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ORIGINAL ARTICLE

Synthesis and Characterization of some new Matals Complexes of (POPIONYL CARBAMOTHIOYL) Valine (PCV)

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ABSTRACT

A new ligand was prepared (PCV) (popionylcarbamothioyl)valine by reacting (popionyl chloride)with ammonium thiocyanate in a ratio of (1:1)mole and adding it to 1mol of valine . The precise analysis of the elements(C,H,N,S) and FTIR spectra and (UV-Vis)measurements of ligand(PCV). The metal ion complexes are created and characterized using (FTIR) and (UV-vis) spectroscopy, magnetic susceptibility, atomic absorption, and conductivity studies. From The formula for calculating the findings is as follows: "$[M(PCV)_2]$ where M^{+2} is Mn, Co,Ni,Cu,Zn,Cd,Hg". since the complexes are thought to have a tetrahedral structure excluding the copper , which has a square planer geometry.

Keywords: Valine , "metal complexes" , popionyl isothiocyanate .

INTRODUCTION

L-Valine is an "essential" of amino acid (`α -amino) in humans[1,2], which means it cannot be synthesized by the body and must be received from diet[3]. It is a branched amino acid[4] that is required for protein biosynthesis[5]. L-Valine is a critical and beneficial chiral amino acid that is used to catalyze asymmetric reactions [6]. And they are broadly dispersed but seldom surpass 10% [7]. may be synthesized from alanine by introducing two methyl groups onto the -carbon atom[8,9]. [N-(acetyl amino)Thioxomethyl]valine was synthesized by (Alia S., 2012) [10], as well as (Bekele Y. et at ,2020) A new derivative of valine called (Ketimine)[11], preparation, spectra, and biological properties of transition metals(II)and(III)Mixed-ligand structures with (5-chlorosalsalic Acid)and L-Valine by (Shatha M. et al., 2019)[12], and also "(Nouria A. Belkher.et al., 2019)"Studies on the constant of some transition metal ion[13]. synthesis and characterization of Co(II)and Ni(II)complexes of Schiff base derived from Nenhydrin and Valine by '(Achalu C. et at ,2020)[14],and also '(Mekuanint H. et at ,2021) synthesis and characterization of Fe(II) and Mn(II)complexes of (Schiff base) derived from Nenhydrin and Valine'[15].

Aims: synthesis of many metal ion complexes by (popionyl carbamothioyl) valine (PCV).

MATERIALS AND METHODS

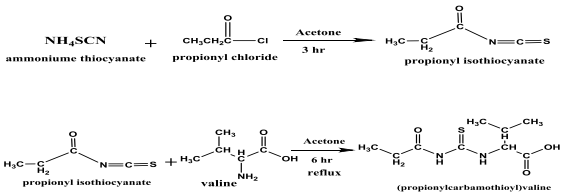
popionyl chloride , valine, hydrated manganese chloride , hydrated cobalt chloride , hydrated nickel chloride , hydrated cupper chloride , Zinc chloride , hydrated cadmium chloride , mercury chloride , All reagents are considered pure by (March and BDH).

Instruments: The FTIR spectra of the KBr disc were acquired using a Shimadzu,FTIR-8300,Infrared spectroscopy. ($H^1$and C^{13}-NMR)was captured at Basra University of Science and technology utilizing an Ultra shield 300Mhz. Electronic spectra were obtained using Shimadzu UV-160A-Visible Recording spectrophotometer. Conductivity was measured by using pw-Digital Meter Conductivity Philips. The MSB-MKT Balanced Magnetic Susceptibility Model was used to acquire magnetic susceptibility data. Stuart's Melting Apparatus was used to determine the melting point. The metals concentrations of the complex were determined using the Shimadzu AA680 GBC 933 plus atomic absorption method. The analysis of microelements (C,H,N,S) was done using the acrlo Euro Vector EA3000A..

Preparation of ligand (PCV):

1 An ammonia thiocyanate solution of 2g and popionyl chloride of 2.26ml were dissolved in 25ml of Acetone for 3 hours, and the filtrated solution was used for the following reaction of (Popionyl isothiocyanate). [16]

2 preparation of **(popionyl carbamothioyl)valine(PCV)** : (3.04g, 1mmol)Valine To sustain strong reflux, that (25ml) ethanol was quickly added. After 6 hours of refluxing, the Re-crystallization of the solid was carried out by washing the sample with Acetone and then ethanol.



