Synthesis and Spectroscopic Study of Transition Elements Complexes with New –β-diketonate Hetero-Ligand

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ABSTRACT

A new ligand 3-[benzothiazolyl]-2,4-pentadione (HL) has been prepared by sequence reactions of 2-mercaptobenzothiazole (I) by methylation and oxidation reactions, then substitution of derivative (III) using sodium hydride as strong base. The product was isolated, studied and fully characterized by appropriate physical measurements; F.T.I.R., UV/Visible, and determination of molecular weight by the depression in freezing point (ΔT_F) in nitrobenzene as solvent. The new ligand (HL) has been used to prepare a series of complexes with Cr(III), Mn(II), Co(II), Ni(II) & Cu(II).

All the prepared complexes have been studied and characterized in solid state by micro elemental anaylsis (C.H.N.M), F.T.I.R. UV/Visible, magnetic moment (μ_{eff}), and measurement of molar conductance (Λ_m) in D.M.F. Molar ratio measurements in solution gave comparable results with those obtained from solid state study.

Introduction

The use of 2-mercaptobenzothinzole (I) as analytical reagent [1-4], and of its complexes in industry and medicine has been known for along time[5-6]. The structures of its complexes with a few metal ions have also been investigated using various physical techniques[7-9]. Such as 3,3'-thiodipropionic acid bis(4-amino-5-ethylimino-2,3-dimethyl-1-phenyl-3-pyrazoline) complexes with Co(II), Ni(II) and Cu(II), which have been synthesized and structurally characterized and the ligand and its complexes have been screened for their antifungal and antibacterial activities against three fungi, and tow bacteria[10].

Benzothiazole containing functional groups like hydroxy, carbonyl and isomethene groups have been reported as antiirradiation agents[11-12], antifungal, and its metal complexes may be light emitting di Iodide (LED)[12-16] with some transition elements like lanthanides where were resulting consequently in a great enhancement of the Lanthanum(III) ion luminescence (ligand sensitized luminescence)[17].

Luminescent properties of a novel terbium complex [Tb(acac)3AAP (acac: acetylacetone, AAP:4-amino-antipyr-ine)] were synthesized and studied. This

complex was used as an emitting center, triple-layer-type device with a different structure of glass exhibited bright characteristic emission of terbium ion upon applying d.c. voltage. The maximum luminance of the device is 56 cd/m2 at 19 V and the maximum luminance efficiency is 0.357 lm/W[18].

The present work focus the attention on such compounds functionalized with β-diketonate group and its metal complexes with some transition elements of the first row.

II. Experimental

Materials:

2-meraptobenzothiazole(MBT), 2,4-pentadione (acetyl acetone), (purity>99%) were obtained from Aldrich chemical and used without further purification.

Instruments:

Elemental analysis were carried out by using Carlo-Erba-5500 elemental analyzer.

I.R. spectra were obtained using Pye-unicam SP3-300 infrared spectrophotometer for the range 4000-200cm^{-1} by using CsI-discs.

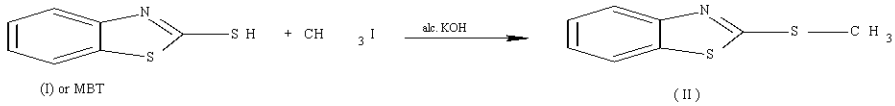
The content of metals in the complexes were determined by Shimadzu AA-670 and Elemental Analyzer-MOD 1006.

Electronic spectra (UV-Vis.) were recorded using shimadzu UD-160A ultraviolet for the range (200-800)nm, in 10^{-3}M solution of DMF.

Magnetic susceptibility (X_g) measurements were done using Bruker Magnet BM6, and conductivity measurements were obtained using Tacussel conductometer type CD6N.

