Compounds of Complex Halo and Pseudohalo Acids of the Group II B Metals, Part I

Etherate, Pyridine and Aniline Compounds of Zn(II)

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The preparation of sixteen new etherate, pyridine and aniline compounds of complex halo and pseudohalo acids of Zn(II) is reported.

The study of some physical and chemical properties as well as the UV and IR spectra of these compounds are discussed. Tetrahedral structures are proposed for all compounds in the solid state.

Introduction

Although a large number of salts of the complex anions $[M^II X_3]^-$ and $[M^II X_4]^{2-}$ is known, the situation with regard to the corresponding acids is not very clear. The study of these acids is of special interest, since a great number of them is used in certain Friedel-Crafts reactions. The catalytic action of the etherate $HAICl_4 \cdot 2 Et_2O$ has been studied [1]. The preparation of etherate and pyridine compounds of the acids $HZnCl_2Br$, $HZnBr_3$ and $HZnI_2Br$ has been reported [2–4]. Recently, we prepared and studied the complex compounds $HZnCl_3 \cdot 3 An$, $HZnBr_2Cl \cdot 3 An$ and $HZnI_2Cl \cdot 3 An$, where An = aniline [5].

The study of compounds of mixed complex metallohaloacids with pseudohalogens is of some theoretical interest. The isolation of the compounds $HZnCl_2(CSN) \cdot 2 Et_2O$ and $HZnBr_2(CSN) \cdot 2 Et_2O$ has been achieved in the past [6]**. The etherate, pyridine and aniline compounds of the acids $HInX_3SCN$ ($X = Cl, Br, I$) have also been prepared and studied [7, 8].

As a continuation of the interest of our laboratory in the complex haloacids and their compounds in this paper we report the preparation, for the first time, of three etherate, five pyridine and eight aniline compounds of complex halo and pseudohalo acids of Zn(II). Thiocyanate was used as a pseudohalogen.

Experimental

Reagents

High purity reagents were used for the preparation of the complex compounds. Diethyl ether was treated as usual for the removal of peroxides and moisture [9]. The organic bases, pyridine and aniline, were doubly distilled under atmospheric pressure.

Preparation of the complexes

The preparation of the etherate complexes $HZnCl_2I \cdot 3 Et_2O$ (**1**) and $HZnBr_2I \cdot 3 Et_2O$ (**2**) was carried out by the "etherohalogenosis" method [3]. As starting materials anhydrous $ZnCl_2$ and $ZnBr_2$ and an ether solution of HI , 0.3 N were used; the last reagent was in 20% excess. The experimental temperature was kept at $-50^\circ C$ (mixture of dry ice and acetone). The preparation of $HZnI_2(CSN) \cdot 3 Et_2O$ (**3**) was achieved by a method previously described [7]. The ether solution of $HSCN$, 0.05 N, was added in 80% excess. The reaction products **1**, **2** and **3**, thick oily liquids, were purified by washing with small portions of absolute ether.

For the preparation of the pyridine and aniline compounds the following procedure was used: To small amounts of freshly prepared etherate complex haloacids a slight excess of pyridine or aniline was added dropwise. The reaction was vigorous and exothermic and was accompanied by the evolution of vapours. Immediately after the addition of the base, the whole reaction mixture solidified. The addition of more base caused dissolution of the solid product and the appearance of a clear solution. Subsequently, the reaction vessel was placed in a vacuum desiccator over concentrated sulfuric acid. The final crystalline product was obtained by repeated pumping. The product was washed with small portions of absolute ether and heated to $35^\circ C$ for 15 min.

Analyses

a) Instruments and apparatus

For the potentiometric determinations of the acidic hydrogen and the organic bases a pH meter Radiometer Copenhagen NV.-Type PHM 26c and

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** Thiocyanate will be indicated as CNS whenever the actual mode of bonding is undetermined.

glass and calomel electrodes were employed. In the determinations of the acidic hydrogen in the pyridine and aniline compounds the saturated aqueous solution KCl of the calomel electrode was replaced by a methanolic one [10]. For the potentiometric determinations of the halogens and the thiocyanate a potentiometer Corning-Eel, model 12 was used with calomel and sulfide electrodes.

b) Analytical procedures

For the quantitative determination of the etherate compounds a solution was prepared by decomposing a definite amount of each compound with water. The acidic hydrogen was determined potentiometrically with a standard 0.1 N KOH solution [11a]. The hydrolysis of Zn(II) was taken into account. Zinc was determined volumetrically with a 0.05 M EDTA solution [11b]. The total halogen was determined volumetrically by the Volhard method [11c] and potentiometrically with a 0.1 N AgNO₃ solution [12]. The iodide ion in the presence of chloride or bromide was determined by the PdCl₂ method [11d]. The sum of iodide and thiocyanate ions as well as each of them in the presence of the other were determined potentiometrically with a 0.1 N AgNO₃ solution [12]. Ether was determined by weight difference.