Scheme 1: preparation ligand (PCV)

Synthesis of metal complexes: (0.46g)(2mmol) of ligand (PCV) in (25ml) of ethanol, (0.12g-2mmol) KOH and the following metal salts were added to: " $MnCl_2.4H_2O$ (0.2g-1mmol),$CoCl_2.6H_2O$ (0.24g-1mmol), $NiCl_2.6H_2O$ (0.24g-1mmol)", and $CuCl_2.2H_2O$ (0.24g-1mmol) The precipitate quickly developed after three hours of constant stirring. Afterward, the precipitate rinsed with distilled water in a vacuum to remove any remaining impurities. Table 1 provides a list of the many physical characteristics.

Table 1: The ligand (PCV) and its metal complexes' physical characteristics

Compound	M.Wt (g/mol)	Color	M.P CO Or dec.	M% Calculation (Found)	Molar condu. Ohm-1.Cm2.mol-1	μeef (B.M)
(PCV)	232	Yellow	120-125	83	2.1	-----
]$Mn(PCV)_2$[	517	Brown	Dec.215	71	6.5	5.93
] $Co(PCV)_2$[	521	Purple	130-132	78	13.2	4.33
] $Ni(PCV)_2$[	520.7	Green	Dec.245	77	9.6	2.99
]$Cu(PCV)_2$[	525.5	Blue	Dec.218	66	7.4	1.73
] $Zn(PCV)_2$[	527.4	White	190-192	62	7.1	0.00
]$Cd(PCV)_2$[	574.4	White	160-162	70	15.2	0.00
]$Hg(PCV)_2$[	662	Yellow	161-163	74	8.2	0.00

Spectral studies 1: Infrared spectra of the free ligand (PCV)"(Fig:1)"revealed bands around (3456)cm^{-1},(1604)cm^{-1} and (1242)cm^{-1}, respectively, due to (N-H), (C=O), and (C=S), whereas another band absorbed at(1728)cm^{-1}. might be regarded as a (COO-)asym, with the (COO-)sym being seen at (1400)cm^{-1}

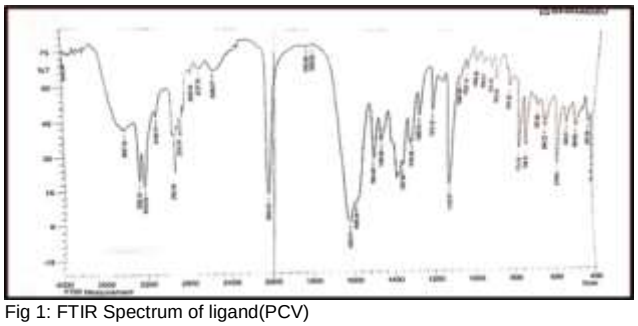


Fig 1: FTIR Spectrum of ligand(PCV)

FT-IR spectra of complexes Fig (2) revealed a significant difference in the frequency of bands belonged to the stretching vibration of the (N-H) in the range (3410-3421)cm^{-1} descreased by (35-46)cm^{-1}, indicating the possibility the ligand(PCV) coordination the nitrogen atom at amine. frequency $(COO^-)_{asym}$ at (1558-1647)and inscreased by(81-170) cm^{-1} . but frequency $(COO^-)_{sym}$ at(1415-1473)cm^{-1} descrease by(11-69)$cm^{-1}$the carboxylic group coordination with metal .The stretching vibration band appears of with (C=O) and (C=S) remain unchanged (1608 cm^{-1} and 1280 cm^{-1}, respectively). As a result,not coordination between (metal–oxygen) interactions were validated using the bending oscillations of (M-O) and (M-N) at frequencies of (470–587) and (416–470)cm-1, respectively. The bands and assignments indicated in Table (2) should be carefully considered for the title compound (PCV) and its complexes.

