SOME NEW COMPLEXES OF ZN(II) AND CD(II) CONTAINING MIXED LIGANDS[+]

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Abstract :

The reaction of acetylacetone bis(thiosemicarbazone)-$ATSCH_2$ and semicarbazone ligands (furfuraldehyde semicarbazone FSCH or 2-chlorobenzaldehyde semicarbazone-ClSCH or benzoin semicarbazone B^-SCH) with zinc(II) and cadmium(II) salts in 1:1:1 molar ratio afforded complexes of formula $[M(ATSCH_2)(LH)]Xn$ (where $M = Zn^{2+}$ or Cd^{2+}, $X = NO_3^-$ or Cl^- or SO_4^{2-}, LH = FSCH or ClSCH or B^-SCH, n = 1 or 2). The coordination of the thiosemicarbazone ligand seemed to occur via the two azomethine nitrogen and the two sulfur atoms, whereas, the coordination of the semicarbazone ligands seemed to occur via the azomethine nitrogen and the carbonyl oxygen atoms. The resulted complexes were characterized by metal ions analysis, relative molecular weights values, molar conductance values, infrared and electronic spectral data. Octahedral structures were suggested for the resulted complexes accordingly.

المستخلص

مفاعلة ليكندات الاسيتيل اسيتون بس (ثايوسميكاربازون) – $ATSCH_2$ والسميكاربازون (فورفوراليهايد سميكاربازون – FSCH او ٢- كلوروبنزالديهايد سميكاربازون – ClSCH او بنزوين سميكاربازون – B^-SCH) مع املاح الخارصين (II) والكادميوم (II) بنسبة مولية ١:١:١ أدت الى تكوين معقدات ذات صيغة $[M(ATSCH_2)(LH)]X_n$ (حيث $Zn^{2+} = M$ او Cd^{2+} ، $NO^{3-} = X$ او Cl^- او SO_4^{2-} ، FSCH = LH او ClSCH او B^-SCH ، n=1 أو 2) . اظهرت أطياف الأشعة تحت الحمراء ان تناسق الثايوسميكاربازون يحدث من خلال ذرتي نيتروجين الازوميثان وذرتي الكبريت ، في حين تناسق ليكندات السميكاربازون يحدث من خلال ذرتي نيتروجين الازوميثان واوكسجين الكاربونيل . شخصت المعقدات الناتجة بالتحليل للعناصر الفلزية والوزن الجزيئي النسبي وقيم الموصلية المولارية وأطياف الأشعة تحت الحمراء والالكترونية. استنادا لذلك اقترحت تراكيب ثمانية السطوح للمعقدات الناتجة .

Introduction

The coordination chemistry of zinc and cadmium in both non-biological and biological areas has been the subject of intensive studies[1]. Cadmium can induced the synthesis of a Cd-binding protein, in fact, the administration of cadmium and zinc to animals induced the synthesis of these proteins called metallothioneins, which played an important role in the metabolism of these elements[1]. Cadmium is a known carcinogen agent that inactivate the DNA mismatch repair pathway. Cd^{2+} is highly inhibitory to the ATP binding

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and hydrolysis activities of MSH_2- MSH_6 , and less inhibitory to its DNA mismatch binding activity. The inhibition of the ATPase activity by Cd^{2+} is prevented by cysteine and histidine, suggesting that these residues are essential for the ATPase activity and are targeted by Cd^{2+} [2] . Zinc is the only metal known to be required for at least one enzyme in each of the major classes of enzymatic activities. Zinc is thiolate ligated and played multifaceted roles in biological system [3].

A good deal of work has been reported on the preparation and structural investigation of thiosemicarbazones and their complexes [4,6] due to their capability of acting as multidentate NS, NNS, SNNS donor with the formation of either mono- or bi- or poly-nuclear complexes [7-9]. In addition to their interesting ligational properties, thiosemicarbazones and their complexes had important biological applications [10-13] .

Semicarbazones are ligands bonding through the nitrogen and oxygen atoms to the central metal ion formed an important class of biologically active ligands [14,15] and provided models for metal-ligand bonding sites in several enzymes [16]. An extremely large number of semicarbazone complexes with transition and non transition metal ions have been known [15-19].

Mixed ligand complexes were of considerable importance in the field of metalloenzymes and other biological activities [20-22]. Hence, a large body of coordination chemistry of mixed ligands with transition and non transition metal ions have been reported recently [20-24]. Due to the importance of such ligands, we took a humble part in the chemistry of mixed ligand complexes, and some articles have been published on their coordination chemistry with transition and non transition metal ions [25-28].

