

Preparation and characterization study of some metal complexes of new ligand derived from benzothiazine

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Abstract:

A new ligand 2-(4-bromo phenyl)-4H-1,3-benzothiazine-4-one, has been prepared and characterized by (FTIR) spectroscopy, C.H.N.S elemental analysis. The new ligand has been used as chelating reagent to prepare Cr(III), Co(II), Mn(II), Cu(II) and Vo(IV), complexes were isolated, and characterized by (FTIR) ,(Uv-vis) spectra, flame atomic absorption technique, in addition to magnetic susceptibility, and conductivity measurements. The study of the nature of the complexes formed in ethanolic medium following the mole ratio method gave results which compound successfully with those obtained from isolated solid state studies as formula $[ML_2(H_2O)_2]Cl_2$ M: Mn(II), Co(II), Cu(II) and $[CrL_2Cl_2]$ and $[VoL_2(H_2O)]SO_4$.

Introduction

The biological activity of many benzodioxine and benzothiozine derivative is now fairly documented⁽¹⁻³⁾. These compounds were described as fungicidal, bactericidal, and hypoglycemic agents⁽⁴⁻⁶⁾. Hydrazino , and mannich bases of such benzothiazine derivatives, have been studied intensively mainly because of their application of organic synthesis especially for preparation dyes⁽⁷⁾, industrial⁽⁸⁾, pharmaceutical , and polymer chemistry⁽⁹⁻¹⁰⁾. Metal complexes of first row of transition elements of benzodioxine, Schiff base of benzodioxine ,mannich bases of benzodioxin and amine compound of benzothiazin have been studied extensively in recent years due to the selectivity and sensitivity of ligands to various metal ions⁽¹¹⁻¹⁵⁾. In present work, we synthesize 2-(4-bromo phenyl)-4H-1,3-benzothiazine-4-one and its metal complexes with metal chlorides of Cr(III), Co(II), Mn(II), Cu(II) and Vo(IV).

1-Experimental

A. Material and methods

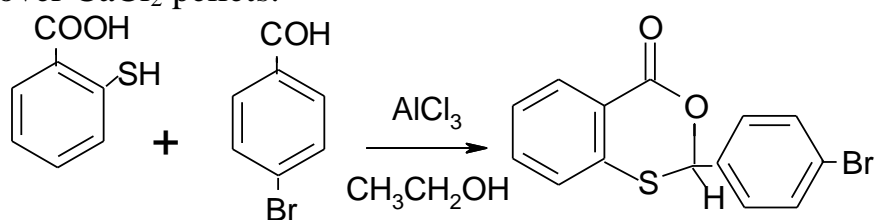
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The chemicals used in this work were obtained from B.D.H and they were all pure grad reagents. Flam atomic absorption of elemental analyzer, shimadzy AA-670 was used for metal determination. FTIR spectra were recorded using shimadzy-8400 spectrophotometer, for the range $4000-400\text{ cm}^{-1}$. Electronic spectra were recorded using varian uv-vis. Spectrophotometer 100 conc. Electrical conductivity was measured by caring conductivity meter 220 and magnetic susceptibility was measured for solid complexes at 30° temperature by Bm6 using faraday 's method.

B. preparation of compound (I)

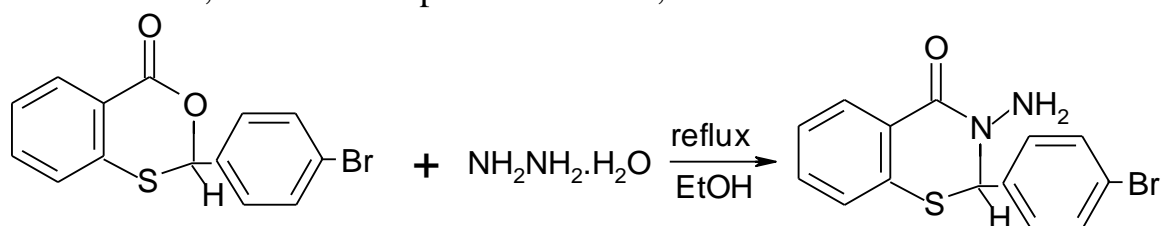
A mixture of (3.85g, 0.025mole) 2-mercobenziocacid and (8.75g , 0.05mole) 4-bromobenzaldehyde in 100ml of ethanol was stirred magnetically , and (2.70g, 20 mmole) of aluminum chloride was gradually added , then stir the mixture for 8 hours at 25°C , then 200ml of distilled water was slowly added , until precipitate formed , which re-crystallized from absolute ethanol , dried over CaCl_2 pellets.



