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Preparation of N-Heterocycle Salts of $[Yb(oxalate)_2]^-$ and $[HoCl_5]^{2-}$

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Three bis(oxalato)ytterbate(III) salts, viz., $(Quinoline{\cdot}H)Yb(C_2O_4)_2{\cdot}3H_2O$, $(Isoquinoline{\cdot}H)Yb(C_2O_4)_2{\cdot}3H_2O$, *and* $(Morpholine{\cdot}H)Yb(C_2O_4)_2{\cdot}4H_2O$, *were prepared by the reaction of* $YbCl_3{\cdot}6H_2O$ *with the corresponding heterocycle and oxalic acid in aqueous medium. The pentachloroholmates(III),* $(Pyridine{\cdot}H)_2HoCl_5{\cdot}H_2O$, $(Isoquinoline{\cdot}H)_2HOCl_5{\cdot}3H_2O$, *and* $(Acridine{\cdot}H)_2HoCl_5{\cdot}5H_2O$ *were obtained by the reaction of* $HoCl_3{\cdot}6H_2O$ *with the azaheterocycle and hydrochloric acid in water. The new compounds were characterized on the basis of their elemental analysis and their infrared spectra. The electronic absorption spectra of the holmium salts were recorded.*

Introduction

In an earlier paper [1] we have described the reaction of uranyl chloride with hydrochlorides and hydrooxalates of nitrogen-containing heterocycles. In the present study we have prepared and characterized six complex ytterbates(III) and holmates(III) containing nitrogen heterocycles as the cations. The bis(oxalato)ytterbates(III) were prepared by the reaction of $YbCl_3{\cdot}6H_2O$ with the corresponding azaheterocycle and oxalic acid in aqueous medium. The pentachloroholmates(III) were obtained from $HoCl_3{\cdot}6H_2O$, the corresponding heterocyclic base, and hydrochloric acid in water.

The $[Yb(oxalate)_2]^-$ salts are insoluble in common organic solvents and water. The pentachloroholmates(III) are soluble in dimethylformamide, dimethyl sulfoxide, and water and insoluble in most other organic solvents. Analytical data on these compounds are summarized in Table I and the details concerning their preparation and some properties are given in Table II.

Experimental

The heterocyclic bases, $YbCl_3{\cdot}6H_2O$ and $HoCl_3{\cdot}6H_2O$, used in the work were reagent grade commercial products. Oxalic acid was 'Analar' grade. Infrared spectra were recorded on a Perkin Elmer model 710 A spectrophotometer in the 4000–600 cm^{-1} wavenumber region using Nujol mull. The ultraviolet and visible spectra were measured in water on a Cary 118 spectrophotometer. Melting points (uncorrected) were determined on a Thomas–Hoover capillary melting point apparatus.

Synthesis of $(Quinoline{\cdot}H)Yb(C_2O_4)_2{\cdot}3H_2O$

To a hot solution of $YbCl_3{\cdot}6H_2O$ (0.97 g, 0.0025 mol) in 30 ml of water, a hot solution of oxalic acid (0.95 g, 0.0075 mol) and quinoline (1.93 g, 0.015 mol) in 30 ml of water were added and the reaction mixture was stirred. After cooling to room temperature, the separated compound was filtered, washed with water and acetone, and dried. Yield 79.3%, m.p. 240 °C (dec.). For elemental analysis, see Table I.

The corresponding isoquinoline and morpholine salts, *viz.*, $(Isoquinoline{\cdot}H)Yb(C_2O_4)_2{\cdot}3H_2O$ and $(Morpholine{\cdot}H)Yb(C_2O_4)_2{\cdot}4H_2O$ were prepared in the same manner (*cf.* Table II).

Synthesis of $(Pyridine{\cdot}H)_2HoCl_5{\cdot}4H_2O$

Holmium trichloride hexahydrate (0.95 g, 0.0025 mol) was dissolved in distilled water (150 ml) and anhydrous hydrogen chloride gas was passed through the solution until it became saturated (3 hr). Pyridine (0.59 g, 0.0075 mol) was added to the solution and more hydrogen chloride gas was passed through the mixture (about 1 hr). The solution was concentrated to 20 ml. Upon cooling, the precipitated crystalline compound was washed 3–4 times with acetone and dried. Yield 83.3%, m.p. 118 °C. For elemental analysis, see Table I.

