Preparation and Characterization of Some New Mixed Ligand Thiosemicarbazone and Benzaldazine Complexes

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Key Words : Thiosemicarbazone, azine, mixed ligand, cobalt(II) complexes, nickel(II) complexes.

Abstract:

The reaction of benzil bis(thiosemicarba- zone) – $BTSH_2$ and benzaldazine – BA with cobalt (II) and nickel (II) salts in 1 : 1 : 1 molar ratio afforded mononuclear complexes of formules $[Co(BTSH_2)(BA)]CO_3$, $[Ni(BTSH_2)(BA)(CO_3)]$, $[M(BTSH_2)(BA)(Ac)]Ac$ and $[M(BTSH_2)(BA)](NO_3)_2$ in neutral medium , whereas the formules $K[M(BTSH)(BA)(CO_3)]$ and $K[M(BTS)(BA)X]$ have been proposed in basic medium {Where M = Co^{2+} or Ni^{2+}, X = NO_3^- or Ac^-, BTSH = deproto- nated $BTSH_2$ ligand (-H) , BTS = deprotonated $BSCH_2$ ligand (-2H)} . The coordination of the thiosemicarbazone ligand seemed to occur via the two azomethine nitrogen and the two sulfur atoms. Meanwhile, the coordination of the azine ligand seemed to occur via either one azomethine nitrogen or the two azomethine nitrogen. The resulted comp- lexes have been characterized physico–chemically and octahedral structures have been suggested accordingly.

Introduction:

A good deal of work has been reported on the preparation and structural investigation of thiosemicarbazones and their complexes (1-3) . This was due partially to their capability of acting as multidentate, NS, NNS, SNNS donor with the formation of either mono– or bi– or poly–nuclear complexes (4-6) . In addition to their interesting ligational properties, thiosemicarbazones and their complexes had important catalytical and biological applications (7-10).

Azines are ligands coordinated to the metal ions in different manners (11) . Azine comp- lexes with some transition ions aroused consider- able interest and a good deal of work has been reported on their complexes (12,13).

There has been growing interest in the formation of mixed ligands chelates involving ligands containing atoms such as sulfur, nitrogen and/or oxygen of different oxidation states (14-18). On the other hand, mixed ligand complexes were of considerable importance in the field of metallo- enzymes and other biological activities (19, 20) . Hence, a large body of coordination chemistry of mixed ligands with transition and non–transition metal ions have been reported recently (21-23) . 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 (24-27).

In the present work, new cobalt (II) and nickel (II) complexes with mixed ligands benzil bis(thiosemicarbazone) and benzaldazine (Figure1) have been prepared and characterized physico – chemically.

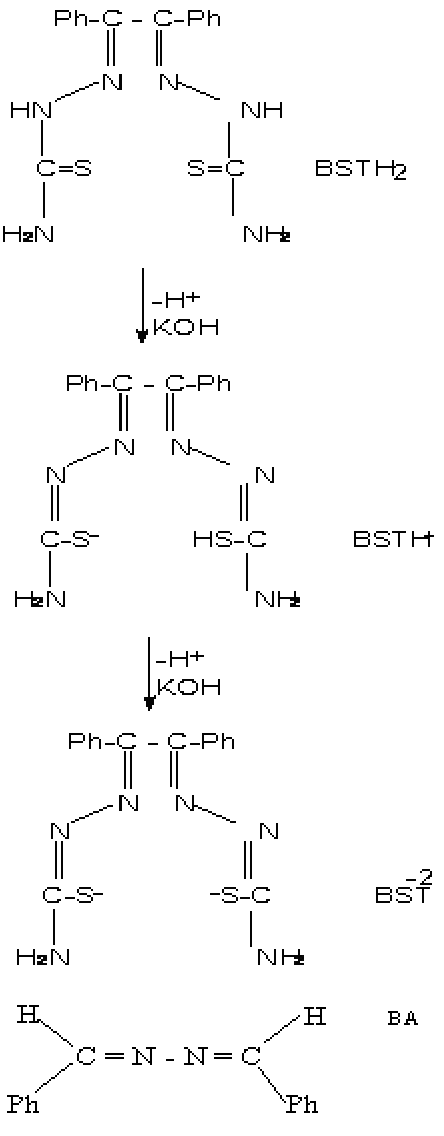


Fig. 1: Structures of the ligands

Experimental:

1-Chemicals:

All the chemicals have been used as supp- lied (Fluka,BDH or Aldrich) except benzaldehyde which was used after purification by distillation.

