# Mixed Ligand Complexes of quinoline-2-carboxylic acid and 4,4<sup>/-</sup>dimethyl-2,2<sup>/</sup>-bipyridyl with V(IV),Cr(III), Rh(III), Cd(II) and Pt(IV)

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### Abstract:

A new mixed ligand complexes were prepared by reaction of quinoline -2-carboxylic acid (L1) and 4,4′dimethyl-2,2′-bipyridyl (L2) with V(IV),Cr(III), Rh(III), Cd(II) and Pt(IV) ions. These complexes were isolated and characterized by (FT-IR) and (UV-Vis) spectroscopy, elemental analysis, flame atomic absorption technique, thermogravimetric analysis, in addition to magnetic susceptibility and conductivity measurements. Most complexes were mononuclear and with octahedral geometry, except Cd (II) with tetrahedral geometry, and V (IV) with square pyramidal geometry. A theoretical treatment of the ligands and the prepared complexes in gas phase was done using two programs Hyperchem.8 and Gaussian program (GaussView Currently Available Versions (5.0.9) along with Gaussian 09 which is the latest in the Gaussian series of programs).

#### Key words: quinoline-2-carboxylic acid, bipyridyl

### **Introduction:**

Quinoline-2-carboxylic acid a biological compound involved in the metabolism of tryptophan. It is a strong chelator providing the donor set similar to that responsible for binding metal ion in pyrroloquinilnequinone (PQQ) cofactor of quinoprotein family [1].

2,2'-bipyridine is known to form stable chelate complexes even with low valent transition metal ions[2]. It has also become a very popular ligand in supramolecular and macromolecular chemistry[3].

The carboxylic acid derivatives of N-heterocycles and N-oxide heterocycles have been used extensively as ligands. Many simple and mixed ligand complexes of various pyridine carboxylic acids with several

divalent transition metal ions[4] and trivalent rare-earth metal ions[5] having nitrogen-oxygen and oxygenoxygen coordination have been investigated thoroughly. A quinoline-2-carboxylic acid and co-ligand 4,4dimethyl-2,2'-bipyridyl not received any attention in spite of well-defined applications of both the molecules. Hence, it was thought that it is worthwhile to study the complexation of quinoline- 2-carboxylic acid and 4,4 dimethyl-2,2 - bipyridyl with а series of transition metal as mixed ligand complexes.

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### Materials and Methods:

### 1. Physical measurements and analysis

Melting points were recorded on Gallen Kamp melting point apparatus and were uncorrected. FT-IR spectra were recorded as CsI discs using FT-IR.3800 Shimadzu in the range of (4000-200 cm<sup>-1</sup>). Electronic spectra were obtained using UV-1650 PC Shimadzu Spectrophotometer at room solvent. temperature in DMF Conductivity was measured bv capacitor analyzer in DMF solution  $(10^{-3})$ M) at room temperature. Elemental analysis was performed by using EM-017 mth instrument. Magnetic susceptibility measurements were obtained at 25 °C Magnetic Susceptibility Balance of Johnson catalytic matty system division, England. The metal percent of the complexes were determined by using GBS-933 Flam plus Atomic Absorption Spectrophotometer. The thermal analysis of all the prepared complexes were carried out by Perkin Elmer TGA 4000 instrument in heat ranges from 30 to 900 at heating rate 20 °C/min

## 2. General method for preparation of the Complexes

solution Α containing (0.173 gm, 1 mmole)of the ligand quinoline-2-carboxylic acid in 10 ml ethanol, and (0.186gm,1mmole) of the ligand 4,4'-dimethyl-2,2'- bipyridyl in 5 ml ethanol were added to a warm solution of each of the metal salts (1mmole) of, [(0.182gm)VOSO<sub>4</sub>.H<sub>2</sub>O, (0.268 gm) CrCl<sub>3</sub>.3H<sub>2</sub>O, (0.227 gm)RhCl<sub>3</sub>.H<sub>2</sub>O, (0.308gm)Cd(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O (0.517 gm) $H_2PtCl_6.6H_2O$ and respectively, in 5 ml of absolute ethanol in molar ratio 1:1:1. The mixture was heated and refluxed with stirring for (3-4) hrs. The color precipitated was filtered, washed several times with ethanol, and finally with ether, and dried under vacuum.