The pentachloroholmates(III) of isoquinoline and acridine, $(Isoquinoline{\cdot}H)_2HoCl_5{\cdot}3H_2O$ and $(Acridine{\cdot}H)_2HoCl_5{\cdot}5H_2O$, were prepared by the same procedure (*cf.* Table II).

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TABLE I. Analytical Data on Ytterbium and Holmium Complex Salts.

Compound	Formula	Mol. Wt.	Analysis									
			Calcd.					Found				
			%C	%H	%N	%Cl	%Yb/Ho	%C	%H	%N	%Cl	%Yb/Ho
(Quinoline·H)Yb$(C_2O_4)_2$·$3H_2O$	$C_{13}H_{14}NO_{11}Yb$	533.3	29.28	2.64	2.62	–	32.45	29.14	2.24	2.65	–	31.03
(Isoquinoline·H)Yb$(C_2O_4)_2$·$3H_2O$	$C_{13}H_{14}NO_{11}Yb$	533.3	29.28	2.64	2.62	–	32.45	29.73	2.10	3.04	–	31.64
(Morpholine·H)Yb$(C_2O_4)_2$·$4H_2O$	$C_8H_{18}NO_{13}Yb$	509.3	18.87	3.56	2.75	–	33.98	18.58	3.09	3.12	–	33.95
(Pyridine·H)$_2$HoCl$_5$·$4H_2O$	$C_{10}H_{20}Cl_5HoN_2O_4$	574.5	20.90	3.51	4.87	30.85	28.71	20.61	4.25	4.95	30.70	28.34
(Isoquinoline·H)$_2$HoCl$_5$·$3H_2O$	$C_{18}H_{22}Cl_5HoN_2O_3$	656.6	32.92	3.37	4.26	26.99	25.12	32.80	4.31	4.54	26.26	24.73
(Acridine·H)$_2$HoCl$_5$·$5H_2O$	$C_{26}H_{30}Cl_5HoN_2O_5$	792.7	39.39	3.81	3.53	22.36	20.80	39.93	4.36	3.74	22.20	20.18

TABLE II. Synthesis of Ytterbium and Holmium Complex Salts.

Compound	$YbCl_3·6H_2O/HoCl_3·6H_2O$ taken (g)	Base added (g)	Oxalic acid added (g)	HCl gas passed (hr)	Color	Yield, %	M.p., °C
(Quinoline·H)Yb$(C_2O_4)_2$·$3H_2O$	0.97	1.93	0.95	–	Off-white	79.3	240 (dec.)
(Isoquinoline·H)Yb$(C_2O_4)_2$·$3H_2O$	0.96	1.94	0.95	–	White	78.4	234 (dec.)
(Morpholine·H)Yb$(C_2O_4)_2$·$4H_2O$	0.95	1.30	0.94	–	White	47.0	348 (dec.)
(Pyridine·H)$_2$HoCl$_5$·$4H_2O$	0.95	0.59	–	4	Off-white	83.3	118
(Isoquinoline·H)$_2$HoCl$_5$·$3H_2O$	0.95	0.97	–	3½	Cream	93.7	265–275
(Acridine·H)$_2$HoCl$_5$·$5H_2O$	0.76	1.07	–	3–3½	Yellow	85.4	245 (dec.)

Analyses

Ytterbium and holmium were determined gravimetrically as Yb_2O_3 and Ho_2O_3, respectively. Chlorine was determined as silver chloride. Carbon, hydrogen and nitrogen microanalyses were performed by the microanalytical laboratory of the Institut de Pétroléochimie et de Synthèse Organique Industrielle, Faculté des Sciences et Techniques de Saint-Jérôme, Université d'Aix-Marseille III, Marseille, France.

Results and Discussion

The method of preparation of the complex ytterbium(III) and holmium(III) salts from the corresponding metal trichlorides and hydrooxalates and hydrochlorides of nitrogen-containing heterocycles was analogous to the preparation of the previously described uranyl chloride complexes [1] as well as of bis(pyridinium)pentachloroferrate(III) [2] and of the morpholinium and ethylenedimorpholinium oxalato cuprates [3].

Whereas the oxalato complexes seem to be straightforward, it is likely that the pentachloro complexes exist in the solid state but that they undergo hydrolysis in aqueous solution. Ryan and Jørgensen [4] have prepared the hexahalo complexes of lanthanides in acetonitrile and demonstrated the ease of their hydrolysis in water. Thus, it is probable that in solution the pentachloroholmates(III) dissociate to form the aquo Ho^{3+} ion and the aquated heterocyclic cation separately.