Scheme(1): preparation of compound (I)

C. Preparation of the ligand(L)

A mixture of (0.01mole, 2.90g) of compound (I) in 50ml of absolute ethanol and 50ml of 98% hydrated hydrazine was stirred at room temperature and refluxed for 6 hours the crystals were collected after evaporate of the solvent, then filtration, washed with petroleum ether, and dried in vacuum.



Scheme(2): Preparation of the ligand(L)

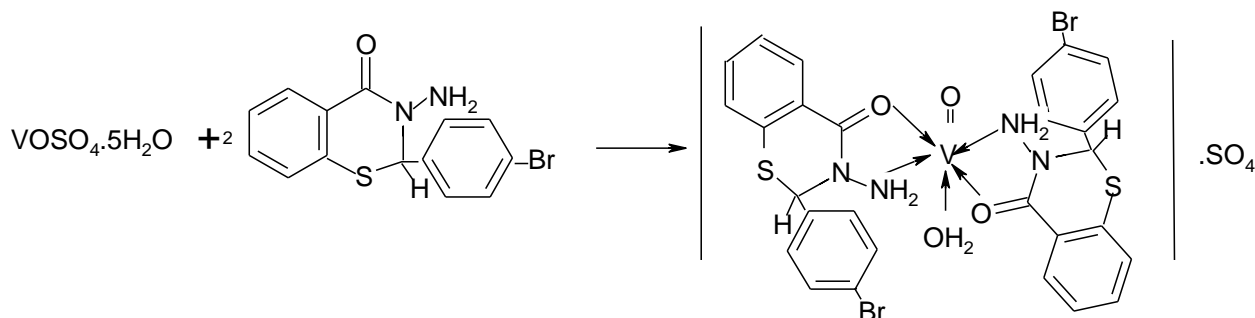
D. Preparation of vanadyl complex

To a (2mmoles , 0.0667g) of 2-(4-bromphenyl)-4H-1,3-benzothiozine-4-one(L) in 10ml ethanol was added (1mmole , 0.248g) of $\text{VoSO}_4 \cdot 5\text{H}_2\text{O}$ in 10ml of water , when colored solid precipitated immediately after refluxing the mixture for approximately 1hour the solid mass was filtered by and washed with

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1:1 ethanol –water mixture and dried in vacuum .



Scheme (3): synthesis of VoL complex

E. Preparation of Cr(III), Mn(II), Co(II) and Cu(II)

Ethanol solution of (2mmole, 0,667g) of ligand was added to 20ml ethanolic solution (1mmole) of metal chloride hydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$). The saturated solution of sodium bicarbonate(NaHCO_3) were added to the mixture, the mixture was heated on a steam bath for 1 hour . After cooling the resulting precipitate was filtered washed with water, ethanol , and then dried which resulted in the formation of their respective metals complexes.