#### **Results and Discussion:**

Some physical properties and data of the ligands (L1) and (L2) with their metal complexes were given in **Table** (1). The molar conductivity in DMF solvent indicated the electrolytic behavior of all complexes.

 Table (1): Some physical and analytical data for the ligands and their metal complexes

Comm	Color	M.P	Viald0/	M.Wt	Elemental analysis Found (Calc			<b>:.</b> )	
Comp.	Color	<i><sup>о</sup>С</i>	1 leta %	g.mol <sup>-1</sup>	С	H	N	S	М
L1	White	154- 156		173.17					
L2	White	172- 174		184.64					
VL <sub>1</sub> L <sub>2</sub>	Olive	340d	68.15	556.67	46.82 (47.43)	3.93 (4.13)	8.02 (7.54)	6.05 (5.75)	12.36 (12.02)
CrL1L2	Green	348d	83.31	533.66	50.16 (49.47)	5.09 (4.49)	8.33 (7.87)		10.00 (9.74)
RhL <sub>1</sub> L <sub>2</sub>	pale Brown	238	90.17	566.53	45.70 (46.60)	2.99 (3.88)	6.52 (7.41)		17.98 (18.16)
CdL <sub>1</sub> L <sub>2</sub>	Off White	162	92.05	549.15	49.39 (48.07)	2.89 (3.64)	10.00 (10.19)		20.86 (20.47)
PtL <sub>1</sub> L <sub>2</sub>	Dark brown	204	85.76	676.25	40.02 (39.04)	3.31 (2.95)	7.10 (6.21)		27.93 (28.84)

d=decomposition degree

### **1. Infrared spectral studies**

Table (2)shows tentative assignments of the IR peaks for the free 2-qinoline carboxylic acid with some metals together with the co-ligand 4,4'dimethyl-2,2' bipyridyl. The (L1) may coordinate with metal ions through monodentate, bidentate chelating and bridging according to Nakamoto[6], Deacon & Phillips[7]. The infrared spectrum of the solid state quinoline-2carboxylic acid, Figure (1), indicates that it exists in two tautomeric forms at the same time, as a neutral molecule (quinoline-2-carboxylic acid) and as a zwitter ion (quinolinium-2carboxylate) [8].In order to predict the coordination mode of metal ions with qinoline-2-carboxylic acid. we compared the difference of the value between the asymmetric and symmetric stretching of  $COO^{-}$ frequencies ( $\Delta v = \mathbf{v}_{sym} COO^{-} - \mathbf{v}_{asym}$ COO<sup>-</sup>) of all complexes, **Table (2)**.

The difference between  $v_{sym}COO$ and  $v_{asym}COO$ ,  $\Delta v$  values, for each of the prepared complexes, indicating the monodentate coordination of the carboxylate group, other very weak intra- and intermolecular interactions can't be excluded, and the bending of  $\delta$  (C=N) in all complexes were shifted and appeared at the range (408-393) cm<sup>-1</sup> with its maximum at (405) cm<sup>-1</sup> [9],this indicates that the nitrogen atom of quinoline-2-carboxylic acid also had coordinated with metal ions. Furthermore, new bands attributed to v (M-O) and v (M-N) which appeared at (570-520) cm<sup>-1</sup> and (420-489) cm<sup>-1</sup> respectively in all complexes confirmed, that L1 with the metal ions coordinated through oxygen atom of carboxylate group and nitrogen atom [6]. The of 4,4'-dimethyl-2,2'coordination bipyridyl is indicated by the positive shift of v(C=C) and v(C=N) ring stretching frequencies and the presence of their deformation modes at 1168 and 1936cm<sup>-1</sup> .The position of the bands found in the spectrum of  $4.4^{\prime}$ -dimethyl-2,2' bipyridyl, Figure (2), was completely changed in the spectra of the complexes (as a co-ligand) and new bands appeared at ~1560-1590 cm<sup>-1</sup> confirming the coordination nature of this ligand, the 424 cm<sup>-1</sup> band of 4,4'dimethyl-2,2' bipyridyl (C-C out of plane bending) was shifted to higher frequency and splitted into two components in the complexes which again confirm the coordination of this ligand through two nitrogen atoms [8], Figure (3). An additional band in the  $cm^{-1}$ range (260-270) was also observed in all complexes indicating nitrogen of the the co-ligand coordination with metal ion [10]. The presence of water molecules caused the appearance of broad O-H stretching bands in the region of 3473-3417 cm<sup>4</sup> in most IR spectra of the complexes [11].



