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Synthesis and Properties of Yttrium(III) Complexes with N-Substituted Salicylideneimines

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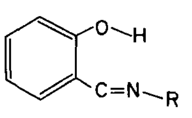
The reaction of yttrium(III) chloride hydrate with N-alkylsalicylideneimines (abbreviated as (Sal-R)H) has yielded yttrium(III) complexes of the type $YCl_3\{(Sal\text{-}R)H\}_3$. *In these complexes, the Schiff bases in their neutral forms are bound with yttrium(III) ion. Their properties are presented and possible structures are discussed.*

Introduction

Although numerous papers have been published about 3*d* transition metal complexes with Schiff bases, little work has been reported on the corresponding complexes of 4*d* and 5*d* transition elements. As part of research projects on such metal complexes, studies of yttrium(III) complexes were undertaken.

In the course of the studies it has recently been found that the reaction of yttrium(III) chloride with N-alkylsalicylideneimines (I, abbreviated as (Sal-R)H) yields a series of yttrium(III) complexes containing neutral Schiff base molecules as ligands. The present paper describes the synthesis and properties of these complexes.



Experimental

Materials

Yttrium(III) complexes of the type $YCl_3\{(Sal\text{-}R)H\}_3$ were prepared by the following general method.

To a solution of yttrium(III) chloride hexahydrate (0.01 mol) in ethanol (100 ml) was added at 80° C an appropriate Schiff base (0.033 mol), and the solution was heated with stirring under reflux at this temperature for about 3 hr. A yellow precipitate was filtered off, while the solution was hot. The precipitate was recrystallized from methanol or ethanol to yield yellow plate-like crystals.

The compounds are soluble in methanol, ethanol and dimethylsulphoxide. In these solvents, however, they are decomposed to a more or lesser extent. In water, they are readily decomposed to form a pale-yellow precipitate. They are insoluble in chloroform, benzene and tetrahydrofuran.

Analytical data of the complexes are shown in Table I.

Measurements

Electronic absorption spectra of the complexes were measured on a Shimadzu MPS-50L spectrophotometer. Infrared absorption spectra were obtained from nujol mulls using a Hitachi EPI-S2 infrared spectrophotometer.

Conductivity measurements were carried out using a calibrated Toa Electronics CG-201 PL conductivity

TABLE I. Analytical Data of Yttrium(III) Complexes of the Type $YCl_3\{(Sal\text{-}R)H\}_3$.

R	M.p. °C	Found, %			Calcd., %			Λ_M[a]
		C	H	N	C	H	N	
CH_3	246	47.46	4.59	6.80	47.98	4.53	6.99	100.0
C_2H_5	237	50.27	5.18	6.55	50.44	5.17	6.54	104.5
n-C_3H_7	235	52.81	5.81	6.17	52.61	5.74	6.14	99.0
i-C_3H_7	205	52.86	5.77	6.14	52.61	5.74	6.14	–

[a] Molar conductivity, $ohm^{-1} cm^2 mol^{-1}$, in dimethylsulphoxide at 20° C, concentration being $10^{-3} M$.

cell, a Toa Electronics Model CM-1DB conductivity bridge, and $10^{-3}M$ solutions of the complexes in dimethylsulphoxide or in methanol.

Results and Discussion

Any attempt to isolate yttrium(III) complexes containing N-substituted salicylideneiminates as ligands has not been successful so far. This is in contrast with a previous result that tris(N-alkylsalicylideneiminato) metal(III) complexes were synthesized for lanthanide (III)[1] and aluminium(III).[2]

The yttrium(III) complexes of the type $YCl_3\{(Sal\text{-}R)H\}_3$ have been isolated in yellow crystals in the present work. It should be noted that the N-alkylsalicylideneimines are bound with yttrium(III) ion in their neutral form and not in an anionic form. In the literature, there have been reported only a small number of those complexes, in which the neutral molecules of N-substituted salicylideneimines are bound with a metal ion. Examples of such complexes are $FeCl_3\{Sal\text{-}p\text{-}CH_3\text{-}C_6H_4)H\}_3$,[3] $CoCl_2\{(Sal\text{-}R)H\}_2$,[4] $SnCl_4\{(Sal\text{-}p\text{-}CH_3\text{-}C_6H_4)H\}_2$,[5,6,7] $UO_2(NO_3)_2\{(Sal\text{-}R)H\}_2$,[8] $WO_2Cl_2\{(Sal\text{-}R)H\}_2$[9] and so on.

