

Synthesis, spectral Characterization and studies of Some Divalent Metal Ion Complexes with Ligand of [3-(1*H*-indol-3-yl)-2-(3-(4-methoxybenzoyl)thiouereido)propanoic acid] (MTP)



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ABSTRACT

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In this work, prepared new ligand[3- (1*H*-indol-3-yl) -2- (3-(4-methoxybenzoyl) thiouereido) propanoic acid](MTP) has been synthesized by reaction of 4-Methoxybenzoyl isothiocyanate with tryptophane(1:1), The ligand was characterized by elemental microanalysis C.H.N.S, FT-IR, UV-Vis and ¹H,¹³C NMR spectra, Some transition metals complexes of this ligand were prepared and characterized by FT-IR, UV-Vis spectra, conductivity measurements, magnetic susceptibility and atomic absorption, From obtained results the molecular formula of all prepared complexes were [M(MTP)₂] (M⁺² =Mn, Co, Ni, Cu, Zn, Cd and Hg), the proposed geometrical structure for all complexes were tetrahedral except copper complex has a square planer geometry around metallic ion with bidentate ligand(MTP).

1.Introduction

α -Tryptophan was reported to inhibit the growth of *Bacterium coli*[1] and to be used as IDO inhibitors[2]. In addition,tryptophan analogues are important building blocks for the synthesis of biologically active compounds ranging from peptide mimetics to natural products[3]. Among various synthetic methods, two strategies have been used for the preparation of tryptophan analogues. The metal complexes derived from amino acid and their derivatives have important pharmaceuticals applications, they have been exploited in cancer multi drugs resistance [4] tested as anti-material[5] and exhibit anti-tumor activity [6].

Metal complexes are gaining importance in recent years particularly in the design of repository, slow release or long acting drug in nutrition and in the study of metabolism [7]. Metal ions are known to accelerate the drug action [8]. The transition metal complexes of tryptophan have been extensively examined due to their wide applications in various fields like biological, pharmacological, clinical, analytical and industrial area. These ligands have been playing an important part in the development of coordination chemistry as they easily form stable complexes with most of the transition metal ions[9]. The interaction of these donors and metal ion give complexes of different geometries and these complexes are potentially biologically active[10]. complexes of transition metals containing ligands with N,O⁻ donors play an essential role in agricultural, pharmaceutical, industrial chemistry [11-12], antifungal, antibacterial, anticancer and

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catalytic activities[13-14]. T. Kavitha and Co Worker reported synthesis Schiff base from tryptophan with naphthylidene-4-aminoantipyrine and also their metal complexes and have the general formale[ML] where M= VO(II), Co(II), Ni(II), Cu(II) and Zn(II)[15]. Also synthesis, characterization and toxicity studies of Schiff based driven from pyridine carboxaldehydes and tryptophan and their metal complexes[16].

The aim of the present study was the synthesis, characterization of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes derived from of tryptophan.

2.Experimental

2.1. Material and measurements

All reagents were analar or chemical pure grade by Sigma-Aldrich, BDH, Merck and Fluka. The chemical tryptophane, Ammonium thiocyanate, 4-Methoxybenzoylchloride, metal chloride salts (MnCl₂.4H₂O), (CoCl₂.6H₂O), (NiCl₂.6H₂O), (CuCl₂.2H₂O), (ZnCl₂), (CdCl₂.H₂O) (HgCl₂) and all solvents were used without purification.

¹H and ¹³C-NMR was recorded using Ultra Shield 300 MHz Switzerl and at University of Al al-Bayt, Jordan. Melting point was recorded by using Stuart- melting point apparatus. FT-IR spectra were recorded as KBr disc using 3800 Shimadzu in the range of (4000-400) cm⁻¹. Electronic spectra were obtained using UV-160 Shimadzu spectrophotometer at room temperature for 10⁻³M solution DMSO with 1.000 ± 0.001 cm matched quartz cell. Molar Conductivity was measured at 25 °C for 10⁻³M solution of DMSO by using Philips PW.Digital.Elemental micro analyses(C.H.N.S) were performed using Acrlo Erba 1106 elemental analyzer. Magnetic susceptibility measurements were obtained by balance magnetic susceptibilityby model MSB-MKI. Metal contents of the complexes were determined by atomic absorption technique by using Shimadzu (AA680G).

