Vibrational spectrum of bismuth subcarbonate

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Since the seventeenth century a variety of bismuth compounds and salts have been used in medicine to alleviate different disorders. In this century they were used to treat syphilis, as diuretics, as antihypertensives, and for the treatment of gastro-intestinal disorders [1, 2]. Recently, renewed interest in some of these compounds has arisen due to the discovery that the bacterium *Helicobacter pylori*, apparently responsible for chronic gastritis and peptic ulcers, can be effectively inhibited by certain bismuth compounds, both *in vitro* and *in vivo* [2].

As part of our present studies, devoted to the spectroscopic characterization of inorganic drugs, we have now investigated the infrared (IR) and Raman spectra of bismuth subcarbonate, one of the most commonly used Bi(III) compounds in pharmacology. This compound is also of interest in the field of materials science because it is a useful precursor for the synthesis of $\square$-Bi$_2$O$_3$ [3], the metastable poly-morphic form in the bismuth–oxygen system [4].

Very pure samples of composition (BiO)$_2$CO$_3\cdot$O$\cdot$5H$_2$O can be obtained by precipitation, according to the following procedure: 1.00 g of Bi(NO$_3$)$_3\cdot$5H$_2$O (C. Erba) was dissolved in a small amount of 20% nitric acid, then the volume of the solution was made up to 710 ml with cold distilled water. A slight excess of a saturated sodium carbonate solution ($\sim$200 ml) was added under continuous stirring. The resulting solution, together with the generated white precipitate, was heated at boiling point for 2 h. The warm solution was filtered off and the precipitate washed several times with about 200 ml of warm distilled water. Finally, the solid was dried for 3 days in an oven at 60 °C.

The Bi(III) content was determined complexometri-cally with ethylenediaminetetreacetic acid (EDTA), using xylenol-orange as indicator [5]. Typical analy-tical results lay around 80.0–80.2% (calculated for (BiO)$_2$(CO$_3$)$\cdot$0.5H$_2$O: 80.54%).

The composition of our samples was further confirmed by thermal analysis, using a Shimadzu thermoanalytical system (model TG-50 and DTA-50), working under an O$_2$-flow and at a heating rate of 10 °C min^{-1}. The decomposition of the material began at virtually 60 °C and occurred in one unique step, which extended up to 520 °C with only one weak break at around 340 °C. The total mass loss was 10.47%, which is in excellent agreement with that theoretically calculated from the equation (BiO)$_2$CO$_3\cdot$O$\cdot$5H$_2$O $\rightarrow$ Bi$_2$O$_3$ + 0.5H$_2$O + CO$_2$ (10.35%). The water loss apparently extended to a wide temperature interval and no differential thermal analysis (DTA) signal accompanied this process. The DTA trace showed three weak exothermic signals; the first one at 332 °C is surely related to the main degradation process of the carbonate; the second (534 °C) and third (704 °C) are probably related to structural changes of the primarily generated $\square$-Bi$_2$O$_3$ oxide ($\square$Bi$_2$O$_3$ $\rightarrow$ Æ-Bi$_2$O$_3$ $\rightarrow$ $\square$Bi$_2$O$_3$) [4].

The structure of the compound, determined by Rietveld analysis of powder neutron diffraction data [3], showed that it belongs to the orthorhombic space group Pna2$_1$ (C$_{2v}^9$, Nr. 33). It can be described as constituted by Bi$_2$O$_2^+$ layers with CO$_3^{2-}$ anions intercalated between them. The disposition of the Bi(III) and the oxide anions was similar to that found in the bismuth oxohalides [6]. The water retained in our samples is surely also located between the layers, and is apparently bonded very strongly, as suggested by the results of the thermal analysis.

The spectra were recorded with a Bruker IFS66 FT-IR instrument provided with an FRA 106 Raman accessory. Excitation of the samples was accom-plished using the 1064 nm line of an Nd:YAG laser.

The obtained spectra, in the range between 2000 and 400 cm^{-1}, are shown in Fig. 1. The proposed assignment is presented in Table I. The "free" carbonate ion (point group symmetry D$_{3h}$) possessed four internal vibrations: the symmetric stretching mode (ν_1, A$_1'$), the corresponding antisymmetric vibration (ν_3, E$'$), the out-of-plane bending (ν_2, A$_2''$) and the in-plane deformation (ν_4, E$'$). Of these vibrations, the A$_2''$ mode presents only IR activity, whereas the E$'$ modes are both infrared and Raman active, and A$_1'$ shows only Raman activity. In the crystal lattice, the anions are located on general positions (C$_1$); therefore, all degeneracies are removed and all of the vibrations become active in the IR and Raman spectra (all of the vibrational modes become A species under C$_1$ site symmetry).

In the higher frequency range (not shown in Fig. 1) the IR spectrum showed a broad weak band centred at 3425 cm^{-1}, which was assigned to the O—H stretching of water. Its position suggests the formation of hydrogen bonds of medium length [7]. The corresponding HOH deformation was only seen as a very weak IR feature at $\sim$1640 cm^{-1}.

