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Indium(III) Complexes with Some Salicylidene Aromatic *Schiff* Bases

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In(III) complexes with salicylidene aromatic *Schiff* bases have been prepared. The nature of the complexes has been studied by microanalysis of the solid complexes, conductometric titration, uv and ir spectrophotometric measurements. The complexes are of the type 1:1 and 2:1 [Ligand: In(III)] depending upon the *Schiff* base. The tendency of the salicylidene *Schiff* base molecule towards complex formation with In(III) is found to depend largely on the strength of the intramolecular hydrogen bond established between the aldehydic OH group and C=N. Furthermore, it is concluded that these *Schiff* bases cordinate to In(III) as tri- or bidentate ligands depending upon the molecular structure of the *Schiff* base (not as monodentate ligand as previously described). The high molar absorbance of the 1:2 In(III) complex with salicylidene-*o*-hydroxyaniline I (17,800 mol^{-1} cm^2) can be applied for the micro determination of small amounts of Indium as low as 0.57 μg/ml solution.

[Keywords: Indium(III) complexes; Schiff bases]

Indium(III)-Komplexe mit aromatischen Schiff-Basen

Es wurden einige In(III)-Komplexe mit (von Salicylaldehyd hergeleiteten) *Schiff*-Basen hergestellt. Elementaranalyse, konduktometrische Titration und UV- sowie IR-Spektroskopie wurden zur Aufklärung der Komplexe herangezogen. Es werden je nach verwendeter *Schiff*-Base 1:1- oder 2:1-Komplexe gebildet. Die Bildungstendenz der Komplexe mit den *Schiff*-Basen als drei- oder zweizähnige Liganden hängt weitgehend von Stärke und Ausbildungsmöglichkeit von H-Brückenbindungen ab. Einer der beschriebenen Komplexe ist zur photometrischen Mikrobestimmung von In(III) geeignet.

Introduction

Very little work has been published on indium(III) complexes with *Schiff* bases. *Lyapina* et al.[1] investigated the In(III) complexes with some salicylidene and β-hydroxynaphthylidene anilines. The formula of

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the synthesized complexes were found to be $InCl_3 \cdot 3\,SB$, where *SB* is a mole of the *Schiff* base. They have shown that the formation of In(III) complexes with *Schiff* bases occur through bond formation between the Indium ion and the unshared pair of electrons on the azomethine nitrogen atom only. In continuation of our earlier work on U(VI), Th(IV), Ce(III) with some salicylidene aromatic *Schiff* bases[2], we now reports the synthesis and properties of In(III) complexes with the same *Schiff* bases. The molecular structures of the different Indium(III) complexes reported in this investigation have been elucidated by microanalysis of the solid complexes, absorption spectra as well as conductometric titration. The effect of molecular structure of the *Schiff* bases under investigation upon its tendency towards complex formation with In(III) is discussed. In addition this work is made with a view to make comparative studies with the results previously described by *Lyapina*[1].

The *Schiff* bases used in this investigation are salicylidene-*o*-hydroxy aniline (**I**), salicylidene-*p*-hydroxyaniline (**II**) and salicylidene-α-naphthylamine (**III**).

Experimental

Materials and Solutions

The chemicals used in the reactions were of reagent grade. Salicylaldehyde was distilled before use.

The *Schiff* bases under investigation were prepared by the condensation of salicylaldehyde with the corresponding amine in the requisite amount in ethanolic medium. The products were recrystallized before use (ethanol).

$10^{-2}\,M$ solutions of the ligands or indium chloride were prepared by dissolving the accurately weighed amount of the compound in absolute alcohol.

Synthesis of Indium(III)—Schiff Base Complexes

These were synthesized by mixing hot saturated solutions of the ligands and $InCl_3$ containing the appropriate quantities of the reactions in molar ratios 1:1, 2:1 and 3:1. The reaction mixture was then refluxed on a water bath for about $^1/_2$-1 h. The deposited metal complexes were filtered, washed with small quantities of absolute ethanol and dried in a vacuum desiccator over dried silica gel. It is worthy to mention that, in case of ligand **II** a resinous substance was obtained which was triturated successively with ether several times to give the solid product. The chelates were then analysed for their carbon, nitrogen and chloride contents. The results of analysis are given in Tab. 1. Despite the different ligand: In(III) molar ratios used in the synthesis only solid complexes of the type 1:1 in case of ligand **I** and 2:1 in case of ligands **II**, **III** were isolated.