2.2. Preparation of ligand(MTP)

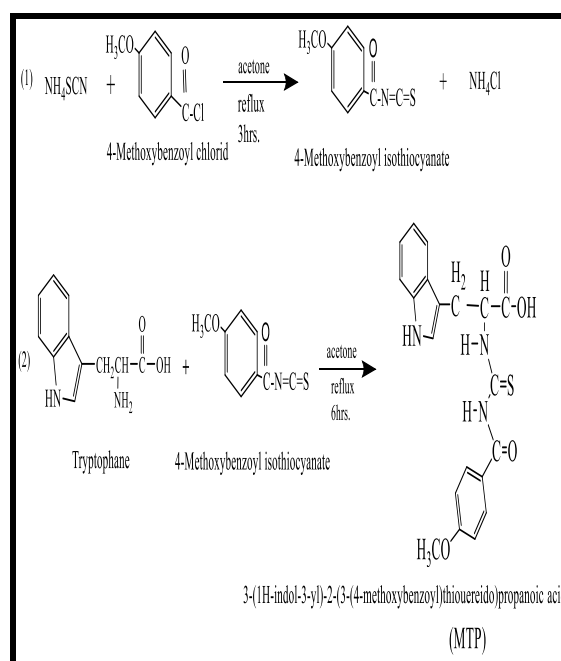
The ligand was prepared by two steps

Step 1. Preparation of the (4-MethoxyBenzoyl isothiocyanate). [17]

Mixture of ammonium thiocyanate (2g, 26mmol) and 4-methoxybenzoyl chloride (3.55ml,26mmol) in (25ml) of acetone was stirred under refluxed for 3hrs and then filtered, the filtrate was used for further reaction.

Step 2. Preparation of 3-(1H-indol-3-yl)-2-(3-(4-methoxybenzoyl) thiouereido) propanoic acid (MTP)

(5.31 g, 26mmol) of tryptophane in (20ml) ethanol was rapidly added to 4-methoxybenzoyl isothiocyanate and maintaining reflux. After refluxing for 6hrs, the resulting solid was collected, washed with acetone and recrystallization from ethanol, Yield(%82), (M.P=250-252)°C, C% found (60.50) calc.(60.45), H% found (4.67), calc.(4.78),N% found (10.40), calc.(10.57),S% found (8.45), calc.(8.06) (scheme:1).



Scheme (1) Preparation of ligand(MTP)

2.3. Synthesis ligand (MTP) complexes

The complexes $[M(MTP)_2]$ have been prepared by the reaction of (0.794g, 2mmol) of ligand(MTP) in (10ml) ethanol containing (0.12gm,2mmol) of KOH with (1mmol) off metal chloride (0.20gm, 0.237gm, 0.170gm, 0.237gm, 0.136gm, 0.20gm and 0.272gm for $MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, $ZnCl_2$, $CdCl_2 \cdot H_2O$ and $HgCl_2$) respectively dissolved in (20ml) absolute ethanol and refluxed with stirring under for 3 hours at room temperature, the precipitate was collected by filtration, washed with(1:1) mixture of water: ethanol and dried in an oven($50^\circ C$). Table(1) exhibit some physical properties of the prepared complexes.

3. Results and Discussion

Ligand and complexes were identified on the basis of elemental analysis and spectral studies. color, yield and elemental analysis data are represented in Table (1).

3.1. Ligand (MTP)

1H -NMR spectrum of the ligand (MTP) fig.(1)which was recorded in $CDCl_3$ as a solvent showed the following signals: singlet at $\delta(1.419)$ ppm for (1H, CH), singlet at $\delta(3.902)$ ppm for (3H, OCH_3), singlet at $\delta(4.663-4.714)$ ppm for (2H, CH_2), multiplet at spcaks at $\delta(6.985-7.015)$ ppm for(4H, aromatic protons), singlet at $\delta(7.184)$ ppm for(1H, NH Sec amine), multiplet peaks at $\delta(7.776-7.852)$ ppm for (4H, indolring), singlet at $\delta(10.486)$ ppm for (1H, COOH).