Fig. (1): FTIR Spectrum of Quinoline-2-carboxylic acid



Fig. (2): FTIR Spectrum of 4,4<sup>7</sup>-dimethyl-2,2<sup>7</sup> bipyridyl



Fig. (3): FTIR Spectrum of Vanadium (IV) Complex

<b>Table (2):</b>	<b>Main FTIR</b>	bands in (cm <sup>-</sup>	<sup>1</sup> ) observed i	n the	spectra	of mixed	ligands
metal ions	complexes						

Comp.	v <sub>asy</sub> .COO <sup>-</sup>	v <sub>sym</sub> .COO <sup>-</sup>	vC=O	vC=N+vC=C	vM-N	vM-O	vM-N (bipy)	Others
L1	1580	1390	1697	1604,1535,1508, 1473				
L2				1604,1519,1481, 1450				
VL1L2	1570	1365	1693	1608, 1535, 1512.1465	489	524	260	$\begin{array}{c} \nu OH{=}3460 \\ \nu (V{=}O){=}975.98 \\ \nu (SO_4){=}1176.58 \\ \delta H_2 O{=}871.8 \end{array}$
CrL1L2	1596	1384		1612,1566, 1512,1465	466	532	262	νOH=3414.00 δH <sub>2</sub> O=860.25
RhL1L2	1595	1385		1608,1558,1520, 1473	474	528	262	vOH=3437 δH <sub>2</sub> O=879 vRh-Cl=308
CdL1L2	1597	1393		1612,1562,1512, 1496	489	520	262	vOH=3460
PtL1L2	1597	1396		1608,1539,1512, 1481,1458	455	528	262	vOH=3464 vPt-Cl=312

### 2. Magnetic properties

The magnetic moment ( $\mu$ eff ) for the V (IV) complex was found to be (1.92) B.M., this higher value may be due to higher orbital contribution. For Cr (III) complex it was recorded at (3.12) B.M., while the ( $\mu$ eff ) of the Pt (IV) complex was (0.572) B.M., this value lie within the expected value which agrees with a lot of results obtained for the octahedral Cr(III)[12] and Pt(IV) [12] complexes. On the other hand, Rh (III), Cd (II), complexes were diamagnetic, **Table (3)**.

### **3.** The Electronic spectra

#### 3.1. Electronic specter of ligands

The electronic spectrum of L1,**Figure(4)** exhibits four main bands appeared at 45045 cm<sup>-1</sup>, 41666 cm<sup>-1</sup>, 34843 cm<sup>-1</sup>, and a shoulder band at 30487 cm<sup>-1</sup> due to  $(\pi \rightarrow \pi^*)$ ,  $(n \rightarrow \pi^*)$ ,  $(n \rightarrow \pi^*)$  $(n \rightarrow \pi^*)$ transition and respectively [13]. While the Electronic spectrum of L2, Figure(5) exhibit two main bands; the first appeared at cm<sup>-1</sup> due to interaligand 41152 transition, the  $(\pi \rightarrow \pi^*)$ second absorption appeared at 33670 cm<sup>-1</sup> arises from  $(n \rightarrow \pi^*)$  transition that may be located on nitrogen atom of -N=C-. A comparative look of electronic absorption spectral data of the ligands and their complexes indicate that  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transition of the ligands were shifted to higher frequencies [14], Table (3).

