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TETRAFLUOROBERYLLATE(2-) IONS AS HYDROGEN-BOND PROTON ACCEPTORS: SPECTROSCOPIC EVIDENCE

Key words : Spectra, infrared spectra, tetrafluoroberyllate, hydrogen bonding, proton acceptors

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ABSTRACT

In the case of isostructural compounds it is easy to intuitively assume that the hydrogen bonds involving fluorine atoms as proton acceptors should be *stronger* than those in which oxygen atoms play the role of proton acceptors. Such an assumption was tested by comparing the infrared spectra of three tetrafluoroberyllate compounds with those of the isostructural sulfates and/or selenates. The experimental results do not support the basic hypothesis, although the elementary calculations based on the concept of equalized electronegativities [1,2] give higher values for the partial relative electric charge on the fluorine atoms in the idealized BeF_4^{2-} anions than are those estimated for the oxygen atoms in either SO_4^{2-} or SeO_4^{2-} ions. On the other hand, the values obtained by *ab initio* methods are more in line with the spectroscopic observations.

INTRODUCTION

As is well known, the hydrogen bonding is a specific interaction (intermolecular or intramolecular) which takes place when a proton bonded to an electronegative atom comes close to another electronegative atom (proton acceptor). The proton acceptor may be a monoatomic ion such as F^- or a larger particle (ion or molecule) containing one or more electronegative atoms which have lone electron pairs. It is reasonable to assume that the larger the electron density (or the partial electric charge) around the proton-acceptor atom is, the stronger the hydrogen bond would be and that the electron density around atoms of more electronegative elements (such as fluorine) would be larger than that around the less electronegative ones (e.g., oxygen or nitrogen).

When the proton-accepting particle is not a monoatomic anion, it is not an easy task to estimate the partial electric charge on the acceptor atoms. This quantity (a better name for it would be partial *relative* electric charge) seems to be important in assessing the ability of the proton-acceptor atom to participate in the formation of hydrogen bonds and in estimating the relative strength of the formed bonds.

One of the possible solutions is based on the rather simple and intuitively appealing model proposed by Sanderson [1,2] according to which the electronegativities of all atoms are *equalized* when a particle is formed from atoms which originally have different electronegativity values. The equalized electronegativity a_{eq} can be calculated [3–5] using the formula

$$a_{eq} = \frac{\sum (va/b) + q}{\sum (v/b)} \quad (1)$$

in which v is the number of atoms of a given kind (e.g., of the species A) in the particle, a is the Mulliken electronegativity of the element, b is the difference between the ionization potential and the electron affinity and q is the overall partial

electric charge of the particle which can then be calculated (see below). Another, certainly better substantiated, approach is to calculate the partial relative electric charges using quantum mechanical methods.

The trends in the values for the partial electric charges on the proton-acceptor atoms could be experimentally tested if the vibrational spectra of compounds containing suitable proton donors (such as water or ammonia molecules, ammonium cations etc.) and various proton acceptor anions are studied. If, namely, the model is correct and if the partial charge on the acceptor atom is the sole (or major) factor governing the hydrogen-bond strength, the stretching frequencies of the proton-donor moieties should be lower when the proton acceptor is such that the partial relative charge on the formally electronegative atoms is high than when this charge is low. If two anions (e.g., of the XY_4^{n-} type) have the same overall charge, one would expect, at least intuitively, the charge on the fluorine atoms in BeF_4^{2-} or BF_4^- to be higher than that on the oxygen atoms in SO_4^{2-} or ClO_4^- ions respectively and the hydrogen bonds formed by the fluorine-containing anions to be stronger than those in which oxoanions act as proton acceptors. The difference between the electronegativities of the sulfur (or selenium) and oxygen atoms is, namely, modest (less than one unit in the Pauling's scale) whereas that between the electronegativities of Be and F atoms is incomparably larger (> 2.4 units). It should be noted, however, that the hydrogen bonds formed by water molecules with sulfate and selenate ions as proton acceptors can be quite strong e.g., in alums (see, for example, [6] and the references given therein).