The acidic hydrogen of the pyridine and aniline compounds was determined potentiometrically with a 0.1 N KOH solution, after dissolving them in absolute DMSO [10]. The content of the organic base was determined by dissolving the compound in glacial CH₃COOH and potentiometric titration with a 0.1 M HClO₄ solution in CH₃COOH or simple titration with 0.1 M HClO₄ and Crystal violet as the indicator [13]; to the sample being analyzed were added 5–8 ml of 6% Hg(CH₃COO)₂ solution in CH₃COOH. Zinc was determined as described above; a 15% aqueous solution of C₂H₅OH was employed as a solvent. The halogens and thiocyanate were determined as described above, the samples being dissolved in 2 N HNO₃. The chloride and bromide ions, the chloride and thiocyanate ions, and the bromide and thiocyanate ions were determined potentiometrically [12].

Stability test for the pyridine and aniline compounds [4]

A small amount of the compound was dissolved in absolute ethanol. No precipitate appeared by the addition of a 0.5% ethanolic solution of AgClO₄. A slight cloudiness appeared after a few minutes. Dilution with water caused the Ag(I) halides and AgSCN to precipitate.

Physicochemical measurements

The m.p. of the pyridine and aniline compounds were obtained in a Büchi 510 apparatus. For the conductivity measurements 10^{−3} M solutions were prepared in CH₃NO₂, which was properly pretreated [14]. A conductivity apparatus, Ehrhardt–Metzger

Nachf. type L21, was employed. The cell constant was $C = 1 \text{ cm}^{-1}$ and the measurements were carried out at $25 \pm 0.1^\circ \text{C}$. The UV spectra of the pyridine and aniline compounds were taken in a Bausch Lomb-Shimadzu Spectronic 210 UV double beam spectrophotometer with a deuterium lamp. The solvent was spectroscopic quality C₂H₅OH, the concentrations 10^{−5}–10^{−4} M and the region scanned 210–320 nm. The IR spectra of these compounds were recorded in Perkin-Elmer spectrophotometers 457 and 577. The samples were used in the form of KBr pellets. The spectra covered the region 4000–250 cm^{−1}.

Results and Discussion

For the preparation of compounds **1** and **2** a low temperature is required, since at high temperatures ether is cleaved by HI [15]. The etherates fume in air and are insoluble in nonpolar solvents. The pyridine and aniline compounds are formed by the complete replacement of the ether by pyridine or aniline:

where Py = pyridine. The pyridine and aniline compounds are crystalline solids and stable in the air. They are insoluble in nonpolar solvents, somewhat soluble in water and alcohols and soluble in other polar solvents. They dissolve readily in dilute mineral acids.

The analytical results, colors, melting points (uncorrected) and Λ_M values are given in Table I.

The stability test for the pyridine and aniline compounds lends a strong support to the assumption that all halide ions and the thiocyanate are coordinated to Zn(II); the new compounds, therefore, are complex compounds and not double salts [4]. The slight cloudiness, appearing after a short time, is attributed to the slight dissociation of the complex ions in ethanol.

From the Λ_M values obtained, it is concluded that all pyridine and aniline complexes in nitromethane behave as 1:1 electrolytes [16].

The UV spectra of the pyridine compounds show absorption maxima at 233, 240, 245, 250, 257 and 263 nm. These maxima are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions [17, 18]. The maximum at 290 nm in the spectra of compounds **4**, **5** and **8** is very peculiar; it cannot be due to an $n \rightarrow \pi^*$ transition [17, 18]. The UV spectrum of pure aniline

Table I. Analytical results, colors, m.p. and Λ_M values of the new etherate, pyridine and aniline compounds of the complex halo and pseudohalo acids of Zn(II).