^{13}C -NMR spectrum of the ligand (MTP) fig.(2)which was recorded in $CDCl_3$ as a solvent showed the following signals : single peak at $\delta(13.260)$ ppm for (CH_2), single peak at $\delta(55.630)$ ppm for (OCH_3), single peak at $\delta(70.234)$ ppm for (CH), single peak at $\delta(111.878-123.511)$ ppm for(aromatic carbons), single at $\delta(130.534-130.155)$ ppm for(carbon in pyrrolering), single at $\delta(160.718-159.586)$ ppm for (carbon in

benzenring), single peak at $\delta(164.409)$ ppm for ($C=O$ sec.amide), single peak at $\delta(164.849)$ ppm for (COOH), single peak at $\delta(189.047)$ ppm for($C=S$) [18-19].

The UV-Vis spectrum of the free ligand (MTP). Fig.(5) exhibits a high intense absorption peaks at $(37313)cm^{-1}$ and (33222) which way attributed to electronic transitions type $\pi \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ [20,21]. The data of electronic spectrum of the free ligand (MTP) were listed in table(3).

3.2. Complexes of the ligand (MTP)

All complexes soluble in some common solvent such as DMF, DMSO and relatively thermally stable. The molar conductivity values of all complexes in DMSO solvent in $10^{-3}M$ at $25^\circ C$ were recorded in rang $(4-12) Ohm^{-1}cm^2mol^{-1}$ indicated non-electrolytic(table-1)[22]. The atomic absorption measurements for all complexes gave approximated values when its comparison with theoretical values, Table(1) includes the physical properties for the ligand and its complexes.

3.3. FT-IR Spectra

These spectra exhibited marked difference between bands Fig. (4) belonging to the stretching vibration of $\nu(COO^-)_{sym}$ in the range $(1354-1465)cm^{-1}$ shifted higher frequencies by $(51-162)cm^{-1}$ and $\nu(COO^-)_{asym}$ $(1581-1695)cm^{-1}$ suggesting shifted lower frequencies by $(135-31)$ of the possibility of the coordination of ligand through the oxygen atom at the carbonyl group[23], while the band caused by $\nu(N-H)$ appeared between $(3317-3390)cm^{-1}$ shifted to lower frequencies by $(85-12)cm^{-1}$ which indicates to the coordination of ligand through the nitrogen atom at $\nu(N-H)$ group [24]. The stretching vibration band $\nu(C=O$ amido) and $\nu(C=S)$ either show no change or very little in their frequencies $(1604)cm^{-1}$ and $(1253-1261)cm^{-1}$ respectively there for indicating do not coordinate to the metal

ion. Metal-oxygen and metal-nitrogen bonds were confirmed by the presence of the stretching vibration of $\nu(\text{M-O})$ and $\nu(\text{M-N})$ around $(452-520)\text{cm}^{-1}$ and $(428-470)\text{cm}^{-1}$ respectively[25], Table(2) describe the important bands and assignment for all prepared complexes and Fig.(4): Infrared spectrum of one from prepared complexes $[\text{Cd}(\text{MTP})_2]$.

3.4. Magnetic moment

The values of observed magnetic moments at room temperature and effective magnetic moment (μ_{eff}) for the Mn(II), Co(II), Ni(II) and Cu(II) complexes are shown in table(1). Mn(II), Co(II), Ni(II) and Cu(II) complexes exhibit μ_{eff} (5.92, 4.82, 2.82 and 1.74)B.M respectively, These values are typical for high spin tetrahedral and squar planer complex for Cu(II) ion geometry coordinated around metale complexes.[26]

3.5. Electronic spectra of complexes

3.5.1 $[\text{Mn}(\text{MTP})_2]\text{d}^5$

The complex of Mn(II) Fig.(6) shows band at $(37174)\text{cm}^{-1}$ due to (L.F) and other bands at $(30395)\text{cm}^{-1}$ and $(21505)\text{cm}^{-1}$ which are caused by the charge electronic transfer (C.T) and ${}^6\text{A}_1 \longrightarrow {}^4\text{T}_{1(\text{G})}$ respectively, suggesting tetrahedral geometry around Mn(II) ion[27].