2-Preparation of the ligands:

Benzil bis(thiosemicarbazone) has been prepared according to previous method (28). It has been prepared by refluxing 1:2 molar ratio of benzil, thiosemicarbazide and sodium carbonate solution for about three hours. The thiosemicarba- zone thus formed has been filtered off from its cold solution , washed with distilled water and recrys- tallized from ethanol (m.p = 178 °C) .

Azine ligand has been prepared according to literature method (29). A mixture of 2 mole hydrazine sulphate in 18 ml. water and 2.4 ml. concentrated ammonium hydroxide solution have been stirred. 2 mole of benzaldehyde has been added with contineuous stirring over a period 30-60 minutes. The mixture has been stirred for a further hour . The solid product was separated by filtera- tion , washed with water, recrystallised from rectified spirit. Yellow crystals were obtained (m.p = 114 – 116 °C) .

3- Preparation of the complexes

The complexes [Co(BTSH$_2$)(BA)]CO$_3$, [Ni(BTSH$_2$)(BA)(CO$_3$)], [M (BTSH$_2$)(BA)(Ac)]Ac and [M(BTSH$_2$)(BA)](NO$_3$)$_2$ have been prepared by the reaction of 0.5g aqueous solution of cobalt (II) salts or nickel (II) salts with ethanolic solution of benzil bis(thiosemcarbazone) and azine ligands in 1:1:1 molar ratio (the amounts in grams have been listed in Table 1) . The mixtures have been refluxed for three hours, evaporated to about half their volumes and cooled. The resulting complexes were filtered off , washed with petroleum ether (b.p =60-80 °C) and then dried. Complexes of the types K[M(BTSH)(BA)(CO$_3$)] and K[M(BTS)(BA)X] have been prepared by the reaction of 0.5g aqueous solution of cabalt (II) salts or nickel (II) salts with ethanolic solution of benzil bis(thiosemicarbazone) and azine ligand in 1:1:1 molar ratio (amounts in grams were listed in Table 1). Ethanolic solution of potassium hydroxide (1M) has been added to the mixture until pH$\approx$8-9. The resulted products have been filtered off, washed with petroleum ether (b.p. = 60-80 °C) and dried.

Table 1: Analytical data and some physical properties of the complexes

No	Complex	wt of BTSH$_2$	Wt of BA	% yield	Color	m.p or d* ^{0}C	^M **	μ$_{eff}$ ***	M% cal.obs.)	M.wt Cal. (obs)
1	[Co(BTSH$_2$)(BA)]CO$_3$	1.36	0.87	74	Dark brown	259	76	4.50	8.64(8.50)	683 (675)
2	[Co (BTSH$_2$)(BSH)Ac]Ac	0.56	0.36	65	Dark brown	174	74	4.45	7.96(7.80)	714 (725)
3	[Co (BTSH$_2$)(BA)](NO$_3$)$_2$	0.55	0.35	56	Dark brown	215	150	4.55	7.90(7.85)	747 (730)
4	K[Co (BTSH)(BA)CO$_3$]	1.41	0.87	74	Dark brown	260	90	4.53	8.18(8.00)	721 (715)
5	K[Co (BTS)(BA)(Ac)]	0.56	0.36	78	Dark brown	248	60	4.50	8.21(8.29)	719 (700)
6	K[Co (BTS)(BA)(NO$_3$)]	0.55	0.35	83	Dark brown	210	92	4.49	8.17(8.10)	722 (715)
7	[Ni(BTSH$_2$)(BA)(CO$_3$)]	1.36	0.87	63	Pale brown	206	28	2.76	8.64(8.60)	783 (675)
8	[Ni (BTSH$_2$)(BA)Ac]Ac	0.66	0.42	65	Dark brown	226	88	2.79	7.96(7.95)	741 (725)
9	[Ni (BTSH$_2$)(BA)](NO$_3$)$_2$	0.55	0.35	74	Pale brown	196	127	2.76	7.90(7.93)	747 (735)
10	K[Ni(BTSH$_2$)(BA)CO$_3$]	1.36	0.87	72	Pale brown	207	61	2.78	8.18(8.15)	721 (708)
11	K[Ni (BTS)(BA)Ac]	0.66	0.42	81	Brown	161	73	2.75	8.21(8.20)	719 (700)
12	K[Ni (BTS)(BA)(NO$_3$)]	0.55	0.35	64	Pale brown	185	83	2.77	8.17(8.15)	722 (715)