No.	Compound	[%]	Acidic hydro- gen	Zn	Cl	Br	I	SCN	B	Color	m.p. [°C]	Λ_M^a [S cm ² mol ⁻¹]
1	HZnCl ₂ I · 3 Et ₂ O	Calcd	0.20	13.44	14.57		26.08		45.70	crimson		
		Found	0.18	13.70	14.33		25.60		46.19			
2	HZnBr ₂ I · 3 Et ₂ O	Calcd	0.17	11.36		27.77	22.05		38.64	crimson		
		Found	0.16	10.99		27.02	21.96		39.87			
3	HZnI ₂ (CSN) · 3 Et ₂ O	Calcd	0.17	10.88			42.31	9.66	36.98	orange-		
		Found	0.17	10.53			43.18	9.86	36.29	red		
4	HZnCl ₂ I · 3 Py	Calcd	0.20	13.04	14.14		25.30		47.32	yellow	110	72
		Found	0.17	13.93	14.28		23.15		48.23			
5	HZnBr ₂ I · 3 Py	Calcd	0.17	11.07		27.07	21.49		40.19	straw	117	86
		Found	0.17	11.28		27.72	20.45		41.22			
6	HZnCl ₂ SCN · 3 Py	Calcd	0.23	15.12	16.42			13.41	54.81	flesh	191	84
		Found	0.23	16.02	16.79			13.69	53.33			
7	HZnBr ₂ SCN · 3 Py	Calcd	0.19	12.54		30.69		11.12	45.45	straw	210	79
		Found	0.18	13.01		31.18		11.31	43.06			
8	HZnI ₂ SCN · 3 Py	Calcd	0.16	10.63			41.27	9.42	38.51	grey	182	76
		Found	0.16	11.03			42.96	10.21	38.24			
9	HZnCl ₂ Br · 3 An	Calcd	0.20	13.17	14.28	16.09			56.26	white	185d	69
		Found	0.18	13.38	13.74	17.28			54.15			
10	HZnBr ₃ · 3 An	Calcd	0.17	11.17		40.94			47.72	pale	162d	87
		Found	0.17	10.99		40.46			47.97	pink		
11	HZnI ₂ Br · 3 An	Calcd	0.15	9.62		11.76	37.35		41.12	light	168–	73
		Found	0.15	9.88		12.34	35.11		42.52	beige	170	
12	HZnCl ₂ I · 3 An	Calcd	0.18	12.03	13.04		23.34		51.40	whitish-	150d	81
		Found	0.16	12.80	13.12		23.02		51.05	yellow		
13	HZnBr ₂ I · 3 An	Calcd	0.16	10.34		25.27	20.06		44.17	yellowish	162–	68
		Found	0.15	10.43		26.13	19.25		43.79		165d	
14	HZnCl ₂ NCS · 3 An	Calcd	0.21	13.78	14.97			12.23	58.81	flesh	238d	77
		Found	0.21	14.03	15.06			12.18	58.59			
15	HZnBr ₂ NCS · 3 An	Calcd	0.18	11.61		28.40		10.29	49.52	pale	245	74
		Found	0.17	12.10		29.04		10.21	50.52	pink		
16	HZnI ₂ NCS · 3 An	Calcd	0.15	9.95			38.64	8.82	42.44	yellow	217	81
		Found	0.16	10.17			39.04	9.04	43.58			

B = Et₂O, Py, An. ^a Values of molar conductance for 10⁻³ M solutions in CH₃NO₂ at 25 °C. d = decomposes.

Table II. IR spectral assignments of some absorption bands of diagnostic value for the pyridine complexes.

Complex	$\nu(\text{C-N})$	$\nu(\text{C-S})$	$\delta(\text{NCS})$	Vibrations of the pyridine ring			$\nu(\text{Zn-Cl})_t$		$\nu(\text{Zn-Br})_t$
4				632 s	420 s	413 sh	323 s	290 s	
5				631 s	421 s	411 sh			251 s
6	2078 s	overlapped by absorption		638 vs	422 s		325 s	295 s	
7	2078 s	bands of the coordinated		638 vs	422 s	418 s			255 s
8	2078 m	pyridine		640 s	425 s	418 m			

s = strong, sh = shoulder, m = medium, vs = very strong.

Table III. IR spectral assignments of some absorption bands of diagnostic value for the aniline complexes.