Preparation of 2-methyl merceptobenzothiazole (II)

This compound was prepared as described by Dave and Vora [19]. Scheme (1)

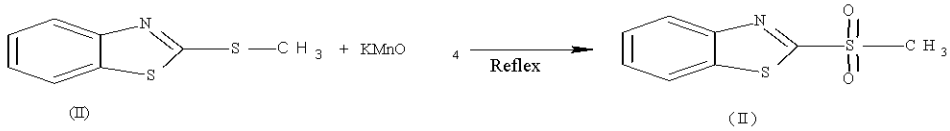


(I) or MBT (II)

Scheme (1)

Preparation of Methyl sulforxyl Benzothiazole (III)

(0.01 mole, 1.81gm) of (II)-compound dissolved in 25ml dioxane, was added step wise with constant stirring to 10% (w/v) solution of $KMnO_4$ in acetic acid. The reaction mixture was refluxed for 3hrs., then cooled at room temperature to yield a dark-yellow powder, which then filtered, washed with dioxane, then petroleum ether, and dried in air, scheme (2)

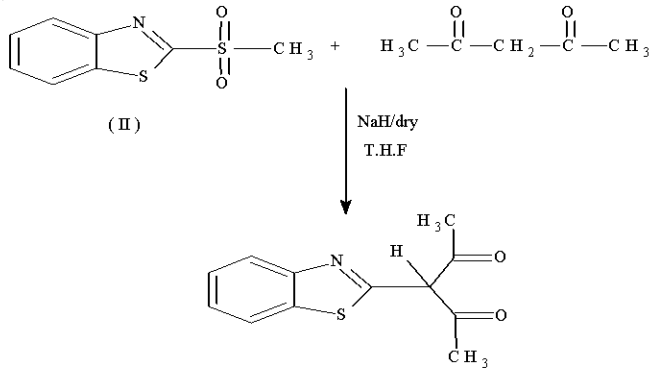


(II) (II)

Scheme (2)

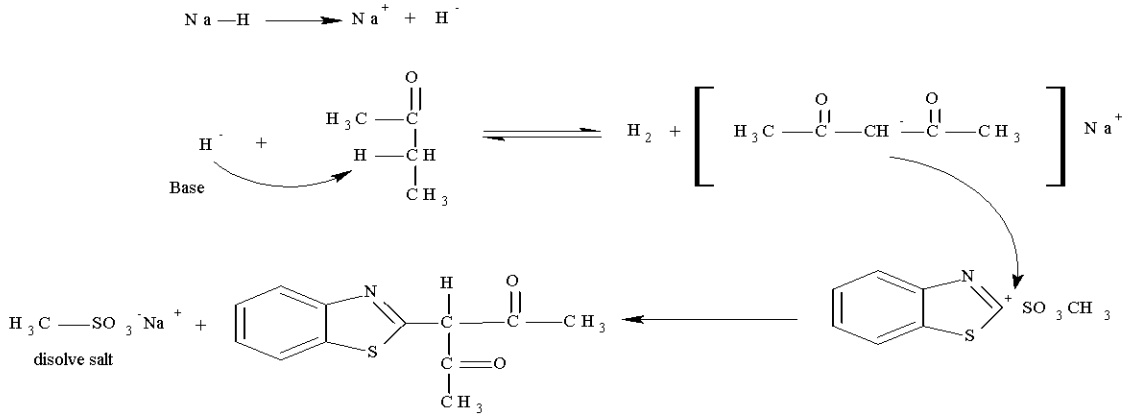
Preparation of 3-[benzothiazolyl]-2,4-pentadione (HL)

A solution of methyl sulfoxide benzothiazole (III) (0.01 mole/1.35gm) in 50mL of dry THF was added drop wise over 2hrs. and stirred solution of 2,4-pentadione (0.01mole, 2.4gm) in 25mL of warm THF containing 1gm NaH in the reaction mixture was stirred on a water bath for 6 hours, then solid mass separated out on cooling, which was kept in a refrigerator for better crystallization. It was then filtered, washed with THF, dioxane, then with petroleum ether, and subsequently dried over anhydrous $CaCl_2$ in a desiccator. The yellow precipitate of (HL) was purified by recrystallization from absolute ethanol, scheme (3):



Scheme (3)

Mechansium of ligand preparation:



Preparation of complexes C_1,C_4 & C_5

(2mmole, 0.466g) of (HL) dissolved in ethanol (50ml) was added gradually with stirring to 20ml of 5% (w/v) potassium-tertiarybutyl oxide. 1mmole of $CrCl_3$ $6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$ in 20ml of distilled water was added to the first solution, then refluxed on water bath for 2hrs., till the complexes precipitated out. The colored complexes filtered, washed with distilled water, ethanol and dried under vacuum. Recrystallization from (DMF:H_2O) yield green, orange and dark green crystals of Cr(III), Ni(II) & Cu(II) complexes respectively. Table (1).