In the present work new zinc (II) and cadmium (II) complexes with mixed ligands acetylacetone bis(thiosemicarbazone) and semicarbazone ligands (Figure 1) have been prepared and characterized physico-chemically, in order to know the coordination mode of these ligands with Zn^{2+} and Cd^{2+}.

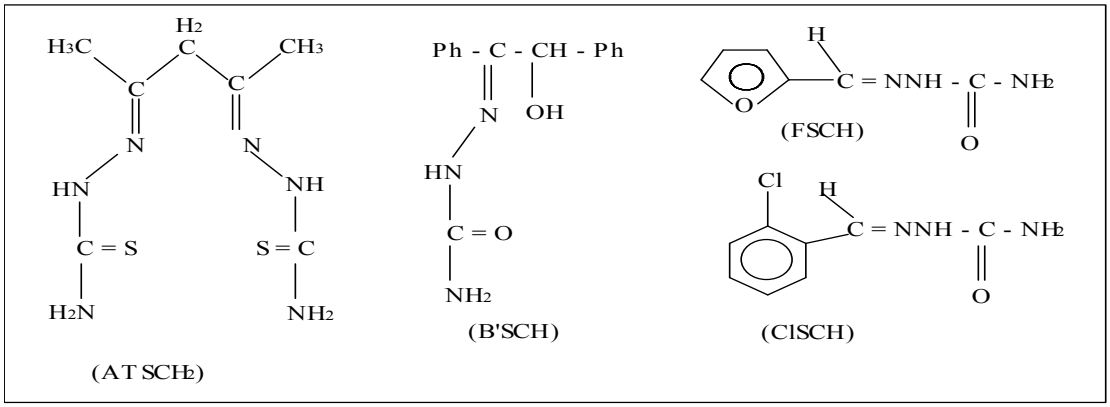

Figure 1 : structures of the ligands

Experimental

1- Materials :

All the chemicals have been used as supplied from Fluka or BDH or Aldrich.

2. Preparation Methods :

Acetylacetone bis(thiosemicarbazone) has been prepared according to the previous method [27}. It has been prepared by refluxing 1:2 molar ratio of acetylacetone and thiosemicarbazide in sodium carbonate solution for about three hours. The thiosemicarbazone thus formed has been filtered off from its cold solution, washed with distilled water and recrystallized from ethanol (M.p = 223^{o}C [27]).

Semicarbazone ligands have been prepared according to the standard method [15,28]. They have been prepared by refluxing 1:1 molar ratio of semicarbazide hydrochloride : corresponding aldehyde and sodium acetate solution for about three hours. The semicarbazone thus formed has been filtered off from its cold solution, washed with distilled water and recrystallized from ethanol.

The complexes [M ($ATSCH_2$)(LH)]Xn have been prepared by the reaction of 5 ml. aqueous solution of 0.5 gm metal salts and 25 ml. ethanolic solutions of acetylacetone bis(thiosemicarbazone) and semicarbazone ligands in 1:1:1 molar ratio (the amounts of metal salts and ligands were listed in Table 1). The mixtures have been refluxed for three hours, evaporated to about half their volumes and cooled. The resulting products have been filtered, washed with cold petroleum ether (60-80^{o}C) and dried.

3. Analytical and physical Measurements :

All the complexes have been decomposed with concentrated nitric acid for analytical purposes. Zinc and cadmium contents have been determined gravimetrically [29]. Relative molecular weights of the ligands and their complexes have been determined cryoscopically [30]. Molar conductivities of the complexes have been measured using 10^{-3}M dimethylformamide solution at 25^{o}C by an electrolytic conductivity measuring set LF-42. Melting or decomposition points were measured using Richert-Jung Hcizubank type MWE. The infrared spectra has been recorded on FT-IR Bruker type Tensor 27 in the range 400-4000 cm^{-1} using KBr pellets. Ultraviolet spectra has been recorded by Shimadzu UV 210A spectrophotometer for 10^{-3} M sohution of the ligald and their complexes in dimethyl-formamide at 25^{o}C.

Results and Discussion :

In continuation of our work [25-28], a number of zinc (II) and cadmium (II) complexes have been prepared. The analytical data (Table 2) showed that the ligands formed mononuclear complexes of the type [M($ATSCH_2$)(LH)]Xn.

The resulted complexes are colored solid (Table 2), insoluble in water and most of the organic solvents, but they are soluble in dimethylformamide and dimethylsulfoxide. The molar conductivities of the Zn (II) and Cd (II) complexes lying in the range 68-88, 132-168 and 141-167or 153-161 Ω^{-1} cm^2 mol^{-1} (Table 3) indicated 1:1 and 1:2 electrolytes [31], respectively.