As can be seen from the results presented in Table I, the predictions of the site symmetry analysis are clearly fulfilled. Only the $\square$ mode could not be identified in the Raman spectrum. The results demonstrate clearly that no correlation field effects operate in this lattice. A factor group analysis, correlating the site symmetry (C$_1$) with the factor
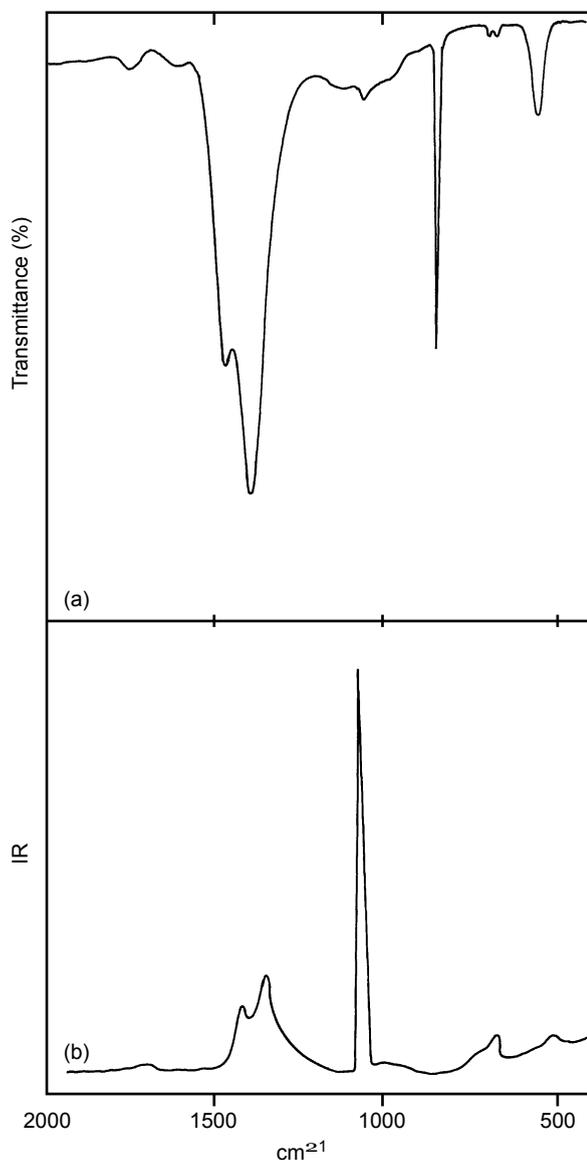
Figure 1 (a) Infrared and (b) Raman spectra of $(BiO)_2CO_3 \cdot O \cdot 5H_2O$.

unit cell were important, a greater number of bands should be observed.

It is worth adding that a series of combinational modes could be identified in the IR spectrum, in a similar way as found, for example, in the alkaline carbonates [8–10]. These modes are also included and analysed in Table I.

The IR band at 553 cm^{-1} has been assigned to the Bi$=$O stretching; in the Raman spectrum only a very weak feature is seen in this region (512 cm^{-1}). The IR band practically lies in the same range in which this vibration is found in the bismuth(III) oxohalides [11].

Finally, it is interesting to compare the present results with those known for other crystalline carbonates. The band positions in $(BiO)_2CO_3 \cdot O \cdot 5H_2O$ lie very close to values measured in $La_2(CO_3)_3$ [12], $PbCO_3$ [13] and $CaCO_3$ (aragonite) [14]. In comparison to the alkaline carbonates, stretching modes are found in a similar range in Na_2CO_3 and K_2CO_3 [8, 9]. However, the bending modes lie somewhat lower. These comparisons show that, apparently, the polarizing effect of the $Bi_2O_2^{2+}$ layers over the anionic carbonate groups is similar to that of Pb(II), a fact which is not totally unexpected, taking into account the position of both metals in the periodic system of the elements [15].

Acknowledgements

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group (C_{2v}), showed that each A species transformed to $A_1 + A_2 + B_1 + B_2$. These species are all Raman and IR active, except A_2, which is only Raman active. This means that, if vibrational coupling in the

TABLE I Assignment of the infrared and Raman spectra of $(BiO)_2CO_3 \cdot O \cdot 5H_2O$ (band positions in cm^{-1})[a]

Infrared	Raman	Assignment
3426 m, br	–	ν(OH)
2922 w/2851 vw	–	$2\nu_2$
2360 w/2335 vw	–	$2\nu_2 + \nu_4$
1756 vw/1730 vw	–	$\nu_1 + \nu_4$
1640 vw	–	δ(H$_2$O)
1468 m/1391 vs	1407 w/1367 m	ν_3(CO$_3^{2-}$)
1125 vw	–	(?)
1067 vw	1070 vs	ν_1(CO$_3^{2-}$)
846 vs	–	ν_2(CO$_3^{2-}$)
698 vw/670 vw	690 vw/669 w	ν_4(CO$_3^{2-}$)
553 m	512 vw	ν(Bi$=$O)
362 s, br	417 sh/369 s, br	
	162 vs	External vibration
	83 m	

[a]vs, very strong; s, strong; m, medium; w, weak; vw, very weak; br, broad; sh, shoulder.