*d= decomposition point ;** ^$_M$ = molar conductivity in ظ$^{-1}$ mol^{-1} cm^2 ; ***μ$_{eff}$ = magnetic moment in B.M.

4. Analytical and physical measurements:

All the complexes have been decomposed with concentrated nitric acid for analytical purposes (30) . Cobalt contents have been determined gravimetrically , whereas nickel contents were determined using Pye-Unicam SPg Atomic Absor- ption Spectrophotometer (30) . Relative molecular weights of the complexes have been determined cryoscopically (31) . Molar conductivities of the complexes have been measured using 10^{-3}M dimethylformamide solution at 25°C by Multiline F/SET-2 WTW Wissenschaftlich-Technische Wer-kstatten. The infrared spectra was recorded on FT–IR Bruker type Tensor 27 in the range 400-400 cm^1 using KBr pellets. Electronic spectra has been recorded by Shimadzu UV Probe type UV – 1601 for 10^{-4} M solution of the ligands and their comp-lexes in dimethylformamide at 25 °C.

Results and Discussions:

In continuation of our work (24-27), we prepared a number of complexes of cobalt (II) and nickel (II) in both neutral and basic medium .The analytical data (Table 1) showed that the ligands formed different types of complexes depending on the medium and the method of preparation . In neutral solution cationic and neutral complexes were obtained . In basic medium , the thiosemi- carbazone ligand lost either one proton or two protons to form anionic complexes .

All the resulted complexes are colored solid, insoluble in water and most of the organic solvents, but they are soluble in dimethylforma- mide . The molar conductivities of the cationic complexes lying in the range 74-88 and 127-150 Ω^{-1} mol^{-1} cm^2 indicated 1:1 and 1:2 elecrolytes whereas the neutral complex 7 was non-electrolyte. Meanwhile, the molar conductivities of the anionic complexes lying in the range 60-92 Ω^{-1} mol^{-1} cm^2 indicated 1:1 electrolytes (32) . The values of magnetic moments observed for Co (II) and nickel (II) complexes were 4.45-4.55 B.M and 2.75-2.79 B.M, respectively, suggested the presence of un- paired electron and the octahedral geometries of the complexes (1,33).

Infrared spectral data (Table2) indicated that coordination in the complexes took place in different ways. For complexes formed in neutral medium, a negative shift of the order 71-99 cm^{-1} was observed for C=N stretching vibrations and a decrease of about 55-91 cm^{-1} in C=S stretching frequencies. Meanwhile, the positions of the bands due to υ_{NH} and υNH_2 remained almost unchanged upon complexation (34) . These negative shifts of $C=N_{(thiosemi)}$ and C=S bands can be regarded as an evidence of coordination through both azomethine nitrogen and thio-sulfur atoms (34) . For complexes in basic medium two different ways of coordination for $BSTH_2$ ligand were observed in the spectra of the complexes {4,10} C=S stretching bands were absent . Instead two bands appeared at 701, 754 cm^{-1} and 2069, 2090 cm^{-1}, which were due to the stretching vibrations of C–S and SH groups, respectively (because of the conversion of the ligand to the thiolic form). Whereas, in the spectra of the complexes {5,6,11 and 12} the C=S stretch- ing bands were absent . Instead one band appeared at 700-753 cm^{-1} which was due to the stretching vibration of C–S group (because of the conversion of the ligand to the thiolic form and the deprotona- tion of the ligand that took place in basic medium) . The C=N stretching vibration in the compexes {4,5, 6,10,11,12} showed a decrease of the order 71-83 cm^{-1}. The NH stretching band was absent in the complexes prepared in basic medium, due to the formation thiol form. Whereas the position of the band due to υNH_2 remained almost unchanged . These negative shifts and the absence of NH band can be regarded as an evidence of coordinating through the azomethine nitrogen and sulfur atom (34-36).

