Etherate, Pyridine, and Aniline Compounds of the Complex Tri- and Tetra-Iodoacids of Zn(II) and Cd(II)

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The preparation, for the first time, and the properties of the title compounds are described. Analytical, conductometric, spectral (infrared and ultraviolet) and data from X-ray powder spectra yield information about the probable structure of the complexes in the solid state. The existence of metal—nitrogen bond for all pyridine and aniline complexes, except $H_2CdI_4 \cdot 4\,An$ (An = aniline), is adduced from infrared and far infrared spectral studies.

[Keywords: Cadmium(II) iodocomplexes; Conductometric measurements; Infrared spectra; Ultraviolet spectra; Zinc(II) iodocomplexes]

Etherate, Pyridin- und Anilin-Verbindungen der komplexen Tri- und Tetra-Jodsäuren von Zn(II) *und* Cd(II)

Die Darstellung und die Eigenschaften der Titelverbindungen werden erstmalig beschrieben. Analytische und konduktometrische Daten, sowie IR, UV und Röntgenpulveraufnahmen ergaben Informationen, aus denen die wahrscheinliche Struktur der Komplexe im festen Zustand abgeleitet wurde. Die Existenz von Metall—Stickstoff-Bindungen für alle Pyridin- und Anilin-Komplexe, mit Ausnahme von $H_2CdI_4 \cdot 4\,An$ (An = Anilin), ergibt sich aus den Daten von IR und fernem IR.

Introduction

Although a large number of salts of the complex metallohalogenoanions $[M^{II}X_3]^-$ and $[M^{II}X_4]^{2-}$ is known, the situation with regard to the corresponding acids is far from clear. The preparation of the etherate compounds of the mixed complex trihalogenoacids of Zn(II), Cd(II) and Hg(II) has been reported[1]. Of the compounds with *Lewis* bases of the complex iodoacids of the group IIB, we have

prepared and studied the compounds $HHgI_3 \cdot 2\,Et_2O$ (Et_2O = diethyl ether) and $HHgI_3 \cdot 2\,Py$ (Py = pyridine)[2]. We have, also, reported the preparation and study of the etherate, pyridine and aniline compounds of the acids HMI_4 (M = Ga, In)[3, 4].

The existence of simple halogenocomplexes with three and four halogen atoms in the inner coordination sphere is referred to as one of the basic properties, which govern the coordination chemistry of Zn(II) and Cd(II).

As a continuation of the interest of our laboratory in the complex halogenoacids and their compounds, the present paper deals with the preparation and properties of twelve etherate, pyridine and aniline compounds of the complex tri- and tetra-iodoacids of Zn(II) and Cd(II). The experimental conditions for the preparation of the compounds of the said acids were also determined. The complexes prepared have been characterized on the basis of data from spectral (UV and IR) and conductivity measurements; the pyridine compounds of the complex tetraiodoacids have also been studied with the aid of X-ray powder spectra.

Experimental

Materials

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

Preparation of the Etherate Complexes

The preparation of the etherate complexes was carried out by the "etherohalogenosis" method[1]. Gaseous HI was passed slowly into 150 ml ether in a special vessel. The passage was carried out at $-50\,°C$ (acetone—dry ice bath) and was continued to the saturation point. The HI concentration of the etherate solution was of the order $0.3\,M$. Subsequently, to an accurately weighed amount of anhydrous ZnI_2 or CdI_2 a definite volume of freshly prepared etherate solution of HI was added with constant stirring (25 °C). Instantaneously, a heavy, oily layer appeared at the bottom of the reaction flask. Stirring was discontinued exactly 0.5 h after the reaction of the last amounts of the solid metal iodide. The oily layer was separated from the supernatant solution and washed with small portions of ether. The oily product was dried completely by vacuum pumping (5 Torr) for 10–15 min at 25 °C and the oily liquid was the final product.

