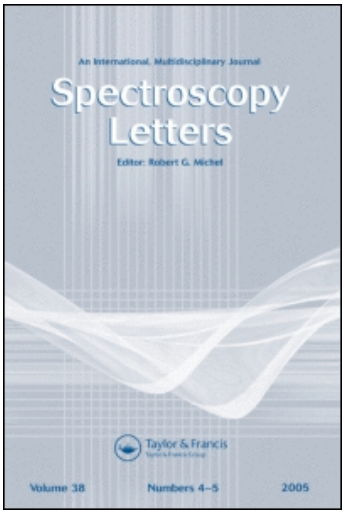

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FT-IR (6600-50 cm⁻¹) and FT-Raman (3500—70 cm^{-1}) Studies of the Tetranuclear Bismuth (III) Complex $(C_5H_5NH)_6Bi_4Cl_{18}$.

G. Bator[a]; Th. Zeegers-Huyskens[b]
[a] Department of Chemistry, University of Wroclaw, Wroclaw, Poland [b] Department of Chemistry, University of Leuven, Heverlee, Belgium

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FT-IR (6600-50 cm^{-1}) and FT-Raman (3500-70 cm^{-1}) Studies of the Tetranuclear Bismuth (III) Complex $(C_5H_5NH)_6Bi_4Cl_{18}$

Key words : Bismuth (III) complex, pyridinium ion, FT-IR and FT-Raman spectra.

G. Bator

Department of Chemistry, University of Wroclaw, F.Joliot-Curie 14, 50 383 Wroclaw (Poland)

Th. Zeegers-Huyskens

Department of Chemistry, University of Leuven, 200F Celestijnenlaan, 3001 Heverlee (Belgium)

ABSTRACT. The FT-IR and FT- Raman spectra of the tetranuclear Bi(III) complex $Bi(C_5H_5NH)_6Bi_4Cl_{18}$ are investigated. The spectroscopic data reflect the non-equivalence of the pyridinium ions and suggest a strong distortion of the octahedral structure for the Bi_4Cl_{18} group. The near-infrared data show that like in the fundamental region, protonation of pyridine results in a frequency increase of several combination bands.

INTRODUCTION.

Bismuth (III) halide salts through clustering of the anion crystallize in a wide range of complex structures. The structures of salts of BiX_4^-, BiX_6^{3-} and

$Bi_2X_8^{2-}$ reveal the general tendency of the Bismuth (III) atom to attain six-coordination, either by association between the ions or by stereochemical activity of the $6s^2$ electron pair [1]. In the tetranuclear Bismuth (III) compound $(C_5H_5NH)_6Bi_4Cl_{18}$ (PBC) the structure is built up of pyridinium ions and $Bi_4Cl_{18}^{6-}$ groups representing another type of halide complex. The $Bi_4Cl_{18}^{6-}$ moeity consists of two pairs of edge sharing octahedra jointed by their top ligands. Of the six Bi-Cl bonds, the three short terminals vary between 2.57 and 2.61 Å and the long bridgings are 2.83 - 2.94 Å [2].

No vibrational data on PBC are available in the literature and in this paper the FT-IR (6500 - 50 cm^{-1}) and the Raman spectra (3500 - 70 cm^{-1}) are investigated.

EXPERIMENTAL.

The FT-IR spectra in the near-infrared and in the far-infrared region have been recorded on the Bruker 66 spectrometer equipped with a tungsten source,a cooled InSb detector and a CaF_2 beamsplitter (6500-3800 cm^{-1}), a globar source,a DTGS/PE detector and a 6μ mylar beamsplitter (400-75 cm^{-1}). The mid infrared spectra were recorded on the Bruker 88 spectrometer using a globar source and a KBr beamsplitter and the Raman spectra were recorded on the Bruker 66 spectrometer equipped with a FRA 106 Raman module. All the spectra were taken at a resolution of 2 cm^{-1} in the solid state (KBr suspension in the mid- infrared and nujol mull in the far- infrared). The spectra were deconvoluted by using the OPUS software.

RESULTS AND DISCUSSION.

The infrared and Raman data between 3250 and 100 cm^{-1} are indicated in Table 1 and FIG.1 reproduces the infrared and Raman spectra in the low frequency region (400-75 cm^{-1}).

