	0.90	0.933	11529.95
7	7609.74	15723.27	22935.77	30120.48	951.22	7609.74	0.80	0.878	30120.48
8	7609.74	16025.64	22935.77	29857.90	951.22	7609.74	0.80	0.878	9131.688
9	8110.32	15723.27	21097.04	31250.00	1013.8	8110.32	0.80	0.935	9732.384
10	7286.99	15723.27	26595.74	31250.00	857.29	7286.99	0.85	0.791	8744.388
11	9187.28	17141.83	22935.77	29940.11	1080.9	9187.28	0.85	0.997	11024.73
12	7955.52	15772.87	22935.77	33783.78	935.99	7955.52	0.85	0.864	9546.624
13	7837.82	15723.27	27247.95	31055.90	922.10	7837.82	0.85	0.851	9405.379
14	9608.29	15723.27	26595.74	31055.90	1011.4	9608.29	0.90	0.933	11529.95
15	9187.28	17141.83	22935.77	30120.48	1080.9	9187.28	0.85	0.997	11024.73
16	8286.04	18867.92	22935.77	30120.48	920.67	8286.04	0.90	0.849	9943.248



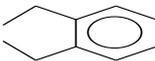
Where Z= Cl⁻, NO₃⁻, CH₃COO⁻; R =  or 

Figure (2): Proposed structures of the complexes.

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