Table 2- Selected I.R. bands of the ligands and their complexes (values in cm^{-1})

Compd.	$\upsilon_{C=N}$ Semi	$\upsilon_{C=S}$ b, sh*	υ_{c-s}	υ_{SH}	υNH_2	υ_{NH} Semi	$\upsilon_{C=N}$ Azine	υ_{M-S}	υ_{M-N}
$BTSH_2$	1621	1325, 1488	-	-	1455	3371	-----	-----	-----
BA	-	-	-	-	1455	-	1624	-----	-----
1	1541	1265, 1444	-	-	1455	3371	1600	618	536
2	1550	1265, 1445	-	-	1455	3371	1597, 1624	617	496
3	1550	1270, 1408	-	-	1455	3371	1598	620	540
4	1550	-	701	2069	1455	-	1572, 1624	621	521
5	1541	-	753	2073	1455	-	1590, 1624	620	520
6	1541	-	715	2284	1455	-	1590, 1624	610	510
7	1541	1265, 1446	-	-	1455	3371	1590, 1624	618	543
8	1522	1234, 1446	-	-	1455	3371	1589, 1624	617	542
9	1522	1235, 1445	-	-	1455	3371	1557	590	495
10	1538	-	754	2090	1455	-	1599, 1624	619	508
11	1541	-	714	2090	1455	-	1556, 1624	619	419
12	1541	-	700	2285	1455	-	1558, 1624	617	500

*b = bending, sh = stretching

The infrared spectra of the complexes {2, 4-8,10-12} containing BA ligand showed two bands at 1624 cm^{-1} and 1557-1600 cm^{-1} due to $\acute{\upsilon}_{C = N(azine)}$ stretching vibrations. This splitting may be due to the coordination of only one azine nitrogen to the metal ion (12). Whereas, in the complexes 1,3 and 9 only one band was observed at 1570-1600 cm^{-1} due to the coordination of the two azine nitrogen to the metal ion (12) . The spectra of complex {1} showed stretching vibration of the carbonate group at 1490-1495 cm^{-1} indicating the ionic nature of this group. Whereas, in the complexes {4,7 and 10} two bands were observed at 1390-1400 cm^{-1} and 1540-1550 cm^{-1} indicating the monodentate nature of the carbonato group (37,38). The spectra of the complexes {2 and 8} showed two kind of stretching vibrations of acetato group at 1520, 1320 cm^{-1} and 1520,1350 cm^{-1}indicating ionic nature of one group and monodentate nature of the other group(37,38). Whereas, the spectra of the complexes {5 and 11} showed two stretching vibrations of symmetric and asymmetric acetato group at 1350 and 1520 cm^{-1} indicating the monodentate nature of this group (37,38). The spectra of the complexes {3 and 9} showed absorption band at 1380 cm^{-1} due to ionic bonding of nitrato group to the metal ion. While complexes {6 and 12} showed bands at 1400 cm^{-1}, 1280 cm^{-1} and 940 cm^{-1} due to $\upsilon_s NO_3$, $\upsilon_{as} NO_3$ and υ_{NO} (υ_2,υ_1 and υ_5), respectively. The difference between $\upsilon_1 - \upsilon_5 = 115$ cm^{-1} which supported the bonding of nitrato group as monodentate ligand through the oxygen atom (37,38). All the complexes showed new bands around 590-621 cm^{-1} and 419-543 cm^{-1} due to υ_{M-S} and υ_{M-N} , respect- ively. The presence of these bands supported the formation of the complexes under investigation.