Table 1.IR and Raman data (3250-100 cm^{-1}) for $(C_5H_5NH)_6Bi_4Cl_{18}$

IR	Raman	Assignment
3217s	3210vw	$\nu(NH^+)$
3160s	3160vw	
3127w		
3100s		20b
	3094	2
3069s		7a
	3005	7b
		8a
1631s	1632m	
1610sh	1610w	8b
1603s	1604m	19b
1530s	1531w	
1482s	1480w	19a
1388w		14
1369w		
1327m		3
1265vw		9b
1247m	1248vw	
1239m	1242w	$\delta(NH^+)$
1194s	1193m	9a
1164w	1164m	15
1057m	1057w	18b
1049s	1050vw	
1028w	1029m	12
1020w	1009vs	1
1007vw		5
986w		
935w		
883m, br	883vw	$\gamma(NH^+)$
745s		4
675s		11
636w	636	6b
610w	610	6a
271w	275s	ν(Bi-Cl) terminal
240s	244m	ν(Bi-Cl) terminal
218m		ν(Bi-Cl) bridged
175vs		ν(Bi-Cl) bridged
	160w	ν(Bi-Cl) bridged
150s		δ(Cl-Bi-Cl)
	122s	

ν = stretching, δ, γ = deformation,vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad, sh = shoulder

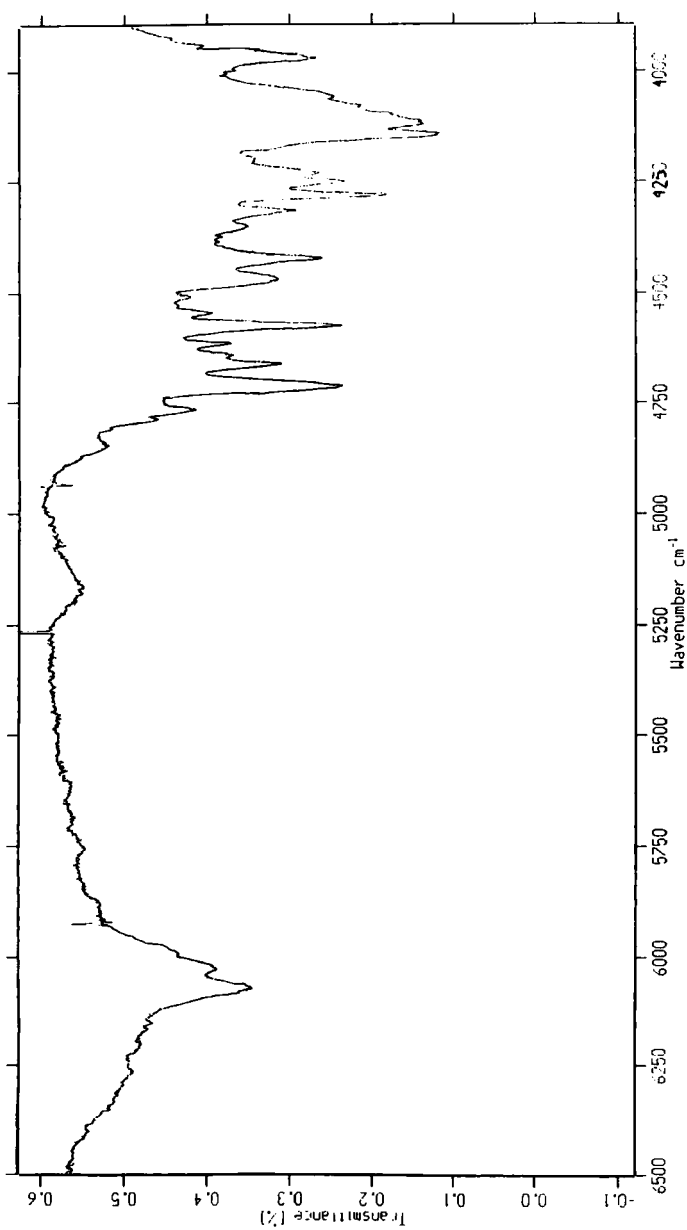

FIG.1. FT-Raman (a) and FT-IR(b) spectrum (350 - 70 cm^{-1}) of $(C_6H_5NH)_6Bi_4Cl_{18}$

1 = experimental spectra

2 = deconvoluted spectra

The $\nu(NH^+)$ vibration is observed as a doublet at 3217 and 3160 cm^{-1}.and the $\gamma(NH^+)$ vibration at 883 cm^{-1}. The two shortest H...Cl contacts of 2.52 and 2.56 Å clearly indicate the presence of NH...Cl hydrogen bonds. in the crystal structure [2]. These hydrogen bonds are weaker than in pyridinium chloride where the H...Cl distance is 1.95 Å and where the $\nu(NH^+)$ and $\gamma(NH^+)$ vibrations are observed at 2450 and 945 cm^{-1}. respectively [3].This is probably related to the fact that in PBC the charge on the Cl^- ion is about $0.5e^-$.

