

Synthesis And Study of New Metal Complexes Derived From 1-[2-(1,3-Benzothiazol-2-Yl Thio) Acetyl]-3-Methyl 2-Pyrazolin-5-one

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Abstract

The ligand 1-[2-(1,3-benzothiazol-2-yl-thio)acetyl]-3-methyl-2-Pyrazolin-5-one was synthesized by the reaction of 2-mercapto benzothiazol with ethyl chloro acetate in an ethanolic solution . The product was reacted with hydrazine in the same solution and the product reacted with ethyl aceto acetate. The complexes of this ligand have been synthesized from the reaction of the ligand with the metal ions [Mn(II),Co(II),Ni(II), Cu(II), Zn(II), Cd(II) and Pt(IV)].Elemental analysis (C.H.N), FT-IR, UV-Visible spectroscopy, atomic absorption , magnetic susceptibility, molar ratio and molar conductance measurements have been determined. Metal to ligand [M:L] ratio obtained for all complexes in ethanol using molar ratio method , Evidence from IR spectra shows that in all the complexes the ligand is coordinated Via the pyrazolin nitrogen, and exo cyclic sulfur m oxygen atom.

الخلاصة

الليكاند (L) 1-[2-(1,3-benzothiazole-2-yl-thio)acetyl]-3-methyl-2-pyrazolin-5-one تم تحضيره من مفاعلة 2-مركبتو بنزو ثيازول مع اثيل كلورواستيت في وسط كحولي ومن ثم مفاعلة الناتج مع الهيدرازين ، بعدها مفاعلة الناتج مع اثيل اسيتو اسيتيت ، اما المعقدات فتم تحضيرها من مفاعلة الليكاند (L) مع الايونات الفلزية [Mn(II),Co(II),Ni(II),Pt(IV),Cd(II),Zn(II),Cu(II)] وقد اعتمدت في التحقق من الصيغ التركيبية لليكاند ومعقداته تقنيات اطياف الاشعة تحت الحمراء (FT.IR) والاشعة فوق البنفسجية والمرئية (UV-Vis) ، تحليل العناصر باستخدام تقنية الامتصاص الذري ، العزوم المغناطيسية والتوصيلية المولارية الكهربائية . وقد تم استخدام طريقة المتغيرات المستمرة لتحديد نسبة الفلز الى الليكاند لجميع معقدات الليكاند في مذيب الايثانول ، ومن دراسة اطياف الاشعة تحت الحمراء لهذه المعقدات وجد ان هذا الليكاند يسلك سلوك ليكاند مخلبي ثلاثي السن ، إذ يرتبط مع الايونات الفلزية عن طريق ذرة النتروجين التابعة لحلقة الباي رازولين وذرة الاوكسجين والكبريت خارج الحلقة .

Introduction

The 2- mercapto benzothiazol derivatives represent very important hetero cyclic compounds for their biological and pharmacological activities⁽¹⁻³⁾. These activities are probably due to the presence of the $-N=C-S$ group. Substituted benzothiazole have been reported to display diverse applications as photostablizer and metal complexing^(4,5).

The insertion of functional groups into the ring of hetero cyclic compound 3-methyl pyrazolin-5- one was reported to produce some compounds of biological activity⁽⁶⁻⁸⁾.

The wide range of application of the ligand and its metal complexes aroused our interest to prepare a new series of some metal complexes.

Experimental

Apparatus :

Melting points were recorded on Gallen Kamp melting point apparatus and were un corrected . The IR spectra of the compounds were recorded with shimadzu FT-IR -3600 spectrophotometer. Electronic spectra were recorded on Shimadzu UV-Visible recording spectrophotometer UV260(200-800nm). The elemental analysis (C.H.N) were recorded on (Carlo-Erba micro analyzer type 1106).

Conductivity measurements were obtained using conductivity Hand – Held meter LF 330 .

These measurement were obtained in (DMF) as a solvent using concentration of ($10^{-3}M$) at $25^{\circ}C$. Magnetic susceptibility measurements (Faraday's Method) at room temperature were

performed using standard instrumentation Cohn 2000(0.001mg) electrobalance.

Chemical :

All chemicals were of highest purity and were used as received.

1-Preparation of ligand

a) 2-(1,3-benzothiazol-2-yl thio) ethyl acetate ((1)).