Physical Measurements

The uv and visible absorption spectra were recorded by the aid of a Unicam SP 8000 spectrophotometer using 1 cm matched glass stoppered silica cells. The ir spectra were recorded on a Beckmann infrared spectrophotometer as KBr discs.

Conductometric titrations were carried out using a PYE conductance bridge at 25 °C and a conducting cell of the dipping type. The conductance was recorded for each addition after allowing for equilibrium attainment.

Results and Discussion

Electronic Absorption Spectra

The electronic absorption spectra of the free ligands under investigation as well as their mixtures with In(III) in 2:1 ratio (where the blank is ethanol or the same concentration as in the mixture) have been recorded in the range 250-500 nm (Fig. 1). It can be seen from Fig. 1 that both the π—π^* and the intramolecular charge transfer bands of the free salicylidene-*o*-hydroxy aniline (ligand **I**) exhibit a large red shift in their λ_{max} upon complexation with In(III). This red shift may be presumably due to the fact that the In(III)—ligand bonding is more ionic in comparison to the H^+—ligand bond. Furthermore, it is found that the complex formation of In(III) with ligands **II** and **III** is observed only at higher concentrations of these ligands relative to that observed in case of ligand **I** ($\geqslant 7 \times 10^{-4}$ *M* in case of ligand **II** and $\geqslant 3.3 \times 10^{-3}$ *M* in case of ligand **III**). This behaviour can be attributed to the difference in the strength of the intramolecular hydrogen bond established in the ligand molecule between the lone pair of electrons belonging to the azomethine nitrogen atom and the *ortho* OH group as previously described[2]. The strength of the intramolecular H-bond in the ligands under investigation is expected to increase in the following order: **I** < **II** < **III**. This will go in the opposite direction to the tendency of these ligands towards complex formation with In(III).

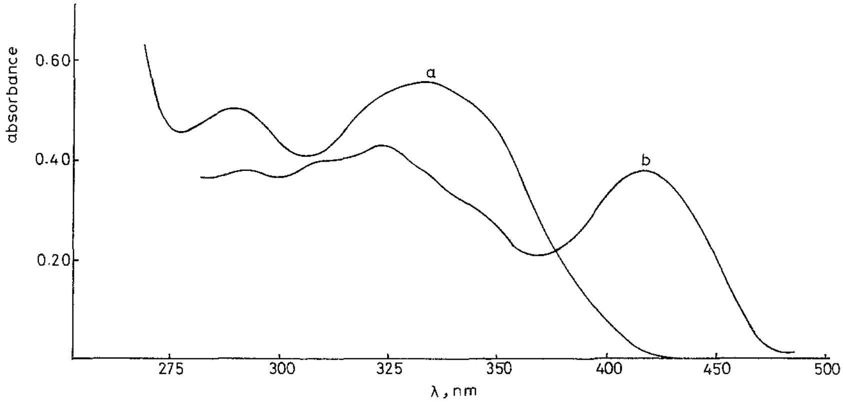

Fig. 1. Absorption spectra of free ligand **I** and 2:1 ligand **I**—In(III) (alcohol as a blank); a) 1×10^{-4} *M* ligand **I**; b) 1×10^{-4} *M* ligand **I**—5×10^{-5} *M* In(III)

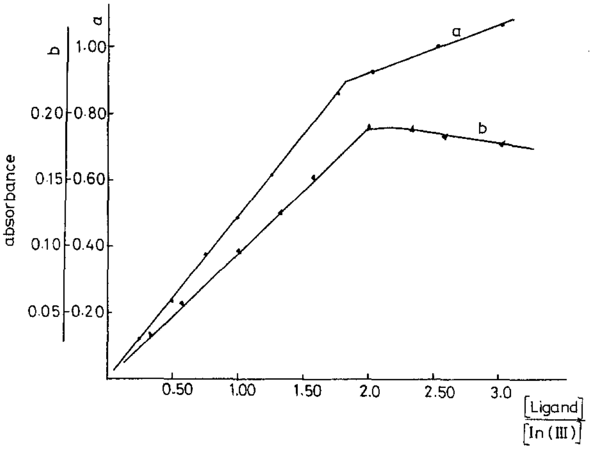

Fig. 2. Molar ratio method; a) ligand **I**, [In(III)] $= 1 \times 10^{-4} M$, $\lambda = 420$ nm; b) ligand **II**, [In(III)] $= 3 \times 10^{-3} M$, $\lambda = 410$ nm