### 3.2. Electronic spectra of [V(L1)(L2)] complex

The spectrum of V (IV) complex, Figure (6) shows three bands; at 14084 cm<sup>-1</sup> , 19047 cm<sup>-1</sup> ,and at  $29411 \text{ cm}^{-1}$ which corresponds to  $^{2}B_{2}g$  $^{2}B_{2}g \rightarrow ^{2}Eg$  $\rightarrow^2 B_1 g$ and  $^{2}B_{2}g \rightarrow ^{2}A_{1}g$  transitions respectively, Table (3). These are in accordance with the proposed square pyramidal geometry of V(IV) [15].

### 3.3 Electronic spectra of [Cr (L1)(L2)] complex

The spectrum of octahedral Cr(III) consist of three bands respectively:  ${}^{4}A_{2}g \rightarrow {}^{4}T_{2}g$  ,  ${}^{4}A_{2}g \rightarrow {}^{4}T_{1}g$ , and  ${}^{4}A_{2}g \rightarrow {}^{4}T_{1}g_{(p)}$  The bands are observed within the range of measurements, they have maximum at about 15923 cm<sup>-1</sup>, 28571,4 cm<sup>-1</sup> and 32154cm<sup>-1</sup>. The  $v_1$ and  $v_2$  transitions are spin allowed and laborite forbidden d-d transition. The values of 10Dq, the nepelauxetic factor  $\beta$  and Racah parameter B' were calculated by fitting the ratio  $v_3/v_1$  to Tanabe-Sugano the diagram for octahedral  $d^3$  system, **Table** (3),these data agree with octahedral geometry around Cr (III) ion ) [12].

### 3.4. Electronic spectra of [Rh(L1)(L2)] complex

Low spin Rh (III) has the electronic configuration d<sup>6</sup>,its spectrum shows a weak band at 12422 cm<sup>-1</sup> which attributed to  ${}^{1}A_{1g} \rightarrow {}^{3}T_{1g}$  transition which may occur when the promoted electron changes its spin and be the two T terms  ${}^{3}T_{1g}$  and  ${}^{3}T_{2g}$ , these transitions are indeed observed in some cases in the region of (1000-14000) cm<sup>-1</sup>[16].

Values of  $B',\beta$ .10Dq were calculated using Tanabe-Sugano diagram for d<sup>6</sup> system by fitting ratio of frequencies (v  $_{3}$ /  $v_{2}$ ) of the observed spin allowed bands to the Tanabe-Sugano diagram which gave value of the interelectronic repulsion parameters B' as well as the crystal field splitting energy10Dq. The value of  $\beta$  nephelauxetic factor is (0.84) refers to a considerable orbital overlap with approximately ionic in metal bond .An octahedral stereochemistry of the ligands around the metal ion was expected [16], Table(3).

### 3.5. Electronic spectra of Cd(L1)(L2) complex

The electronic spectrum of Cd(II) complex shows no d-d transition as it

belongs to  $d^{10}$  [17]. The prepared complex is off white in color with diamagnetic property which is expected for  $d^{10}$  ion too. The ultraviolet-visible spectrum of this complex showed relative change in the bands position compared to that of free ligands as listed in **Table (3)** due to charge transfer between Cd (II) ion and the ligands.