3.5.2. $[\text{Co}(\text{MTP})_2]\text{d}^7$

The spectrum of the complex gave four bands at $(37174)\text{cm}^{-1}$, $(29239)\text{cm}^{-1}$, $(17090)\text{cm}^{-1}$ and $(12048)\text{cm}^{-1}$ attributed to (L.F) and C.T_{mix} with ${}^4\text{A}_{2(\text{F})} \longrightarrow {}^4\text{T}_{1(\text{P})}$, ${}^4\text{A}_{2(\text{F})} \longrightarrow {}^4\text{T}_{1(\text{F})}$ and ${}^4\text{A}_{2(\text{F})} \longrightarrow {}^4\text{T}_{2(\text{F})}$ respectively and the rachinter electronic repulsion parameter (B^-) was found to be $(679)\text{cm}^{-1}$, from the relation $\beta=B^-/B^0$, $[\beta]$ was found to be equal(0.70), these parameter are accepted to Co(II) tetrahedral complex[28].

3.5.3. $[\text{Ni}(\text{MTP})_2]\text{d}^8$

The spectrum of complex of Ni(II) has revealed the following (L.F) and C.T, ${}^3\text{T}_{1(\text{F})} \longrightarrow {}^3\text{T}_{1(\text{P})}$, ${}^3\text{T}_{1(\text{F})} \longrightarrow {}^3\text{A}_2$ and ${}^3\text{T}_{1(\text{F})} \longrightarrow {}^3\text{T}_{2(\text{F})}$ transition at $(37174)\text{cm}^{-1}$, $(30303)\text{cm}^{-1}$, $(25641)\text{cm}^{-1}$, $(18867)\text{cm}^{-1}$ and $(10989)\text{cm}^{-1}$ respectively, the(B^-) value found to be $(769.4)\text{cm}^{-1}$, while β was equal to (0.739) these are the characteristics for tetrahedral complexes of Ni(II).[29,30]

3.5.4. $[\text{Cu}(\text{MTP})_2]\text{d}^9$

The spectrum of complex of Cu(II) show four bands at $(37174)\text{cm}^{-1}$, $(30303)\text{cm}^{-1}$, $(15267)\text{cm}^{-1}$ and $(13315)\text{cm}^{-1}$ caused to (L.F), (L.F), ${}^2\text{B}_{1\text{g}} \longrightarrow {}^2\text{A}_{1\text{g}}$, ${}^2\text{B}_{1\text{g}} \longrightarrow {}^2\text{B}_{2\text{g}}$ transition respectively, which was a good agreement for squar planer complex for Cu(II) ion fig.(8)[31,32].

3.5.5 $[\text{Zn}(\text{MTP})_2]$, $[\text{Cd}(\text{MTP})_2]$ and $[\text{Hg}(\text{MTP})]$

Shows only charge transfer (C.T) and (L.F) of ($\text{M} \rightarrow \text{L}$) in range $(22675-31645)\text{cm}^{-1}$ and $(28985-37174)$ respectively [33,34]. All transition with their assignments are summarized in Table(3).

4. Conclusions

New ligand (MTP) and their metal complexes were prepared and characterized by spectral and analytical data. The synthesized ligand act as bidentate, coordinating via oxygen and nitrogen atoms of (COO^-) and (N-H) groups respectively as ill ustration fig.(7). Magnetic and electronic studies reval "tetrahedral" structure for all complexes except Copper complex has a "square planer" geometry.

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Table No. (1): Some physical properties of the ligand (MTP) and its complexes

Compound	M.wt (gm/mole)	Color	M.p°C	M% Calculation (Found)	Molar Cond. $\text{Ohm}^{-1} \text{cm}^2 \text{Mol}^{-1}$ in DMSO	μ_{eff} (B.M)
Ligand (MTP)	397	Brown	250-252°C	–	2	–
[Mn(MTP) ₂]	846.94	Deep Yellow	115-117°C	6.49 (6.19)	12	5.92
[Co(MTP) ₂]	850.93	Blue	158-160°C	6.93 (6.82)	11	4.82
[Ni(MTP) ₂]	850.71	Green	165-168°C	6.93 (6.85)	9	2.82
[Cu(MTP) ₂]	855.54	Deep Brown	105-108°C	7.42 (7.33)	4	1.74
[Zn(MTP) ₂]	857.38	Light Yellow	181-183°C	7.62 (7.28)	5	0
[Cd(MTP) ₂]	904.4	Deep Yellow	185-187°C	12.42 (12.09)	4	0
[Hg(MTP) ₂]	992.59	Yellow	113-115°C	20.25 (19.98)	9	0

