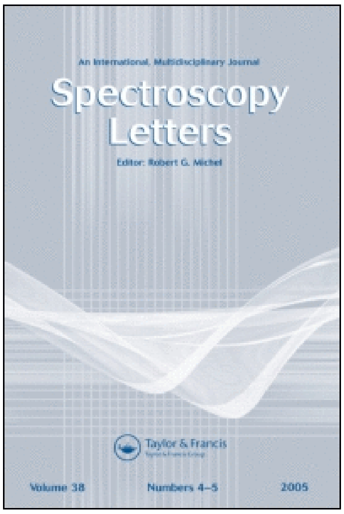

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IR Spectra of $Be(IO_3)_2.nH_2O$ (n = 4, O) and of the Deuterated Analogue

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IR SPECTRA OF $Be(IO_3)_2.nH_2O$ (n = 4,0) AND OF THE DEUTERATED ANALOGUE

Key words: beryllium iodites, IR spectra

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SUMMARY

The compounds of beryllium - $Be(IO_3)_2.4H_2O$, its deuterated analogue and $Be(IO_3)_2$ were studied by IR-spectroscopy over the range of 200 to 4000 cm^{-1}.

The presence was unequivocally proved of two structural groups making up $Be(IO_3)_2$, namely, the regular tetrahedron of $[Be(H_2O)_4]^{2+}$ and the IO_3^- ion which is with lower symmetry.

In $Be(IO_3)_2$ the tetraherdal coordination of Be^{2+} was realized through bidentate coordination of the iodate groups, which lowers the point group symmetry to C_s. The data also indicate disrupted symmetry of the other structural group, namely BeO_4.

There were no X-ray or spectroscopic data in pertinent literature about the beryllium iodate-hydrate and the anhydrous salt. The recording and interpretation of their IR-spectra was of interest, because the data obtained can provide information about the state of the structural groups making up the compounds, as well as the interactions between them.

EXPERIMENTAL

$Be(IO_3)_2.4H_2O$ was initially obtained as described earlier[1]. The deuterated analogue was obtained by the dissolution of $Be(IO_3)_2$ in heavy water and recrystallization over concentrated H_2SO_4. This operation was carried out twice. Strict observance of the conditions was necessary in order to avoid the formation of a greasy mass. The anhydrous $Be(IO_3)_2$ was isolated by thermal dehydration of $Be(IO_3)_2.4H_2O$ at 280°C. The sample was heated at this temperature for two hours and then kept under dry argon to avoid the absorption of moisture from the air. Under these conditions $Be(IO_3)_2$ was obtained in a crystalline state. It was isolated, identified and investigated by us for the first time.

The compounds obtained were identified by the methods of quantitative analysis described[2,3]. Their IR-spectra were recorded in an interval of 4000 cm^{-1} to 400 cm^{-1} in tablets of KBr, also from 400 cm^{-1} to 1500 cm^{-1} in Hostaflon and from 1500 cm^{-1} to 250 cm^{-1} in suspension of Nujol. A comparison between the spectrum in Nujol and that recorded in KBr tablets revealed that the very weak absorptions of Nujol at 720, 650 cm^{-1} did not affect the strong absorption bands observed in this region in the spectrum of the investigated compound.

TABLE 1

Data from the IR spectra of $Be(IO_3)_2.4H_2O$ and $Be(IO_3)_2.4D_2O$

H	D	ν_H/ν_D	Nature of the vibrations
3180 w	2370 w	1.34	$\nu(OH)$
3040 s	2250 s	1.34	
2930 ss	2190 ss	1.34	
2250 w			$\delta(H_2O) + \nu_L$
1660 m			$\delta(H_2O)$
1630 w	1215	1.34	
990 m	890 m	1.12	$\nu(Be\text{-}OH_2)$
860 sw	645 w	1.33	$\rho_r(H_2O)$
795 w	795 w	-	$\nu_3(E)(IO_3)$
780 s	770 s		$\nu_3(F_2)[Be(H_2O)_4]^{2+}$
760 s	760 s		$\nu_3(E)(IO_3)$
740 s	740 s		$\nu_1(A_1)(IO_3)$
725 sh	560 w	1.33	ν_{ω}, H_2O
620 sw	465 w	1.34	
390 w	390 w		$\nu_2(IO_3)$
360 w	360 w		$\nu_4(IO_3)$
340 sw	340 sw		
315 w	305 w	1.03	$\nu_4[Be(H_2O)_4]^{2+}$