Preparation of Pyridine and Aniline Compounds

To a definite amount of freshly prepared etherate compound of the complex iodoacid was added dropwise and with continuous stirring, small excess of pyridine or aniline. The reaction was vigorous and exothermic, accompanied by the evolution of fumes. The solidification of the whole system commenced

immediately after the addition of the organic base; the addition of more base caused complete dissolution of the solid product and formation of a clear solution. The reaction vessel was then placed in a vacuum desiccator over concentrated H_2SO_4. The final crystalline product was obtained by repeated pumping. The solid product was washed with small portions of absolute ether and heated at 35 °C for 20-25 min. The yield ranged from 75 to 95% for all compounds, except **12, 14** where it was 50%.

The hydroiodic salts of pyridine and aniline were also prepared by standard methods; the ultraviolet and infrared spectra of the salts were obtained under experimental conditions identical to those for the spectra of the pyridine and aniline compounds.

Analyses, Stability Test of the Compounds and Physicochemical Measurements

The instruments, apparatus, procedures for the quantitative analysis of all compounds prepared and the stability test for the pyridine and aniline compounds have been described in detail[5,6]. Cadmium was determined volumetrically with a standrad 0.05 M $EDTA$ solution and Xylenol Orange as an indicator.

The instruments for most of the physicochemical measurements have been mentioned previously[6]. For the molar conductance measurements of the pyridine and aniline compounds, solutions were prepared in absolute acetone and nitromethane in concentration $\sim 1 \cdot 10^{-3} M$; the measurements were carried out at 25 ± 0.1 °C.

For the ultraviolet spectra of the pyridine and aniline compounds, in the form of solutions, ethanol (210-400 nm) and dichloromethane (235-400 nm), both of spectroscopic quality, were used as solvents. The concentrations of the solutions were $5 \cdot 10^{-5} - 5 \cdot 10^{-4} M$.

Infrared absorption spectra, for all compounds prepared, covered the region 4,000-250 cm^{-1}.

The spectra of the oily etherate compounds were taken by forming a thin layer of the compound between CsI crystals. The samples of the pyridine and aniline compounds were used in the form of KBr pellets; their spectra were also taken in the form of nujol and hexachlorobutadiene paste between CsI crystals. For the compounds $HCdI_3 \cdot 3 Py$ and $H_2CdI_4 \cdot 4 An$ the region 250-50 cm^{-1} was also scanned in a Polytec FIR 30 spectrophotometer; the solid samples were suspended by polythene plates in nujol mull.

The X-ray powder spectra of the compounds $H_2MI_4 \cdot 5 Py$ (M = Zn, Cd) were taken in a Philips diffractometer which operated at a power of 700 W. As a source of X-ray primary beam a Cu anticathode ($\lambda_{CuK_{a1}} = 1.5418$ Å) was employed. These spectra covered the region of the angle 2ϑ from 3° to 60°.

Results and Discussion

The preparative data for the etherate complexes are shown in Table 1. These complexes are viscous, oily liquids, fume in the air and are insoluble in nonpolar solvents.

For the preparation of the complex **1**, a small excess of HI in ether was used. When the value of the ratio mol HI : mol ZnI_2 was 1.34, the analytical data for the prepared oil showed that this corresponded to the formula $HZnI_3 \cdot 3 Et_2O$. When the value of this ratio was 7.82, the
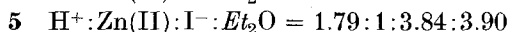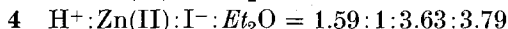
analytical data for the prepared oil showed that this corresponded to the formula $H_2ZnI_4 \cdot 4\,Et_2O$. For a large number of values of the ratio between 1.50 and 7.50, oily products were obtained which were mixtures of $HZnI_3 \cdot 3\,Et_2O$ and $H_2ZnI_4 \cdot 4\,Et_2O$. By increasing the value of the molar ratio, increased the percentage of **2** in the mixture. Three of the mixtures obtained appear in Table 1 as products **3, 4** and **5**. Thus,

Table 1. *Preparative data for the etherate compounds of the complex tri- and tetra-iodoacids of* Zn(II) *and* Cd(II)