Table (2): The characteristic infrared band in cm^{-1} for free ligand (MTP) and its metal complexes

Compounds	$\nu(\text{O}-\text{Hi})$ $\nu(\text{N}-\text{Hi})$	$\nu(\text{COO})$ asym	$\nu(\text{COO})$ sym	$\Delta\nu$ (COO)	$\nu(\text{C}=\text{O})$ Amide	$\nu(\text{C}=\text{S})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
Ligand MTP	3078(m) 3402(m)	1716(m)	1303(w)	413	1604 (s)	1211(s)	–	–
[Mn(MTP) ₂]	3348(b)	1654(s)	1419(s)	235	1604(s)	1211(m)	478(w)	428(w)
[Co(MTP) ₂]	3390(b)	1581(s)	1354(s)	227	1604(s)	1257(m)	479(w)	457(w)
[Ni(MTP) ₂]	3344(b)	1581(s)	1373(s)	208	1604(w)	1257(w)	462(w)	432(w)
[Cu(MTP) ₂]	3387(b)	1666(s)	1435(s)	231	1604(w)	1257(m)	452(w)	447(w)
[Zn(MTP) ₂]	3390(b)	1654(s)	1423(s)	231	1604(s)	1211(s)	478(w)	443(w)
[Cd(MTP) ₂]	3317(b)	1662(s)	1396(s)	266	1604(S)	1211(S)	462(w)	447(w)
[Hg(MTP) ₂]	3390(b)	1695(s)	1465(s)	230	1604(S)	1253(w)	520(w)	428(w)

Table (3) Electronic spectral data of ligand (MTP) and its complexes in DMSO solvent

Compounds	λ (nm)	ν (cm^{-1})	ABC	ϵ_{max} molar $^{-1}\text{cm}^{-1}$	Transitions
Ligand MTP	268	37313	1.272	1272	$\pi \rightarrow \pi^*$
	301	33222	0.927	927	$n \rightarrow \pi^*$
	269	37174	1.490	1490	L.F.
[Mn(MTP) ₂]	329	30395	2.212	2212	C.T
	465	21505	0.041	41	${}^6A_1 \rightarrow {}^4T_{1(G)}$
	269	37174	1.525	1525	L.F.
	342	29239	2.041	2041	C.T Mix whit ${}^4A_2 \rightarrow {}^4T_1$
[Co(MTP) ₂]	585	17090	0.028	28	${}^4A_2 \rightarrow {}^4T_{1(F)}$
	830	12048	0.018	18	${}^4A_2 \rightarrow {}^4T_{2(F)}$
	269	37174	1.352	1352	L.F.
	330	30303	1.819	1819	C.T
[Ni(MTP) ₂]	390	25641	0.030	30	${}^3T_{1(F)} \rightarrow {}^3T_{1(P)}$
	530	18867	0.030	30	${}^3T_{1(F)} \rightarrow {}^3A_2$
	910	10989	0.020	20	${}^3T_{1(F)} \rightarrow {}^3T_{2(F)}$
	269	37174	1.536	1536	L.F.
	330	30303	2.360	2360	L.F.
[Cu(MTP) ₂]	655	15267	0.022	22	${}^2B_{1g} \rightarrow {}^2A_{1g}$
	751	13315	0.020	20	${}^2B_{1g} \rightarrow {}^2B_{2g}$
	269	37174	1.279	1279	L.F.
	310	32258	0.952	952	L.F.
[Zn(MTP) ₂]	316	31645	0.967	967	C.T
	369	77174	1.327	1327	L.F.
	319	31347	1.173	1173	L.F.
[Cd(MTP) ₂]	441	22675	0.220	220	C.T
	269	37174	1.500	1500	L.F.
	345	28985	2.209	2209	C.T
[Hg(MTP) ₂]	357	28011	1.170	1170	C.T

