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Etherates and Pyridinium Compounds of Mixed Complex Iodoacids of Gallium(III)

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The preparation of etherates and pyridinium compounds of mixed complex iodoacids of Ga(III) is reported together with some physical and chemical properties, as well as conductometric measurements and the ultraviolet and infrared spectra of the new compounds. From the analytical, conductometric, stability and spectral data, some information is gained about the probable structure of the complexes.

[Keywords: Conductometric measurements; Gallium(III) mixed iodoacids; Infrared spectra; Ultraviolet spectra]

Etherate und Pyridin-Verbindungen von gemischtkomplexen Jodosäuren von Gallium(III)

Es wird über die Darstellung von Ether- und Pyridiniumverbindungen gemischter komplexer Jodosäuren von Ga(III), sowie über einige physikalische und chemische Eigenschaften, konduktometrische Daten und die UV- und IR-Spektren dieser neuen Verbindungen berichtet. Auf Grund von analytischen, konduktometrischen, spektroskopischen und Stabilitätsbefunden wurden Informationen über die wahrscheinliche Struktur dieser Komplexe gewonnen.

Introduction

Complex chloro- and bromoacids of Ga(III), simple and mixed, have been prepared in the form of etherates[1–3], pyridine[4], aniline[4] and aquo[5] compounds. Also kown are compounds of $HGaI_4$ with ether, pyridine and aniline[6].

On the contrary, there are no compounds known of mixed iodoacids of Ga(III).

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 four etherates and four pyridinium compounds of mixed iodoacids of Ga(III).

Experimental

Materials

The chemical reagents used were of high purity. Anhydrous gallium(III) halides and gaseous hydrogen halides were used from ampoules and lecture bottles, respectively. Diethyl ether (Et_2O) was pretreated for the removal of peroxides and moisture. Pyridine (Py) was doubly distilled under atmospheric pressure.

Preparation of the Etherates

The preparation of the etherates, as well as of the pyridinium compounds, was carried out in a specially designed apparatus[7], which facilitated the transfer of Ga(III) halides into the reaction flask, by vacuum sublimation, and did not allow moisture to enter the reaction vessel.

The preparation was carried out by the method of "etherohydrohalogenosis"[2]:

$$\mathrm{Ga}X_3 + \mathrm{H}X' \xrightarrow{Et_2\mathrm{O}} \mathrm{HGa}X_3X' \cdot y\, Et_2\mathrm{O}$$

where $X = \mathrm{Cl}$, Br and $X' = \mathrm{I}$, or $X = \mathrm{I}$ and $X' = \mathrm{Cl}$, Br, and $y = 2$.

An ether solution of anhydrous gaseous $\mathrm{H}X'$ ($X' = \mathrm{Cl}$, Br, I) was added, with constant stirring, to an ether solution of $\mathrm{Ga}X_3$ ($X = \mathrm{Cl}$, Br, I). Almost instantaneously a heavy oily layer appeared at the bottom of the reaction flask. Stirring was continued, in all cases, for 20-30 min. The oily layer was separated from the supernatant solution by vacuum pumping of the solution, washed with ether and dried completely by vacuum pumping (3-4 Torr) for 15-20 min at room temperature. An oily liquid was the final product.

Preparation of Pyridinium Compounds

Pure pyridine was added to the etherate compounds. A vigorous reaction took place with simultaneous evolution of vapours (ether) and formation of a solid, which subsequently dissolved in excess base.

$$\mathrm{HGa}X_3X' \cdot y\, Et_2\mathrm{O} \xrightarrow[-Et_2\mathrm{O}]{Py} \mathrm{HGa}X_3X' \cdot z\, Py$$

where $X = \mathrm{Cl}$, Br and $X' = \mathrm{I}$, or $X = \mathrm{I}$ and $X' = \mathrm{Cl}$, Br, $y = 2$ and $z = 4$.

The solution was transferred to a *Petri* dish, placed in a vacuum desiccator and the excess base was removed by continuous pumping. After a few days crystalline solids of various colours were obtained. The solid products were washed with small portions of absolute ether and dried at 35 °C for half an hour.

