Monatshefte für Chemie 109, 1475—1479 (1978) Monatshefte für Chemie

Aniline and Quinoline Compounds of Mixed Complex Haloacids of Indium(III) With Thiocyanate

Short Communication

Andreas G. Galinos* and **Theodore F. Zafiropoulos**

Department of Inorganic Chemistry,
University of Patras, Patras, Greece

(Received 12 June 1978. Accepted 1 August 1978)

In the present paper the preparation and some properties of compounds of aniline and quinoline with mixed complex haloacids of Indium(III) with thiocyanate are reported. Their UV and IR spectra are discussed.

Anilin- und Chinolin-Verbindungen gemischter komplexer Halogenosäuren des Indium(III) mit Thiocyanat (Kurze Mitteilung)

Es wird über die Darstellung von gemischten Thiocyanaten komplexer Halogenosäuren des Indium(III) mit organischen *Lewis*basen (Anilin und Chinolin) und über einige ihrer Eigenschaften berichtet. Die IR- und UV-Spektren dieser Verbindungen werden diskutiert.

Introduction

Ether compounds of mixed complex haloacids of different metals with thiocyanate—among them $H[InCl_3SCN] \cdot 2\,Et_2O$ and $H[InBr_3SCN] \cdot 2\,Et_2O$ (Et_2O = ether)—have been reported[1]. Recently the pyridine compounds of the form

$$[InX_3SCN(Pyr)_2]^-[Pyr\ldots H\ldots Pyr]^+ (X = Cl, Br, I \text{ and } Pyr = \text{pyridine})$$

were prepared[2].

In the present paper the preparation and the study of some physical and chemical properties of aniline and quinoline compounds of mixed complex haloacids of In(III) with thiocyanate are described. On the basis of analytical results and the study of their UV and IR spectra a possible structure is proposed.

0026-9247/78/0109/1475/$ 01.00

Preparation

In the freshly prepared compounds $H[InCl_3SCN] \cdot 2\,Et_2O$ and $H[InBr_3SCN] \cdot 2\,Et_2O$, pure aniline and quinoline were added in excess and displacement of ether molecules by molecules of the organic base took place. The reaction was exothermic and was accompanied by the evolution of ether vapors. The excess of the organic base was then removed by continual pumping in a vacuum desiccator over concentrated sulfuric acid. The crystalline compounds obtained are insoluble in water and nonpolar solvents but soluble in acetone, dimethylsulfoxide (*DMSO*), acetic acid, $2N$-nitric acid, and partially soluble in ethyl alcohol.

Chemical Analysis

The hydrogen cation (H^+) was determined in absolute *DMSO* by potentiometric titration with $0.1N$-NaOH solution[3]. Indium was determined gravimetrically with 8-hydroxyquinoline. The sum of halogen ions and thiocyanate ions as well as the separation of chloride or bromide ions from thiocyanate ions were determined potentiometrically with $0.1N$-$AgNO_3$, with calomel and sulfide electrodes. Aniline and quinoline were determined potentiometrically[4]. The experimental mole ratio, the m.p. and color of the compounds are given below:

$H(InCl_3SCN) \cdot 4An$; $H:In:Cl:SCN:An = 1.05:1.09:3.04:1.00:3.99$; 205 °C; Brown.
$H(InCl_3SCN) \cdot 3Qu$; $H:In:Cl:SCN:Qu = 1.00:1.07:3.02:1.01:3.07$; 120 °C; Brown.
$H(InBr_3SCN) \cdot 4An$; $H:In:Br:SCN:An = 1.15:1.17:2.98:1.00:3.85$; 137 °C; Beige.
$H(InBr_3SCN) \cdot 3Qu$; $H:In:Br:SCN:Qu = 1.04:1.08:3.00:1.00:2.86$; 108 °C; Brown.

IR Spectra

The IR spectra of the compounds were taken in KBr pellets with a P.E. Spectrophotometer, model 577 covering the region 4,000-250 cm^{-1}. The spectra of the aniline compounds show absorption bands in the region 3,350-2,500 cm^{-1}, at 2,070 cm^{-1}, in the region 1,650-1,400 cm^{-1} and in the region 1,350-250 cm^{-1}.