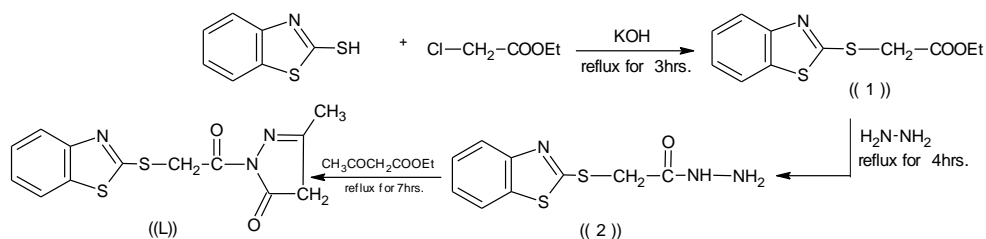
To a hot ethanol solution of 2-mercapto benzothiazole (0.1mole), ethyl chloro acetate (0.1mole) in presence of KOH as a basic media was added. The mixture was refluxed for (3hrs), The solid product was collected and crystallized from ethanol gave a white crystals (m.p. $42^{\circ}C$, yield 75%).

b) 2-(1,3-benzothiazol-2-yl thio)aceto hydrazide((2)).

To a solution of compound ((1)) (0.1mole) in absolute ethanol, hydrazine (0.1mole) was added . The mixture was refluxed for (4hrs), the solvent was removed and the solid product was collected and crystallized from ethanol gave a white needles (m.P $165^{\circ}C$, yield 72%).

c) 1-[2-(1,3-benzothiazol-2-yl thio)acetyl]-3-methyl-2-Pyrazolin-5-one (L).

To a hot solution of compound((2)) (2.39gm, 10mmole) in absolute ethanol (10ml), ethyl aceto acetate(10ml) was added. The mixture was refluxed for (7hrs), the solvent was removed and the solid product was collected and crystallized from methanol .The physical properties of the prepared ligand is described in Table(1), the synthetic route is shown in scheme 1.



2-Preparation of metal complexes:

a. Complexes with Co(II) Ni(II) , Cd(II) and Cu(II):

The complexes were prepared by interaction between the metal chloride (1mmole) and ligand (L) (1mmole) using ethanol as solvent. The resulting mixture was refluxed for (1hr.) . Then filtered and recrystallized from a mixture of (DMSO:ethanol)(30:70).

b. Complexes with Mn(II) and Zn(II):

A solution of (1mmole) of the ligand (L) dissolved in (10ml) of absolute ethanol and (1mmole) of metal chloride dissolved in (10ml) of absolute ethanol were mixed. The resulting mixture was refluxed for (2hrs), cooled, filtered and recrystallized from hot absolute ethanol.

c. Pt(IV) complex:

A solution of (1mmole) of the ligand (L) dissolved in (10ml) of absolute ethanol and (1mmole) of K_2PtCl_6 dissolved in a mixture of (ethanol:water) (50:50). Then the mixture was refluxed for (1hr.) , cooled, filtered and recrystallized from a mixture of (DMSO: ethanol) (30:70).

Study of complex formation is solution

Complexes of (L) with metal ions were studied in solution using ethanol as a solvent , in order to determine [M:L] ratio in the complex following Molar ratio methods⁽⁹⁾. A series of solutions were prepared having a constant concentration [$10^{-3}M$] of the metal ion and (L) . The [M:L] ratio was determined from the relationship between the absorption of the absorbed light and the mole ratio of [M:L]. The results of complex formation in solution were listed in table(1).

Table 1: Physical data for (L) and its metal complexes.