The yttrium(III) complexes obtained in the present work are stable in the solid state. In solution, however, they undergo decomposition in various ways, which depend upon the solvent employed. In water, they are decomposed very fast to form a pale-yellow precipitate, due possibly to hydrolysis.

Although no precipitate appears in dimethylsulphoxide, no precise measurements of the conductivity can be made in this solvent because of its fast increase until a plateau of 100–120 $ohm^{-1}cm^2mol^{-1}$ is reached, which corresponds to the value for a 3:1 electrolyte.[10] It is likely that the chloride ions originally bound with the yttrium(III) ion are readily replaced by dimethylsulphoxide (DMSO) molecules, yielding a 3:1 electrolyte, $[Y(DMSO)_2\{(Sal\text{-}R)H\}_3]Cl_3$, in the solution.

In methanol, the decomposition is much slower. Immediately after dissolution, the conductivity is about 160 $ohm^{-1}cm^2mol^{-1}$, which corresponds to the value for a 1:1 electrolyte,[10] although it increases slowly with time. This finding seems to suggest a possible formula $[YCl_2\{(Sal\text{-}R)H\}_3]Cl$ for these yttrium(III) complexes in the solid state.

The electronic absorption spectra of the yttrium(III) complexes in dimethylsulphoxide show well-defined absorption bands at about 25.5–26.0 kK (ε 1000–1800) and 31.7–31.9 kK (ε 12500–18000), which are considered to be due to electronic transitions within the salicylideneimine molecules coordinated to the yttrium (III) ion. These bands are found to be shifted toward very slightly higher frequencies, as compared with those of the free ligand, for example, (Sal-n-propyl)H, which shows the corresponding bands at about 24.2 kK (ε 250) and 31.6 kK (ε 4000) respectively.

A similar slight hypsochromic shift is observed for complexes of the type $UO_2(NO_3)_2\{(Sal\text{-}alkyl)H\}_2$, which show the corresponding bands due to intraligand transitions at about 25.3–25.5 kK (ε 6300–8000) and 31.7–31.8 kK (ε 4500–6300).[8] It should be noted that the frequencies of these band maxima are very close to those for $YCl_3\{(Sal\text{-}R)H\}_3$.

Main infrared bands of these yttrium(III) complexes are shown in Table II. They show a strong band at about 1635–1640 cm^{-1}, which is assigned to $\nu(C{=}N)$ of the Schiff bases.[11] Those complexes cited above which were concluded to contain neutral salicylideneimines coordinated to a metal ion show the corresponding band at about 1640 cm^{-1}. This frequency region is found to be higher than the free ligand value around 1620 cm^{-1}. It is well known that the bidentate N-substituted salicylideneiminate anion bound with a metal ion exhibits the corresponding band at about 1610–1620 cm^{-1}.

In agreement with the formulation involving the neutral Schiff bases, the complexes $YCl_3\{(Sal\text{-}R)H\}_3$ show a band at about 3000–3100 cm^{-1}, which is indicative of hydrogen bonded NH or OH group of the Schiff base. The Schiff base in the unionized neutral form is known to show the corresponding band at about 2800–2900 cm^{-1} and in the anionic bidentate form no absorption band of this sort appears in this region. Previous studies[3,4,5] have shown that similar complexes of cobalt(II) and iron(II) halides with salicylideneimines show related infrared bands at about 2600–2800 cm^{-1}.

Based upon the argument given above and also taking into consideration that the coordination number of yttrium(III) often exceeds six, the yttrium(III) complexes obtained in the present work may be formulated as $[YCl_2\{(Sal\text{-}R)H\}_3]Cl$, in which the yttrium (III) ion probably achieves a coordination number eight with two chloride ions and three bidentate Schiff base molecules. The hydrogen bonding may occur either between the two adjacent ligands, or within one salicylideneimine molecule coordinated to the metal ion. The latter possibility seems much less likely; an intraligand hydrogen bonding makes it impossible for the Schiff base to act as a bidentate ligand not only for steric reasons but also for electronic ones.

TABLE II. Main Infrared Bands of Yttrium(III) Complexes $YCl_3\{(Sal\text{-}R)H\}_3$.

R	$\nu(C{-}O)$	$\nu(C{=}N)$	$\nu(O\cdots H\cdots N)$
CH_3	1525	1640	3100
C_2H_5	1530	1640	3100
$n\text{-}C_3H_7$	1525	1635	3050
$i\text{-}C_3H_7$	1530	1635	3050

Another structure, however, might not be ruled out. Instability of these complexes in appropriate solvents did not allow measurements of molecular weight or proton magnetic resonance spectra. The definitive conclusion about the structure of these complexes must await further studies including X-ray structural work.

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