Since we have been long involved in the study of hydrates of sulfate, selenate, phosphate, arsenate and similar salts, it appeared interesting to study the proton-acceptor ability of the tetrafluoroberyllate compounds. Studied were pairs (or triads) of compounds in which one member is a tetrafluoroberyllate salt whose spectroscopic features were compared with those of the isotypic (preferably isomorphous) compound(s) containing SO_4^{2-} and/or SeO_4^{2-} anions. When both sulfate

and selenate salts were studied, a comparison was made of *their* spectral properties as well.

EXPERIMENTAL

All studied compounds were prepared by standard methods.

The infrared spectra were recorded at room temperature (RT) and temperatures down to the boiling temperature of liquid nitrogen (LNT) on a Perkin–Elmer 580 infrared spectrophotometer.

The quantum mechanical calculations were carried out using the Gaussian 92 quantum mechanical package [7]. The optimizations were performed using the Fletcher–Powell method [8] and the default Gaussian convergence criteria at the Hartree–Fock level [9] as well as at the second–order Møller–Plesset perturbation level [10]. The preliminary optimizations were performed with the 3–21G basis set, and then, in order to obtain a better description of the ionic species, the 6–311++G* basis set with diffuse functions [11] was employed.

RESULTS AND DISCUSSION

Spectral data

The appearance of the infrared spectra of the studied compounds in the O–H (or, when appropriate, the N–H/O–H) stretching region can be seen in Figs. 1–3. In all of them comparison is made of the tetrafluoroberyllate salts and the corresponding sulfate (or sulfate and selenate) analogues. As seen, the stretching frequencies of the proton-donating water and ammonia molecules or ammonium cations are similar, irrespective of the nature of the anion (sulfate or selenate, on the one hand or tetrafluoroberyllate, on the other). In other words, the spectral data do not lend

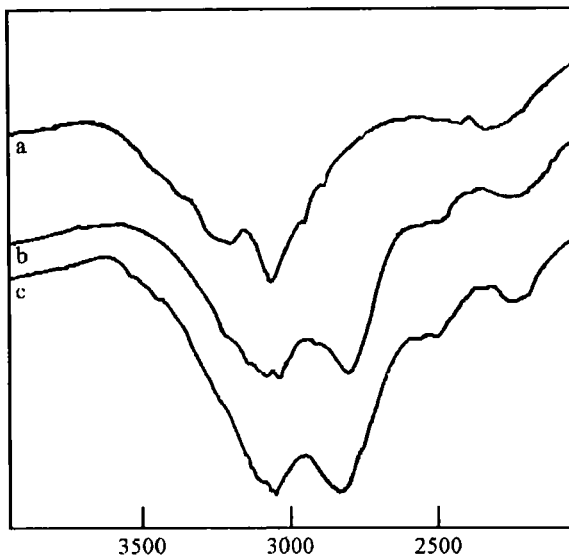


Fig. 1. The O-H stretching region of the spectra of $[\text{Cu}(\text{bpy})]\text{BeF}_4 \cdot 2\text{H}_2\text{O}$ (a), $[\text{Cu}(\text{bpy})]\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (b) and $[\text{Cu}(\text{bpy})]\text{SeO}_4 \cdot 2\text{H}_2\text{O}$ (c)

support to the notion that the BeF_4^{2-} anions are better proton acceptors than either the sulfate or the selenate ions.

Electronegativity arguments

In order to be more quantitative, we decided to employ the concept outlined in the introduction and estimate the partial relative electric charges on the fluorine atoms in the idealized tetrafluoroberyllate anion and compare them with the existing values for the sulfate and selenate anions. On the basis of the described model, Meek [12] has calculated the partial relative electric charges on the oxygen atoms in a number of oxoacids and their anions. Values of -0.415 and -0.409 were obtained for the partial relative charge on the oxygen atoms in the idealized, strictly