Table(1): Physical data , elemental analysis of the ligand and its metal complexes

Compound	M.P c°	Color	Yield%	C%	H%	N%	M%
				Cal. (Found)	Cal. (Found)	Cal. (Found)	Cal. (Found)
$\text{C}_{14}\text{H}_{11}\text{N}_2\text{OSBr(L)}$	290	Yellow	65	51.31 (51.85)	3.03 (3.08)	8.35 (8.64)	-
$[\text{Cr}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{OSBr})_2\text{Cl}_2]\text{Cl}$	330 d°	Green	70	41.51 (41.94)	2.41 (2.49)	6.89 (6.99)	5.73 (5.91)
$[\text{Vo}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{OSBr})_2(\text{H}_2\text{O})_2]\text{SO}_4$	318-320	Olive	69	40.55 (40.77)	2.39 (2.42)	6.57 (6.79)	5.38 (5.58)
$[\text{Mn}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{OSBr})_2(\text{H}_2\text{O})\text{Cl}_2]$	350 d°	Pink	70	41.32 (41.79)	2.45 (2.48)	6.85 (6.96)	6.19 (6.21)
$[\text{Co}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{OSBr})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	366 d°	Brown	60	41.25 (41.58)	2.42 (2.47)	6.81 (6.93)	6.75 (6.68)
$[\text{Cu}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{OSBr})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	370d°	Green	65	40.95 (41.37)	2.35 (2.46)	6.79 (6.89)	6.95 (7.14)

2- Result and discussion

2.1 Brief synthetic comments :

Complexes of Cr(III), Mn(II), Co(II), Cu(II) and Vo(IV) with the ligand were prepared by the simple reaction of metal chloride and vandyl sulfate under basic medium (NaHCO_3) employing 1:2 molar ratio.

2.2- Analytical data of ligand and their metal complexes elemental analysis of the ligand and its metal complex are reported in table(1).The

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elemental analysis data agreed well with the proposed formula for the complexes was studied in various solvent . Most of the complexes are soluble in DMSO and DMF while in soluble in common solvent such as methanol , ether, chloroform, n-hexan and carbontetrachlorid.

2.3- Characterization of the ligand and its metal complexes
spectroscopic measurements, the FTIR spectrum table(2) of the ligand a medium band at 3320 cm^{-1} which may be to NH_2 group the thiazining showed C-H stretching at 3010 cm^{-1} while bending vibration appeared at 735 cm^{-1} . The stretching frequency at 1675 cm^{-1} can be attributed to carbonyl C=O group of the heterocyclic ring . other band and 1109 and 1192 cm^{-1} are due to stretching vibration of (C-S) and (C-N)⁽¹⁶⁻¹⁷⁾ . Abroad band obtained in the range ($3350\text{-}3180$) cm^{-1} for the spectrum of metal complexes, is much less broad the NH_2 the free ligand , which indicates the participation of NH_2 group to coordination to metal ion more ever ,the appearance of medium band in the rang ($450\text{-}570$) cm^{-1} reveal the formation of metal nitrogen Linkage (M-N)⁽¹⁸⁾. As well as the red shift of C=O group in the rang C=O ($13\text{-}30$) supports the linkage of oxygen of carbonyl group to metal ion, this concedes the behavior of the ligand as bidentate ligand forming five-member ring system which is thermodynamically stable⁽¹⁹⁾. Other band such as at ($920\text{-}970$) cm^{-1} as strong to (V=O) group in vanadium(IV) complex⁽²⁰⁾.

Table(2): I.R(v cm^{-1}) spectral data of the ligand(L) and its metal complexes

Compound	vNH_2	vC=O	Vc-s, VC-N	VM-N, VM-O	Other bands
$\text{C}_{14}\text{H}_{11}\text{N}_2\text{OSBr(L)}$	3443,3346(m)	1759(s)	819(w), 1153-1190(s)	-	2994(Ar c-H)
$[\text{VO}(\text{L}_2(\text{H}_2\text{O})_2)]\text{SO}_4$	3180,3200(m)	1695(s)	890(w), 1160-1180(s)	450(m), 420(w)	920-970(S) Vv=O 3480(br)
$[\text{CrL}_2\text{Cl}_2]\text{Cl}$	3250(br)	1670(s)	910(w), 1170-1182(s)	(470-515) 250(M-cl)	2987-2992(s)
$[\text{MnL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$	3205,3113(br)	1687(s)	1068-1155(s)	430-452(m)	3590(br) $\delta\text{ o-H}$
$[\text{CoL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$	3117,3500(br)	1730(s)	1043-1074(s)	434-511(w)	2978-2740(C-H)
$[\text{CuL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$	3443(m)	1683(s)	887(w),1228(m)	400-580(w)	3875(br.) $\delta\text{ o-H}$