Compound	Color	Melting point °C	Yield%	Elemental analysis Calc.(found)				M:L (in EtOH)
				C	H	N	M	
C ₁₃ H ₁₁ N ₃ O ₂ S ₂ (L)	Light brown	210-212	80	51.14 (50.46)	3.60 (3.34)	13.77 (12.96)		
[Mn(L)Cl]Cl	Pale green	238-340	70	36.19 (36.56)	2.55 (2.01)	9.74 (9.41)	12.74 (13.25)	1:1
[Co(L) ₂]Cl ₂	Brown	224-226	78	42.16 (42.79)	2.97 (2.71)	11.35 (12.02)	7.96 (7.53)	1:2
[Ni(L)Cl]Cl	Green	220 ^{d*}	67	35.88 (35.19)	2.53 (2.79)	9.66 (9.51)	13.50 (13.96)	1:1
[Cu(L)Cl]Cl	Dark green	230-232	75	35.49 (35.21)	2.50 (2.16)	9.55 (9.97)	14.45 (14.93)	1:1
[Pt(L)Cl ₃]Cl	Deep orange	218-220	70	24.29 (24.90)	1.71 (1.94)	6.54 (6.05)	30.38 (31.22)	1:1
[Zn(L)Cl]Cl	Pale Yellow	214 ^{d*}	82	35.34 (34.75)	2.49 (2.13)	9.51 (8.99)	14.81 (14.12)	1:1
[Cd(L)Cl]Cl	White	240 ^{d*}	85	31.94 (31.13)	2.25 (2.11)	8.59 (8.08)	23.01 (23.09)	1:1

Results and Discussion

The physical analytical data for the ligand and the prepared complexes are given in table(1) indicated that the M:L stoichiometry was 1:1 for all complexes except for CoL which was 1:2.

The data of (C.H.N) and metal analysis were obtained using flame atomic absorption technique. The calculated values were in a good agreement with the experimental values. The suggested molecular which are formulas also supported by subsequent spectral and molar ratio, as well as magnetic moment.

Infra red spectroscopy: The structure of compound ((1)) was confirmed by the presence of bands at 1695cm⁻¹, 1032cm⁻¹ and 699cm⁻¹ were assigned to the stretching of C=O, C-O and C-S-CH group respectively ⁽¹⁰⁾. The reaction of compound((1)) with hydrazine hydrate afforded the compound((2)), the appearance of (IR) new absorption bands at 3320cm⁻¹, 3200cm⁻¹, 1650cm⁻¹ and 755cm⁻¹ assigned to stretching vibration of NH₂, NH, C=O and C-S stretching vibration respectively ⁽¹¹⁾. Moreover treatment of -NHNH₂ in

compound ((2)) with ethyl aceto acetate to give new ligand (L) shows new bands at 1655cm⁻¹, 758cm⁻¹ which may be attributed to C=O, C-S and bonding C=N of 2-pyrazolin ring ⁽¹²⁾. In the IR spectra of all the complexes these bands appeared at lower wave numbers about (5-20cm⁻¹), (5-25cm⁻¹) and (6-26cm⁻¹) for the C=N, C=O and C-S group stretching vibration respectively ⁽¹³⁾.

New bands were observed for the coordination (M←N=C), (M←O=C), (M-S) and (M-Cl) bands appeared in the regions (470-492cm⁻¹), (500-545cm⁻¹), (363-410cm⁻¹) and (255-320cm⁻¹) respectively ⁽¹⁴⁾, table (2).

Electronic spectra, Magnetic moment and Conductance measurements:

The UV spectrum of the ligand (L) showed intense bands at 305 nm and at 372 nm which belong to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively⁽¹⁵⁾, table (3).

The electronic spectrum of Mn(II) complexes showed bands at (18933 cm⁻¹), (24872 cm⁻¹) and (29855 cm⁻¹) assignable to ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$, ${}^6A_{1g} \rightarrow {}^4E_{1g}$, ${}^4A_{1g}(G)$ and ${}^6A_{1g} \rightarrow {}^4E_{1g}(D)$ respectively and the magnetic moment values of the Mn(II) complex is (5.53 B.M) supported the tetrahedral geometry⁽¹⁶⁾.

The electronic spectrum of (Co(II) complex showed bands at (11961 cm⁻¹), (18163 cm⁻¹) and (21495 cm⁻¹) assignable to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ respectively and the magnetic values of the Co(II) complex is (4.7 B.M) supported the octahedral geometry⁽¹⁸⁾.

The electronic spectrum of the Ni(II) complex showed bands at (18769 cm⁻¹), (23952 cm⁻¹) and (26819 cm⁻¹) due to ${}^1A_{1g} \rightarrow {}^1A_{2g}$, ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1E_g$

respectively supported the square planar geometry⁽¹⁹⁾ and the magnetic moment values of the Ni(II) is diamagnetic indicating a square planar geometry⁽²⁰⁾.

