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SYNTHESIS AND STRUCTURAL,SPECTROSCOPIC STUDY OF NOVEL BIDENTATE LIGANDS(1,3,4-THIADIAZOLE DERIVATIVES) AND THEIR COMPLEXES WITH Ni(II), pd(II) and pt(IV)

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Abstract:

This work reports the synthesis and characterization of two new ligands

5-(p-phenoxy)-1,3,4-thiadiazole - 2- thioacetic acid(HL) and 5-(p-toluyl)-1,3,4-thiadiazole-2-thioacetic acid(HL^-). Also complexes of two new ligands (HL) and (HL^-) with $Ni^{(II)}$, $pd^{(II)}$ and $pt^{(IV)}$ in formulas $[Ni(L)_2].2H_2O$, $[Ni(L^-)_2].H_2O$,$[pd(L)_2]$, $[pd(L^-)_2]$,$[pt(L)_2(H_2O)_2]Cl_2$ and $[pt(L^-)_2(H_2O)_2]Cl_2.3H_2O$ were prepared . All compounds have been characterized by spectroscopic methods [FT-IR,UV-VIS, Atomic absorption], microanalysis(C.H.N) along with conductivity measurements and magnetic susceptibility . From the above data, the proposed molecular structure for $Ni^{(II)}$ and $pd^{(II)}$ complexes are tetrahedral and square planar geometry respectively, while $pt^{(IV)}$ complexes are forming octahedral geometry.

Introduction :

There has been an extensive interest in the chemistry of thiadiozole derivatives which are formed by cyclization of semicarbazaide or thiosemicarbazide in presence of alkaline solution of carbondisulfide(1). The (-SH) group attached to a hetrocyclic nucleus may induce fungicial activity(2,3). Compounds containing acetyl or acetate groups in the position(2) of thiadiozole rings have been reported as irradiation, analytical agents(4-6).

The complexation properties of such compounds with various metal ions have also been investigated. The bidentate nature of such ligands reported to coordinate through sulfur and nitrogen atoms(7-9). Recently, we have been concered with the study of hetroaromatic system and their complexes(10,11) ,here we reported the synthesis and characterization of 5-(p-phenoxy)-1,3,4-thiadiazole-2-thioacetic acid and 5-(p-toluyl)-1,3,4-thiadiazole-2-thioacetic acid and their metal complexes with Ni(II), pd(II) and pt(IV) ions.

Experimental :

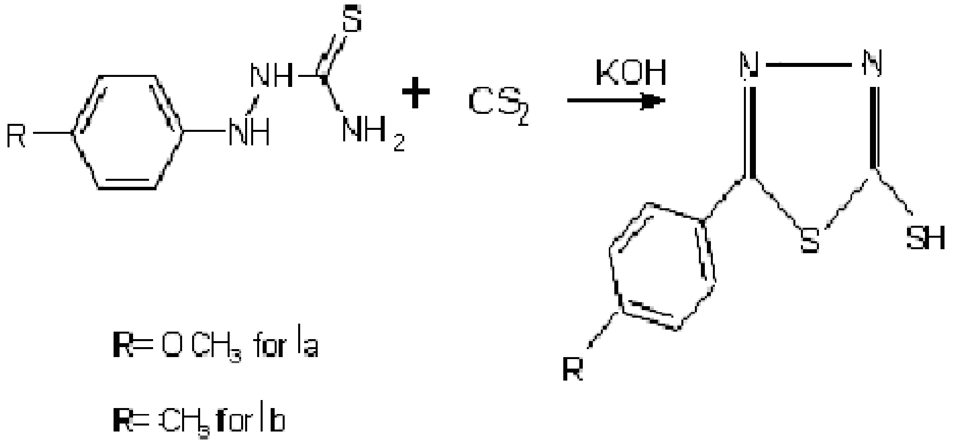
Materials , physical measurements and analysis:

All the chemicals were used as received of highest purity available . Melting points were recorded on Gallen Kamp melting point apparatus and were uncorrected .FT-IR spectra were recorded using FT-IR 8400 Shimadzu spectrophotometer in the range 4000-200cm^{-1}by using CsI disk. Electronic spectra were obtained by using UV-160 Shimadzu spectrophotometer at room temperature in the region 200-1000 nm for10^{-3}M solutions in DMF with 1.000±0.001cm matched quartz cell. While metal contents of the complexes were determined by AA680 G atomic absorption (AA) technique using a shimadzu AA 680 G atomic absorption spectrophotometer. Elemental microanalysis were performed by using C.H.N Elementary Analyzer of Perkin-Elmer-240B.Conductivity measurements were obtained by using (WTW) conductometer at 25C° for 10^{-3}M solutions of the samples in DMF solvent. Magnetic susceptibility measurements were obtained at 25C° on the solid state appling faradys, method using Bruker BM6 instrument.

Preparation of the compounds:

1-preparation of 5-(p-phenoxy)-1,3,4-thiadiazole-2-thiol(Ia) and 5-(p-toluyl)-1,3,4-thiadiazole-2-thiol(Ib):

They synthesised and purified according to the literature method(12) , see Scheme-1 :



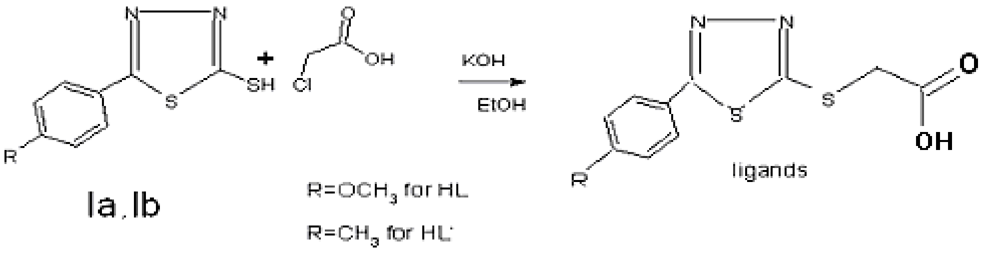
Scheme-1

2-preparation of ligand 5-(p-phenoxy)-1,3,4-thiadiazole-2-thioacetic acid(HL):

A mixture of (10mmole , 2.24g) from (Ia) and KOH (10mmole ,0.56g) in ethanol (50ml) was prepared and refluxed for 1hr. A solution of (10mmole, 0.95g) chloroacetic acid in 10ml ethanol was added dropwise with stirring , the mixture was refluxed for 3hrs., the compound wich precipitated , was filtered , washed several times with hot distilled water , petroleum ether and recrystallization from ethanol to afford bright yellow crystals , (sceme-2).

3-preparation of ligand 5-(p-toluyl)-1,3,4-thiadiazole-2-thioacetic acid(HL$^-$):

A similar procedure to that described for the ligand (HL) was used to prepare ligand (HL$^-$) but with (10mmole , 2.1g) from Ib inplace of (Ia) , scheme-2.



Scheme-2

4-preparation of complexes (C$_1$--------C$_6$):

C$_1$ complex [Ni(L)$_2$].2H$_2$O :

A (2.0mmole , 0.56g) of ligand (HL) dissolved in ethanol (40ml) was added to(1.0mmole, 0.238g) of NiCl$_2$. 6H$_2$O in(10ml) ethanol .The mixture was refluxed for a bout 2hrs. , the brown precipitate on adding sodium acetate as buffering agent , the isolated brown crystals were filtered off, washed several times with hot distilled water , ethanol dried under vacuum over anhydrous calcium chloride.

C_2 complex $[Ni(L^-)_2]. H_2O$:

The method used to prepare C_2 complex was analogous to the procedure given for the C_1 complex but with (2.0mmole , 0.53g) of(HL^-) instead of (HL), to give a brown precipitate which was filtered off, washed several times with hot distilled water, ethanol and dried under vacuum over anhydrous calcium chloride.