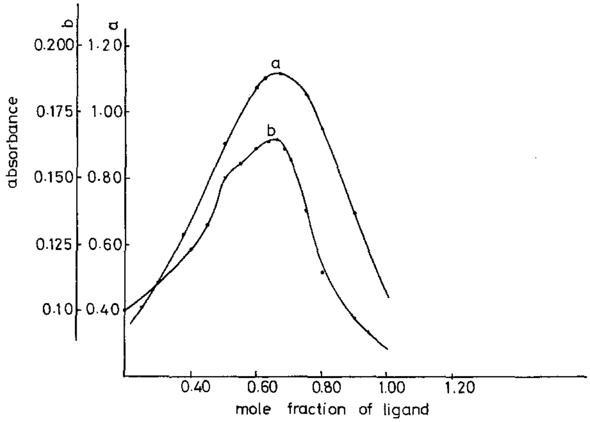

Fig. 3. Continuous variation method; a) ligand **I**, $\lambda = 420$ nm, Total concentration $= 4 \times 10^{-4} M$; b) ligand **II**, $\lambda = 420$ nm, Total concentration $= 1 \times 10^{-2} M$

Stoichiometry of the Complexes

The stoichiometry of Indium complexes with ligands **I** and **II** in alcoholic medium is determined using conventional spectrophotometric methods. The molar ratio and continuous variation methods revealed the existence of 2 : 1 [*L* : In(III)] complexe in case of ligand **I** and 1 : 1, 2 : 1 complexes in case of ligand **II**. The stoichiometry of these complexes is also proved by conductometric titration of 50 ml 10^{-3} *M* $InCl_3$ solution with 10^{-2} *M* solution of ligands **I** and **II**. The titration curves shown in Fig. 4 are characterized by two breaks at molar ratios 1:1 and 2:1 [*L*:In(III)]. The general increase in conductance as the amount of ligand is increased can be explained by the liberation of hydrogen ions through the interaction of ligands **I** and **II** with $InCl_3$ as indicated by the following equations:

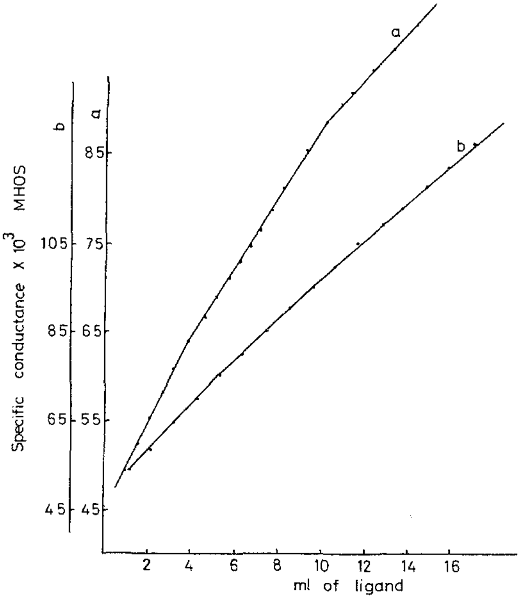

Fig. 4. Conductometric titration of 50 ml 10^{-3} *M* In(III) with 10^{-2} *M* ligand; a) with ligand **I**; b) with ligand **II**

I: $InCl_3 + H_2L \rightleftharpoons [InL]Cl + 2\,HCl$
$InCl_3 + 2H_2L \rightleftharpoons [InL_2]\,H + 3\,HCl$
II: $InCl_3 + H_2L \rightleftharpoons [In(HL)]Cl_2 + HCl$
$InCl_3 + 2\,H_2L \rightleftharpoons [In(HL)_2\,Cl + 2\,HCl$

This behaviour is supported by the results of the micro analyses of the solid complexes (cf. Tab. 1).

It is worthwile to mention that it is quite difficult to trace the step wise formation of the Indium complex with ligand **III** by spectrophotometric or conductometric titration methods due to the instability of this complex in solution This is expected as a result of the strong intramolecular H-bond in ligand **III** (good electron donor properties of the amine moiety).