Preparation of C_2 and C_3 complexes

2mmole, 0.466g of ligand (HL) in 50ml of ethanol, was gradually added to 20ml of 5% w/v potassium-tertiary bentyl oxide. Upon adding 1mmole of $MnCl_2.4H_2O$ or $CoCl_2.6H_2O$ in 20ml distilled water to the above solution, colored precipitate separated immediately, which then filtered, washed with water, ethanol, dried under vaccum, recrystalization form (DMF:H_2O) yield brown and green crystals of Mn(II) & Co(II) complexes respectively. Table (1)

Table (1): Physcial properties of elemental analysis of the prepared compounds

Compound Symbol	M.P°C/color	Yield%	Microelemental anaylsis Cal.(Founed)				** Mwt for HL and complexes g/mole Cal.(founed)	Formula
			C%	**H%**	**N%**	**M%***		
HL	White/yellow (140-142)	65	61.8 (60.9)	4.72 (4.01)	6.00 (5.81)	-----	233.035 (230.95)	$C_{12}H_{11}NSO_2$
C_1	Green /190-192	80	46 (45.89)	3.19 (3.01)	4.47 (4.33)	8.3 (8.19)	627 (630.1)	$K[Cr(L)_2Cl_2]$
C_2	Brown /180-182	75	55.50 (54.31)	3.86 (3.12)	5.40 (4.85)	10.56 (9.77)	520 (522.1)	$[Mn(L)_2]$
C_3	Green/198[d]	70	55.07 (51.33)	3.87 (2.92)	5.35 (4.43)	11.27 (10.44)	525 (526.1)	$[Co(L)_2]$
C_4	Orange 215[d]	85	55.17 (54.43)	3.83 (3.22)	5.36 (4.46)	11.22 (10.35)	524 (524.1)	$[NiL_2]$
C_5	Green/215-217	95	42.57 (41.88)	2.95 (2.25)	4.13 (3.98)	9.38 (8.82)	678 (679.1)	$K_2[CuL_2Cl_2]$

M%*=Metal content was determined by S.F.A.A.S

**=Depression in freezing point ΔT_f to deduec Fut. of complexes

Table (2): Infra-red spectra of β-diketonate (HL) ligand and their metal complexes

Compound	I.R. $\upsilon(cm^{-1})$ $\upsilon_{C=0}$, υ_{C-H}, $\upsilon_{C=N}$, M-O
HL	1760(s), 2943, 1627, 3481[a] (O-H)
C_1	1750(s), 2960, 1610, 415(m), 295(Cr-Cl)
C_2	1747, 2894, 1620(s), 490, 395(m)
C_3	1743, 2943-2894(m), 459(w)
C_4	1748(s), 2962(m), 415-500 (Ni-O)
C_5	1745(s), 2950(m), 415(Cu-O)(w), 295-315(Cu-Cl)

[a] band at 3481 (br) alcoholic group referred to tautomerism of β-diketone ligand
s=strong, m=medium and w=weak

Table (3): Molar conductance, magnetic and other properties of the prepared complexes

Complex	Λm ohm^{-1} cm^2 mol^{-1}	μ_{eff} (B.M)	M:L ratio	Suggested Symmetry
C_1	75	2.5	1:2	Octahedral
C_2	20	3.9	1:2	Tetrahedral
C_3	45	1.6	1:2	Square planar
C_4	30	0.0	1:2	Square planer
C_5	180	1.30	1:2	Octahedral

a =molar conductance were measured in DMF solutions

Table (4): Electronic spectra of the prepared compounds in ethanol spectrosol and DMF (10^{-3}M)

Compound	Uv/visible λ_{max} nm($\in_{max}$)			
	π→ π`	n→ π`	C.T	d-d-transition
HL	240	350	365(31,000)	
C_1	220	315	370(40,000)	450(90),600(120)
C_2	215	340	390(35,000)	
C_3	230	325	365(33,000)	645(115)
C_4	220	318(1500)	395(159000)	550(120)
C_5	249	350(7500)	380(25500)	508(95)

