

NEW COMPLEXES OF INDIUM (111) CONTAINING MIXED LIGANDS (SEMICARBAZONES and BENZALDAZINES).

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Abstract

Mixed ligand complexes of indium (111) have been synthesized by the reaction of $\text{InCl}_3 \cdot 6\text{H}_2\text{O}$ with semicarbazone (SCH) and benzaldazine (BA) ligands in neutral and basic medium. Complexes of the type $[\text{In}_2(\text{BA})_2(\text{LH})_4]\text{Cl}_6$ and $[\text{In}_2(\text{BA})_2(\text{L})_4]\text{Cl}_2$ (where BA = benzaldazine, LH = semicarbazone ligands (SCH) and L = deprotonated semicarbazone ligands (SC)) have been proposed in neutral and basic medium, respectively. The complexes are characterized physicochemically.

Key words: Ligands, semicarbazone, benzaldazine, indium.

Résumé

Un mélange de ligands complexes d'indium (111) est synthétisé par la réaction de $\text{InCl}_3 \cdot 6\text{H}_2\text{O}$ sur des ligands semicarbazone (SCH) et benzaldazine (BA) dans des milieux neutre et basique. Des complexes de type $[\text{In}_2(\text{BA})_2(\text{LH})_4]\text{Cl}_6$ et $[\text{In}_2(\text{BA})_2(\text{L})_4]\text{Cl}_2$ (où BA = benzaldazine, LH = semicarbazone ligands (SCH) and L = deprotonated semicarbazone ligands (SC)) sont proposés dans des solutions respectivement neutre et basique. Les complexes sont caractérisés physicochimiquement.

Mots clés: Ligands, semicarbazone, benzaldazine, indium.

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ملخص

يتضمن البحث تحضير معقدات للأنديوم III مع مزيج من ليكاندين وذلك بمفاعلة كلوريد الأنديوم $\text{InCl}_3 \cdot 6\text{H}_2\text{O}$ مع ليكاندات البنزالدازين و السميكاربازون في الوسط المتعادل و القاعدي. ولقد اقترحت الصيغ التالية للمعقدات الناتجة $[\text{In}_2(\text{BA})_2(\text{LH})_4]\text{Cl}_6$ و $[\text{In}_2(\text{BA})_2(\text{L})_4]\text{Cl}_2$ حيث BA تمثل ليكاند البنزالدازين و LH تمثل ليكاندات السميكاربازون و L تمثل ليكاندات السميكاربازون مزال عنها البروتونات في الوسط المتعادل و القاعدي على التوالي، و قد شخصت المعقدات الناتجة بطرق فيزيائية كيميائية.

الكلمات المفتاحية: ليكاندات، السميكاربازون، البنزالدازين، الأنديوم.

Azine complexes with some ions have aroused considerable interest [1]. Study of these complexes suggested that the azine ligands coordinate in different manners [2]. Recently an increasing number of metal complexes with some ions have been studied [3-5].

Semicarbazones bonding through the nitrogen and oxygen atoms to the central metal ion form an important class of biologically active ligands and provide models for metal-ligand bonding sites in several enzymes [6, 7]. In biological systems, the enzymes are frequently strongly dependent, as far as their reactions are concerned, on the presence of small amounts of metal ions. Semicarbazone complexes of some transition elements have been reported [8-10].

In recent years, there has been considerable interest in the study of mixed ligands complexes, of transition and non-transition metals [11, 12], due to their important role in biological processes [12, 13].

In view of this, and since mixed ligand complexes with indium (111) ion have not yet been reported, it is a matter of interest to determine the extent to which the biological properties of these ligands would be affected by incorporating the In (111) ion. This information can be gained by biological examination of the various complexes derived from azine and semicarbazones which would be synthesized.

In the present work, new indium (111) complexes with mixed ligands (benzaldazine, (BA) and semicarbazones such as: benzaldehyde semicarbazone (BSC), 4- dimethylaminobenzaldehydesemicarbazone (DMSC), 3, 4-dimethoxybenzaldehydesemicarbazone (DMBSC), 2-fluorobenzaldehydesemicarbazone (FSC) 3-fluorobenzaldehydesemicarbazone (FBSC)) (Fig.1), have been synthesized and characterized physicochemically.