The electronic spectra (Table 3) of Co (II) comp- lexes showed absorption bands at 9407-9500 and 18814-20630 cm^{-1} due to υ_1 and υ_3 , respectively {attributed to $^4T_1g(F)\rightarrow{}^4T_2g(F)$ and $^4T_1g(F)\rightarrow{}^4T_1g(P)$ transitions} expected for d^7 system in octahedral field. υ_2 {assigned to $^4T_1g(F)\rightarrow{}^4A_2g(F)$ transition} was calculated by literature method (39,40) . The electronic spectra of Ni (II) complexes showed absorption bands at 14594-15889 and 19417- 20790 cm^{-1} due to υ_2 and υ_3 {attributed to $^3A_2g(F)\rightarrow{}^3T_1g(F)$ and ^3A_2g $(F)\rightarrow{}^3T_1g$ (P) transitions} respectively . υ_1 {assigned to ^{3} A_2g $(F)\rightarrow{}^3T_2g$ (F) transition} was calculated by literature method (39). The free ion value of B were 701-823 and 690-770 cm^{-1} compared to the reported value of B (1120 and 1080 cm^{-1}) for Co(II) and Ni(II) comp- lexes, respectively , The 10Dq values of the complexes indicated that the ligands were produced a weak field . Energy calculation pointed out to the high spin nature of the complexes . The values of β f the complexes were between 0.71-0.84 clearly indicated the covalent character of the bond concerned . The values of Dq/B, υ_3/υ_1 and υ_3/υ_2 confirmed the octahedral geometry for all the for all the prepared complexes (39, 40) .

Table – 3 : Electronic spectral data of the prepared complexes

No.	υ_1 cm^{-1}	υ_2 cm^{-1}	υ_3 cm^{-1}	C.T. cm^{-1}	B cm^{-1}	10Dq cm^{-1}	Dq/B	β	υ_3/υ_2	υ_3/υ_1	C.F.S.E. cm^{-1}
1	9455	16162*	18910	22500	702	10450	1.49	0.72	1.17	2.00	8360
2	9433	15723*	18868	28000	703	10550	1.49	0.72	1.20	2.00	8440
3	9407	16080*	18814	29500	705	10580	1.50	0.73	1.17	2.00	8464
4	9500	16504*	20630	28500	823	10710	1.30	0.84	1.25	2.17	8568
5	9416	15695*	18834	28500	708	10530	1.49	0.72	1.20	2.00	8424
6	9460	15899*	18920	27500	701	10450	1.49	0.72	1.19	2.00	8360
7	10729*	15021	19417	28600	698	10400	1.49	0.72	1.29	1.81	12480
8	10695*	15508	19569	28900	700	10220	1.46	0.72	1.26	1.83	12264
9	10526*	13999	19120	28000	695	10216	1.47	0.72	1.37	1.82	12259
10	10593*	15889	19920	28600	770	11473	1.49	0.80	1.25	1.88	13767
11	10905*	14594	20790	28000	700	10360	1.48	0.72	1.44	1.91	12432
12	10976*	14814	19801	28000	690	10350	1.50	0.71	1.34	1.80	12420

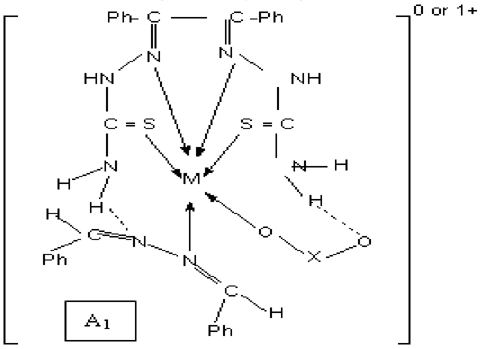
* calculated

Conclusion:

According to the physico – chemical studies some observations have been achieved reading to establish the following points :,

1. Benzil bis(thiosemicarbazone) acted as tetradentate chelating ligand joint to the metal ions through the two azomethine nitrogen and the two thio – sulfur .
2. Benzaldazine acted as either monoden- tate or bidentate chelating ligand.
3. Nitrato group in the complexes {3 and 9} joint in an ionic manner to the metal ions , whereas in the complexes 6 and 12 joint as monodentate ligand through the oxygen atom.
4. Carbonato group in complex (1) joint in an ionic manner , while in the complexes {4,7 and 10} it joint as monodentate ligand through the oxygen atom .
5. Acetato group in the complexes {2 and 8} joint to the metal ions in two manner one group acted as monodentate ligand and the other one joint in ionic manner , whereas in the complexes {5 and 11} it joint as monodentate ligand through the oxygen atom .