### 3.6 Electronic spectra of [Pt(L1)(L2)] complex

The Pt (IV) complex spectrum shows four bands; a weak band at 10341 cm<sup>-1</sup> which assigned to the spinforbidden transition  ${}^{1}A_{1}g \rightarrow {}^{3}T_{1}g$ , the other appeared at 15384 cm<sup>-1</sup> refers to  ${}^{1}A_{1}g \rightarrow {}^{1}T_{1}g$  transition and the third one appeared at 22222 cm<sup>-1</sup> which assigned to  ${}^{1}A_{1}g \rightarrow {}^{1}T_{2}g$ , also another band appeared at 32786 cm<sup>-1</sup> which is due to charge transfer from the donor atoms of ligands to the platinum ion , L $\rightarrow$ PtCT [13],**Table (3).** 



Fig. (4): Electronic Spectrum of Quinoline-2-carboxylic acid



Fig. (5): Electronic Spectrum of 4,4<sup>'</sup>-dimethyl-2,2<sup>'</sup> bipyridyl



Fig. (6): Electronic Spectrum of Vanadium (IV) complex

<b>Table (3):</b>	Electronic	spectra,	conductance	in	DMF	solvent	and	magnetic
moment (B.N	A) for ligand	ls and the	eir metal comp	plex	es			

Comp.	L1	L2	VOL1L2	CrL1L2	RhL1L2	CdL1L2	PtL1L2
Absorption	30487(sh) 34843 41666 45045	33670 41152	14084 19047 24411	26666 29850 30769	12422 14285 22624 25641	41666 34482	10341 15384 22222 32786
Assignment	$n \rightarrow \pi^*$ $n \rightarrow \pi^*$ $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	${}^{2}B_{2}g \rightarrow {}^{2}Eg$ ${}^{2}B_{2}g \rightarrow {}^{2}B_{1}g$ ${}^{2}B_{2}g \rightarrow {}^{2}A_{1}g$		$^{1}A_{1}g \rightarrow ^{3}T_{1}g$ $^{1}A_{1}g \rightarrow ^{1}T_{1}g$ $^{1}A_{1}g \rightarrow ^{1}T_{2}g$ $L \rightarrow RhCT$	ILCT ILCT	$^{1}A_{1}g \rightarrow ^{3}T_{1}g$ $^{1}A_{1}g \rightarrow ^{1}T_{1}g$ $^{1}A_{1}g \rightarrow ^{1}T_{2}g$ $L \rightarrow PtCT$
B°				918			
<b>B</b> <sup>/</sup>				888.20			
β				0.96			
Dq/B <sup>/</sup>				1.8			
10Dq				15987.6			
15 B <sup>/</sup>				13578.47			
$\mu_{eff}$			1.92	3.12	0.00	0.00	0.572
μ <sub>scm</sub> -1			92.1	57.6	62.7	45.5	62.1
Suggested Structure			Square pyramidal	O.h	O.h	T.d	O.h

ILCT: Internal ligand charge transfer, sh: Shoulder



### **3.4** Thermal analysis

Thermal analyses were done to confirm the presence of water molecules as suggested in the new prepared complexes following the degradation steps in TG curves, the results obtained in thermogravimetric analysis agree with the suggested structures from other analyses, **Table** (4).

Table (4): Thermal analytical data ofthe water molecule for the newlyprepared complexes

Compounds	Weight loss found (Calc.)%	Temp range in TG (°C )
VL1L2	5.74(6.46)	64.31-126.16
CrL1L2	10.06(10.11)	84.63-363.66
RhL1L2	7.45(6.35)	70.29-197.06
CdL1L2	3,58(3.27)	62.23-195.90
PtL1L2	2.95(2.66)	121.22-174.97

## 3.5 Suggested structures of new complexes

### 4. Theoretical studies

The heat of formation  $(\Delta H^{o}_{f})$ . binding energy  $(\Delta E_b)$  and dipole moment  $(\mu)$  for the free ligands and their metal complexes were calculated using ZINDO/I, PM3 and AMBER methods at 298 K. It was found that the complexes are more stable than their ligands Table (5); Furthermore, the electrostatic potential for free ligands was calculated to investigate the reactive site of the molecules, PM3 was used to evaluate the vibrational spectra of free ligands, and these obtained frequencies agreed well with those values experimentally found, in addition, the calculation helped to assign unambiguously the most diagnostic bands Table (6). Electronic spectra measurements for the ligands were calculated theoretically by using ZINDO/S method and comparing it