C.T= Charge transfer, $\in_{max}$ (L.ml^{-1}.cm^{-1})

III. Results & Discussion

Microanalytical, molar conductance, and magnetic moment data, TG-DTA of the ligand (HL) and its metal complexes, are given in tables (1 and 3). The stoichiometries of the ligand and its complexes were confirmed by their elemental analyses. The molar conductance measured in 10^{-3}M DMF solutions of the complexes fall in the range (90-45) ohm^{-1} cm^2 mol^{-1} for C_2,C_3 and C_4 complexes, indicating non-electrolytic behavior[19,20], where C_1 and C_5 complexes behave as electrolyte in 1:1 and 2:1 ratio respectively .

The reactions of the transition metal chloride with the ligand (HL), are represented by the following equations:

$$2HL + CrCl_3.6H_2O \xrightarrow[H_2O]{2Bu^t-\bar{O}K^+} K[CrL_2Cl_2] + 2Bu^t - OH + KCL$$

$$MCl_2.xH_2O + 2HL \xrightarrow{2Bu^t-\bar{O}K^+} [ML_2] + xH_2O + 2KCl + 2Bu^t - OH$$

$$CuCl_2.2H_2O + 2HL \xrightarrow{2Bu^t-\bar{O}K^+} K_2[CuL_2Cl_2] + 2H_2O + 2Bu^t - OH$$

The metal/ligand mole ratio was found to be 1:2 according to elemental analyses and spectrophotometric studies obtained from continuous variation using Job`s methods.

The observed magnetic moment of Cr (III) complex was 2.58B.M this value suggested octahedral stereochemistry due to orbital contribution of $(t_2g)^3$ with π* of β-diketonate ligand[21].

The observed magnetic moment of Mn (II) & Co (II) complexes were 3.9 to 1.6 B.M., these indicate the tetrachedral and square planer geometries respectively[19].

However, copper complex showed magnetic moment (1.30B.M) of unpaired electron, suggesting the octahedral symmetry [22, 23].

The nickel complex is diamagnetic. The diamagnetism is very strong indication that the spatial arrangement of the ligand molecules around the nickel ion is square planer [24].

I.R. Spectra

The important features for the ligand (HL) and metal complexes may be summarized as follow:

The strong band that appeared in the spectrum of ligand (Fig.(1))at 1760cm^{-1}, is assigned to vibration of carbonyl group, and the tautomersm of acidic proton of C=O carbonyl may investigate tautomersm of alcoholic group υ_{OH} at 3481cm^{-1}.The intensity of these bands is considerably lowered in formed metal complexes, moreover, the bands are broad, and the number of bands decreases in this region. Therefore, the blue shift in carbonyl group in the range (10-17)cm^{-1} indicates the coordination of metal ion via oxygen atoms of β-diketonato group[25]. However the appearance of low frequency vibrational modes in range of (395-500)cm^{-1}, may be attributed to M-O bond [26].

Finally, the infrared spectra of the octahedral complexes Cr(III)& Cu(II) show only one band for each one, in the far-infrared region at 295 and 315cm^{-1} respectively, these bands were assigned for υ_{M-Cl} of trans-octahedral isomers[27]. (Figures 2 and 3).