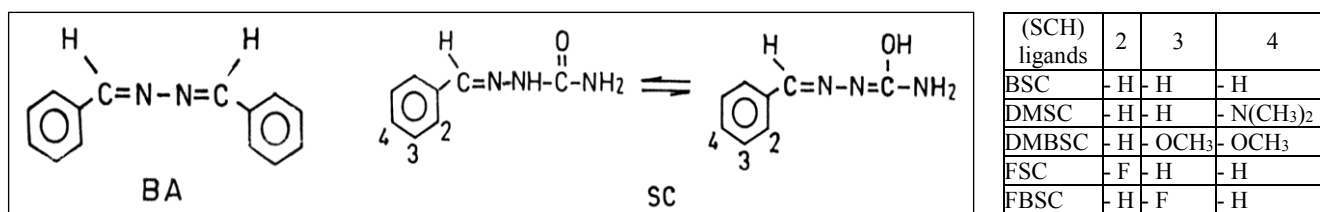


Figure 1: Model structures of the ligands.

EXPERIMENTAL

A. Analytical and physical measurements

IR spectra have been recorded on Pye-Unicam 1100 spectrophotometer in the 400-4000 cm^{-1} range using KBr pellete.

UV spectra have been recorded on Pye-Unicam 8000 spectrophotometer for 10^{-5} M solutions of the ligands and their complexes in DMF at 25 °C, using a 1 cm cell.

^1H NMR spectra have been recorded in deuterated DMSO on Hitachi Perkin Elmer NMR spectrometer (60 μ Hz).

Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring set IF-42 using 10^{-3} M DMF at room temperature.

Elemental analyses for some complexes have been carried out on a CHN Analyser, Type 1106 (Carlo – Erba) at the department of Chemistry, College of Science, University of Mosul, Iraq. Chloride contents have been determined by applying Mohr method [14].

B. Starting materials

The chemicals $\text{InCl}_3 \cdot 6\text{H}_2\text{O}$, 4-dimethylamino benzaldehyde, dimethylformamide (Fluka) and 3, 4-dimethoxybenzaldehyde, hydrazine sulphate, semicarbazide hydrochloride, diethylether, ammonium hydroxyde (BDH) are used as supplied. Whereas the chemicals benzaldehyde, 2-fluorobenzaldehyde and 3-fluorobenzaldehyde (Fluka) are used after purification by distillation.

C. Preparation of the ligands

Benzaldazine (BA) has been prepared according to the standard method [15]. A mixture of 0.0184 mole powdered hydrazine sulphate in 2.4 ml ammonium hydroxide solution and 18 ml water have been stirred. 0.0434 mole of benzaldehyde is added with continuous stirring over a period of 30-60 minutes. The mixture has been stirred for a further hour. The solid product is separated by filtration, washed with water, recrystallised from 8 ml rectified spirit. Yellow crystals are obtained (m.p 114 °C).

Semicarbazone ligands have been prepared according to standard method [5]. 0.0896 mole of semicarbazide hydrochloride and 0.0163 mole sodium acetate dissolved in 10 ml water are mixed with 0.0940 mole of the aldehyde. The mixtures are shaken until clear solutions are produced, followed by heating on a waterbath for few minutes then cooled. The products are separated by filtration, washed with cold water and recrystallised from ethanol. White crystals are obtained (m.p of BSC = 200°C, DMSC = 234d, DMBSC = 212d, FSC = 240d and FBSC = 230 °C).

D. Preparation of the complexes

a/ Neutral medium

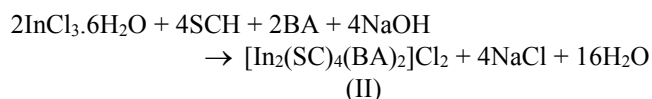
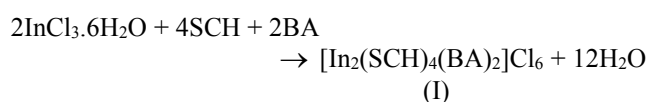
Complexes having the formula $[\text{In}_2(\text{SCH})_4(\text{BA})_2]\text{Cl}_6$ have been prepared by the reaction of aqueous solution of indium (III) chloride with ethanolic solutions of the semicarbazones and benzaldazine ligands in 2:4:2 molar ratios using 20 ml ethanol. The mixtures are refluxed for 3h, evaporated to about half their volumes and cooled. The resulting complexes are filtered off, washed with diethylether and dried. The percentage yields of the complexes are in the range 80-85%.

b/ Basic medium

Complexes of the type $[\text{In}_2(\text{SC})_4(\text{BA})_2]\text{Cl}_2$ have been prepared by the reaction of aqueous solution of indium (III) chloride with the semicarbazones and benzaldazine ligands in 2:4:2 molar ratios using 20 ml ethanol as a solvent. NaOH solution is added to the mixture until pH \approx 8 - 8.5. The mixture is cooled in ice bath and the products are filtered off, washed with diethyl ether and dried.