$[pd(L)_2]$ (C_3) and $[pd(L^-)_2]$ (C_4) complexes:

Asimilar procedure to that desirable for $C_1$and C_2 complexes was used to prepare C_3 and C_4 complexes respectively but with (1.0mmole, 0.3g) of Na_2pdCl_4 replace $NiCl_2.6H_2O$.The quantities of the other reagents were adjusted accordingly and an identical work-up procedure gave orange precipitate.

$[pt(L)_2(H_2O)_2]Cl_2$ (C_5) and $[pt(L^-)_2(H_2O)_2]Cl_2.3H_2O$ (C_6) complexes:

The method used to prepare C_5 and C_6 was analogues to the procedure given for $C_1$and C_2 complexes respectively but with (1.0mmole, 0.486g) of K_2ptCl_6 instead of $NiCl_2.6H_2O$, to give a green precipitate.

Results and discussion :

Elemental analysis :

The physical properties and the results of the elemental analysis of the ligands (HL and HL^-) and their complexes (C_1--------C_6) are listed in table-1. on the basis of elemental analysis data, the molecular formula of their complexes was assigned to be: $[Ni(L)_2].2H_2O$, $[Ni(L^-)_2]. H_2O$, $[pd(L)_2]$, $[pd(L^-)_2]$, $[pt(L)_2(H_2O)_2]Cl_2$, $[pt(L^-)_2(H_2O)_2]Cl_2.3H_2O$

The suggested molecular formula (fig.1) was also supported by spectral measurement as well as molar conductivity and magnetic moments.

Molar conductance:

The molar conductance of the prepared complexes(C_1------C_6) in DMF solvent in 10^{-3} M at 298° K (table-3) indicated no electrolytic nature for $Ni^{(II)}$ and $pd^{(II)}$ complexes (C_1-------C_4) , while indicating electrolytic nature with 2:1 ratio for $pt^{(IV)}$ complexes (C_5 and C_6)(13,14) .

Magnetic moment:

The measured magnetic moment (μeff.) for the prepared complexes (C_1-------C_6) are shown in table-3. Ni complexes (C_1 and C_2) exhibit magnetic moment 3.21 B.M and 3.18 B.M respectively which can be a normal value for high- spin $Ni^{(II)}$ complexes compared with that has been found in the literature(15).while the values of magnetic moment for $pd^{(II)}$ and $pt^{(IV)}$ complexes (C_3-----C_6) were found to be (0.42-0.00)B.M and (0.26-0.00)B.M respectively which are a good evidence for low –spin complexes(16) .

Infrared spectroscopic study:

The IR spectral data of two new ligands (HL and HL^-) and their complexes (C_1-------C_6) are summarized in table-2. these spectra are complicated owing to:

1- The IR spectral data of two new ligands (HL and HL^-) indicated the absence of SH stretching vibration at 2540cm^{-1} which has been observed in spectra of the starting materials (Ia , Ib), this indicates that the displacement of H for (SH) group by mean of ($-CH_2-COOH$).On the other hand two weak bands had been observed at 3040cm^{-1} and 2950cm^{-1} in the ligands spectra which are due toν(C-H) aromatic and aliphatic respectively(17) .

2- The spectra of ligands showed two bands ,the first at (1640, 1650)cm^{-1} for HL and HL^- respectively , due to $\nu_{asy}coo^-$ and the second at (1400, 1390)cm^{-1} for HLand HL^- respectively due to ν_{sy} coo^- . The bands $\nu_{asy}coo^-$ and ν_{sy} coo^- were shifted to a lower frequency in the IR spectra of their complexes(18). Also $\nu_{C=O}$ appeared at 1695$cm^{-1}$and 1700cm^{-1} in the spectra of HLand HL^- respectively , while in the complexes spectra these bands were shifted to lower frequency . The shift in the position of ν_{asy}coo$^-$, ν_{sy} coo$^-$ and $\nu_{C=O}$ indicated the coordination of metal ions Ni$^{(II)}$, pd$^{(II)}$ and pt$^{(IV)}$ with ligands via oxygen atom of carboxylato group(19) .