Complex	$\nu(\text{C-N})$	$\nu(\text{C-S})$	$\delta(\text{NCS})$	$\nu_{\text{asym}}(\text{N-H})$	$\nu_{\text{sym}}(\text{N-H})$	$\nu(\text{Zn-An})$	$\nu(\text{Zn-Cl})_t$		$\nu(\text{Zn-Br})_t$
9				3270 m	3225 m	400 sh	357 s	290 s	274 sh
10				3263 m	3220 m	399 sh	355 s		< 250
11				3262 m	3219 m	400 sh	341 s		250 s
12				3265 m	3220 m	400 w	358 s	290 s	275 sh
13				3270 m	3224 m	400 sh	347 m		252 m
14	2090 s	overlapped		477 m	3260 vs	3220 vs	405 m	365 s	296 s
15	2090 s	by bands of the		475 m	3260 vs	3220 vs	400 s	357 s	< 250
16	2080 s	coordinated							
		aniline		471 m	3265 s	3215 s	395 m	343 s	

in ethanol shows absorption maxima at 235 and 285 nm. The spectra of the salts AnHX ($X = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$) in ethanol also show regular maxima at 235 and 285 nm as well as succeeding absorptions in the form of shoulders at 255, 260 and 265 nm. These shoulders are due to the AnH^+ ion [19]. The maxima at 230 and 285 nm in the spectra of all aniline complexes obtained are due to electronic transitions of aniline, since they appear in the spectra of aniline, AnHX and coordination compounds of aniline [20]. The shoulder at 260 nm in the spectra of most aniline complexes is attributed to the AnH^+ ion [19].

Some characteristic and of diagnostic value IR frequencies (cm^{-1}) of the pyridine and aniline complexes are given in Tables II and III, respectively.

Study of IR spectra of the pyridine complexes

The two or three weak absorption bands in the region $3220\text{--}3100\text{ cm}^{-1}$ in the spectra of the pyridine complexes are due to the PyH^+ ion; their low intensity indicates that the PyH^+ ion is involved in hydrogen bridging [21]. The absence, also, of a strong broad band just below 3000 cm^{-1} excludes the presence of hydrogen bonding of the cation-anion type, $\text{N}^+\text{--H}\cdots\text{X}^-$ [21]; this is, of course, expected since, all halide ions and the thiocyanate are coordinated to Zn(II). The presence of PyH^+ ion in the molecules of the prepared complexes is clearly indicated by the absorption bands at 1630, 1600, 1525, 1480, 1325, 1240 and 1185 cm^{-1} [22, 23].

The two absorption bands at 1570 and 1445 cm^{-1} as well as the strong ones at $1215, 1150, 1065, 1040, 1010, 750$ and 695 cm^{-1} are due to coordinated pyridine [23]. The strong bands at 635 and 420 cm^{-1} are thought of being shifts of the bands at 604 (an in-plane ring deformation) and 405 (an out-of-plane ring deformation) cm^{-1} of free pyridine. The shifting of these bands to higher frequencies indicates coordinated pyridine [22, 24]; consistent with this is the splitting of the band at 420 cm^{-1} in the spectra of the complexes **4**, **5**, **7**, and **8** [22, 24]. The band at 635 cm^{-1} indicates a tetrahedral environment around Zn(II) [24, 25]. Absorption bands due to Zn–N(Py) stretching vibrations appear below 250 cm^{-1} [24–26].

The strong bands in the region $325\text{--}290\text{ cm}^{-1}$ in the spectra of compounds **4** and **6** are attributed to Zn–Cl terminal stretching vibrations, $\nu(\text{Zn--Cl})_t$, since they are absent in the spectra of chlorine-free complexes; the frequencies of these bands clearly

show that the structure of compounds **4** and **6** is tetrahedral [24, 26]. Likewise, the strong bands at 251 and 255 cm^{-1} in the spectra of **5** and **7**, respectively are attributed to $\nu(\text{Zn--Br})_t$ and their frequencies indicate a tetrahedral ligand arrangement around Zn(II) [24]. The Zn–I stretching vibrations occur below 250 cm^{-1} [24].

The thiocyanate group has three diagnostic IR regions; C–N stretching $\nu(\text{C--N})$, C–S stretching $\nu(\text{C--S})$ and NCS bending $\delta(\text{NCS})$. The absorption bands in these regions are affected by different types of coordination. The absorption bands in the CN region appear at 2078 cm^{-1} in our spectra, a fact indicating the absence of bridged -SCN-groups [27] or free thiocyanate ions [28]. The C–S stretching region has been well dealt with in the chemical literature and has been used as a diagnostic region for the type of bonding of the thiocyanate group in the complexes. Turco and Pecile [29], studying IR spectra of complexes of known structure showed that the $\nu(\text{C--S})$ for the S-bonded complexes occurs in the region $690\text{--}720\text{ cm}^{-1}$ and in the region $780\text{--}860\text{ cm}^{-1}$ for the N-bonded ones. Since our spectra do not show absorption bands in the region $780\text{--}860\text{ cm}^{-1}$, the presence of Zn–NCS bond is excluded. The assignment of $\nu(\text{C--S})$ in the region $690\text{--}720\text{ cm}^{-1}$ is impossible due to the simultaneous appearance of absorption bands of coordinated pyridine. The thiocyanate complexes show absorption bands in the region $440\text{--}400\text{ cm}^{-1}$ and the isothiocyanate ones in the region $490\text{--}450\text{ cm}^{-1}$ [30, 31]. In our case, the absence of a band in the region $490\text{--}450\text{ cm}^{-1}$ excludes or rules out the presence of Zn–NCS bond; in the region $440\text{--}400\text{ cm}^{-1}$ coordinated pyridine absorbs too.