The magnetic moment values ($\mu_{\text{eff}} = 1.77 \text{ B.M}$) for Cu(II) complex corresponds to one unpaired electron. The electronic spectrum of the Cu(II) complex showed one band at (17220 cm⁻¹) attributable to ${}^2B_{1g} \rightarrow {}^2E_g$ transition in the square planar geometry⁽²¹⁾.

The Zn(II) and Cd(II) complex were diamagnetic as expected for d¹⁰ ions, so that no d-d transition can be expected in the visible region, this supports the tetrahedral geometry complexes^(22,23).

The Pt(IV) complex showed three bands at 21153, 25476 and 26715 cm⁻¹ which indicate an octahedral geometry⁽²⁴⁾ and the magnetic moment value of the Pt(IV) complex is (2.41 B.M) supported the Octahedral geometry⁽²⁵⁾.

Molar Conductance measurement in dimethyl formamide (DMF) as a solvent at 25°C showed that the complexes were to be ionic⁽¹⁵⁾, table (3)

Table 2: IR Analytical data (cm⁻¹) of (L) and its metal complexes.

Compound	$\nu \text{ C=N}$	$\nu \text{ C=O}$	$\nu \text{ C-S}$	$\nu \text{ M-O}$	$\nu \text{ M-S}$	$\nu \text{ M-N}$	$\nu \text{ M-Cl}$
C ₁₃ H ₁₁ N ₃ O ₂ S ₂ (L)	1610	1655	758				
[Mn(L)Cl]Cl	1595	1645	750	545	410	482	320
[Co(L) ₂]Cl ₂	1591	1630	742	512	391	489	318
[Ni(L)Cl]Cl	1590	1643	740	523	385	477	265
[Cu(L)Cl]Cl	1593	1640	747	525	363	490	255
[Pt(L)Cl ₃]Cl	1592	1638	752	543	397	492	300
[Zn(L)Cl]Cl	1600	1650	745	500	367	479	290
[Cd(L)Cl]Cl	1605	1648	732	505	375	470	333

Table 3: Electronic spectra, Conductance (in DMF) and Magnetic moment (B.M) for (L) and its metal complexes.

Comp.	Wave number(cm^{-1})	Transitions	Molar Cond. $\text{ohm}^{-1}.\text{cm}^{-2}.\text{mol}^{-1}$	μ_{eff} (B.M)	Suggested structure
$\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_2\text{S}_2(\text{L})$	26881 32750	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$			
$[\text{Mn}(\text{L})\text{Cl}]\text{Cl}$	18933 24872 29855	${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{1\text{g}}(\text{G})$ ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{E}_{1\text{g}}, {}^4\text{A}_{1\text{g}}(\text{G})$ ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{E}_{1\text{g}}(\text{D})$	82.78	5.53	Tetrahedral
$[\text{Co}(\text{L})_2]\text{Cl}_2$	11961 18163 21495	${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{2\text{g}}(\text{F})$ ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{A}_{2\text{g}}(\text{F})$ ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{1\text{g}}(\text{P})$	166	4.70	Octahedral
$[\text{Ni}(\text{L})\text{Cl}]\text{Cl}$	18769 23952 26819	${}^1\text{A}_{1\text{g}} \rightarrow {}^1\text{A}_{2\text{g}}$ ${}^1\text{A}_{1\text{g}} \rightarrow {}^1\text{B}_{1\text{g}}$ ${}^1\text{A}_{1\text{g}} \rightarrow {}^1\text{E}_{\text{g}}$	84.82	Diamagnetic	Square planer
$[\text{Cu}(\text{L})\text{Cl}]\text{Cl}$	17220	${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{E}_{\text{g}}$	76.56	1.77	Square planer
$[\text{Pt}(\text{L})\text{Cl}_3]\text{Cl}$	21153 25476 26715	${}^1\text{A}_{1\text{g}} \rightarrow {}^3\text{T}_{1\text{g}}$ ${}^1\text{A}_{1\text{g}} \rightarrow {}^3\text{T}_{2\text{g}}$ ${}^1\text{A}_{1\text{g}} \rightarrow {}^1\text{T}_{1\text{g}}$	87.00	2.41	Octahedral
$[\text{Zn}(\text{L})\text{Cl}]\text{Cl}$	30847 32398	Charge transfer	65.80	Diamagnetic	Tetrahedral
$[\text{Cd}(\text{L})\text{Cl}]\text{Cl}$	32100 33985	Charge transfer	71.80	Diamagnetic	Tetrahedral