2.4- Magnetic moment and electronic spectra

The effective magnetic moment was measured. Data were corrected for diamagnetic contribution using the Pascal's constants⁽²¹⁾. Oxavandium(IV) complex shows magnetic value 1.2 BM, which is accordance with values reported for VO(IV) complexes shows magnetic value 1.25 BM, which is in accordance with the values reported for V(IV) complexes with one unpaired electron⁽²²⁾ ,indicating that the (VOL) complexes is monomeric . The magnetic

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moment of CrL, MnL, CoL and CuL complexes in the rang reported for high spin octahedral complexes⁽²²⁾. The ligand solution in ethanol (10^{-3}), show two absorption peak at 261 and 268 nm, which are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ ⁽²³⁾. All the complexes solution in DMF(10^{-4}) show a red and blue shift for the ligand field spectrum due to complexes of metal ion to the ligand especially of charge transfer of ligand to metal ($L \rightarrow M$)⁽²⁴⁾ in the rang (345-375)nm. All the compexes show d-d transition in the visible region as weak absorptions which are well agree with the reported octahedral structures of Cr(III), VO(IV), Mn(II), Co(II) and Cu(II)⁽²⁵⁻²⁹⁾.

Table(3): Electronic transitions , magnetic moments and molar conductivities of the prepared compounds.

Compound	Absorption $\lambda_{\max}(\text{nm})$	Transition	(BM) μ	Molar Conductivities($\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$)	Proposed geometry
$\text{C}_{14}\text{H}_{10}\text{N}_2\text{OSBr(L)}$	261 212 268	$\pi \rightarrow \pi^*$ charge transfer $n \rightarrow \pi^*$	-	-	-
$[\text{CrL}_2\text{Cl}_2]\text{Cl}$	217 213 450 468	$\pi \rightarrow \pi^*$ C.T $A_2g^4 \rightarrow T_2g^4$ $A_2g^4 \rightarrow T_1g^4$	3.59	85	Octahedral
$[\text{VoL}_2(\text{H}_2\text{O})_2]\text{SO}_4$	220 280 658 708	C.T C.T(V=O) $T_2g^2 \rightarrow E_g^2$ $T_2g^2 \rightarrow A_1g^2$	1.65	95	Octahedral
$[\text{MnL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$	220 282 418 593	$\pi \rightarrow \pi^*$ C.T $A_1g^6 \rightarrow T_2g^4$ $A_2g^6 \rightarrow T_2g^4(G)$	5.82	185	Octahedral
$[\text{CoL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$	260 419	C.T $T_1g^4 \rightarrow T_1g^4(P)$	3.03	169	Octahedral
$[\text{CuL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$	205 446	C.T $B_2g^2 \rightarrow B_1g^2$	1.05	199	Distorted octahedral

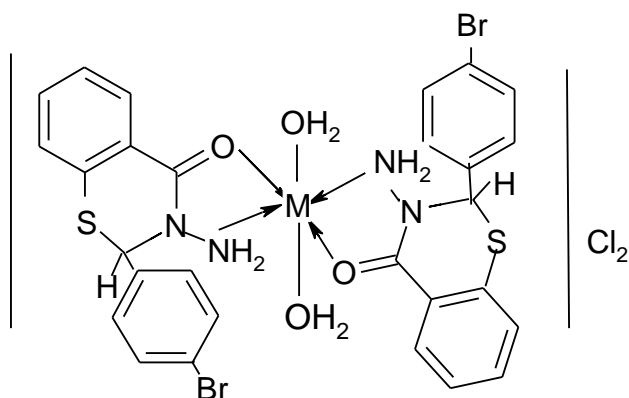
3- Conclusions:

The structural , geometrical and thermodynamic properties of the prepared complexes have been investigated on their elemental and spectroscopic analyses according to the results obtained from infra-red ,Uv-visible spectra, magnetic moments and molar conductivity of the solid and solution of metal complexes, the proposed structures or geometric of CrL, MnL, VoL, CoL and CuL are show

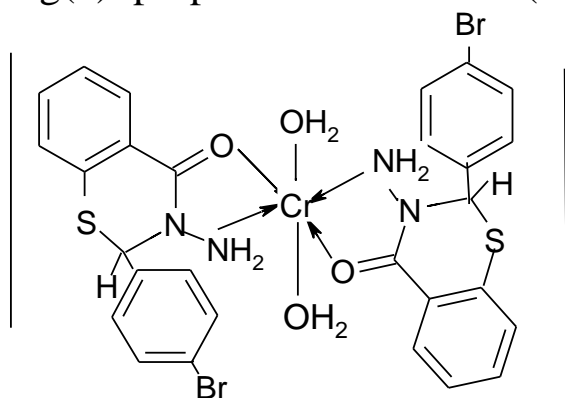
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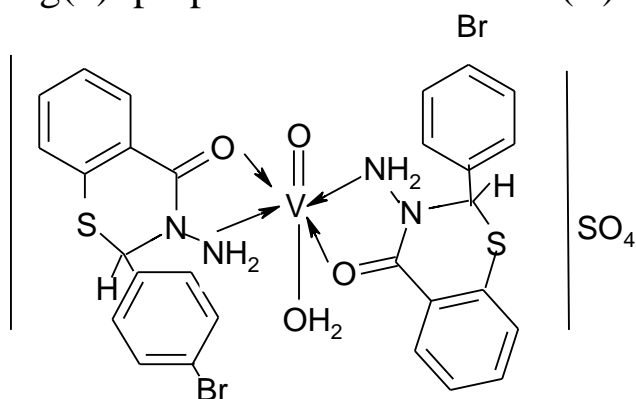
as below:



Fig(1): proposed structures of (Mn(II), Co(II), Cu(II) complexes



Fig(2): proposed structure of Cr(II) complex



Fig(3): proposed structure of oxo vanadium complex

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المخلص :

تم تحضير 2-(4- بروموفنيل)-H-4- 3.1 - ينزو ثايازين-4- اون ودراسته وتشخيصه بالطرق الطيفية المعروفة (طيف الاشعة تحت الحمراء المعززه بتحويلات فورير- طيف الاشعة فوق البنفسجية- المرئية) التحليل الدقيق للعناصر (C.H.N.S) كذلك تم استخدام المشتق الجديد كليكند جديد لتحضير فلزات الكروم الثلاثي، الكوبلت، المنغنيز، النحاس الثنائي، الفناديوم الرباعي و ثم عزل المعقدات الصلبة وتشخيصها بالطرق الطيفية F.T.IR و uv-vis وتحديد كمية الفلز بواسطة طيف الامتصاص الذري الالهي F.AA.S بالاضافة الى قياس العزم المغناطيسي المؤثر للمعقدات الصلبة وتعيين التوصيل المولاري في مذيب ثنائي مثيل فورماميد. اثبتت الدراسات الطيفية والتحليل ان الليكاند (L) يتفاعل بنسبة (2:1) (L:M) مع الفلزات المذكوره و ثم اقتراح الشكل الهندسي ثماني السطوح لجميع المعقدات بالصيغه $[ML_2(H_2O)_2]Cl_2$ حيث $M=CO, Cu, Mn(II)$ و $[CrL_2Cl_2]Cl$ ومعقد الفناديوم الرباعي بالصيغة $[VOL_2(H_2O)]SO_4$

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