The infrared spectra of thiosemicarbazone ligand (Table 4) showed a strong band at 1645 cm^{-1} attributed to C=N group [4,5]. A negative shift of the order 43-76 cm^{-1} was observed for C=N stretching vibration on coordination due to the decrease of the bond order as a result of metal nitrogen bond formation [5,6]. The next strong band at 1488 cm^{-1} attributed to C=S group [5,6]. A negative shift of the order 23-91 cm^{-1} was observed in C=S

stretching frequency on coordination indicating the coordination of thio sulfur to the metal ion [5,6,8]. The position band of the ligand in the range 3200-3300, 3390-3494 and 1450 cm^{-1} due to υ_{NH}, υ_{NH_2} and δ_{NH_2} , respectively, remained unaltered indicating that there is no coordination through these groups and the metal ion [5,6].

The infrared spectra of semicarbazone ligands (Table 4) showed a strong band at 1580-1620 cm^{-1} due to C=N group [16,17]. A negative shift of the order 19-106 cm^{-1} was observed for this group on complexation which can be regarded as an evidence of coordination through azomethine nitrogen [16,17]. The other strong band at 1670-1700 cm^{-1} assigned to C=O group [16,17]. The negative shift of the order 13-95 cm^{-1} was observed for C=O group, indicating the coordination of carbonyl oxygen to the metal ion [16,17]. The bands in the range 3200-3300, 3400-3500 and 1450 cm^{-1} attributed to υ_{NH}, υ_{NH_2} and δ_{NH_2}, respectively, remained unaltered in the complexes indicating that there was no coordination through these groups and the metal ions [16,17,19]. This wide range was due to the presence of hydrogen bonding and presence of different groups at the same position [16,17,19].

Complexes 1-3 and 10-12 showed a band at 553-587 cm^{-1} which was attributed to the presence of ionic chloride [31]. Complexes 7-9 showed a band at 1384-1397 cm^{-1} due to the presence of ionic nitrate [31]. Complexes 4-6 showed bands at 613-616 cm^{-1} and 1117-1140 cm^{-1} which were attributed to the presence of ionic sulfate [32].

On the other hand, the spectra of the complexes showed new bands around 417-583 cm^{-1}, 557-661 cm^{-1} and 598-683 cm^{-1} due to υ_{M-N} , υ_{M-O} and υ_{M-S} , respectively [5,6, 32]. The presence of these bands supported the formation of the complexes under investigations.

The ultraviolet spectral data of the ligands and their complexes are listed in Table 5. The ligands showed two absorption bands in the region 40323, 29070 cm^{-1} and 39216-39526, 32258-32787 cm^{-1} (for thiosemicarbazone and semicarbazone ligands, respectively) corresponding to π-π^* and n-π^* transitions [33], respectively. On complexation a blue shift has been observed due to the polarization in the C=N bond caused by the metal ligand electron interaction during the chelation. A new band was observed in the ultraviolet spectra of the complexes which could be related to additional transition involving metal and ligand orbitals indicating the participation of the ligand molecules in complexes formation.

Conclusion :

According to the analytical, physical and spectral studies the resulted complexes had the formula $[M(ATSCH_2)(LH)]Xn$ (where M = Zn^{2+} or Cd^{2+}, X =NO_3^- or Cl^- or SO_4^{2-}, LH = FSCH or ClSCH or B^-SCH, n = 1 or 2). The study supported that the metal ion in all the complexes have hexa-coordinated and the complexes had octahedral geometries. The proposed structures of the prepared complexes are shown in Figure 2.