3- HLand HL$^-$ ligands spectra showed two bands at (1026-1030)cm^{-1} and (682-686)cm^{-1} are considered to be $\nu_{c\text{-}s}$ and $\nu_{c\text{-}s\text{-}c}$ respectively(20,21) , this two bands shifted to higher frequencies in the metal complexes spectra, this may refer to the linkage of metal ion with the sulfer atom of the side chain(-2-thioacetic acid) (22) .

4- A broad band was observed a round (3350-3440)cm^{-1} in the spectra of Ni$^{(II)}$ and pt$^{(IV)}$ complexes, assigned to $\nu_{O\text{-}H}$ and suggested the presence of H_2O in the crystal lattice of these complexes . But this band disappeared in IR spectra of pd$^{(II)}$ complexes, while in IR spectra of pt$^{(IV)}$ complexes, in addition of this band, a new band appeared a round 865cm^{-1} which due to coordinated H_2O molecule with pt$^{(IV)}$ (23,24) .

5- $\nu_{N\text{-}N}$ and $\nu_{C=N}$ in IR spectra of all complexes showed a little change in the position and intensity when they are comparison with that of free ligands , this indicates non involvement of C=N and N-N groups in the coordination(25) .

6- The above observation were further indicated by the appearance of new bands in IR spectra of all complexes at (415-440)cm^{-1} and (480-510)cm^{-1} due to $\nu_{M\text{-}S}$ *and* $\nu_{M\text{-}O}$ respectively(26) .

Electronic Spectroscopic Study:

The ligands:

The uv-vis spectral data for the ligands (HL, HL^-) (table-3) exhibit a high intense absorption peaks 250nm and 220nm respectively , which are attributed to electronic transition type ($\pi \rightarrow \pi^*$) , also the spectra displayed absorption peaks at 315nm and 295nm respectively , which are assigned to electronic transition type ($n \rightarrow \pi^*$)(27) .

The complexes:

The uv-vis spectral data for all complexes (C_1-------C_6) were summarised in table-3 , the uv-vis spectra of all complexes displayed a high intense two absorption peaks , the first at range (218-270) nm assigned to ligand field and the second at range(350-395)nm assigned to charge transfer transition(28).

Ni(II) complexes:

The electronic spectra of $C_1$and C_2 exhibit a new absorption peaks at 515nm and 520nm respectively which are attributed to (d-d) electronic transition type ($^3T_1 \rightarrow {}^3T_{1\,(P)}$) suggesting tetrahedral geometry about Ni(II) (29) .

pd(II) complexes :

The uv-vis spectra of C_3 and C_4 complexes appeared a new peaks at 532nm and 541nm respectively , assigned to (d-d) electronic transition type ($^1A_{1g} \rightarrow {}^1B_{1g}$) which is a good evidence for square planar structure of pd(II) complexes(29,30) .

pt(IV) complexes:

in the electronic spectra of C_5 and C_6 complexes a new two absorption peaks , the first at(450nm and

→ →

435nm) and the second at (560 nm and 575 nm) respectively which were attributed to (d-d) electronic transition type (${}^1A_{1g}$ ${}^1T_{2g}$) and (${}^1A_{1g}$ ${}^1T_{1g}$) respectively , these indicated octahedral geometry about pt$^{(IV)}$ ion(29,31) .

conclusion:

In conclusion ,our investigation this suggest that the ligands (HL, HL$^-$) behave on complexation as bidentate chelating agent coordinating via oxygen atom of carboxylato group and sulfer atom of the side chain (-2-thioacetic acid) of thiadiazol ring , forming tetrahedral , square planar geometry about Ni$^{(II)}$, pd$^{(II)}$ respectively (fig.1) and octahedral geometry about pt$^{(IV)}$ (fig.2) .