The frequencies of the fundamental vibrations of the pyridine moeity (ring modes, ν(CH) and δ(CH) modes) are very similar to those observed in pyridinium chloride [3-4]. In the present case however, a splitting of the ring stretching modes (8b, 14, 12), of the in-plane CH deformation (18b) and of the ν(NH+) and δ(NH+) vibrations is clearly observed. These splittings can be accounted for by the non-equivalence of the pyridinium ions in the crystal structure [2].

The $Cs_2NaBiCl_6$ complex is strictly octahedral and only five vibrations (two IR, three Raman) are active [5]. In PBC, five IR and five Raman bands are observed. PBC belongs to the space group C2/m and the $Bi_4Cl_{18}^{6-}$ has as a whole, the 2/m (C_{2h}) symmetry [2]. There is a strong distortion of the octahedral structure, the six Sb-Cl distances and the corresponding angles of the $SbCl_6$ subunit being different. The bands observed at about 270 and 240 cm^{-1} are assigned to the ν(Sb-Cl) vibrations of the terminal SbCl bonds characterized by the shortest distances (2.61, 2.56 and 2.59Å). The bands at 218, 175 and 160 cm^{-1} are assigned to the ν(Sb-Cl) vibrations of the bridged SbCl bonds characterized by much longer distances (2.83, 2.94 and 2.85 Å). The lower frequency absorptions originate from the δ(Cl-Bi-Cl) deformations. In the $(C_5H_5NH)_2BiBr_5$ complex, the highest frequency modes have also been assigned to the ν(Bi-Br) vibrations of the external bonds [6].

The near infrared spectrum of PBC is reproduced in FIG.2 and the spectral data and the assignment of the bands are indicated in Table 2. The vibrational overtone spectra (5800-6000 cm^{-1}) of the CH stretching modes of pyridine derivatives has been recently analyzed [7-9] but there are no data on the combinations modes observed between 5500 and 4000cm^{-1}. Table 2 also reports the anharmonicity coefficients (X_{11}) or the coupling coefficients (X_{12}) defined as

$$X_{11} = \nu_{01} - \nu_{02}/2 \qquad X_{12} = (\nu^1_{01} + \nu^2_{01}) - \nu_{02}.$$

where the subscripts 01 and 02 refer to the fundamental and first excited level and the superscripts 1 and 2 to two different fundamental transitions.

The overtones of the CH stretching vibrations of pyridine have been recorded in dilute tetrachloride solution and are somewhat different than those observed in pure pyridine (5835,5867,5907 and 5956 cm^{-1})[9]. This is probably ascribable to the existence of weak CH...N hydrogen bonds in the pure compound. In PBC, the overtone of the (CH) stretching vibrations are badly resolved and are broader than in pyridine. The band at 6000 cm^{-1} assigned to the first overtone of the ν(NH+...Cl) vibration is characterized by an anharmonicity constant of 162 cm^{-1}. This constant is higher than that of the overtone of the free ν(NH) vibration (between 45 and 80 cm^{-1}) and this is in line with the observations of C.Sandorfy and coworkers [10-12].In free pyridine, four absorptions are observed between 4656 and 4487 cm^{-1}. These absorptions are tentatively assigned to combinations involving the ν(CH) stretching vibrations and the 8a,8b,19a and 19b ring vibrations. In the pyridinium ion, these bands are shifted upward and our assignment is reinforced by the fact that in the fundamental region, the 8 and 19 ring vibrations are shifted to higher wavenumbers upon protonation of pyridine [3,4,13]. These combinations bands are characterized by coupling constants between 4 and 21 cm^{-1}. Two new bands at 4470 and 4423 cm^{-1} appear in PBC. These absorptions probably originate from the ν(NH+) and