TABLE 2

Data from the IR spectra of $Be(IO_3)_2$

Absorpt.bands observed	Nature of vibrations	Absorpt.bands observed	Nature of vibrations
1060 sw		635 m	
1030 sm		535 sw	$\nu_1(A_1)(BeO_4)$
895 sh		440 w	$\nu_2(A_1)(IO_3)$
880 sh	$\nu_3(F_2)(BeO_4)$	410 sw	$\nu_4(E)(IO_3)$
830 sh		390 w	
780 s	$\nu_3(E)(IO_3)$	340 w	$\nu_4(F_2)(BeO_4)$
730 s	$\nu_1(A_1)(IO_3)$	305 sw	
675 w		265 sw	

The spectra were recorded with a UR-10 Zeiss, and from 400 cm^{-1} to 200 cm^{-1} with UR-75. Fig. 3 presents the diagrams showing the interplanar distances of $Be(IO_3)_2.4H_2O$ (a), $Be(IO_3)_2.4D_2O$ (b) and $Be(IO_3)_2$ (c).

EXPERIMENTAL DATA AND DISCUSSION

The absorption bands of $Be(IO_3)_2.4H_2O$ and of the deuterated analogue are presented in Table 1, while those of the anhydrous product are presented in Table 2. Fig. 1 a,b shows the spectra of $Be(IO_3)_2.4H_2O$ and of $Be(IO_3)_2.4D_2O$, respectively, in the interval of 1000 cm^{-1}

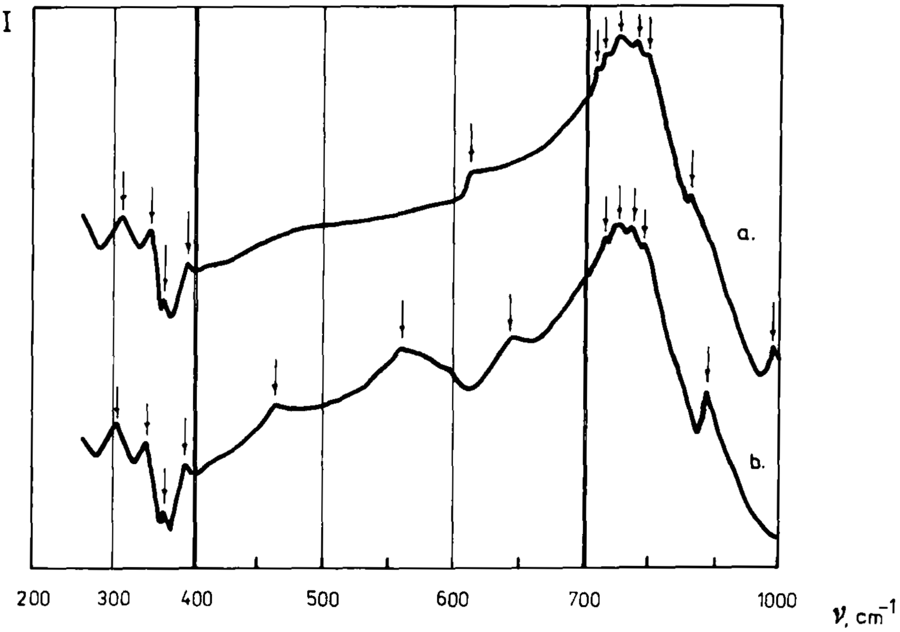

Fig. 1. IR spectra of: (a) $Be(IO_3)_2 \cdot 4H_2O$; (b) $Be(IO_3)_2 \cdot 4D_2O$.

to 250 cm^{-1}, while Fig. 2 shows the spectrum of $Be(IO_3)_2$ for the same interval.