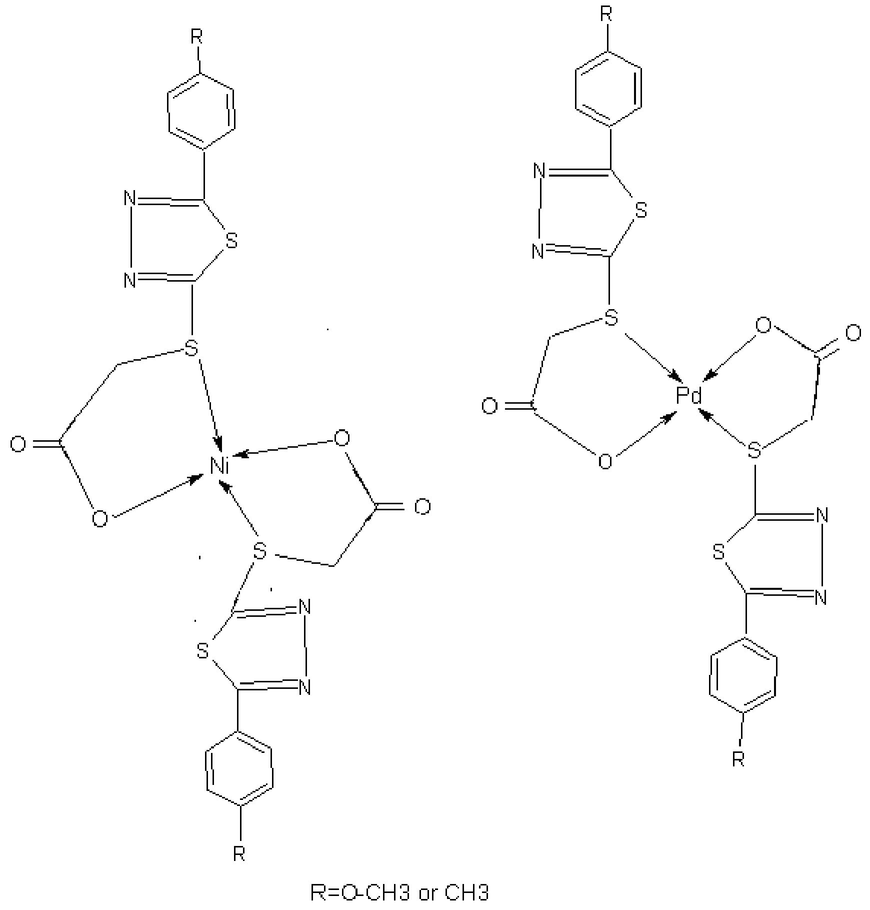
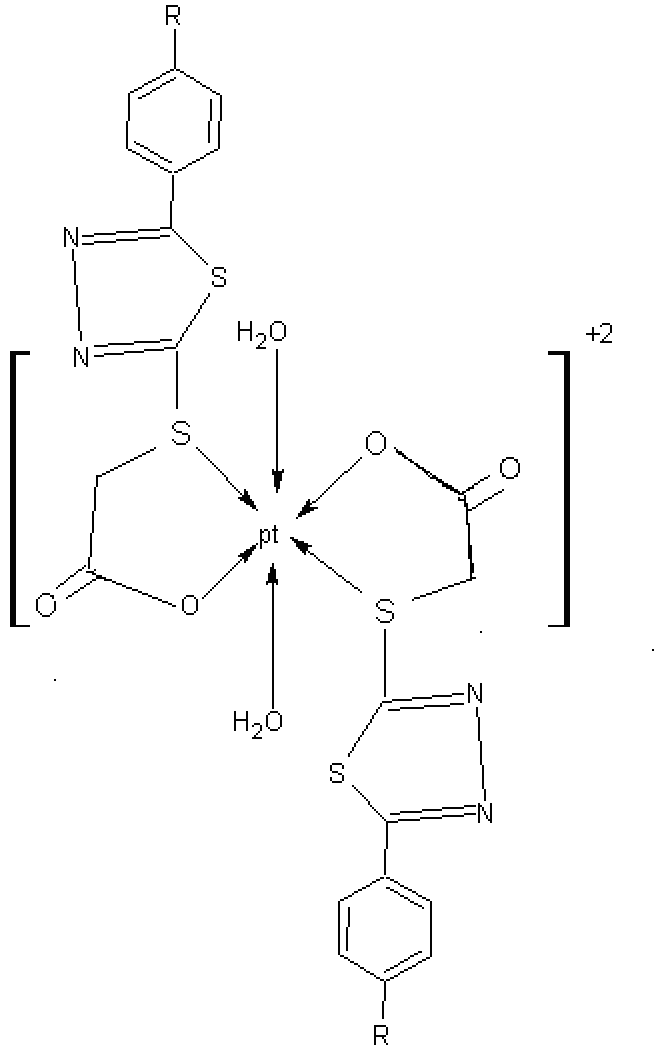