No.	Complex or Product	$M I_2$ (mmol)	HI (mmol)	$\dfrac{\text{mol HI}}{\text{mol } M I_2}$	Yield (%)
1	$HZnI_3 \cdot 3\,Et_2O$	3.20	4.30	1.34	97
2	$H_2ZnI_4 \cdot 4\,Et_2O$	3.07	24.00	7.82	87
3[a]	product of indefinite chemical composition	3.19	11.60	3.64	
4[a]	product of indefinite chemical composition	3.76	19.20	5.11	
5[a]	product of indefinite chemical composition	3.21	20.50	6.39	
6	$HCdI_3 \cdot 3\,Et_2O$	2.78	4.30	1.55	98
7	$H_2CdI_4 \cdot 4\,Et_2O$	2.83	17.40	6.15	94
8[b]	product of indefinite chemical composition	2.63	8.50	3.23	
9[b]	product of indefinite chemical composition	2.19	10.00	4.57	
10[b]	product of indefinite chemical composition	5.40	32.30	5.98	

[a] Starting halide ZnI_2. [b] Starting halide CdI_2.

the experimentally found molar relationships of the constituents of **3, 4** and **5** are as follows:

3 $H^+ : Zn(II) : I^- : Et_2O = 1.20 : 1 : 3.25 : 3.32$
4 $H^+ : Zn(II) : I^- : Et_2O = 1.59 : 1 : 3.63 : 3.79$
5 $H^+ : Zn(II) : I^- : Et_2O = 1.79 : 1 : 3.84 : 3.90$

Similar observations can be made for the values of the ratio mol HI : mol CdI_2, on the basis of the data in Table 1 (again three of the mixtures obtained appear as products **8, 9** and **10**). All the aforementioned are valid for a constant reaction time (0.5 h).

Presently, two points must be stressed:

1. The fact that when the value of the ratio mol HI : mol $M I_2$ (M = Zn, Cd) becomes a little larger than 2 the compound

Table 2. Physicochemical and analytical data of the etherate, pyridine and aniline compounds of the complex tri- and tetra-iodoacids of Zn(II) and Cd(II)

No.	Complex	M.P. (°C)	$\Lambda_M{}^a$ (S cm² mol⁻¹) acetone	$\Lambda_M{}^a$ nitromethane	Color	% of Acidic Hydrogen Found (Calcd.)	% of Metal Found (Calcd.)	% of Iodide Found (Calcd.)	% of B Found (Calcd.)
1	$HZnI_3 \cdot 3\,Et_2O$				Crimson	0.14 (0.15)	9.70 (9.77)	55.60 (56.87)	34.66 (33.21)
2	$H_2ZnI_4 \cdot 4\,Et_2O$				Blood-red	0.23 (0.23)	7.70 (7.50)	57.76 (58.25)	34.31 (34.02)
6	$HCdI_3 \cdot 3\,Et_2O$				Crimson	0.14 (0.14)	15.72 (15.69)	53.23 (53.14)	30.91 (31.03)
7	$H_2CdI_4 \cdot 4\,Et_2O$				Crimson	0.21 (0.22)	12.40 (12.24)	54.32 (55.26)	33.07 (32.28)
11	$HZnI_3 \cdot 3\,Py$	143	130	86	Brown	0.15 (0.15)	9.45 (9.55)	53.11 (55.63)	35.51 (34.67)
12	$H_2ZnI_4 \cdot 5\,Py$	134	217	170	Brown	0.20 (0.21)	7.19 (6.74)	50.76 (52.30)	41.85 (40.75)
13	$HZnI_3 \cdot 3\,An$	181	125	71	White	0.14 (0.14)	8.96 (9.00)	51.92 (52.40)	38.58 (38.46)
14	$H_2ZnI_4 \cdot 4\,An$	175	196	140	Yellow	0.21 (0.21)	6.99 (6.90)	52.77 (53.57)	39.92 (39.32)
15	$HCdI_3 \cdot 3\,Py$	86	143	92	White	0.15 (0.14)	15.49 (15.37)	52.66 (52.05)	33.31 (32.44)
16	$H_2CdI_4 \cdot 5\,Py$	80	227	179	Gray	0.20 (0.20)	11.46 (11.05)	49.49 (49.89)	38.25 (38.87)
17	$HCdI_3 \cdot 3\,An$	65	142	92	Brown	0.13 (0.13)	13.91 (14.53)	48.37 (49.22)	37.76 (36.12)
18	$H_2CdI_4 \cdot 4\,An$	72	200	163	Olive-green	0.20 (0.20)	11.12 (11.30)	52.05 (51.04)	37.63 (37.46)

a. Molar conductance in acetone (left column) and in nitromethane. $B = Et_2O$, Py, An.