with the experimental results. It was found that the results were close between the theoretical and experimental spectra, Table (7). While Gaussian program semi-empirical (PM3) method was used to calculate, the geometry optimization, dipole moment  $(\mu)$  and total energy **Table (8)**. Electrostatic potential, ELUMO and EHOMO was obtained; evaluate the vibrational spectra of free ligands, and these obtained frequencies agreed well with those values experimentally found Electronic Table spectra (9). measurements for the ligands were calculated theoretically by using the job type: Single point energy (SP) along with ZINDO method and also the job type Frequency (Freq) used along with CIS method (3-21G) and compare both methods with the experimental results **Table** (10). It was found that there was a close agreement between the theoretical and experimental spectra.

Table (5): Conformation energetic in (Kcal.mol<sup>-1</sup>) and dipole moment (in Debye) for ligands and their metal complexes using hyperchem-8 program

	PM3				AMBER		
Compound	$\Delta H^{o}_{f}$	ΔE <sub>b</sub>	μ	$\Delta H^{o}{}_{f}$	ΔE <sub>b</sub>	μ	$\Delta H^{o}_{f} = \Delta E_{b}$
L1	-39.8326	-2345.56	3.027	-4515.74	-6821.47	3.324	
L2	329.69	-2259.59	4.589	-4860.72	-7450.01	5.209	
VL1L2							130.19
CrL1L2				-10798.55	-16376.61	10.59	
Rh L1L2				-12401.00	-18351.2	9.3681	245.07
Cd L1L2	70.385	-5111.86	6.913				
PtL1L2							277.99

Table (6): Comparison of experimental and theoretical main vibration frequencies for Qinoline-2-carboxylic acid (L1) and 4,4-dimethyl -2,2-bipyridyl(L2)using hyperchem-8program

Symb.	v(C=O)	v(C=N+C=C)	δ(C-O)	v(O-H)
	1980.78	1631.59	1394.36	3852.17
L1	1697.36*	1604*	1261.45 *	2939 *
	(16.69)	(1.68)	(10.54)	(4.47)
Symb.	v(C=N+C=C)	v(C-H)aliph.	v(C-H)arom.	δ(C-N)
	1780.43	3170.58	3035.50	1233.03
L2	1604.77*	2981.95*	3078.39*	1273.02*
	(10.94)	(2.99)	(0.033)	(-3.14)

Table (7): Comparison of experimental and theoretical electronic transition for ligands from ZINDO/S calculation and Experiment method using hyper chem-8 program

Symbols	Transition	Experimental	Theoretical(ZINDO/S)
	n→π	328sh	306
T 1	n→π*	287	279.4
LI	n→π*	240	229
	$\pi \rightarrow \pi^*$	222	214
	n→π*	297	274.55
1.2	$\pi \rightarrow \pi^*$	243	
LZ	n→π*		237.02
	$\pi \rightarrow \pi^*$		195.0

Table (8): Conformation energetic in (Kcal.mol<sup>-1</sup>) and dipole moment (in Debye) for ligands (L1,L2) using Gaussian program.

Compound	Total energy	μ
L1	-32.44762449	3.3846
L2	45.4167809	3.4377

Table (9): Comparison of experimental and theoretical vibration frequencies for Qinoline-2-carboxylic acid (L1) 4,4-dimethyl-2,2-bipyridyl (L2)using Gaussian programs

Symb.	v(C=O)	v(C=N+C=C)	δ(C-O)	v(O-H)
т 1	2065.71	1628.07	1282.41	3239.37
LI	(17.83)	(1.47)	(1.63)	(9.27)
Symb.	v(C=N+C=C)	v(C-H)aliph.	v(C-H)arom.	δ(C-N)
	1745.74	3170.22	3031.92	1228.28
L2	1604.77*	2981.95*	2981.95*	1273.02*
	(8.07)	(5.93)	(1.63)	(-3.64)

Table (10): Comparison of experimental and theoretical electronic transition for ligands from CIS and ZINDO calculation and Experiment method using Gaussian program.