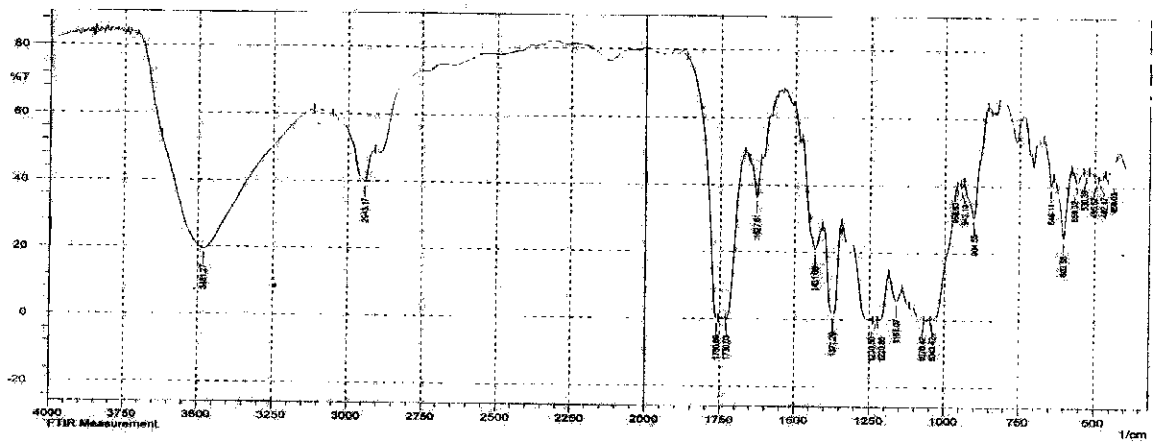


Fig.(1): F.T.I.R Spectrum of ligand (HL) in KBr - disc.

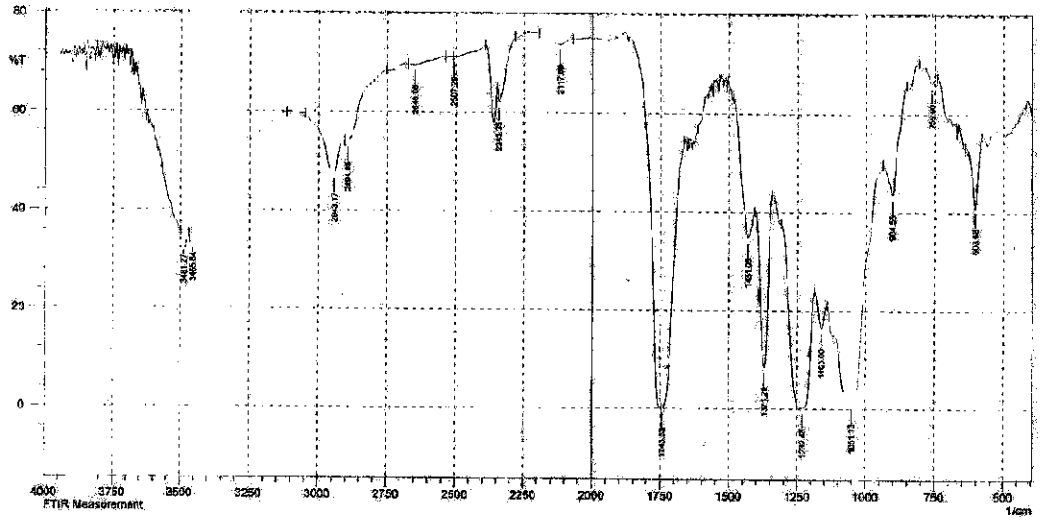


Fig.(2): F.T.I.R Spectrum of Cr(III) complex in CsI - disc.