L.F = ligand field , C.T = charge transfer

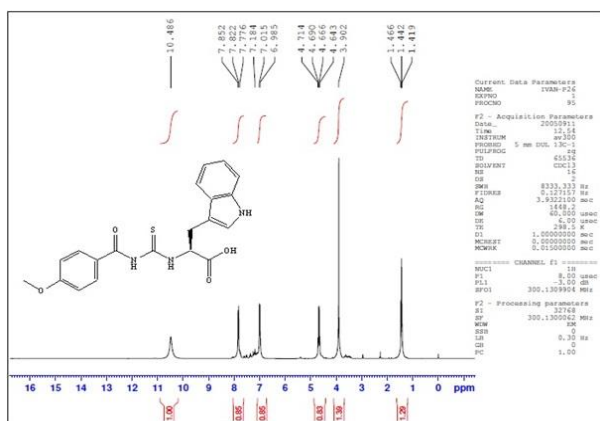


Figure No(1) : ¹H-NMR spectrum of ligand (MTP)

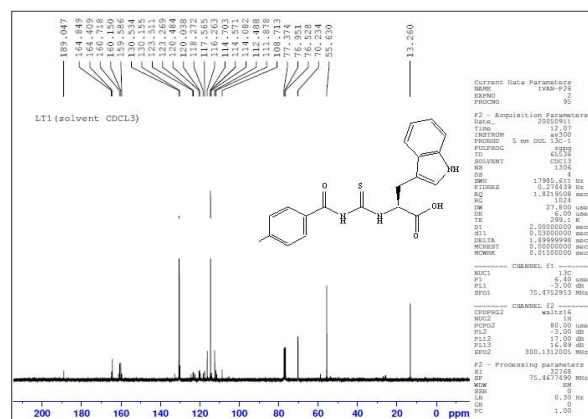


Figure No. (2): ¹³C-NMR spectrum of ligand (MTP)

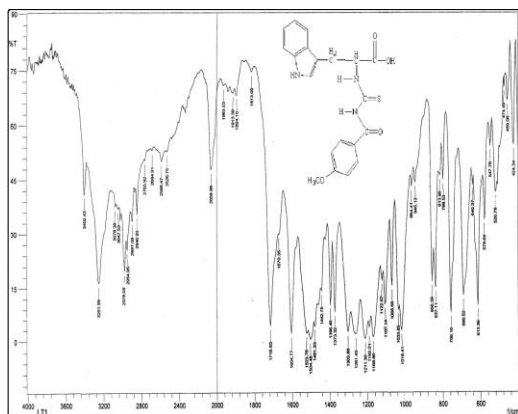


Figure No. (3): Infrared spectrum of ligand (MTP)

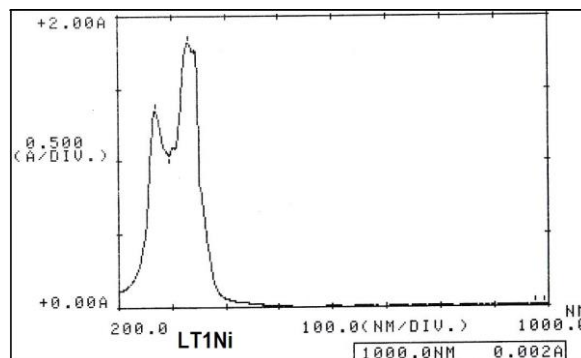


Figure No. (6): U.V spectrum of complex [Ni(MTP)₂]

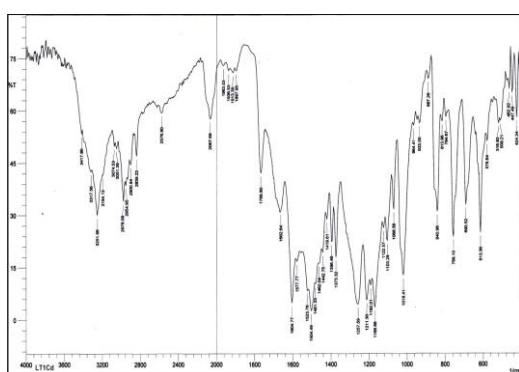


Figure No. (4): Infrared spectrum of complex [Cd(MTP)₂]