Table 1. *Analytical data of the etherates and pyridinium compounds of the complex mixed iodoacids of Gallium(III)*

No.	Complex	%Acidic Hydrogen Found (Calcd.)	%Ga Found (Calcd.)	%Cl Found (Calcd.)	%Br Found (Calcd.)	%I Found (Calcd.)	% of B Found (Calcd.)
1	$HGaCl_3I \cdot 2Et_2O$	0.21 (0.22)	16.02 (15.42)	23.14 (23.52)		28.21 (28.06)	32.42 (32.78)
2	$HGaI_3Cl \cdot 2Et_2O$	0.15 (0.16)	10.49 (10.98)	5.13 (5.58)		59.71 (59.94)	24.52 (23.34)
3	$HGaBr_3I \cdot 2Et_2O$	0.16 (0.17)	11.12 (11.91)		39.75 (40.93)	21.53 (21.67)	27.44 (25.32)
4	$HGaI_3Br \cdot 2Et_2O$	0.15 (0.15)	11.31 (10.26)		10.95 (11.76)	56.14 (56.02)	21.45 (21.81)
5	$HGaCl_3I \cdot 4Py$	0.16 (0.16)	11.15 (11.24)	17.00 (17.14)		21.11 (20.46)	51.32 (51.00)
6	$HGaI_3Cl \cdot 4Py$	0.12 (0.13)	8.57 (8.68)	4.43 (4.41)		48.35 (47.39)	37.41 (39.39)
7	$HGaBr_3I \cdot 4Py$	0.14 (0.13)	9.08 (9.25)		31.54 (31.80)	17.02 (16.84)	42.10 (41.98)
8	$HGaI_3Br \cdot 4Py$	0.12 (0.12)	8.09 (8.22)		9.12 (9.43)	43.40 (44.91)	38.68 (37.32)

Et_2O = Diethyl Ether, Py = Pyridine, $B = Et_2O$, Py.

Chemical Analysis, Stability Test of the Compounds and Physicochemical Measurements

The prepared compounds, analysed in aqueous solutions by methods referred to below, gave results which correspond to formulae shown in Table 1.

The protic hydrogen (H^+) was determined potentiometrically with 0.1 *N* NaOH, using a *pH* meter Radiometer Copenhagen, model 26. Gallium was determined gravimetrically with 8-hydroxyquinoline. The total halide content was determined volumetrically by the *Volhard* method. The determination of a specific halide ion was made potentiometrically with 0.1 *N* $AgNO_3$, using a *pH* meter Corning-Eel, model 12, with saturated calomel and selective sulfide[8] electrodes. The iodide ion was, in addition, determined by the gravimetric method with palladous chloride. In all cases the results were exactly the same. Ether was calculated by difference, and pyridine was determined potentiometrically[9] with 0.1 *N* $HClO_4$ in glacial acetic acid, using the Radiometer *pH* meter with saturated calomel and glass electrodes. The samples for the determination of pyridine were dissolved in glacial acetic acid.

The m.p.'s of the pyridinium compounds were taken in a Büchi 510 apparatus and are shown in Table 2.

The stability of the compounds was tested qualitatively, by adding an ethanolic solution of $AgClO_4$ to an ethanolic solution of the sample.

For the conductometric measurements an apparatus Ehrhardt-Metzger Nachf., type L 21 was used. The solutions were prepared in absolute ethanol, in concentrations $\sim 1 \cdot 10^{-3}\,M$, and the measurements were carried out at $25 \pm 0.1\,°C$, by using a thermostat Haake N/6 with thermometer 0-50 °C and accuracy $\pm 0.1\,°C$. The cell constant was $c = 1\,cm^{-1}$. The results are shown in Table 2.

Table 2. *Physicochemical data of the etherates and pyridinium compounds of the complex mixed iodoacids of Gallium(III)*

Complex	Colour	M.P. (°C)	Λ_M (S cm^2 mol^{-1})	ν(Ga—X) (cm^{-1})
1	Yellow			370
2	Yellow-brown			360
3	Brownish yellow			276
4	Chestnut brown			272
5	Pale yellow	91	47	
6	Yellow-green	168 d	50	
7	Yellow-brown	129-131 d	44	
8	Yellow-brown	173 d	48	

X = Cl or Br, d = decomposes.

The ultraviolet spectra of the compounds were taken in a double-beam Bausch-Lomb, Spectronic 210 UV spectrophotometer and cover the region 210-400 nm. The solvent, ethanol, was of spectroscopic quality and the concentrations of the solutions were of the order 10^{-5}-$10^{-4}\,M$.

The infrared spectra were taken in a double-beam P-E 577 spectrophotometer and cover the region 4000-250 cm^{-1}. The samples of the etherate compounds were used in their oily form between CsI windows, 0.1 mm in thickness, and of the pyridinium compounds in the form of KBr pellets.

Results and Discussion

The etherate compounds are very hygroscopic, viscous, oily liquids, fuming in air. They are insoluble in nonpolar solvents, soluble in ethanol, and decompose in water, yielding acidic solutions.