The absorption bands at 3,338 and 3,268 cm^{-1} are due to antisymmetric and symmetric stretching vibrations of the NH_2 group of coordinated aniline[5]. The bands at 3,220, 3,120, and 3,050 cm^{-1} are assigned to the NH_3^+ stretching vibrations[6]. The band at 2,070 cm^{-1} is due to the pseudosymmetric stretching vibration of the SCN group (commonly referred to as νCN)[7].

The absorption bands in the region 1,650-1,400 cm^{-1}, namely at 1,630 (weak), 1,608 (shoulder), 1,600 (very strong), 1,570, 1,530, 1,490, 1,470, and 1,450 cm^{-1}, appear also in the spectra of *An*HCl and *An*HBr with slight shifts. It must be mentioned that the band at 1,570 cm^{-1} is absent in the spectrum of aniline[6].

The bands below 1,350 cm^{-1} for compounds containing AnH^+ (i.e. *An*HCl, *An*HBr) appear also in the spectra of the prepared aniline compounds. Additionally, shifts and splitting of the spectral bands are observed in the region 1,000–1,050 cm^{-1}, at 798 and 746 cm^{-1}, indicating the existence of the In ← *An* bond[8]. The band at 698 cm^{-1} is assigned to the C—S stretching vibration and indicates a S-bonded type complex[9]. The band at 420 cm^{-1} is attributed to the SCN bending vibration and is indicative of a S-bonded thiocyanate complex to the exclusion of a N-bonded one[10]. The band at 355 cm^{-1} is attributed to the In ← *An* bond, while the band at 275 in the spectrum of the compound $H[InCl_3SCN] \cdot 4\,An$ indicates an In—Cl bond[11]. The spectra of the quinoline compounds show absorption bands in the region 3,300–2,800 cm^{-1}, at 2,075 cm^{-1}, in the region 1,650–1,380 cm^{-1} and in the region 1,320–250 cm^{-1}. The bands in the region 3,300–2,800 are due to the N—H vibrations and C—H stretching modes. The band at 2,075 cm^{-1} is the pseudosymmetric stretching vibration of the SCN group[7]. There are seven medium to strong, absorption bands in the region 1,650–1,380 cm^{-1} (1,630, 1,595, 1,555, 1,500, 1,465, 1,430, and 1,385 cm^{-1}), which also appear in the spectra of coordinated compounds of inorganic halides with quinoline[12]. The bands in the region 1,320–250 cm^{-1} are due to the in-plane and out-of-plane C—H vibrations[12], while the splitting and shifting of the bands at 800 and 750 cm^{-1} indicate the presence of In ← *Qu* bond[13]. The band at 780 cm^{-1} is due to a C—S stretching vibration and indicates a N-bonded complex[9], while the band at 470 cm^{-1} is the NCS bending vibration, which arises in N-bonded complexes[10]. Finally the band at 275 cm^{-1} in the spectrum of the compound $H[InCl_3SCN] \cdot 3\,Qu$ indicates an In—Cl bond[11].

UV Spectra

The UV spectra were obtained in a double beam spectrophotometer, OPTICA CF 4 R, in the region 220–320 nm. The compounds were used as solutions in absolute ethanol with concentrations in the range

Table 1. *The values of ε at the wavelengths of maximum absorption*

Compounds	$\varepsilon_{\lambda\,max}$ $mol^{-1}\ l\ cm^{-1}$
$H[InCl_3SCN]4\,An$	$\varepsilon_{237} = 19{,}000$; $\varepsilon_{252} = 11{,}400$; $\varepsilon_{258} = 8{,}000$; $\varepsilon_{264} = 5{,}100$; $\varepsilon_{286} = 2{,}950$
$H[InCl_3SCN]3\,Qu$	$\varepsilon_{227} = 112{,}000$; $\varepsilon_{231} = 100{,}000$; $\varepsilon_{277} = 11{,}200$; $\varepsilon_{282} = 10{,}900$; $\varepsilon_{288} = 10{,}350$ $\varepsilon_{294} = 9{,}100$; $\varepsilon_{301} = 10{,}200$; $\varepsilon_{306} = 7{,}700$; $\varepsilon_{313} = 11{,}400$
$H[InBr_3SCN]4\,An$	$\varepsilon_{237} = 21{,}200$; $\varepsilon_{252} = 9{,}850$; $\varepsilon_{258} = 5{,}000$; $\varepsilon_{264} = 2{,}700$; $\varepsilon_{286} = 2{,}300$
$H[InBr_3SCN]3\,Qu$	$\varepsilon_{227} = 93{,}000$; $\varepsilon_{231} = 83{,}000$; $\varepsilon_{277} = 8{,}900$; $\varepsilon_{282} = 8{,}700$; $\varepsilon_{288} = 8{,}300$ $\varepsilon_{294} = 7{,}350$; $\varepsilon_{300} = 8{,}140$; $\varepsilon_{306} = 6{,}200$; $\varepsilon_{313} = 9{,}700$