The interpretation of the spectra in relation to the structural groups making up $Be(IO_3)_2 \cdot 4H_2O$, namely, $[Be(OH_2)_4]^{2+}$ and IO_3^-, was difficult due to the identical range in which their IR-active normal vibrations appeared. Thus $\nu_3(E)$ and $\nu_1(A_1)$ of IO_3^- and $\nu(F_2)$ of the aquacomplex must appear in the range of 700 - 800 cm^{-1}, while the bending vibrations $\nu_4(F_2)$ of $[Be(H_2O)_4]^{2+}$ and $\nu(E)$ of IO_3^- must appear in the range of 350 - 250 cm^{-1}.

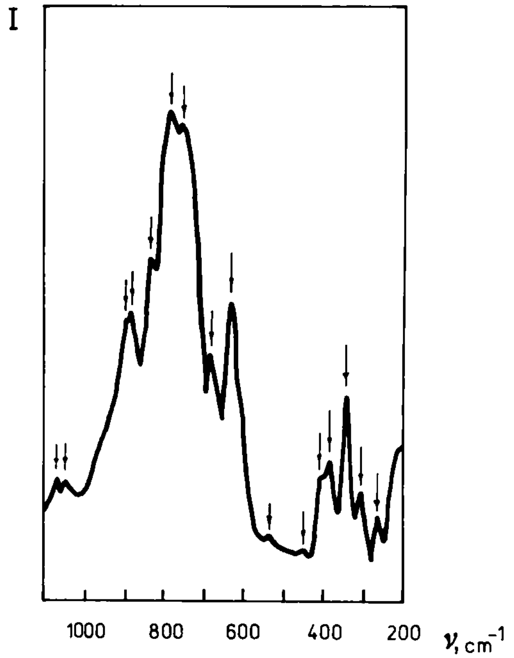

Fig. 2. IR spectrum of $Be(IO_3)_2$.

It was difficult to differentiate between them on the basis of the isotopic shift which was very small for the aquacomplex - about 1.1 to 1.05. Hence information about the symmetry of these groups could be obtained from the number of absorption bands observed in the above ranges, as well as from the presence of certain other vibrations.

For instance, in the strong absorption band observed between 800 - 700 cm^{-1} it was possible to record very well the maximums at 795 cm^{-1}, 780 cm^{-1}, 760 cm^{-1} and 740 cm^{-1}. These same maximums, without any essential changes, were to

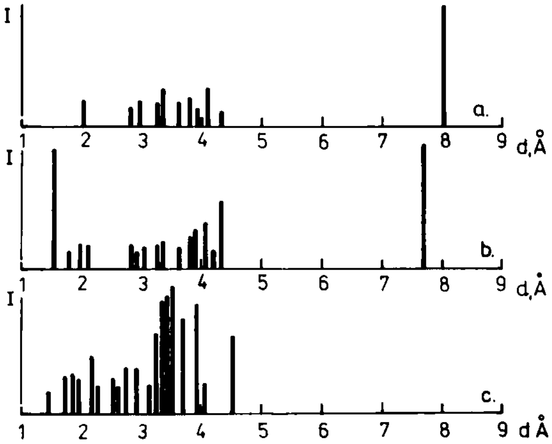

Fig. 3. Interplanar distances of: (a) $Be(IO_3)_2 . 4H_2O$; (b) $Be(IO_3)_2.4D_2O$; (c) $Be(IO_3)_2$.

be observed also in the spectrum of the deuterated sample. However, their number was indicative of disrupted symmetry of one of the groups examined.

The question "Which one of them ?" may be answered by the fact that the absorption band $\nu_1(A_1)$ of $[Be(H_2O)_4]^{2+}$ was not found in the spectrum at 540 cm^{-1}. This is considered as spectroscopic proof of the regular tetrahedral symmetry of the aquacomplex, since the vibration $\nu_1(A_1)$ was IR-active only upon a decrease of the T_d symmetry. Therefore, only one of the four vibrations of the examined range belonged to that ion. According to data from pertinent literature [4-10], most probably this is the maximum, with average intensity at 780 cm^{-1}.

The remaining three vibrations belong to the IO_3 ion, namely, 795 cm^{-1} and 700 cm^{-1} of the split $\nu_3(E)$ vibration, while 740 cm^{-1} belongs to $\nu_1(A_1)$. The value of the latter vibration was relatively low, according to data published about the free ion, with symmetry C_{3v}. However, such values have been observed in iodates of other metals [11,12].