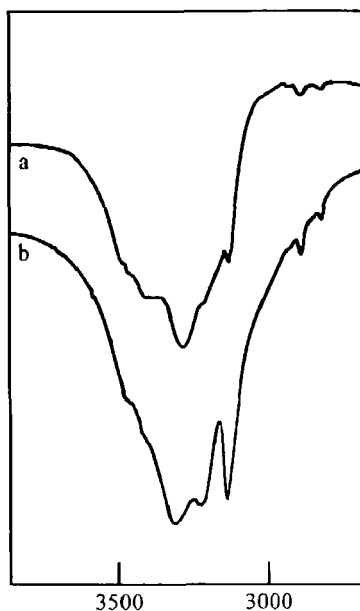


Fig. 2. The O-H stretching region in the spectra of $[\text{Cu}(\text{NH}_3)_4]\text{BeF}_4 \cdot \text{H}_2\text{O}$ (a) and $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ (b)

tetrahedral, SO_4^{2-} and SeO_4^{2-} ions respectively. No values of this nature seem to be available for anions in which fluorine atoms act as proton acceptors, e.g., tetrafluoroberyllate(2-) or tetrafluoroborate(1-) ions.

The essential ideas behind the calculations are as follows. If the equalization of the electronegativities does take place, it would bring about the appearance of partial relative electric charges on the individual atoms of the A type within the particle. These charges can be calculated using the equation (2)

$$\delta_A = \frac{a_{\text{eq}} - a_A}{b_A} \quad (2)$$

Using the same method and the same set of initial data as those utilized by Meek

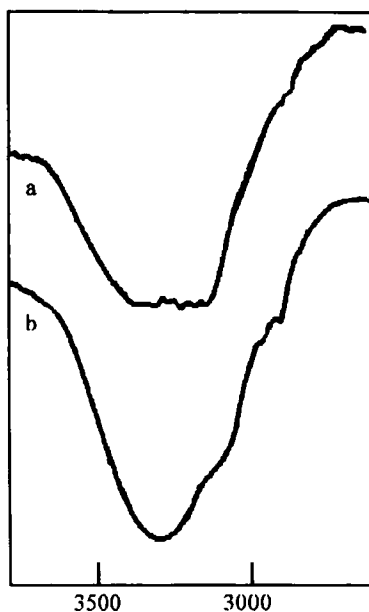


Fig. 3. The O-H stretching region in the spectra of $(\text{NH}_4)_2\text{Ni}(\text{BeF}_4)_2 \cdot \text{H}_2\text{O}$ (a) and $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (b)

[12], for the BeF_4^{2-} ions we obtained the values given in Table I. For comparison, the Meek's values for the SO_4^{2-} and SeO_4^{2-} anions are also included.

As seen, according to the employed model, the partial relative electric charge on the fluorine atoms in the BeF_4^{2-} ions is expected to be considerably higher than that on the oxygen atoms in either the isostructural sulfate and selenate anions. Nonetheless, as already pointed out, the frequencies of stretching bands of the proton donors in the case of the tetrafluoroberyllate compounds are not significantly lower (or not lower at all) than those in the spectra of the corresponding sulfate or selenate analogues (Figs. 1–3). Consequently, the hydrogen bonds in the former case could not be considered as appreciably stronger than those in the case of the iso-

Table I. The equalized Mulliken electronegativities and the calculated partial electric charges on the Y atoms of some XY_4^{2-} ions

XY_4^{2-}	BeF_4^{2-}	SO_4^{2-} [12]	SeO_4^{2-} [12]
α_{eq}/eV	5.32	7.57	7.66
δ_Y	-0.561	-0.415	-0.409

morphous sulfate and/or selenate compounds. Furthermore, our previous experience with pairs of sulfate and selenate compounds [13–15] has shown that, practically invariably, the stretching frequencies in the selenate compounds are *lower* than in the analogous sulfate ones. This is again in variance with the expectations based on the higher calculated partial relative electric charge on the oxygen atoms in the selenate than in the sulfate anions (cf. Table I).

The discrepancy between the expectations and the experimental results indicates that the conclusions based on the simple model are not adequate and that more sophisticated methods should be used to calculate the partial electric charges. In fact, a preliminary *ab initio* calculation indicates that the partial relative electric charge on the sulfate oxygen atoms (-0.771) is *larger* than that on the fluorine atoms in BeF_4^{2-} anions (the latter value was found to be -0.628). However, it should be remembered that the charge distribution was assigned from the Mulliken population analysis scheme [16] and that the atomic charges in a molecule are not a quantum mechanical observable and are not unambiguously predicted from the first principles. It is the *molecular* charge distribution that *can* be calculated and measured, but they can not be uniquely partitioned among the atomic centers.

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