Symbols	Transition	Experimental	Theor	retical
	n→π	328sh	CIS	ZINDO
T 1	n→π*	287		
LI	n→π*	240	(222)max	(311.59)max
	$\pi \rightarrow \pi^*$	222		
	n→π*	297	CIS	ZINDO
L2	$\pi \rightarrow \pi^*$	243	(185)max	(270, 77) may
	$\pi \rightarrow \pi^*$		(105)111ax	(2/9.77)IIIax

### **Conclusion:**

In this paper, the mixed ligands of (Quinoline-2-carboxylic acid and 4,4dimethyl-2,2'-bipyridyl) with some heavy and light metal ions were succeeded to prepare. The new solid metal complexes were isolated and characterized using available conventional techniques. The results indicated that the ligand Quinoline-2carboxylic acid behaves as bidentate through the nitrogen and oxygen atoms, while the co-ligand 4.4 dimethyl-2,2'-bipyridyl behaves as bidentate ligand, but through the two nitrogen atoms with these metals. Moreover, the results obtained for the ligands and their complexes which isolated in solid state, were compared with the results obtained from gas phase study using Hyper Chem-8 and Gaussian programs exhibiting almost identical results between these states.

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### معقدات الليكندات المختلطة (كوينولين \_2\_ حامض الكاربوكسيلي و 4,4 ً داي مثيل 2,2 ٌ باي برديال) مع فناديوم(IV)،كروم (III) ,روديوم(III) ،كادميوم (IV) والبلاتين (IV)

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#### الخلاصة:

تم تحضير معقدات جديدة من مفاعلة كوينولين -2- حامض الكربوكسيلي و 4,4'-داي مثيل،2,2'-باي بريديال مع ايونات الفلزات: فناديوم(IV)،كروم(III) ,روديوم(III)،كادميوم (II) والبلاتين (IV).تم عزل وتشخيص المركبات المحضرة بالطرق الطيفية والفيزيائية كطيف الاشعة تحت الحمراء والاشعة فوق البنفسجية-المرئية والتحليل الدقيق للعناصر وتعيين نسبة الفلز والتحليل الحراري بالاضافة الى القياسيات الحساسية المغناطيسية والتوصيلية . معظم المعقدات المحضرة مونمرية وذات شكل هندسي ثماني السطوح ماعدا معقدات الفناديويوم والتوصيلية معظم المعقدات المحضرة مونمرية وذات شكل هندسي ثماني السطوح ماعدا معقدات الفناديويوم بالتوصيلية . معظم المعقدات المحضرة مونمرية وذات شكل هندسي ثماني السطوح ماعدا معقدات الفناديويوم والتوصيلية . معظم المعقدات المحضرة مونمرية وذات شكل هندسي ثماني السطوح ماعدا معقدات الفناديويوم بالتوصيلية . معظم المعقدات المحضرة مونمرية وذات شكل هندسي شاني السطوح ماعدا معقدات الفناديويوم والتوصيلية . معظم المعقدات المحضرة مونمرية وذات شكل هندسي شاني السطوح ماعدا معقدات الفناديويوم والتوصيلية . معظم المعقدات المحضرة مونمرية وذات شكل هندسي شاني السطوح ماعدا معقدات الفناديويوم والتوصيلية . معظم المعقدات المحضرة مونمرية وذات شكل هندسي شاني السطوح ماعدا معقدات الفاديويوم مربع هرمي والكادميوم رباعي السطوح . تم اجراء معالجة نظرية لهذه الليكندات المحضرة في الطور الغازي المربع مربي والكادميوم رباعي السطوح . تم اجراء معالجة نظرية لهذه الليكندات المحضرة في الطور الغازي . والتحدام برنامجي ( Buyer chem.8 and Gaussian program (GaussView Currently Available ) باستخدام برنامجي ( S.0.9) along with Gaussian 09 which is the latest in the Gaussian series of programs).