Further information about the state of the two structural groups was given by the absorptions in the range of 350 - 250 cm^{-1}. In this case the spectrum showed three absorptions - at 360 cm^{-1}, 340 cm^{-1} and 315 cm^{-1}. An isotopic shift of 1.03 corresponded only to the latter, and that was why we ascribed it to $\nu_4(E)$ of the aquacomplex. The first two were components of $\nu_4(E)$ of IO_3, since its twofold degeneration had been eliminated.

Ensuing from the data discussed it is possible to draw the conclusion that while $[Be(H_2O)_4]^{2+}$ participates in the crystalline structure of $Be(IO_3)_2.4H_2O$ with regular tetrahedral coordination (as in the case of $Be(ClO_4)_2.H_2O$ [3,4]), the position symmetry of the IO_3 ion is lower, i.e. the spectrum shows six IR-active vibrations belonging to it, since the degeneration is eliminated for $\nu_3(E)$ and $\nu_4(E)$.

The state of the coordination water in $Be(IO_3)_2.4H_2O$ was characterized by means of its stretching, bending and librational vibrations. In the broad absorption band due to the stretching vibrations of the water it was possible to record maximums at 3180, 3040 and 2930 cm^{-1} (Table 1), to which absorptions with isotropic shift 1.34 - 1.35 corresponded in the spectrum of the deuterated sample.

The character and the position of the absorption band examined indicated participation of the water molecules in strong hydrogen bonds, as was to be expected in view of the covalent character of the Be $\longleftarrow$ OH_2 bonds in the aquacomplex. This covalency determined a considerable redistribution of the electron density along the OH-bond, hence an increase of the positive charge of the hydrogen ion, which is favourable for its interaction with the adjacent proton-accepter particles and for the formation of strong hydrogen bridges. It is quite possible that, in the particular case [13], they lead to protonation of the coordinated water molecules.

However, if this is so, the spectrum of the compound must show absorptions characteristic of the vibrations of the bond I - O - H , namely, absorption in the range around 1100 - 1200 cm^{-1} of δ (I-OH) and 640 cm^{-1} of ν (I-O(H)). Their absence, however, rules out the possibility for complete protonation of the water molecules in the investigated compound, perhaps due to the presence of certain steric factors.

In this case, from the position of the stretching vibration ν (OH) it is difficult to calculate the energy of the hydrogen bonds which have emerged, because both they and the coordination of the water molecules around Be act univalently on it. The character of their planar bending vibration (δ(H_2O)) observed as absorption band with maximums at 1630 cm^{-1} and 1660 cm^{-1} is a spectroscopic criterion for the presence in the structure of the compound of two types of crystallochemical unequal water molecules.

Information on their symmetry is obtained from the librational vibrations (ρ_r and ρ_ω) observed in their spectrum. They are well manifested in the spectrum of the deuterated sample free from other absorptions. Thus the absorption at 645 cm^{-1} for D_2O and the one corresponding to it at 860 cm^{-1} for H_2O with isotopic shift $\nu_H/\nu_D = 1.33$ may be ascribed to $\rho_r(H_2O)$, while the other two appearing at lower frequencies (560 cm^{-1} and 465 cm^{-1} for D_2O and at 725 cm^{-1} and 620 cm^{-1} for H_2O) can be ascribed to The one more vibration expected of the ρ_r type was not to be observed, probably due to overlapping with another vibration.

The librational vibrations recorded in the spectrum of $Be(IO_3)_2.4H_2O$ were of low intensity due to their immediate proximity to the broad absorption region of the stretching vibrations of the two structural groups $[Be(H_2O)_4]^{2+}$ and IO_3^-. According to Elsken & Robinson [14] the number of librational vibrations observed confirms the presence of two types of structurally different water molecules participating in different types of H-bonds of the kind of $H_2O ... H_2O$ and $O_3I ... H_2O$. The presence of asymmetric water molecules was proved by the disrupted difference between the symmetric and asymmetric stretching vibrations of the OH groups, namely, $\Delta\nu = 250$ cm^{-1}, as well as by

Teller-Redlich's rule (0.56) and by the character of the δ(HDO) vibration which appeared split.