RESULTS AND DISCUSSION

The reaction of $\text{InCl}_3 \cdot 6\text{H}_2\text{O}$ with semicarbazones and benzaldazine ligands in 2:4:2 molar ratio in both neutral and basic medium may be represented by the following reactions:



The resulted complexes are coloured, solids, moderately soluble in ethanol, soluble in DMF and DMSO. The elemental analyses reveal that the complexes have the composition $[\text{In}_2(\text{SCH})_4(\text{BA})_2]\text{Cl}_6$ and $[\text{In}_2(\text{SC})_4(\text{BA})_2]\text{Cl}_2$ in neutral and basic medium respectively (Table 1). The molar conductivities of the complexes in 10^{-3} M MDF are determined, the values (Table 1) approach those expected for 1:6 and 1:2 electrolytes [16] for (I) and (II) respectively.

According to the analytical and physical data for the metal complexes, the central metal atoms are probably hexacoordinated and binuclear complexes are resulted.

The infra red spectra of semicarbazone ligands show a strong band at about 1675-1695 cm^{-1} which is attributed to

N°	Compound	mp °C	Colour	Λ_M $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	Med.	Analysis Calc./Obs. (%)			
						C	H	N	Cl
1	$[\text{In}_2(\text{BSC})_4(\text{BA})_2]\text{Cl}_6$	146	yellow	500	neutral				
2	$[\text{In}_2(\text{DMSC})_4(\text{BA})_2]\text{Cl}_6$	210d	orange	500	neutral	48.5 49.02	4.75 4.31	16.64 15.89	12.66 13.00
3	$[\text{In}_2(\text{DMBSC})_4(\text{BA})_2]\text{Cl}_6$	188	orange	510	neutral				
4	$[\text{In}_2(\text{FSC})_4(\text{BA})_2]\text{Cl}_6$	149	pale yellow	505	neutral	45.44 45.61	3.54 3.31	12.13 13.03	13.46 13.50
5	$[\text{In}_2(\text{FBSC})_4(\text{BA})_2]\text{Cl}_6$	216	pale yellow	505	neutral				
6	$[\text{In}_2(\text{BSC})_4(\text{BA})_2]\text{Cl}_2$	236d	yellow	155	basic	52.61 52.11	4.38 4.55	16.37 15.88	5.19 5.50
7	$[\text{In}_2(\text{DMSC})_4(\text{BA})_2]\text{Cl}_2$	120	brown	170	basic				
8	$[\text{In}_2(\text{DMBSC})_4(\text{BA})_2]\text{Cl}_2$	150d	orange	170	basic	50.73 51.01	4.10 4.54	13.92 14.97	4.41 4.50
9	$[\text{In}_2(\text{FSC})_2(\text{BA})_2]\text{Cl}_2$	218	pale yellow	140	basic				
10	$[\text{In}_2(\text{FBSC})_2(\text{BA})_2]\text{Cl}_2$	214	pale yellow	140	basic	49.98 51.01	4.30 4.54	15.55 14.97	4.93 4.80

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

n (*)	VC=N Azine	VN-N Azine	VN-H	VC=N Semi	VC=O Semi	VC-O Semi	ν_{NH_2}	VM-O	VM-N	Other bands
BSC & BA	1630	950	3400-3500	1580	1675		1450			
1	1570	990	3400-3500	1540	1650		1450	460	550	
6	1570	990	3400-3500	1540		1350	1450	450	550	
DMSC & BA	1630	950	3510	1580	1670		1450			VC-N 1190
2	1590	980	3510	1550	1650		1450	550	600	VC-N 1190
7	1590	980	3510	1560		1360	1450	520	570	VC-N 1190
DMBSC & BA	1630	950	3500	1575	1675		1450			VC-O-C 1180
3	1590	975	3500	1530	1650		1450	500	570	VC-O-C 1180
8	1590	975	3500	1530		1360	1450	450	520	VC-O-C 1180
FSC & BA	1630	950	3505-3400	1580	1680		1440			VC-F 1150
4	1590	970	3505-3400	1550	1640		1440	470	550	VC-F 1150
9	1590	970	3510-3400	1540		1350	1440	450	560	VC-F 1150
FBSC & BA	1630	950	3500	1595	1695		1430			VC-F 1150
5	1580	980	3500	1560	1650		1430	460	550	VC-F 1150
10	1580	980	3500	1535		1340	1430	450	560	VC-F 1150

Table 2: IR spectra of the ligands and their complexes (values in cm^{-1}).