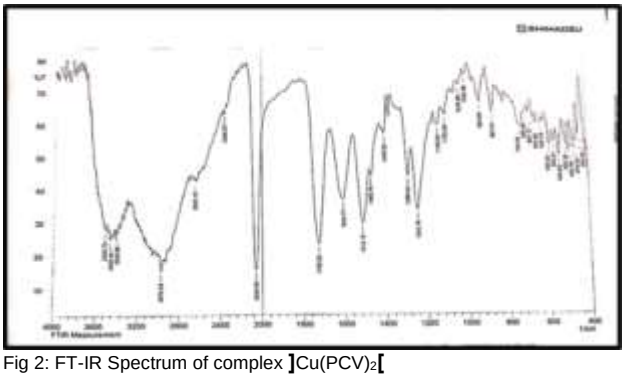


Fig 2: FT-IR Spectrum of complex]Cu(PCV)$_2$[

Table 2: FT-IR frequencies in (cm^{-1}) for ligand (PCV)

Complex	$\upsilon(COO)^{asym}$	$\upsilon(COO)^{sym}$	Δ υ	υ(N-H) υ(O-H)	υ (C=S)	υ (C=O) amide	υ(M-N)	υ(M-O)
Ligand(PCV)	1728s	1400	-	3456(b) 3390(b)	1242	1604w	-	-
[Mn(PCV)$_2$]	1597s	1415s	182	3437m	1269m	1604w	424w	474w
[Co(PCV)$_2$]	1631s	1465m	166	3217m	1257m	1604w	412w	455w
[Ni(PCV)$_2$]	1593s	1411s	182	3344m	1269w	1627m	428w	474w
[Cu(PCV)$_2$]	1589m	1465m	124	3437m	1215m	1620m	424w	489w
[Zn(PCV)$_2$]	1593m	1415m	178	3275m	1269m	1604w	424w	470w
[Cd(PCV)$_2$]	1581m	1465m	116	3356m	1219w	1612w	435w	470w
[Hg(PCV)$_2$]	1597m	1469m	128	3429m	1238w	1604w	410w	516w

s=strong , m=medium, w=weak

2)^{1}H and ^{13}C-NMR spectra:

^{1}H-NMR spectrum: for ligand(PCV)in "Using DMSO as the solvent, Fig (3) revealed the following signals: doubled at (0.82) parts per million for ($2CH_3$,6H), triplet at (0.98)ppm for (CH_3,3H) propionyl group, multiplet at δ(1.132)ppm for($CH(CH_3)_2$,1H),singlet at δ(2.53)ppm for DMSO ,triplet at δ(3.73)ppm for(CHCOOH,1H) ,quartet at (2.173)ppm for (CH_2,2H) propionyl group, singlet at δ(7.28)ppm for (NH_{amine},1H), singlet at δ(7.460)ppm for (NH_{amide},1H), singlet at δ(8.191) ppm for(COOH,1H)".

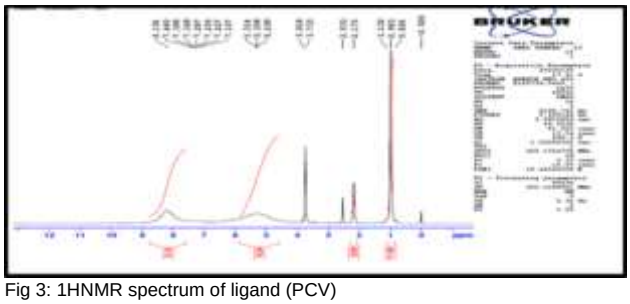


Fig 3: 1HNMR spectrum of ligand (PCV)

^{13}C- NMR spectrum: in DMSO for the ligand (PCV) The following signals were shown in Fig(4): for signal at (0.56 ppm) (CH_3), signals at (18.23-18.47)ppm for($2CH_3$),signal at (29.49)ppm for ($CH(CH_3)_2$), signals at(29.80)ppm for (CH_2-CO), signals at (39.19-40.44)ppm for DMSO, signal at (57.66)ppm for(CHCOOH), signal at (130.50)ppm for (C=O), signal at (170.83)ppm for (COOH), signal at(170.89)ppm for(C=S).Table (4) includes the spectral data for ligand (PCV) .

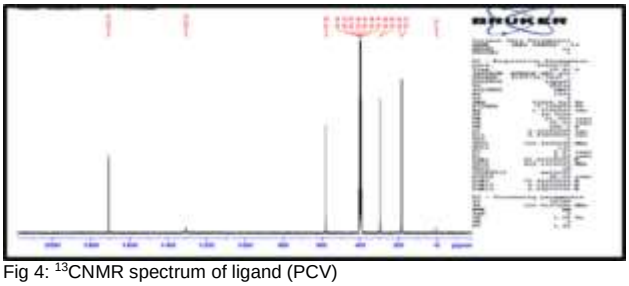


Fig 4: ^{13}CNMR spectrum of ligand (PCV)

Table 3: ^{1}H-NMR spectral data for ligand (PCV)