In the spectrum of $[Be(H_2O)_4](IO_3)_2$ there was absorption with mean intensity at 990 cm^{-1} for H_2O and at 890 cm^{-1} for D_2O, with isotopic shift 1.12. According to F. Bertin[8] this absorption is ascribed to the librational vibrations. Having in mind the value of the calculated isotopic shift and the fact that such absorption was not to be observed in the spectrum of the anhydrous product (Table 1), it follows that this was not a case of vibration of the water molecule.

It is more verisimilar for this absorption to be related to the vibrations of the $Be{-}OH_2$ group. This was confirmed by the fact that it was to be observed also in the spectra of other beryllium hydrates[3,4].

The spectrum of the anhydrous $Be(IO_3)_2$ was rich in absorption bands in the range of 900 cm^{-1} to 200 cm^{-1} (Table 2, Fig. 2). However, its interpretation calls for taking into account certain electrostatic considerations according to which the anhydrous salt may be realized by the formation of BeO_4 tetrahedrons at the bidentate coordination of IO_3 around Be^{2+}, whereby the first ones are arranged in such a manner as to provide for local compensation of all charges in the system. Consequently, the spectrum of $Be(IO_3)_2$ must show IR-active vibrations of the two structural groups BeO_4 and IO_3^-, the latter being bidentate combined. According to published data[9,11,14] their normal vibrations lie precisely in the range of 900 cm^{-1} to 200 cm^{-1}.

If we begin the interpretation of the spectrum with the observed absorption band at 540 cm^{-1}, which may belong to the symmetric stretching vibration $\nu_1(A_1)$ of BeO_4 and which is IR-active only upon disrupted tetrahedral symmetry of BeO_4, it follows that the other two normal vibrations, $\nu_3(F_2)$ and $\nu_4(F_2)$, will also appear as twofold split, i.e. their degeneration will be partially eliminated. Consequently, five of the absorption bands observed in the spectrum will belong to BeO_4, two of them lying in the range around 700 - 800 cm^{-1} and two in the range below 300 cm^{-1} [15].

On the other hand, the bidentate coordination of IO_3^- determined a decrease of its point symmetry to C_s (the local one could not be determined, and there were no data for the space group), that is why the spectrum must show six of its IR-active vibrations, namely: $\nu_1(A_1)$, $\nu_2(A_1)$, $\nu_3(E)$ and $\nu_4(E)$, the last two being split. Their degeneration was eliminated and they appeared with two absorption bands each. Consequently, in addition to the bands of BeO_4, the range of 850 - 600 cm^{-1} will show also three bands of IO_3^- - $\nu_1(A_1)$ and two components of $\nu_3(E)$, while in the range of 350 - 250 cm^{-1} also two $\nu_4(E)$ IO_3.

Having in mind the data published about the IR spectra of other iosates studied[11,12], it is possible for the absorption band observed at 440 cm^{-1} to be ascribed to $\nu_2(A_1)$, while those at 780 cm^{-1}, 730 cm^{-1} and 675 cm^{-1} accordingly to $\nu_3(E)$ and $\nu_1(A_1)$. The differention of the latter is, however, unreliable.

Belonging to $\nu_4(E)$ of IO_3^-, duly split, were also the two absorption bands in the lower range, and it is precisely to them that we ascribe the vibrations 410 cm^{-1} and 390 cm^{-1}. The latter were higher in values than had been expected, and to all probability this was due to the influence of the vibrations $\nu_4(F_2)$ of BeO_4, which must appear close to the former ones. An analysis of the published data about the IR spectra of beryllium compounds - hydrates containing the BeO_4 group - shows that to these vibrations belong the absorptions at 340 cm^{-1} and 305 cm^{-1}, while to $\nu_3(F_2)$ belong the absorption bands at 880 cm^{-1} and 830 cm^{-1}.

Finally it must be pointed out that the identification of the normal vibrations of BeO_4 and IO_3 may involve certain inaccuracies, but their number fully coincides with the one determined on the basis of the existing symmetry of that group. In the future, it will be possible to resolve quite accurately certain problems, after some X-ray data about $Be(IO_3)_2$ had been obtained.

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