Table 1. *Elemental analysis of the* In(III)-*Schiff base complexes*

Ligand	Formula	% Carbon		% Nitrogen		% Chloride	
		Found	Calc.	Found	Calc.	Found	Calc.
I	[In $C_{13}H_9NO_2$]Cl	43.35	43.20	3.76	3.88	9.75	9.83
II	[In $(C_{13}H_{10}NO_2)_2$]Cl	54.22	54.50	5.02	4.88	6.48	6.19
III	[In $(C_{17}H_{13}NO)_2$]Cl_3	57.45	57.06	3.85	3.92	15.60	14.89

Table 2. *Evaluation of the apparent formation constant* (K_f) *for the 1:2 (metal: ligand) indium(III) complexes*

Method	With ligand **I**	With ligand **II**
M.R.	3.35×10^{10}	3.5×10^8
C.V.	2.40×10^{11}	1.50×10^8

Microdetermination of Indium

The very high molar absorption coefficient of the In(III) complex with salicylidene-*o*-hydroxyaniline (**I**) ($\varepsilon = 17{,}800\,\mathrm{mol^{-1}\,cm^2}$) suggests the application of this ligand for the microdetermination of Indium. Applying the *Beer-Lambert* law, it is found that the lowest Indium(III) concentration to be estimated with good accuracy would be in the range of $5 \times 10^{-6}\,M$ (0.57 μg/ml of solution).

Apparent Formation Constants

The results of the molar ratio and continuous variation methods can be utilized in calculating the apparent stability of the Indium complexes with ligands **I** and **II**[3]. It is evident from the results shown in Tab. 2 that the 2:1 complex with ligand **I** is more stable than the corresponding one with ligand **II**. This difference in stability goes in accord with the weak tendency of ligand **II** (relative to ligand **I**) towards complex formation with In(III) as discussed above.

Infrared Spectra

Tentative assignments of some of the imporatnt bands belonging to the ligands and their In(III) complexes are recorded in Tab. 3. Careful examination of the results indicate that complex formation between

Table 3. *Some infrared frequencies (in* cm^{-1}*) of the Schiff bases and their* In(III) *complexes*

Ligand **I**	1:1 Ligand **I**: In(III) complex	Ligand **II**	2:1 Ligand **II**: In(III) complex	Ligand **III**	2:1 Ligand **III**: In(III) complex	Assignment
		3320[a]	3380[a]		3060[b] w	OH-stretching
2540	—	2560	—	2620	—	Intramolecular H-bonded OH
1605	1612	1618	1612	1596	1618	C=N stretching vibration
1290	1285	1288	1280	1284	1302	Phenolic C—O stretching

[a] Free —OH, [b] chelating —OH.

ligands **I**, **II**, **III** and Indium(III) probably occur through coordination of In(III) with the azomethine group and formation of an oxygen—In(III) bond in case of ligands **I**, **II** and an oxygen → In(III) bond in case of ligand **III**. This conclusion is based on following observations:

a) The disappearance of the broad and weak band responsible for the intramolecular H-bonded OH stretching in the free ligands upon their complexation with In(III).

b) The shift observed in the frequency of the phenolic C—O or C = N stretching bands of the free ligands either to shorter or longer frequencies on comparing with the corresponding ones belonging to the complexes.

c) The appearance of a weak band at 3,060 cm^{-1} in the ir spectra of the In(III) complex with ligand **III** in comparsion to the corresponding one of the free ligand **III**. This band can be assigned to the stretching of the chelating O—H group.

The above spectrophotometric and conductometric studies as well as the results of the microanalysis of the solid complexes support the conclusion that ligand **I** coordinates to In(III) as tridentate ligand, whereby the ligand anions (L^{--}) are coordinated to the central Indium ion to form complexes of the type 1:1 and 2:1. On the other hand ligands **II** and **III** react with In(III) as bidentate ligands where the anions of the former ligand ($\mathrm{H}L^{-}$) and the molecules of the latter one are coordinated to the central metal, to form complexes of stoichiometry 1:1, 2:1 in case of ligand **II** and 2:1 in case of ligand **III**. These facts are quite different from those previously described by *Lyapina* et al.[1] where the salicylidene *Schiff* base molecules are reported to coordinate to In(III) as monodentate ligand to form complexes of the type 3:1.

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