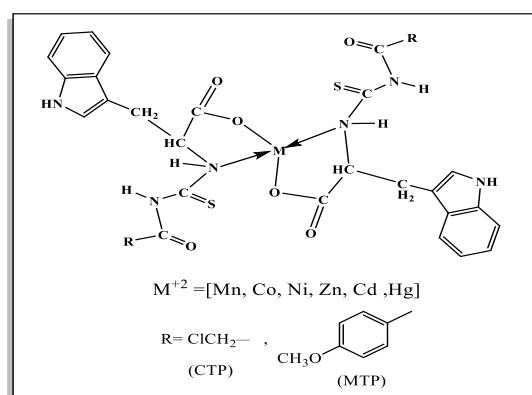


Figure No. (7): The proposed tetrahedral structure of the complexes [M(MTP)₂].

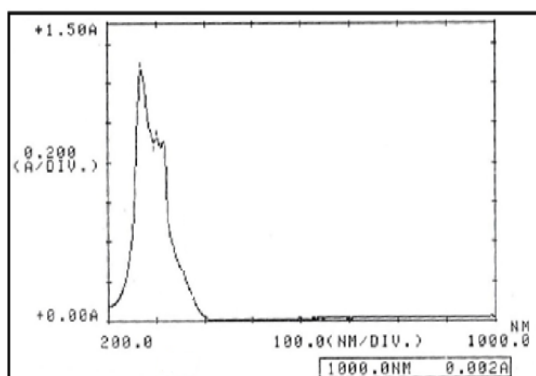


Figure No. (5): U.V spectrum of ligand (MTP)

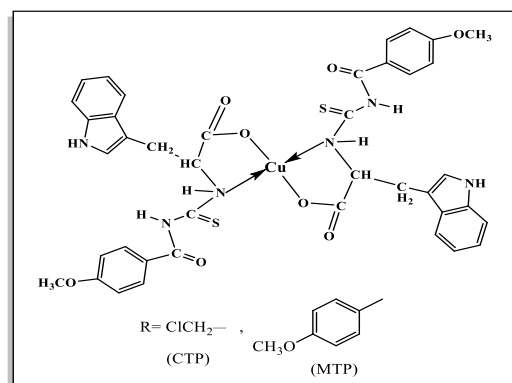


Figure No. (8): The proposed square planar structure complex for [Cu(MTP)₂].

تحضير تشخيص طيفي ودراسة بعض المعقدات الفلزية ثنائية التكافؤ مع الليكاند [3-(هيدروجين 1-اندول-2-3)-4-ميثوكسي بنزويل(ثايويوريديو) حامض بروبانويك]

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الخلاصة:

في هذا العمل حضر الليكاند الجديد [3-(هيدروجين 1-اندول-2-3)-4-ميثوكسي بنزويل(ثايويوريديو) حامض بروبانويك] (MTP) وذلك من مفاعله (4-ميثوكسي بنزويل أيزوثايبوسيانات) مع الحامض الاميني التربتوفان وبنسبة (1:1) وشخص بوساطة التحليل الدقيق للعناصر (C.H.N.S) والأشعة تحت الحمراء والأشعة فوق البنفسجية- المرئية وطيف الرنين النووي المغناطيسي, كما حضرت وشخصت معقدات أملاح بعض ايونات العناصر الانتقالية الثنائية التكافؤ (Hg, Cd, Zn, Cu, Ni, Co, Mn) مع الليكاند (MTP) وشخصت المعقدات المحضرة باستخدام الأشعة تحت الحمراء والأشعة فوق البنفسجية - المرئية والتوصيلية المولارية والحساسية المغناطيسية والامتصاص الذري واستنتج إن المعقدات لها شكل رباعي السطوح ماعدا معقد النحاس له شكل مربع مستوي حول الايون الفلزي مع الليكاند (MTP) ثنائي السن.

الكلمات المفتاحية : تربتوفان, 4-ميثوكسي بنزويل أيزوثايبوسيانات, أيونات فلزية ثنائية التكافؤ, معقدات.