10^{-5}-$10^{-6}M$. The absorption maxima and the corresponding values of the extinction coefficient, ε, are given in Table 1.

The absorption bands in the spectra of the aniline compounds appear also in the spectrum of *An*HCl, which was also recorded, with slight shifts. This fact indicates the existence of the AnH^+ ion. The large values of ε for the aniline compounds in comparison to those of *An*HCl, in the same solvent, suggest complexation and, probably, the existence of hydrogen bridge. Finally, the bands in the spectra of quinoline compounds appear also in the spectrum of *Qu*HSCN (also recorded), a fact which supports the view of the existence of the QuH^+ ion.

Discussion

From the study of the IR spectra it is concluded that:

a) All the compounds contain coordinated molecules of the organic base, also in the form BH^+ (B = Aniline and Quinoline).

b) The absorption band at 275 cm^{-1} in the spectra of the compounds $H[InCl_3SCN] \cdot 4\,An$ and $H[InCl_3SCN] \cdot 3\,Qu$ suggests an octahedral structure for these complex compounds[11].

c) In the aniline compounds the central atom of indium is bonded to the SCN group via the S atom (In ← SCN), whereas in the quinoline compounds it is bonded via the N atom (In ← NCS). Similar cases have been reported in the literature[14].

From the study of the UV spectra it is concluded that the compounds contain the QuH^+ and AnH^+ ions of which the latter is involved in hydrogen bridging. On the basis of the analytical results and the study of the IR and UV spectra the following structures for the prepared compounds are proposed:

$$[InX_3(SCN)An_2]^-[An\text{---}H\text{---}An]^+ \quad \text{and}$$
$$[InX_3(NCS)Qu_2]^-QuH^+ \quad (\text{where } X = Cl, Br).$$

References

1 *A. G. Galinos*, J. Inorg. Nucl. Chem. **24**, 1555 (1962).

2 *A. G. Galinos* and *Th. F. Zafiropoulos*, Z. Naturforsch. **326**, 1149 (1977).

3 *K. K. Barnes* and *C. K. Mann*, Anal. Chem. **36**, 2502 (1964).

4 *J. S. Fritz* in: Acid-Base Titrations in Nonaqueous solvents, pp. 60-62 and 126-127. U.S.A.: Allyn and Bacon Inc. 1973.

5 *M. A. J. Jungbauer* and *C. Curran*, Spectrochimica Acta **21**, 641 (1965).

6 *B. Chenon* and *C. Sandorfy*, Can. J. Chem. **36**, 1181 (1958).

7 *A. A. Newman*, Chemistry and Biochemistry of Thiocyanic Acid, and its Derivatives, p. 74. London: Academic Press. 1975.

8 *A. G. Galinos* and *D. M. Kaminaris*, Chimika Chronika New Series **2**, 59 (1973).

[9] *J. Lewis, R. S. Nyholm*, and *P. W. Smith*, J. Chem. Soc. **1961**, 4590.

[10] *J. Bertini* and *A. Sabatini*, Inorg. Chem. **5**, 1025 (1966).

[11] *D. M. Adams, A. S. Carty, P. Carty*, and *D. G. Tuck*, J. Chem. Soc. **A 1968**, 162.

[12] *S. S. Singh*, Z. anorg. allg. Chem. **348**, 81 (1971).

[13] *D. M. Kaminaris*, Doctorate Thesis, Patras, Greece (1972).

[14] *A. Turco* and *C. Pecile*, Nature **191**, 66 (1961).