$H_2MI_4 \cdot 4\,Et_2O$ is not formed, but a mixture of the etherates of tri- and tetra-iodoacids.

2. The fact that the preparation of **7** is successful for a smaller value of the molar ratio than that of **2**. This may, possibly, be due to steric hindrance. The Zn^{2+} ion is smaller than the Cd^{2+} ion. Consequently, the steric hindrance, due to bulky I^- ions, is larger in $[ZnI_3]^-$ than in $[CdI_3]^-$, and as a result of this, the entrance of the fourth I^- ion in the coordination sphere is kinetically faster for the case of **7**.

The pyridine and aniline compounds are formed by the complete substitution of the ether molecules in the etherate complexes with pyridine or aniline molecules, since the latter are stronger *Lewis* bases than ether. They are crystalline substances and stable in the air. The compound **18**, on standing, loses its original crystalline form. These compounds are insoluble in nonpolar solvents, somewhat soluble in water, alcohols and dichloromethane and soluble in nitromethane, *DMF*, *DMSO* and dilute acid solutions.

The analytical data, colors, m.p. (uncorrected) and the Λ_M values are shown in Table 2.

The stability test for the pyridine and aniline compounds constitutes a strong indication that all iodide ions are coordinated to the central metal[7].

Conductometric Measurements

From the Λ_M values obtained it is concluded that the complex compounds **11, 13, 15** and **17** behave in nitromethane and acetone as 1:1 electrolytes, while the **12, 14, 16** and **18** as 2:1 electrolytes in both solvents[8].

Ultraviolet Spectra

The spectra of the pyridine complexes, in both solvents employed, are similar; they show absorption maxima at about 240, 245, 250, 257 and 264 nm.

These maxima are attributed to $\pi \to \pi^*$ and $n \to \pi^*$ electronic transitions[9,10]. The appearance of two maxima at 290 and 360 nm is very peculiar.

The maximum at 290 nm cannot be due to an $n \to \pi^*$ transition[9,10]; these maxima, also, cannot be due to charge transfer transitions between the ligands and the central atom, since they appear in the spectrum of *Py*HI too.

The UV spectrum of pure aniline in ethanol shows absorption maxima at 235 and 285 nm. The spectrum of *An*HI in ethanol shows regular maxima at 223, 285 and 355 nm as well as successive absorptions, in the form of shoulders, at 255, 261 and 264 nm, which are due to

the AnH^+ ion[6]. The maxima at 225 and 285 nm in the spectra of the aniline compounds (in ethanol) are due to electronic transitions of the aniline molecule, since they appear also in the spectra of aniline, AnHI and coordination compounds of aniline[11]. In dichloromethane the shorter wavelength maximum is absent and the longer wavelength maximum shows a bathochromic shift. The shoulder at 260 nm in all the spectra of aniline complexes and in both solvents, is attributed to the presence of the AnH^+ ion in the solution[6].

Infrared Spectra of the Etherate Compounds

These spectra are similar. The only absorption bands that do not correspond to bands of the spectrum of diethyl ether, are a broad band of medium intensity at $3,350\,cm^{-1}$ and two others at 2,900 and $1,095\,cm^{-1}$. The first of these bands probably shows that the Et_2OH^+ is involved in hydrogen bonding[12].

There are no bands due to $M \leftarrow O$ bonds (M = Zn, Cd).

Infrared Spectra of the Pyridine Complexes

For the pyridine and aniline complexes and for a given compound the IR spectra obtained by each of the three techniques (KBr, nujol, hexachlorobutadiene) are alike, except in the absorption regions of the mulling agents.