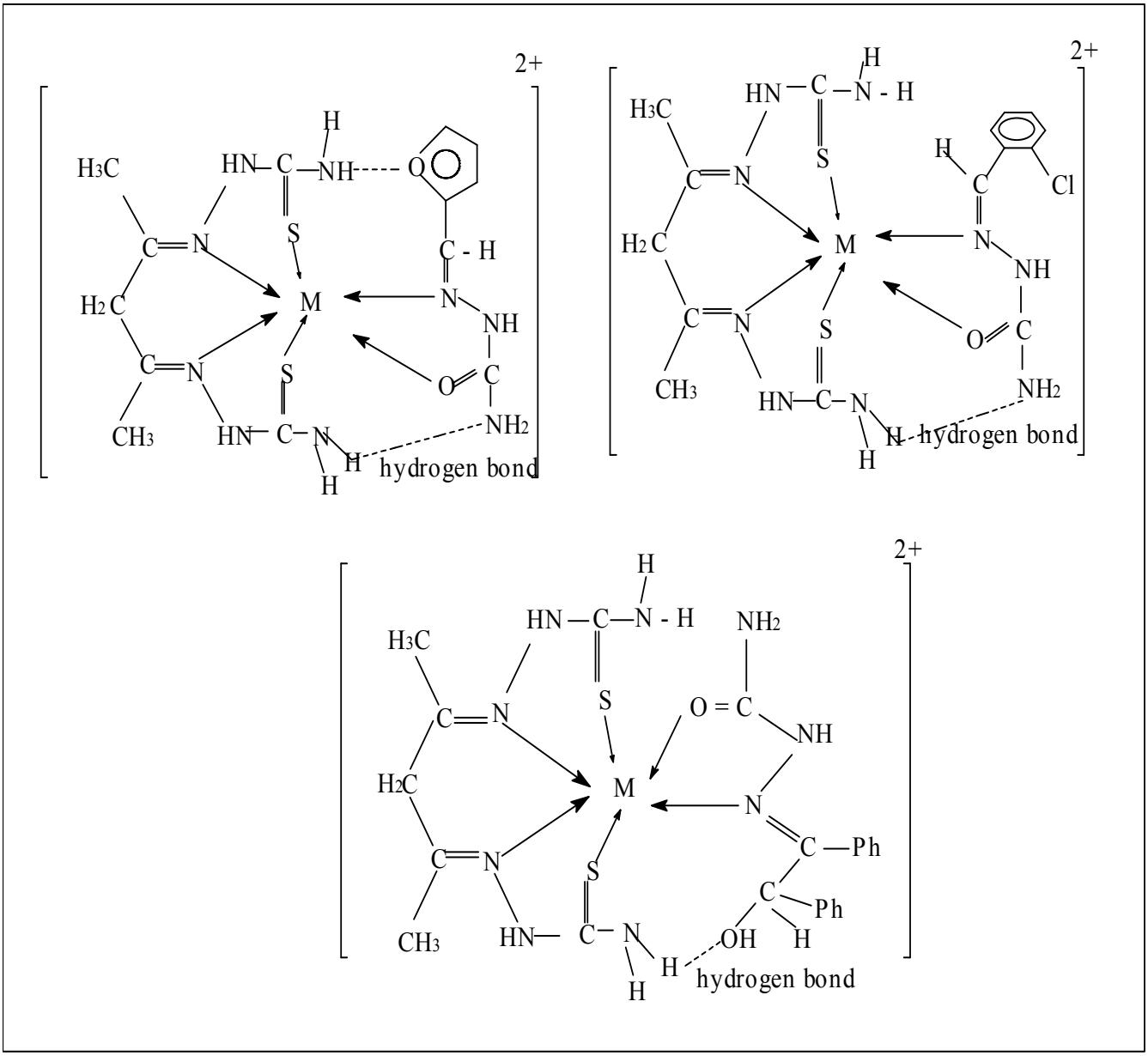

Figure 2 : Proposed structures of the complexes.

Table 1 : Amounts of metal salts and ligands

No.	Complexes	Wt of metal salts	Wt of $ATSCH_2$	Wt of semicarbazone ligands	% yield
1	$[Zn(ATSCH_2)(FSCH)]Cl_2$	0.50	0.902	0.561	74.1
2	$[zn(ATSCH_2)(ClSCH)]Cl_2$	0.50	0.902	0.724	69.4
3	$[Zn(ATSCH_2)(B^-SCH)]Cl_2$	0.50	0.902	0.986	77.9

4	$[Zn(ATSCH_2)(FSCH)]SO_4$	0.50	0.428	0.266	63.9

No.	$\upsilon_{C=N}$	$\upsilon_{C=S}$	$\upsilon_{C=O}$	υ_{Cl^-} or $\upsilon_{NO_3^-}$ or $\upsilon_{SO_4^{-2}}$	$\upsilon_{M.N}$	$\upsilon_{M.S}$	$\upsilon_{M.O}$	Other band

5	$[Zn(ATSCH_2)(ClSCH)]SO_4$	0.50	0.428	0.343	67.1
6	$[Zn(ATSCH_2)(B^-SCH)]SO_4$	0.50	0.428	0.468	66.5
7	$[Cd(ATSCH_2)(FSCH)](NO_3)_2$	0.50	0.399	0.248	72.5
8	$[Cd(ATSCH_2)(ClSCH)](NO_3)_2$	0.50	0.399	0.320	59.8
9	$[Cd(ATSCH_2)(B^-SCH)](NO_3)_2$	0.50	0.399	0.436	70.7
10	$[Cd(ATSCH_2)(FSCH)]Cl_2$	0.50	0.670	0.417	70.2
11	$[Cd(ATSCH_2)(ClSCH)]Cl_2$	0.50	0.670	0.538	62.3
12	$[Cd(ATSCH_2)(B^-SCH)]Cl_2$	0.50	0.670	0.733	63.4

Table 2 : Analytical and some physical properties of the complexes.