Fig.1: the suggested structures for Ni$^{(II)}$, pd$^{(II)}$ complexes



$R=OCH_3$ or CH_3

Fig.2 rhe suggested structure for pt(IV) complex

Table-1: Elemental analysis and physical data of prepared compounds

Symbol* of compounds	Formula	M.wt	colour yield%	M.p C°	. found% , (Calcu.)%			
					C	H	N	metal
HL	$C_{11}H_{10}N_2S_2O_3$	282	Yellow 86	162	45.71 (46.80)	3.01 (3.45)	9.20 (9.92)	-----
HL^-	$C_{11}H_{10}N_2S_2O_2$	266	Yellow 84	171	49.02 (49.62)	3.34 (3.75)	9.81 (10.52)	------
C_1	$[Ni(L)_2].2H_2O$	657	Brown 84	212	39.66 (40.18)	2.98 (3.34)	7.94 (8.52)	8.23 (8.98)
C_2	$[Ni(L^-)_2]\ H_2O$	607	Brown 82	213	42.96 (43.49)	2.94 (3.29)	9.00 (9.22)	9.22 (9.71)
C_3	$[pd\ (L)_2]$	668	Orange 80	250	39.14 (39.52)	2.42 (2.69)	7.90 (8.38)	15.16 (15.86)
C_4	$[pd(\ L')_2]$	636	Orange 81	240	40.98 (41.50)	2.54 (2.83)	8.10 (8.80)	15.91 (16.66)
C_5	$[pt(L)_2(H_2O)_2]Cl_2$	864	Green 90	260	30.12 (30.55)	2.02 (2.54)	5.84 (6.48)	21.96 (22.56)
C_6	$[pt(L')_2\ (H_2O)_2]Cl_2.3H_2O$	886	Green 84	270	29.24 (29.79)	2.82 (3.16)	5.81 (6.32)	21.61 (22.00)

* $L = C_{11}H_9N_2S_2O_3$
$L^- = C_{11}H_9N_2S_2O_2$

Table-2:Characteristic vibrational frequencies(cm^{-1})located in the I.R spectra for the prepared compounds:

Symbol of compound	νC=O	νasy.COO$^-$	ν C-S	ν C-S-C	ν C=N	ν M-O	ν M-S
	νO-H	νsy .COO$^-$			νN-N		
HL	1695(S) 3000(b)	1640(vs) 1400(vs)	1026(s)	682(ms)	1600(s) 980(m)	—	—
HL$^-$	1700(s) 2990(b)	1650(vs) 1390(vs)	1030(s)	686(ms)	1613(s) 960(m)	—	—
C_1	1685(s) 3350(b)	1615(ms) 1342(ms)	1048(ms)	696(s)	1600(s) 972(w)	520(m)	413(w)
C_2	1692(s) 3382(b)	1620(ms) 1310(ws)	1052(s)	708(ms)	1590(s) 962(w)	480(m)	420(w)
C_3	1686(s) —	1610(vs) 1332(ws)	1046(s)	712(ms)	1595(s) 970(w)	470(m)	395(w)
C_4	1695(s) —	1614(ms) 1312(ms)	1044(ms)	732(ms)	1599(s) 962(m)	460(w)	389(w)
C_5	1678(s) 3438(b)	1612(ms) 1360(ms)	1050(ms)	724(ms)	1595(s) 972(m)	515(m)	410(w)
C_6	1688(s) 3440 (b)	1624(vs) 1328(ws)	1054(s)	738(s)	1590(s) 974(w)	500(w)	400(w)