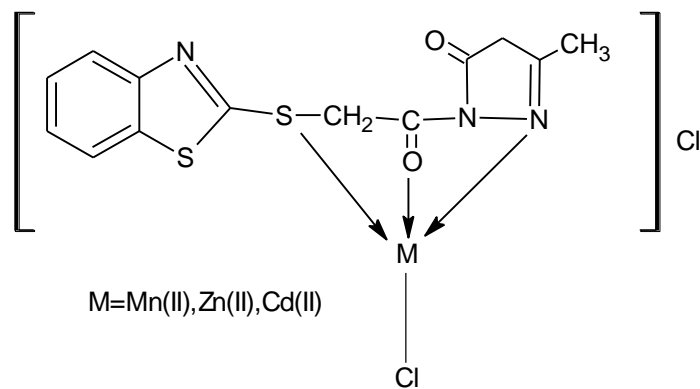


Figure (1)

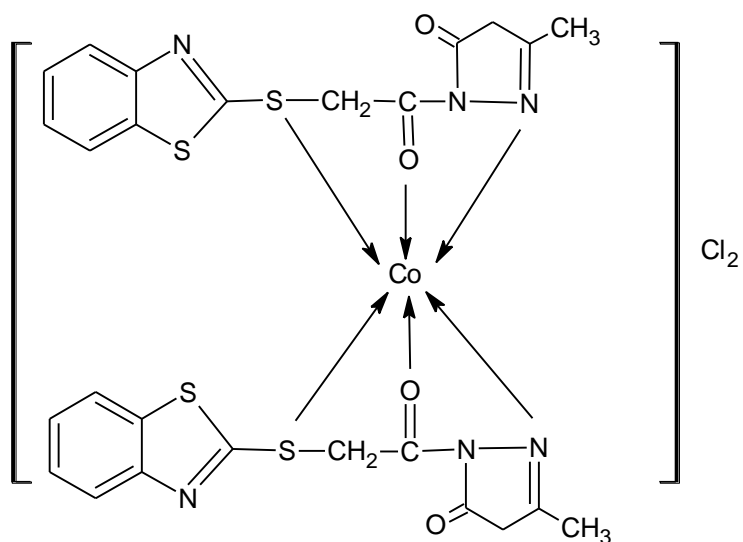


Figure (2)

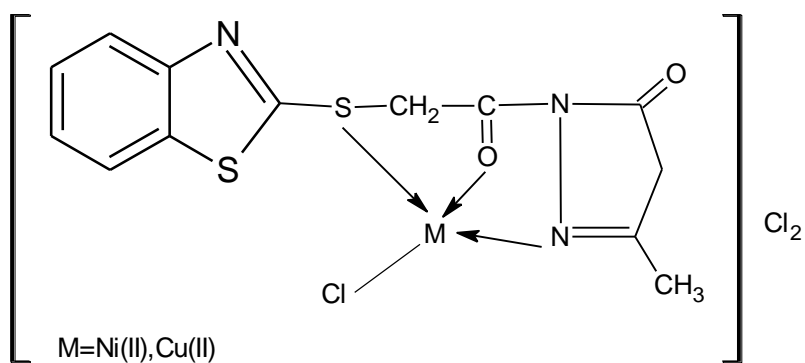


Figure (3)

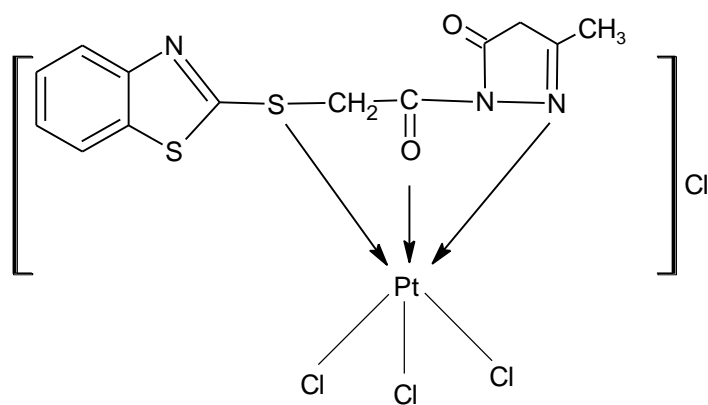


Figure (4)

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