No	Colors	*M.P d °C	M% Cal/(obs)	M. wt Cal(obs)	*No*	Colors	*M.P d °C	M% Cal/(obs)	M. wt Cal(obs)
1	Dark yellow	240d	12.22 (11.93)	535.40 (529.98)	7	Yellow	254	17.69 (17.19)	635.40 (628.31)
2	Dark yellow	252d	11.05 (11.02)	591.90 (558.11)	8	Yellow	261	16.25 (16.36)	691.90 (663.24)
3	Dark yellow	266d	9.86 (9.65)	663.40 (649.22)	9	Yellow	255d	14.72 (14.48)	763.40 (750.43)
4	Yellowish-brown	266d	11.67 (11.29)	560.40 (548.29)	10	Yellow	263d	19.30 (18.92)	582.40 (571.86)
5	Yellowish-brown	257	10.60 (10.57)	616.90 (587.18)	11	Pale yellow	243	17.59 (17.87)	638.90 (607.68)
6	Yellowish-brown	242	9.50 (9.24)	688.40 (674.55)	12	Dark yellow	250	15.82 (15.78)	710.40 (692.79)

*d = decomposition point.

Table 3 : Molar conductivities of the complexes (Ω^{-1} cm^2 mol^{-1}

No	Non electr.	1:1 electr.	1;2 electr.	No	Non electr.	1:1 electr.	1;2 electr.
DMF	0 - 30	65 - 90	130 - 170	DMF	0 - 30	65 - 90	130 - 170
1			132	7			141
2			137	8			167
3			168	9			163
4		68		10			153
5		73		11			156
6		88		12			161

Table 4 : IR spectra of complexes (values in cm^{-1}).

$ATSCH_2$	1645	1488	-	-	-	-	-	υ_{NH} 3200 υ_{NH_2} 3494
FSCH	1590	-	1690	-	-	-	-	υ_{C-O-C} 1520
ClSCH	1580	-	1670	-	-	-	-	υ_{C-Cl} 720
B^-SCH	1620	-	1700	-	-	-	-	υ_{C-O} 1250, υ_{OH} 3500-3600
1	1570,1550	1432	1616	586	425	680	660	υ_{NH} &υ_{NH_2} 3200-3522
2	1594,1561	1449	1649	587	425	681	642	υ_{NH} &υ_{NH_2} 3200- 3480
3	1572,1507	1464	1624	556	417	677	659	υ_{NH} &υ_{NH_2} 3200-3440
4	1602,1541	1420	1617	616,1224	480	680	655	υ_{NH} &υ_{NH_2} 3200-3509
5	1590,1498	1428	1657	613,1117	465	672	567	υ_{NH} &υ_{NH} 3208-3490
6	1602,1550	1427	1620	613,1140	466	670	557	υ_{NH} &υ_{NH} 3208-3500
7	1569,1507	1397	1621	1397	426	661	586	υ_{NH} &υ_{NH_2} 3200-3440
8	1572,1508	1421	1605	1386	466	598	561	υ_{NH} & υ_{NH_2} 3200-3396
9	1572,1522	1465	1624	1384	583	675	657	υ_{NH} &υ_{NH_2} 3200-3553
10	1573,1484	1465	1605	585	485	672	657	υ_{NH} &υ_{NH_2} 3200-3395
11	1574,1540	1465	1621	553	453	669	648	υ_{NH} &υ_{NH_2} 3200-3564
12	1590,1520	1451	1624	564	520	683	645	υ_{NH} &υ_{NH_2} 3200-3530

Table 5 : UV spectral data of the ligands and their metal complexes in 10^{3-} M dimethylformamide (values in cm^{-1}).

No.	**υ_1**	**υ_2**	**υ_3**
$ATSCH_2$	40323	29070	-
FSCH	39216	32787	-
ClSCH	39526	32258	-
B^-SCH	39370	32362	-
1	39216	28090	26316
2	38168	28090	26810
3	37594	27473	25840
4	38911	27701	26385
5	38168	27933	26385
6	38023	27855	25317
7	38610	28011	26178
8	38760	28169	26738
9	38760	27322	25974
10	38911	27624	26316
11	38462	28011	26667
12	39216	27397	26110

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