S=sharp , vs= very sharp , b=broad , w=weak , ms=middle sharp , ws=weak sharp, m= middle

Table-3:Electronic spectral data, molar conductance(M.C)(ohm^{-1}. Cm^{2} .mol^{-1}) and magnetic moment (B.M) for prepared compounds:

Symbol of compounds	λ (nm^{-1})	$\bar{\nu}$ cm^{-1}	(ϵ_{max}) M^{-1}.Cm^{-1}	Assignment	M.C	$\mu_{eff.}$	Suggested structure
HL	250 315	40000 31746	926 1108	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	----	---	------
HL^-	220 295	45455 33898	912 1026	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	----	----	-----
C_1	260 360 515	38462 27778 19417	846 1232 80	Ligand feild Charge transfer $^3T_1 \rightarrow {}^3T_1$ (p)	25	3.21	tetrahedral
C_2	260 380 520	38462 26318 19231	1021 1162 40	Ligand feild Charge transfer $^3T_1 \rightarrow {}^3T_1$(p)	30	3.18	tetrahedral
C_3	240 370 532	41667 27027 18797	1048 1142 42	Ligand feild Charge transfer $^1A_1g \rightarrow {}^1B_1g$	40	0.42	Square planar
C_4	265 395 541	37736 25316 18484	986 1182 38	Ligand feild Charge transfer $^1A_1g \rightarrow {}^1B_1g$	35	0.00	Square planar
C_5	218 350 450 560	45872 28571 22222 17857	948 1200 28 32	Ligand feild Charge transfer $^1A_1g \rightarrow {}^1T_2g$ $^1A_1g \rightarrow {}^1T_1g$	140	0.26	octahedral
C_6	260 365 435 575	38462 27397 22989 17391	1056 1188 39 42	Ligand feild Charge transfer $^1A_1g \rightarrow {}^1T_2g$ $^1A_1g \rightarrow {}^1T_1g$	180	0.00	octahedral

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تحضير ودراسة تركيبية وطيفية لليكاندات ثنائية السن جديدة(مشتقات1, 3, 4- ثايادايازول) ومعقداتها مع النيكل(II),البلاديوم(II) والبلاتين(IV)

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الخلاصة :

تضمن هذا البحث تحضير الليكاندين 5- (بارا-فينوكسي)-4،3,1 ثايودايوزول-2-ثايوحامض الخليك(HL) و 5 –(باراتوليـل)-4,3,1-ثايـادايوزول-2-ثايوحـامض الخليـك (HL^-) كـذلك تـم تحضير معقداتهما مع الايونات : النيكل(II),البلاديوم (II) والبلاتين(IV) .شخصت جميع المركبات المحضرة بالطرائق الطيفية (الاشعة تحت الحمراء, الاشعة فوق البنفسجية –المرئية), التحليل الكمي الدقيق للعناصر والتوصيلية المولارية فضلا عن قياس الحساسية المغناطيسية وتعيين نسبة الفلز بوساطة طيف الامتصاص الذري اللهبي للمعقدات المحضرة فقط.

من النتائج التي تم الحصول عليهامن التقنيات السابقة فان الشكل الفراغي المقترح هو رباعي السطوح لمعقدات النيكل(II) وشكل المربع المستوي لمعقدات البلاديوم(II) بينما اتخذت معقدات البلاتين(IV) الشكل ثماني السطوح.