Careful examination of the spectra of all prepared pyridine compounds clearly shows the absence of characteristic bands of free pyridine; hence these compounds contain no lattice pyridine [32].

Study of IR spectra of the aniline complexes

The spectra of all aniline complexes show two strong and broad bands at 2850 and 2580 cm^{-1} , which are indicative of the AnH^+ ion involved in hydrogen bridging [33, 34]. The numerous weak bands in the region $2550\text{--}1650\text{ cm}^{-1}$ are mainly combination bands and overtones, some of which are due to the absorption of the $-\text{NH}_3^+$ group [33, 35]. The assignments in the region 1620 to 1500 cm^{-1} are difficult, since bands in this region

are due to stretching vibrations of the benzene ring and bending vibrations of the -NH_3^+ group [33]. The bands at 1600, 1560, 1515, 1490, 1465, 1325, 1290, 1190, 1175, 1150, 1110, 1080, 1025, 1000, 960, 900, 840, 800, 740, 680, 615, 525 and 380 cm^{-1} are due to AnH^+ ion since these appear also in the spectra of AnHX .

The spectrum also shows that aniline is coordinated to Zn(II). All spectra show two absorption bands in the region $3300\text{--}3200\text{ cm}^{-1}$. The band at the higher frequency is attributed to -NH_2 anti-symmetric stretching vibration while the one at the lower frequency to -NH_2 symmetric stretching vibration. The frequencies of these bands (significantly lower than the corresponding in free aniline) indicate coordinated aniline [20, 36]. The shifting and splitting of the bands at 740, 680, 615 and 525 cm^{-1} show also coordinated aniline [37]. The two bands in the region $405\text{--}341\text{ cm}^{-1}$ of every spectrum are attributed to Zn-N(An) stretching vibration or to vibration modes of aniline; the latter have, possibly, shifted or become infrared active upon the coordination of aniline [36, 38].

From the $\nu(\text{Zn-Cl})_t$ and $\nu(\text{Zn-Br})_t$ values (see Table III) it is concluded that the complexes **9**, **10**, **11**, **12**, **13** and **14** have tetrahedral structure [24, 26, 36, 38]. The absence of a band, due to Zn-Br stretching vibration, above 250 cm^{-1} in the spectrum of compound **15**, is reasonable, since this band often occurs slightly below 250 cm^{-1} for tetrahedral complexes of Zn(II) [26, 38].

The presence of the SCN group in the inner sphere of the aniline complexes is shown by the appearance of bands at 2090 and 475 cm^{-1} .

The position of the C-N stretching rules out the presence of the thiocyanate group in the ionic or bridged form. The position also of the NCS bending

shows that the bonding of the thiocyanate group to Zn(II) is via the nitrogen atom.

Finally, the absence of lattice aniline is certain.

Correlation of the data regarding the stereochemistry of the pyridine and aniline complexes in the solid state

From the stability test it is concluded that the new compounds are complex compounds; the UV spectra also show that the aniline compounds contain the AnH^+ ion.

From the IR spectral analysis it is concluded that:

- All compounds contain coordinated organic base.
- In all complexes the PyH^+ and AnH^+ ions are involved in hydrogen bonding.
- All complex anions are tetrahedral monomers.
- None of these compounds contains lattice pyridine or aniline.
- None of these compounds contains ionic or bridged thiocyanate. The pyridine complexes, containing the thiocyanate, are S-bonded, while the corresponding aniline complexes are N-bonded.

On the basis of all these findings the following general structural formula is proposed for the new pyridine and aniline compounds:

where $\text{X} = \text{Cl, Br, I}$; $\text{Y} = \text{Br, I, SCN}$; $\text{B} = \text{Py, An}$.

The symbol $\cdots$ represents a hydrogen bridge between the protonic hydrogen and two nitrogen atoms of two molecules of the organic base in the outer sphere of the complex; such a hydrogen bond has been observed in numerous compounds of complex haloacids [4, 5, 7, 8, 37].

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