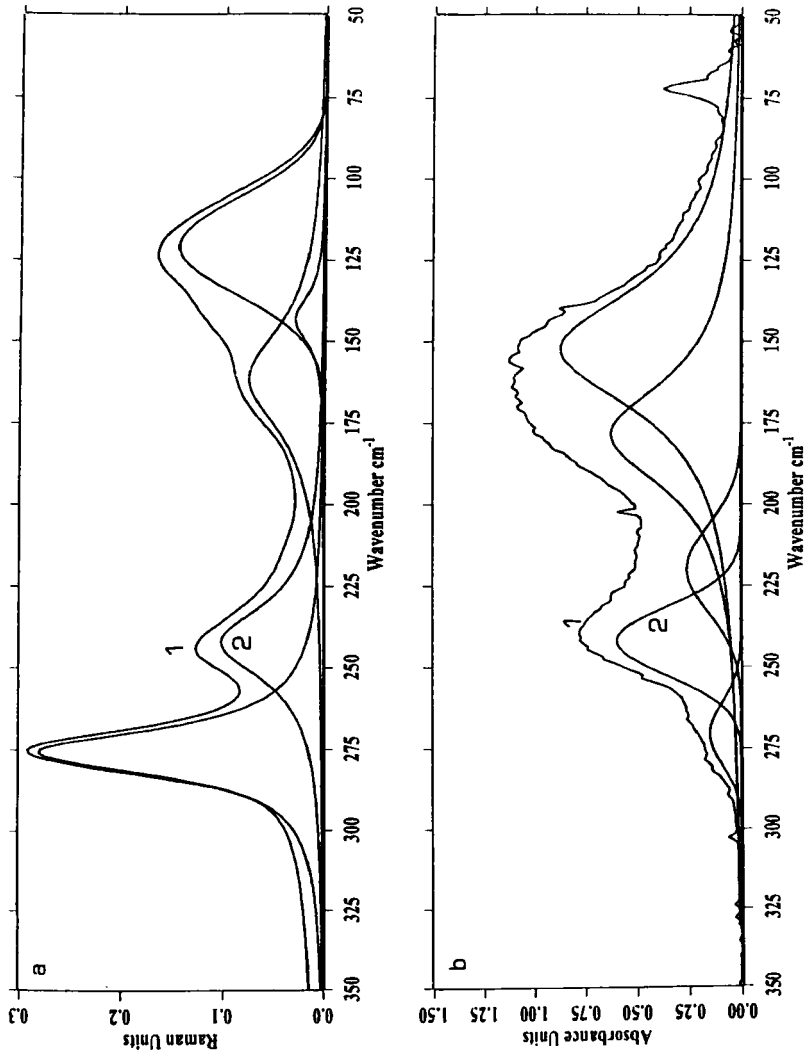

FIG.2. Near infrared spectrum (6500-3800 cm^{-1}) of $(C_6H_5NH)_6Bi_4Cl_{18}$

Table 2. Near infrared data (6500-4000 cm^{-1}) for $(C_5H_5NH)_6Bi_4Cl_{18}$

Free Pyridine		PBC	
Experimental ν (cm^{-1})	Assignment	Experimental ν (cm^{-1})	Assignment
6106 w	2 x 3080 (22)	6072 m;br	2 x 3100 (64)
6057 w	2 x 3054 (37)	6029 m,br	2 x 3069 (55)
5998 w	2 x 3054 (37)		
5960 w	2 x 3025 (45)		
		6000 w	2 x 3162 (162)
4656 s	3080 + 1583 (7)	4711 s	3100 + 1632 (21)
4598 s	3054 + 1572 (28)	4663 m	3069 + 1604 (10)
4555 s	3036 + 1482 (31)	4618 w	3100 + 1531 (13)
4487 s	3054 + 1439 (6)	4576 s	3100 + 1480 (4)
		4470 m	3217 + 1232 (-21)
		4423 m	3160 + 1247 (-16)
			3100 + 1327 (4)
4262 w	3054 + 1068 (10)	4280 s	3100 + 1192 (12)
4241 w	3036 + 1218 (17)	4250 m	3069 + 1192 (11)
4115 vs	3054 + 1068 (7)	4143 vs	3100 + 1057 (14)
	2 x 1572 + 992 (21)		2 x 1604 + 1007(72)
4080 vs		4122 s	3100 + 1028 (6)
		4118 s	3100 + 1020 (2)

vs = very strong, s = strong, m = medium, w = weak, br = broad;

δ(NH+) combinations. They are characterized by negative coupling coefficients and this probably originate from a coupling betwwen the fundamental δ(NH+) mode and vibrations of the pyridine. This coupling is evidenced by the fact that the 19b , 3 and 9a vibrations are markedly different in pyridine-H+ and pyridine-D+[3]. The absorptions between 4150 and 4000 cm^{-1} are also very sensitive to protonation. The band at 4115 cm^{-1} (4143cm^{-1} in PBC) is assigned to the ν(CH) and 18b combination. Another possible assignment is the combination between the first overtone of the 8b vibration and the ring breathing vibration which shifts from 992 to 1007 cm^{-1} upon protonation of pyridine.

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