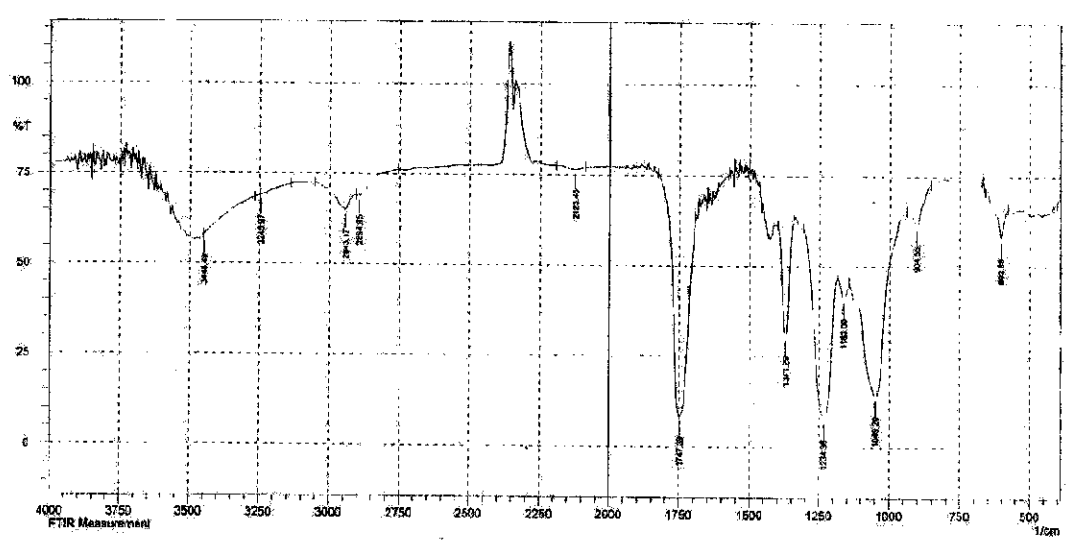


Fig.(3): F.T.I.R Spectrum of Cu(II) complex in CsI - disc.

H[1]NMR spectra:

The resonance signals for (HL) ligand in d6-DMSO solvent showed distinct peaks at (7-8)ppm, a high assigned to absorptions resonance for protons of aromatic benzothiazole ring[28], while the resonance signals in the deshielding region(□ppm=q ppm)referred to acidic proton (-OH) , which suffering shifting

upon complexation with metal ions. As well as the multiple signals at (2-4ppm), are attributed to aliphatic (-CH,-CH_3) groups[28], Fig. (4).

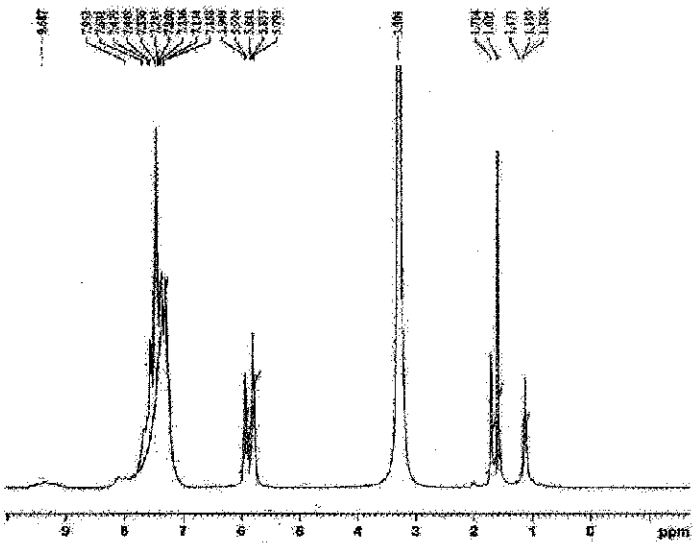


Fig.(4):H^1NMR of diketonate ligand(HL) in d6-MSO

Electronic spectra

The uv/visible spectra of ligand solution in absolute ethanol (10^{-3}M) and complexes solutions in D.M.F. (10^{-3}M) were recorded in the range (200-800)nm.

C_1: The Cr(III) complex solution showed two overlapped bands at 450 and 600nm of low intensity which were assigned to spin forbiddn of ${}^4A_2g \rightarrow {}^4T_2g$ and ${}^4A_2g \rightarrow {}^4T_1g$ respectively [29], this suggest the octahedral geometry of d^3 complexes.

C_2: The brown solution of Mn(II) complex exhibits high intensity peak at 390nm which is attributed to charge transfer of Mn→L[30],and suggests to be tetrahedral symmetry of Mn(II) complexes.

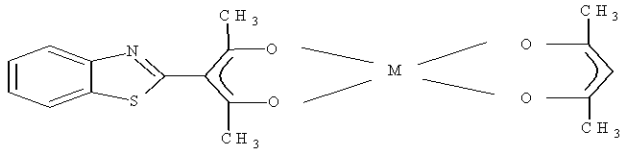
C_3: The greenish solution of Co(II) complex in DMF exhibit, abroad band at 645nm, was assigned to spin orbital transition, of ${}^2E_2g \rightarrow {}^1T_2g$ and $E_2g \rightarrow {}^1T_1g$ which indicate the square planar symmetry of low spin Co(II) complex.[31]

C_4: A band at 550nm of Ni(II) comple has been assigned to $A_2^1g \rightarrow A_2^2g$, this suggests the square planar geometry of Ni(II) complex.[32]