Compound	No of protens	(ppm)δ
Ligand (PCV)	d ($2CH_3$, 6H)	0.82
	t (CH_3 , 3H)	0.98
	m($CH(CH_3)_2$,1H)	1.132
	q(CH_2,2H)	2.173
	t(CHCOOH ,1H)	3.73
	s (NH amine ,1H)	7.28
	s (NH amide ,1H)	7.46
	s (COOH , 1H)	8.191

Table 4: ^{13} C-NMR spectral data for ligand (PCV)

Compound	Function group	(ppm)δ
Ligand (PCV)	CH_3	0.56
	$2CH_3$	18.23-18.47
	$CH(CH_3)_2$	29.49
	CH_2-CO	29.80
	CHCOOH	57.66
	C=O	130.50
	COOH	170.83
	C=S	170.89

The metal complexes exhibit the following magnetic properties: "Magnetic moment" (μeef) Numerous spin-only complexes have been identified, including those combining the metal complexes $Mn^{+2}(d^5)$ and $Co^{+2}(d^7)$equal (5.93 B.M.) (4.33 B.M., respectively)[17] .The $Ni^{+2}(d^8)$ complex has a μeff value due to the orbital contribution (2.99 B.M) [18].The μeef of the $Cu^{+2}(d^9)$ combination was determined to be (1.73) B.M, within the expected range for a single electron. [19] (1).

The electronic spectra: "The UV-visible spectra of ligand(PCV)in(0.001M)(DMSO),fig(5) show band at(36496) cm-1 that have been ascribed to $\pi \rightarrow \pi^*$ and (28653)cm^{-1} due to $n \rightarrow \pi^{*'}$ [20].

"$[Mn(PCV)_2]$ d^5: the yellow complex's spectrum Mn^{+2}, bracelets on display at (36630) $cm^{-1}$and (14204) cm^{-1},(14025) cm^{-1} due to (ligand filed) and $^6A_1 \rightarrow {}^4T_{1\,(G)}$, $^6A_1 \rightarrow {}^4T_{2\,(G)}$ respectively".

" $[Co(PCV)_2]$ d^7: the spectrum of green complex of Co^{+2}: show bands at (36630) cm^{-1} ,(25974) cm^{-1} ,(14534) cm^{-1} and (10080) cm^{-1} attributed to (ligand field) , (C.T mix) with $^4A_2 \rightarrow {}^4T_{1\,(p)}$, $^4A_2 \rightarrow {}^4T_{1\,(F)}$and $^4A_2 \rightarrow {}^4T_{2(F)}$ according to the connection, and the rachi inter molecular repulsion parameter (B-) was determined to be (687.2) cm^{-1}. $\beta = B/B_o$:was found to be equal (0.70),these parameter are accepted to Co^{+2} tetrahedral complex" .

"[$Ni(PCV)_2$] d^8 : the spectrum of deep brown complex of Ni^{+2}: show bands at (37174) cm^{-1} ,(26666) cm^{-1} ,(15503) cm^{-1} and (10050) cm^{-1} attributed to(ligand field) , [C.T mix with $^3T_{1(F)} \rightarrow {}^3T_{1(P)}$] , $^3T_{1(F)} \rightarrow {}^3A_2$ and $^3T_{1(F)} \rightarrow {}^3T_{2(F)}$ respectively."

$[Cu(PCV)_2]$ d^9: the spectrum of" Cu^{+2} deep green complex Fig(6): shows lines at (37453)cm^{-1}, (13531)cm^{-1}, and (12391)cm^{-1} that really are due to the (ligand field),"$^2B_{1(g)} \rightarrow {}^2A_{1(g)}$ and $^2B_{1(g)} \rightarrow {}^2B_{2(g)}$" respectively.

$Zn(PCV)_2]$, $[Cd(PCV)_2]$, and $[Hg(PCV)_2]$ complexes The table summarizes the only [ligand field] and [C.T]of (M-L) transitions at (36630,26041)cm^{-1},(37037,28735)cm^{-1},and (36630,14204) cm^{-1}, respectively (5).