The two or three weak absorption bands in the region $3,220\text{-}3,100\,cm^{-1}$ in the spectra of the pyridine complexes are due to N^+—H stretching vibrations and indicate the presence of the PyH^+ ion[13]. The appearance of a broad band at $2,900\,cm^{-1}$ in the spectra of **11** and **15** is a very strong indication of hydrogen bonding[13]. Since all the iodide ions are coordinated to the central metal ion, it is thought impossible for the resulting complex anion to be involved in hydrogen bonding with the PyH^+ ion[13]. The presence of PyH^+ in the molecules of the prepared complexes is also indicated by the bands at 1,630, 1,600, 1,525, 1,480, 1,325, 1,240, and $1,185\,cm^{-1}$[14,15].

The two absorption bands at 1,570 and $1,445\,cm^{-1}$ as well as strong ones at 1,215, 1,150, 1,065, 1,040, 1,010, 750 and $685\,cm^{-1}$ are due to vibration modes of coordinated pyridine[15]. Consistent with the existence of coordinated pyridine is also the splitting in two of the band at $685\,cm^{-1}$ in the spectra of **15** and **16**[14]. The strong bands at 630 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[14,16]; consistent with this is the splitting of the band at $420\,cm^{-1}$ in the spectra of the complexes **11** and **12**[14,16].

Absorption bands due to stretching vibrations of the Zn—N, Cd—N, Zn—I and Cd—I appear below 250 cm^{-1}, lowest limit of the spectrophotometer used[16-18].

The far IR spectrum of **15** (250-50 cm^{-1}) shows absorption bands at 187, 165, 157, 143, 108, 97, 88, 75, 66 and 55 cm^{-1}. The strong band at 187 cm^{-1} is attributed to Cd—N stretching vibration. The bands at 165, 157, and 143 cm^{-1} are attributed to Cd—I terminal stretching vibrations ν(Cd—I)$_t$; their frequencies show the existence of tetrahedral ligand environment around Cd(II)[17, 18]. The bands at 55-97 cm^{-1} are due to bending and deformation vibrations of the Cd—I bonds as well as lattice vibrations, but they are not indicative of the stereochemistry.

The pyridine compounds, also, do not contain lattice pyridine[19].

Table 3. *IR spectral assignments of some absorption bands of diagnostic value for the aniline complexes*

Complex	ν_{asy}(N—H)	ν_{sym}(N—H)	ν (M—N)	AnH$^+$ vibration	ν (M—I)$_t$
13	3268 m	3218 m	396 sh 345 m	384 m	< 250
14	3275 m	3220 m	340 m	380 m	< 250
17	3290 m	3225 m	332 m	370 m	< 250
18*	—	—	—	371 s	149 m 135 s 122 wbr

s = sharp, m = medium, sh = shoulder, wbr = weak broad.

* There are, also, data for the region below 250 cm^{-1}.

Infrared Spectra of the Aniline Complexes

Some characteristic and of diagnostic value IR frequencies (cm^{-1}) of the aniline complexes are given in Table 3.

The spectra of all the aniline complexes show two strong and broad absorption bands at 2,900 and 2,560 cm^{-1}, which are indicative of the AnH$^+$ ion involved in hydrogen bridging[20].

The bands at 1,600, 1,560, 1,490, 1,465, 1,325, 1,285, 1,190, 1,175, 1,150, 1,080, 1,025, 995, 960, 830, 795, 735, 680, 610, 520, 465 and 375 cm^{-1} are due to vibration modes of the AnH$^+$ ion, since they appear also, with slight shifts, in the spectrum of AnHI. It is noted that, the band at 795 cm^{-1} in the spectrum of **18** appears much weaker than the corresponding band of the other aniline complexes.