(*) n corresponds to the number N of the complex in table 1.

the C=O group [10-17]. This value shifts towards a lower frequency on coordination, in neutral medium, indicating the formation of a chelation between the oxygen of the C=O group and the metal ion [10]. Meanwhile, in basic medium, this band disappears in the complexes and a new band is observed at 1340-1360 cm^{-1} due to C-O group, thereby establishing coordination of the ligand through the

enolic oxygen atom [10]. The next strong band at 1575-1595 cm^{-1} which is attributed to C=N group [9] shifts towards a lower frequency on coordination [8] which is due to the decrease of the bond order as a result of metal nitrogen bond formation [8]. The position of the ligands in the range 3400-3510 cm^{-1} remains unaltered in the complexes indicating that there is no coordination through the NH group [10].

The spectra of benzaldazine show a strong band in the region 1630 cm^{-1} as due to C=N stretching vibration [1]. This band shifts towards lower frequency (Table 2), what demonstrates that the two azine nitrogen are coordinated to the metal ion [1]. Moreover, the positive shift in the N-N vibration band on complexation can be added as further support to the coordination of the azine nitrogen to the metal ion.

The spectra of all the complexes show new bands around 450-550 and 550-600 cm^{-1} due to $\nu_{\text{In-O}}$ and $\nu_{\text{In-N}}$, respectively. The presence of these bands strongly support the coordination of the ligands under investigation with the metal atom [17, 18].

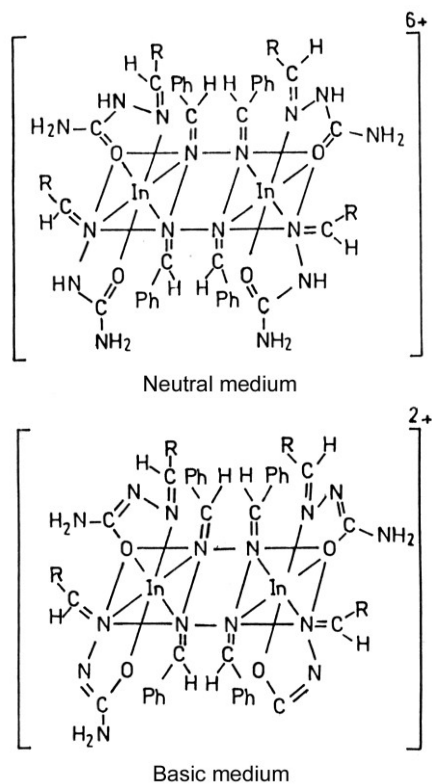
The electronic spectra of the ligands and their complexes in DMF solution have been recorded. The maximum at about 260-280 nm in the case of the ligands are due to $\pi-\pi^*$ (benzenoid) electronic transition [8].

This band is almost unchanged in the complexes. Moreover, the spectra of the ligands show a broad band at about 325-335 nm which is due to $n-\pi^*$ transitions within the C=N chromophore. On complexation, a blue shift is observed due to the polarization in the C=N band caused by the metal ligand electron interaction during the chelation [8]. This shift is due to the donation of nitrogen lone pair of

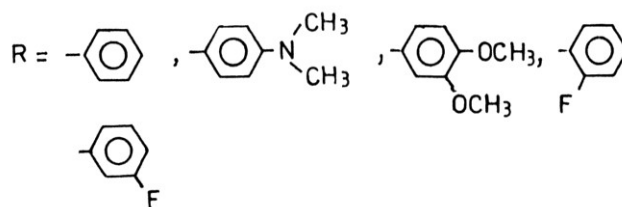
the azomethine group to indium atom [19]. However, in the visible region at about 410-440 nm a band observed which can be related to a charge transfer from ligand to metal orbitals. This ligand to metal charge transfer absorption band is possibly the band responsible for the colours of these complexes [5].

The coordination of the ligands have been further substantiated by the ^1H NMR spectra of the ligands and some of their complexes with indium (III). In the spectra of the ligands, the protons observed at (δ 8.0-8.1 ppm) shift downfield in the spectra of the complexes (δ 8.5-8.6 ppm), this deshielding is possibly due to the donation of the lone pair of electrons by the azomethine nitrogen to the metal atom resulting in formation of a coordination bond [8]. The other protons NH and NH_2 remain unaltered in the complexes and confirm the bonding through the C=O and C-O groups in neutral and basic medium, respectively.

From the present study we can conclude that the complexes having the formula $[\text{In}_2(\text{SCH})_4(\text{BA})_2]\text{Cl}_6$ and $[\text{In}_2(\text{SC})_4(\text{BA})_2]\text{Cl}_2$ in neutral and basic medium respectively, have the following proposed geometry (Fig.2):



where:



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