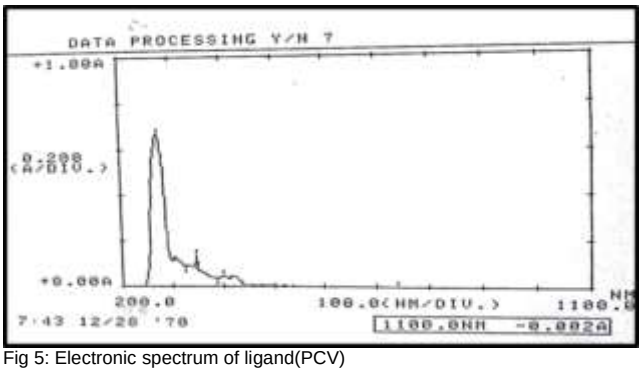


Fig 5: Electronic spectrum of ligand(PCV)

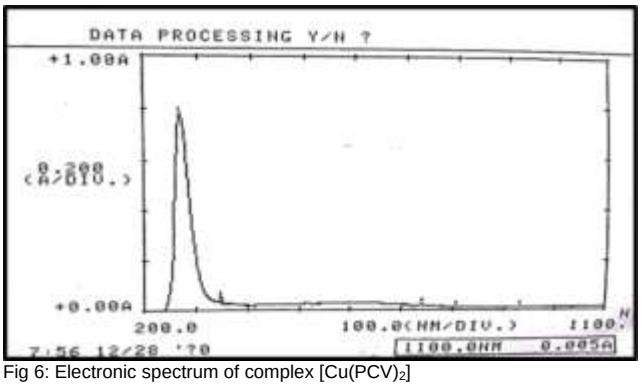


Fig 6: Electronic spectrum of complex $[Cu(PCV)_2]$

Table 5: the peaks electronic transition and structure geometries of (PCV) and its complexes

No	Complex	λ_{max}(nm)	ABC	Wav number cm^{-1}	ϵ_{max} $L.mol^{-1}.cm^{-1}$	الملاحظات
-1	Ligand(PCV)	274 349	0.667 0.136	36496 28653	667 136	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
-2	$[Mn(PCV)_2]$	273 704 713	0.500 0.043 0.046	36630 14204 14025	500 43 46	L.F $^6A_1 \rightarrow {}^4T_{1(G)}$ $^6A_1 \rightarrow {}^4T_{2(G)}$
-3	$[Co(PCV)_2]$	273 385 688 992	1.863 0.380 0.077 0.025	36630 25974 14534 10080	1863 380 77 25	L.F C.T mix $^4A_2 \rightarrow {}^4T_{1(p)}$ $^4A_2 \rightarrow {}^4T_{1(F)}$ $^4A_2 \rightarrow {}^4T_{2(F)}$
	$[Ni(PCV)_2]$	269 375 645 995	1.237 0.225 0.100 0.105	37174 26666 15503 10050	1237 225 100 105	L.F C.Tmix $^3T_{1(F)} \rightarrow {}^3T_{1(p)}$ $^3T_{1(F)} \rightarrow {}^3A_2$ $^3T_{1(F)} \rightarrow {}^3T_{2\,(f)}$
-5	$[Cu(PCV)_2]$	267 739 807	0.782 0.025 0.021	37453 13531 12391	782 25 21	L.F $^2B_{1(g)} \rightarrow {}^2A_{1(g)}$ $^2B_{1(g)} \rightarrow {}^2B_{2(g)}$
-6	$[Zn(PCV)_2]$	273 384	0.694 0.388	36630 26041	694 388	L.F C.T
7	$[Cd(PCV)_2]$	270 348	0.578 0.198	37037 28735	578 198	L.F C.T
-8	$[Hg(PCV)_2]$	273 704	0.399 0.082	36630 14204	399 82	L.F C.T

CONCLUSION

The new ligand in the presented study was prepared through reaction from the(propionyl isothiocyanate) with valine , ligand has been characterized through: Element micro analysis (C.H.N.S.), FTIR, UV-Visible, and ^1H,^{13}C-NMR spectra. Ligands and transition metals have been synthesized and studied using FTIR, UV-visible spectroscopy. ', magnetic measurements, conductivity measurements, the suggested geometrical structure with regard to complexes have been tetrahedral geometry except for the copper, has square planer

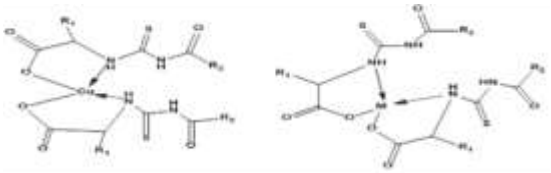


Figure 7: structure of complexes $[M(PCV)_2]$

M^{+2}=Mn,Co,Ni,Zn,Cd,Hg

R_1=$CH(CH_3)_2$

R_2=$CH_2.CH_3$

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