The pyridinium compounds are crystalline substances, fairly stable in air; this is a good indication that they do not contain $Py\mathrm{H}X$ or $\mathrm{Ga}X_3$ ($X = \mathrm{Cl, Br, I}$), all of which are extremely hygroscopic. They are insoluble in nonpolar solvents, but dissolve in ethanol, *DMSO*, glacial acetic acid and pyridine; they decompose in water.

The results of the stability test constitute a strong indication that all halide ions are coordinated to the central atom[10–12], a fact that is supported by the spectral (IR) data of the etherate compounds.

Conductometric Measurements

From the Λ_M values obtained it is concluded that the prepared pyridinium compounds behave in absolute ethanol as 1:1 electrolytes[13].

Ultraviolet Spectra

The spectra of all etherates show absorption maxima at 220, 290 and 360 nm. These maxima are, probably, due to charge transfer transitions[14–16] and appear, also, in the spectra of the pyridinium compounds. In the spectra of the latter compounds there are also maxima at 239, 245, 251, 256 and 262 nm, which are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions of pyridine[17].

Infrared Spectra

The spectra of the etherate compounds are almost identical with the spectrum of diethyl ether. Main differences are a broad band of medium intensity at 3350 cm^{-1}, two others at 2900 and 1095 cm^{-1} and the medium to strong bands shown in Table 2. These last bands are in a very good agreement with the values of the ions $[\mathrm{Ga}X_3X']^-$, where $X \neq X'$ and $X, X' = \mathrm{Cl, Br, I}$[18]. The broad band at 3350 cm^{-1} may indicate that $Et_2\mathrm{OH}^+$ is involved in hydrogen bonding[12,19,20].

The two or three weak absorption bands in the region 3225-3100 cm^{-1} and a broad, medium to strong band between 2880 and 2800 cm^{-1}, appearing in the spectra of all the pyridinium compounds, are indicative of the $Py\mathrm{H}^+$ ion[21–25]. The intensity and broadness of the latter band, in comparison with the weakness of the former ones, is confirmatory of a $Py\mathrm{H}^+$ ion, involved in hydrogen bonding[21–25]. This broad band appears in the spectra of $Py\mathrm{H}X$ ($X = \mathrm{Cl}$, Br, I) at frequencies increasing noticeably (more than 150 cm^{-1}) with increasing size of the halide ion[24–26]. In spectra of pyridinium compounds with polyatomic anions the N^+—H absorption frequencies move to much higher wavenumbers, losing their broadness[26]. In the spectra of all the prepared pyridinium compounds the constancy of the frequency of this intense and broad band is noteworthy, a constancy which appears also in the spectra of similar pyridinium compounds of Ga(III)[4]. For all the aforementioned reasons, we propose a hydrogen bond between $Py\mathrm{H}^+$ and a second molecule of pyridine, rather than between $Py\mathrm{H}^+$ and the anion of each compound. Such a bonding, being found in many cases[4,12,27,28], enlarges the size of the cation, making thus the whole lattice more stable.

The presence of $Py\mathrm{H}^+$ in the molecules of the prepared complexes is also indicated by the bands at 1632, 1608, 1528, 1482, 1328, 1245, 1198, 1163, 1045, 1025, 1005 and 745 cm^{-1}[23,26,29,30].

The absorption bands at 1602, 1448, 1215, 1150, 1065, 1040, 1010 and 685 cm^{-1} are due to vibrational modes of coordinated pyridine[23,26,30]. The spectra, also, do not indicate lattice pyridine[31].

In the spectra of the compounds $\mathrm{HGaCl_3I}\cdot 4Py$ and $\mathrm{HGaBr_3I}\cdot 4Py$ there are weak to medium bands at 362 and 270 cm^{-1}, respectively. These bands may be due to the Ga—X ($X = \mathrm{Cl}$, Br) stretching vibrations[18].

Structure of the Prepared Compounds

On the basis of all aforementioned data, we may propose as the most probable structure for the etherate compounds the formula $(Et_2\mathrm{O})_2\mathrm{H}^+[\mathrm{Ga}X_3X']^-$, where $X = \mathrm{I}$ and $X' = \mathrm{Cl}$, Br or $X = \mathrm{Cl}$, Br and $X' = \mathrm{I}$. The proposed formula is in agreement with many such etherate compounds of gallium(III) haloacids[1–3], in which the metal has a coordination number 4.