The formation of a coordinate bond $M \leftarrow$ N(An) in the compounds

13, 14 and **17** is ascertained readily by examining the region 3μ of the spectrum. Thus in the region $3,300$-$3,200 \, cm^{-1}$ the spectra of the aniline complexes, except that of **18**, show two absorption bands. The band of the higher frequency is attributed to the $-NH_2$ antisymmetric stretching vibration, while the one of lower frequency is attributed to the $-NH_2$ symmetric stretching vibration. The frequencies of these bands (significantly lower than the corresponding of the free aniline) indicate coordinated aniline[21]. In the spectrum of **17** these two bands appear at higher frequencies as compared with the corresponding bands of the Zn(II) complexes; this is in agreement with previous observations[21]. The shifting and splitting of the bands at 740, 680 and $525 \, cm^{-1}$ in the spectra of **13, 14** and **17** show also coordinated aniline[22]. Likewise, the spectacular increase of the intensity of the $795 \, cm^{-1}$ band in the spectra of **13, 14** and **17** is connected with the coordination of aniline[22]. In the region 400-$330 \, cm^{-1}$ appears only one strong absorption band in the spectra of AnHI and **18**, whereas two or three bands appear in the spectra of the remaining aniline complexes. These additional bands are attributed to metal—nitrogen stretching vibrations or to vibration modes of aniline; the latter have, possibly, shifted or become infrared active upon the coordination of aniline[21].

The far IR spectrum of **18** (250-$50 \, cm^{-1}$) shows absorption bands at 203, 149, 135, 122, 90, 73 and $52 \, cm^{-1}$. The bands at 149, 135 and $122 \, cm^{-1}$ are attributed to Cd—I terminal stretching vibrations $\nu \, (Cd—I)_t$, and they indicate tetrahedral structure[17,18]. The bands at 90-$52 \, cm^{-1}$ are due to bending and deformation vibrations of the Cd—I bonds, as well as lattice vibrations.

Finally, the absence of lattice aniline is certain.

X-Ray Powder Spectra

The X-ray powder patterns of the pyridine complexes **12** and **16** are similar; consequently, these compounds are isomorphous. Both patterns suggest, by the multitude of the reflections, that the crystals formed are of low symmetry.

Final Correlation of the Data Regarding the Stereochemistry of the Pyridine and Aniline Complexes in the Solid State

For the elucidation of the structure of the complexes a complete X-ray crystallographic analysis is required; unfortunately, our compounds could not be obtained as single crystals. On the basis, however, of all aforementioned data we can predict the stereochemistry, arranging the prepared complexes in the following general classes:

Class A

In this class belong the complexes **11, 13, 15** and **17**, for which we propose tetrahedral structure of the type $[MI_3B]^- [B$—H—$B]^+$, where M = Zn, Cd and $B = Py$, An. The symbol—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. We have established such an arrangement for other Zn(II) and Cd(II) complexes too[5, 6, 23]. The preparation of pseudotetrahedral complexes with an inner sphere $[ZnX_3Py]^-$, where X = Cl, Br, I, has been mentioned only once in the past[24].

Class B

In this class the complex **14** is placed, with octahedral arrangement of the type $[ZnI_4An_2]^{2-} \cdot 2[AnH]^+$. Complexes containing the octahedral anions $[MI_4B_2]^-$, where M = Ga, In and $B = Py$, An, have been mentioned in the literature[3, 4].

Class C

The tetrahedral complex **18** with the structural formula $[CdI_4]^{2-} \cdot 2[An$—H—$An]^+$ belongs in this class. The absence of aniline molecules in the inner coordination sphere of **18** is, most probably, due to steric hindrance of the four bulky iodide ions. In the compound $H_2CdI_2Cl_2 \cdot 4\,An$, in which the steric hindrance is clearly, lesser, two aniline molecules are coordinated to cadmium and thus the octahedral structure is obtained[23].

For the ligand arrangement in **12** ane **16** no prediction is possible. For these compounds the coordination number of the central metal probably takes the values five or seven. In conclusion, we note that coordination numbers five and seven have been established for complex and chelate compounds of Zn(II) and Cd(II)[25, 26].

Note added in proof: Very recent experiments in our laboratory have shown that the 290 and 360 nm maxima in the UV spectra of the pyridine complexes are due to the $\sigma_g \to \sigma_u{}^*$ and $\pi_g \to \sigma_u{}^*$ transitions of the I_3^- ion, respectively[27].

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