All the complexes have been Probably hexa-coordinated leading to octahedral geometry (Figure 2) .



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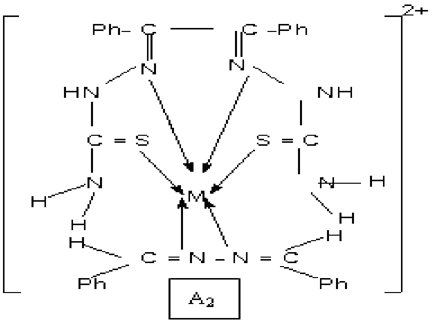

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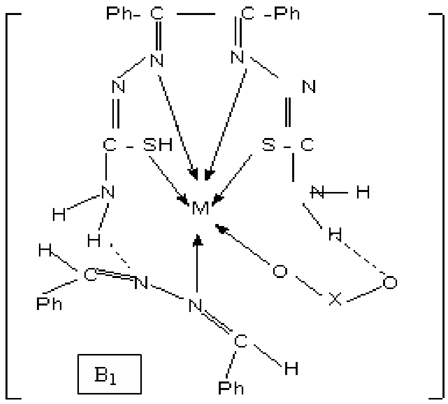

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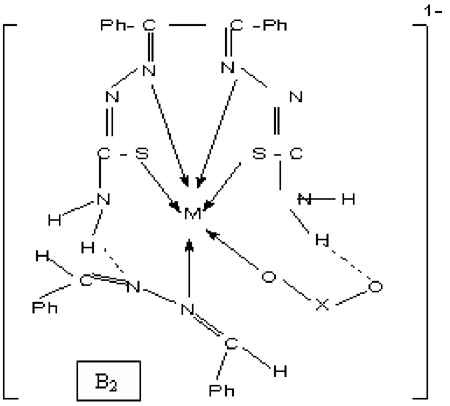

B2

Fig. 2 : Proposed structures of the complexes

M= Ni^{2+} ,Co^{2+} ; X= -CO, CH_3C- or –NO;

A_1 & A_2 = in neutral medium ; B_1 & B_2 – in basic medium .

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تحضير وتشخيص بعض المعقدات الجديدة لمزيج من ليكاندات الثايوسميكاربازون والبنزالدازاين

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الكلمات المفتاحية : ثايوسميكاربازون ، أزاين ، مزيج من الليكاندات ، معقدات الكوبلت (II) ، معقدات النيكل (II) .

الملخص:

يتضمن البحث تفاعل بنزل بس (ثايوسميكاربازون) – $BSTH_2$ والبنزالدازاين – BA مع املاح الكوبلت (II) والنيكل (II) بنسبة مولية ١:١:١ مكونا معقدات أحادية النواة ذات صيغ $[Co(BTSH_2)(BA)]CO_3$ و$[Ni(BTSH_2)(BA)CO_3]$ و $[M(BTSH_2)(BA)(Ac)]Ac$ و $[M(BTSH_2)(BA)](NO_3)_2$ في الوسط المتعادل، في حين اقترحت الصيغ $K[M(BTSH)(BA)CO_3]$ و$K[M(BTS)(BA)X]$ في الوسط القاعدي(حيث $M=Co^{2+}$ أو Ni^{2+} ، BTSH = الليكاند $BTSH_2$ مزال منه بروتون واحد ، و BTS = الليكاند $BTSH_2$ مزال منه بروتونين) . تتناسق الليكاندات في المعقدات أحادية النواة عن طريق ذرتي نتروجين الازوميثين وذرتي الكبريت في الثايو سميكاربازون بينما ليكاند الازاين فيتناسق اما من خلال ذرة واحدة من نتروجين الازوميثين أو من خلال ذرتي نتروجين الازوميثين . شخصت المعقدات الناتجة باستخدام تقنيات فيزيائية–كيميائية واستنادا لذلك اقترحت لها تراكيب ذات شكل ثماني السطوح .