Our attempts to prepare pentachloroytterbates(III) and bis(oxalato)holmates(III) did not lead to compounds of defined composition.

Infrared Spectra

The oxalate group is characterized by the presence of bands at ~1625 and ~1440 cm^{-1} due to asymmetric C=O stretching and symmetric C–O stretching vibrations, respectively. The absorptions arising from water of crystallization lie at ~3400 and 1600 cm^{-1} and are assigned to the stretching ν(O–H) vibration and the bending δ(H–O–H) vibrations, respectively [5]. The presence of the morpholinium ion in $(Morpholine{\cdot}H)Yb(C_2O_4)_2{\cdot}4H_2O$ is indicated by the presence of a band at 2950 and a medium intensity band at 1600 cm^{-1} due to the stretching and bending modes of protonated nitrogen group, $\overset{+}{N}H$ [6].

The presence of pyridinium [7], quinolinium, isoquinolinium, and acridinium cations in their respective compounds is shown by the peaks observed in their spectra. The C–H stretching frequency at ~2950 cm^{-1}, the ring stretching vibrations at about 1640, 1595, 1475, and 1370 cm^{-1}, the C–H in-plane deformation at or near 1320, 1255, 1200, and 1045 cm^{-1}, the ring breathing modes at or near 1010 cm^{-1}, and the C–H out-of-plane deformation at or near 725 cm^{-1} are such bands. The N–H group is indicated by the appearance of a peak at ~890 cm^{-1} which corresponds to the N–H stretching (symmetrical) [8] and a strong band at or near 1540 cm^{-1} arising from the N–H bending. Thus, the infrared spectral studies confirm the presence of pyridinium, quinolinium, isoquinolinium, and acridinium cations in these complex salts.

Electronic Absorption Spectra

Because of the insolubility of the bis(oxalato)-ytterbates(III) in common solvents, we were not able to measure their electronic spectra. However, the electronic spectra of the pentachloroholmates(III) were recorded in water. The spectra of these compounds in the ultraviolet region are very similar to those of the corresponding heterocyclic cations, *i.e.*, the pyridinium, isoquinolinium, and acridinium cation. Thus, the spectrum of $(Pyridine{\cdot}H)_2HoCl_5{\cdot}4H_2O$ exhibited absorption maxima at 197 (log ϵ 3.86), 248 (4.02), 253 (4.08), and 258.5 sh nm (3.91) (in water). The ultraviolet spectrum of pyridine taken in 10% methanol–0.1 *N* aq. HCl is characterized by absorption bands at 248 (log ϵ 3.85), 252.5 (3.91), and 258 nm (3.74). An analogous situation is observed with the $(Isoquinoline{\cdot}H)_2HoCl_5{\cdot}3H_2O$ and $(Acridine{\cdot}H)_2HoCl_5{\cdot}5H_2O$ salts whose ultraviolet spectra resemble those of the corresponding heterocyclic cations (for the spectra of the pyridinium and isoquinolinium cations, see [9]; the spectrum of the acridinium cation has been reported in [10]).

The ultraviolet spectra of the pentachloroholmates(III) thus confirm the presence of the respective heterocyclic cations in these compounds.

The holmium absorption bands were measured in the 360–660 nm region. The spectra of $(Pyridine{\cdot}H)_2HoCl_5{\cdot}4H_2O$ and $(Isoquinoline{\cdot}H)_2HoCl_5{\cdot}3H_2O$ have a pronounced fine structure and the positions of the band maxima are generally in good agreement with the data reported for the Ho^{3+} ion [11]. Thus, *e.g.*, the most intense absorption bands in the case of $(Pyridine{\cdot}H)_2HoCl_5{\cdot}4H_2O$ are at 358, 414, 449, 482, 534, and 639 nm (between 400 and 650 nm, literature [11] reports for the Ho^{3+} ion in 0.1 *M* $HClO_4$: 416, 451, 485, 537, and 641 nm). Ryan and Jørgensen [4] reported the following internal $4f^{10}$ transitions for the $[HoCl_6]^{3-}$ ion: 362, 383, 397.5, 421, 453.8, 488, 542, and 648 nm.

Our results seem to support the independent existence of the Ho^{3+} cation and of the respective heterocyclic cation in aqueous solution.

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