C_5: Cu(II) is (d^9) and term symbol in the ground state is (Eg) in o.h., therefore only one electronic (d-d) transition was expected. The dark-green solution of Cu(II) complex show transition at 508nm due to $E_2g \rightarrow {}^2T_2g$.[32]

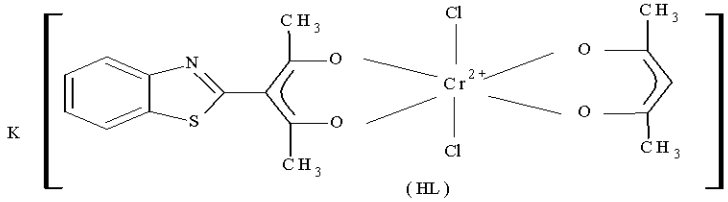
Suggested stereochemical structure

According to the results obtained from elemental, and spectral ananylsis, the structures of the above mentioned complexes, can be illustrated as follows:
M=Mn(II), Cu(II), Ni(II)
Bis[3(benzothiazolyl)-2,4-Pentedionato] Metal (II)
Potassium-bis [3-(benzothiazolyl)-2,4-pentodinate] chromate(III)
Potassium-bis[3-(benzothiaolyl)-2,4-Pentodionate) Cupprate (II)



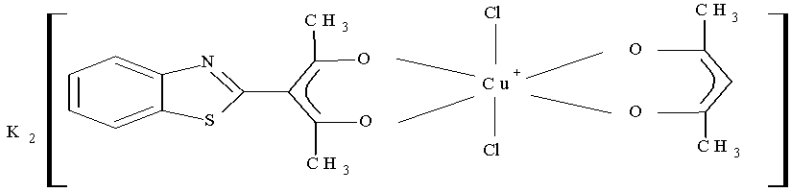
(HL)

M=Mn $^{+2}$, Co $^{+2}$, Ni $^{+2}$
Bis[3 -(benzothiazolyl)-2,4 -Pentadonoato]Cobalt(II) or Nickel(II)



(HL)

Potassium -bis[3 -(benzothiozolyl)-2,4 -pentodionato dichloro Chromate(III)



Potassium -bis[3 -(benzothiozolyl)-2,4 -pentodionato dichloro Cupperate(II)

Conclusion:

Previously the metal complexes of earth lanthanide elements with hetero-β-diketonates, reassembly to our recent work have been showed chemilumscence and possessed wide range of applications in emitting light diodes synthesis, therefore, the new metal complexes in the recent work (paper) may have furtural forward investigation in this significant field of photochemistry.

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تحضير ودراسة طيفية لمعقدات لبعض الفلزات الانتقالية مع ليكاند جديد مشتق من بيتا-ثنائي كيتون غير المتجانس

الخلاصة :

تم تحضير ليكاند جديد ثنائي السن احادي القاعدة بيتا –ثنائي الكيتون (HL) مشتق من التفاعل الاستبدالي النيوكلوفيلي ثنائي النواة لـ 2- ميركابتو-بنزوثايازول و اسيتيل اسيتون باستخدام هدريد الصوديوم كقاعدة .

استخدام المشتق الجديد كليكاند ثنائي السن لتعقيد ايونات الكروم الثلاثي ، المنغنير ، الكوبلت ، النيكل والنحاس الثنائية وتم عزلها بالحالة الصلبة وتشخيصها طيفياً بالطرق الطيفية المعروفة (طيف الاشعة تحت الحمراء وطيف الاشعة فوق البنفسجية –المرئية وقياس العزم المغناطيسي للمعقدات الصلبة بطريقة فارادي والتحليل الدقيق للعناصر (كاربون-هيدروجين-نتروجين) وقياس نسبة الفلز في المعقدات بطريقة الامتصاص الذري اللهبي (F.A.A.S) فضلاً عن تحديد الوزن الجزيئي لليكاند الجديد (HL) بطريقة الانخفاض بدرجة الحرارة (ΔT_f). وقياس الموصلية المولارية لمحاليل المعقدات في محاليل (10^{-3}) مولاري في (N-N)-ثنائي مثيل فورماميد (DMF) كما قيست النسبة المولية (M:L).