For the pyridinium compounds the most probable structure is $(Py\ldots\mathrm{H}\ldots Py)^+[\mathrm{Ga}X_3X'Py_2]^-$, where $X = \mathrm{I}$ and $X' = \mathrm{Cl}$, Br or $X = \mathrm{Cl}$, Br and $X' = \mathrm{I}$. The proposed formula is in agreement with the analytical, conductometric and spectral data, the results of the stability test and the tendency of Ga(III) to form complexes with coordination numbers 4 and 6[4,6,32]. Finally, the fact that the halide ions are coordinated to the metal atom before the addition of pyridine, may make their replacement rather difficult in the inner sphere of the complexes, because of the relatively high energy required to break the metal—halogen bond in $[\mathrm{Ga}X_4]^-$ ($X = \mathrm{Cl}$, Br) ions[33].

References

[1] *Wiberg, E., Schmidt, M., Galinos, A. G.*, Angew. Chem. **66**, 443 (1954).
[2] *Galinos, A. G.*, J. Amer. Chem. Soc. **82**, 3032 (1960).
[3] *Clark, R. J. H., Crociani, B., Wassermann, A.*, J. Chem. Soc. (A) **1970**, 2458.
[4] *Raptis, D., Galinos, A. G.*, Rev. (Roumaine) Chim. **24**, 1307 (1979).
[5] *Picotin, G., Roziere, J., Potier, J., Potier, A.*, Adv. Mol. Relax. Processes **7**, 177 (1975).
[6] *Raptis, D., Kaminaris, D., Kouinis, J., Galinos, A. G.*, Mh. Chem. **107**, 345 (1976).
[7] *Raptis, D.*, Ph.D. Thesis, University of Patras, Greece (1980).
[8] *Bazzele, W. E.*, Analyt. Chim. Acta **54**, 29 (1971).
[9] *Fritz, J. S.*, Acid-base Titrations in Nonaqueous Solvents, p. 127. Boston: Allyn and Bacon. **1973**.
[10] *Galinos, A. G.*, J. Inorg. Nucl. Chem. **19**, 69 (1961).
[11] *Perlepes, S. P.*, Ph.D. Thesis, University of Patras, Greece (1979).
[12] *Galinos, A. G., Perlepes, S. P., Kouinis, J. K.*, Mh. Chem. **111**, 829 (1980).
[13] *Nicholson, A. R., Sutton, G. J.*, Austral. J. Chem. **22**, 1543 (1969).
[14] *Smith, M., Symons, M. C. R.*, Trans. Faraday Soc. **54**, 338 (1958).
[15] *Awtrey, A. D., Connick, R. E.*, J. Amer. Chem. Soc. **73**, 1842 (1951).
[16] *Katzin, L. I.*, J. Chem. Phys. **23**, 2055 (1955).
[17] *Stephenson, H. P.*, J. Chem. Phys. **22**, 1077 (1954).
[18] *Grigor'ev, A. N., Grigor'ev, A. I., Mikheeva, L. M., Baranovskii, I. B.*, Russ. J. Inorg. Chem. **17**, 1965 (1972).
[19] *Lehmann, E., Kouinis, J., Galinos, A.*, Mh. Chem. **106**, 499 (1975).
[20] *Kouinis, J., Galinos, A. G.*, Mh. Chem. **108**, 835 (1977).
[21] *Nuttall, R. H., Sharp, D. W. A., Waddington, T. C.*, J. Chem. Soc. **1960**, 4965.
[22] *Evans, R. F., Kynaston, K.*, J. Chem. Soc. **1962**, 1005.
[23] *Gill, N. S., Nuttall, R. H., Scaife, D. E., Sharp, D. W. A.*, J. Inorg. Nucl. Chem. **18**, 79 (1961).
[24] *Chenon, B., Sandorfy, C.*, Canad. J. Chem. **36**, 1181 (1958).
[25] *Brissette, C., Sandorfy, C.*, Canad. J. Chem. **38**, 34 (1960).
[26] *Cook, D.*, Canad. J. Chem. **39**, 2009 (1961).
[27] *Galinos, A. G., Perlepes, S. P.*, Bull. Soc. Chim. Fr. **1979**, I-46.
[28] *Galinos, A. G., Sotiropoulos, D.*, Mh. Chem. **109**, 259 (1978).
[29] *Greenwood, N. N., Wade, K.*, J. Chem. Soc. **1960**, 1130.
[30] *Mitchell, P. C. H.*, J. Inorg. Nucl. Chem. **21**, 382 (1961).
[31] *Graddon, D. P., Heng, K. B., Watton, E. C.*, Austral. J. Chem. **19**, 1801 (1966).
[32] *Ivanov-Emin, B. N., Rabovik, Ya. I.*, Russ. J. Inorg. Chem. **4**, 1015 (1959).
[33] *Gearhat, R. C., jr., Beck, J. D., Wood, R. H.*, Inorg. Chem. **14**, 2413 (1975).