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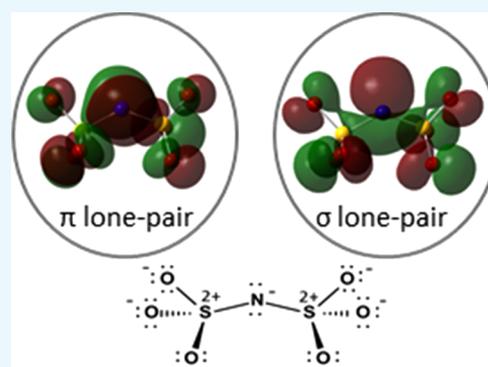
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Ab Initio Assessment of the Bonding in Disulfonates Containing Divalent Nitrogen and Phosphorus Atoms

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ABSTRACT: The iminodisulfonate, $[\text{N}(\text{SO}_3)_2]^{3-}$, and phosphinodisulfonate, $[\text{P}(\text{SO}_3)_2]^{3-}$, ions have been investigated by performing ab initio MP2/6-311+G** calculations. The nitrogen and phosphorus atoms as part of the ions are shown to be divalent with a negative charge and two lone pairs on the nitrogen and phosphorus atoms. The experimentally known calcium sodium iminodisulfonate trihydrate and the analogous unknown compound calcium sodium phosphinodisulfonate trihydrate have also been investigated using the MP2/6-311+G** calculations. For the nitrogen compound, only minor changes occur in the iminodisulfonate ion when it becomes part of the calcium sodium iminodisulfonate trihydrate. For the phosphorus compound, the geometry of the phosphinodisulfonate ion changes significantly as part of calcium sodium phosphinodisulfonate trihydrate. Furthermore, the charges associated with the atoms in calcium sodium phosphinodisulfonate trihydrate are quite different from those of the phosphinodisulfonate ion. For calcium sodium iminodisulfonate trihydrate, the Raman spectrum has been measured, and it compares well with the spectrum derived using HF/6-311+G** calculations.



1. INTRODUCTION

At the Enstedvaerk power plant, Aabenraa, Denmark, some insoluble crystals were discovered in the water pipelines of the flue gas cleaning systems removing sulfur dioxide. In 2002, Fogh et al. carried out X-ray diffraction investigations of these crystals, and the crystalline compound was identified as calcium sodium iminodisulfonate trihydrate, $\text{CaNa}[\text{N}(\text{SO}_3)_2] \cdot 3\text{H}_2\text{O}$.¹ In 2003, Rasmussen et al.² published powder diffraction data for the same compound.

The $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{NH}(\text{SO}_3)_2]^{2-}$ anions have been prepared in combination with cations potassium, sodium, and calcium by several groups.^{3–7} Calcium sodium iminodisulfonate was first prepared in 1892 by Divers and Haga, as described in their study on imidosulphonates where they suggested the name imidosulphonate.⁵ In 1896, Divers and Haga published a comprehensive review of a previous work on several imidosulphonate salts.⁶

In 1956, Jeffrey and Jones analyzed the crystal structure of the potassium salt of the aminodisulphonate ion, $[\text{NH}(\text{SO}_3)_2]^{2-}$, by X-ray diffraction.⁸ The focus was on measuring the S–N bond length and establishing the configuration of nitrogen. They determined the S–N bond length to be 1.655 Å, which they interpreted as a partial double bond between S and a sp^2 -hybridized N atom. In addition, Cruickshank and Jones¹⁰ refined the crystal structure of potassium iminodisulphonate based on the data from Jeffrey and Jones.⁸ Their results essentially confirmed the results obtained by Jeffrey and Jones.⁸ Hodgson et al.¹¹ tried to locate the hydrogen in $[\text{NH}(\text{SO}_3)_2]^{2-}$ and to establish the configuration around the nitrogen atom by neutron diffraction. The structure was refined

to give 4-fold bonding to two sulfur atoms. Furthermore, the structure was refined with two half hydrogen atoms about the twofold axis; therefore, they rejected trigonal bonding for nitrogen. Barbier et al.¹² carried out X-ray diffraction studies of $\text{K}_3[\text{N}(\text{SO}_3)_2] \cdot \text{H}_2\text{O}$ and $\text{K}_2[\text{NH}(\text{SO}_3)_2]$. Their results for $[\text{NH}(\text{SO}_3)_2]^{2-}$ confirmed the structure obtained by Cruickshank and Jones¹⁰ and by Hodgson et al.¹¹ Barbier et al.¹² also determined the mean bond length between N and S in $\text{K}_2[\text{N}(\text{SO}_3)_2] \cdot \text{H}_2\text{O}$ to be 1.606 ± 0.002 Å and the mean bond angle S–N–S to be $120.83 \pm 0.11^\circ$. Hall et al.¹³ supplemented their X-ray diffraction measurements of $\text{K}_3[\text{N}(\text{SO}_3)_2] \cdot \text{H}_2\text{O}$ with IR and Raman spectroscopy. They observed that the S–N bond lengths in $[\text{N}(\text{SO}_3)_2]^{3-}$, 1.609 ± 0.002 Å, are markedly shorter than those of the S–N bonds in compounds containing $[\text{NH}(\text{SO}_3)_2]^{2-}$.

In the present work, the $[\text{N}(\text{SO}_3)_2]^{3-}$ ion is investigated by carrying out ab initio Hartree–Fock (HF) calculations in the Roothaan formalism¹⁴ and also by performing second-order Møller–Plesset (MP2)¹⁵ calculations. In addition, the analogous phosphinodisulfonate ion, $[\text{P}(\text{SO}_3)_2]^{3-}$, is also investigated by performing HF and MP2 calculations. The initial structure of $[\text{N}(\text{SO}_3)_2]^{3-}$ is based upon the structure obtained by Fogh et al.¹ The geometry of the investigated ions was optimized using MP2/6-311+G** calculations, and the results elucidate the bonding properties of the ions. Furthermore, the electrostatic charges associated with the atoms in $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$ were determined on the basis of the

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optimized structures, and the results are compared with the standard Lewis structures of the ions.

In addition, *ab initio* MP2/6-311+G** studies were performed on calcium sodium iminodisulfonate trihydrate and for the analogous calcium sodium phosphinodisulfonate trihydrate. The bond lengths and angles determined by the *ab initio* calculations are compared to the known experimental data. The location of hydrogen and the configuration of nitrogen in $[\text{NH}(\text{SO}_3)_2]^{2-}$ were elucidated by the MP2/6-311+G** calculation.

The Raman spectrum has been measured for the calcium sodium iminodisulfonate trihydrate salt obtained from the Enstedvaerk power plant, Denmark. In addition, Raman spectra were obtained for $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$, as well as for $\text{CaNa}[\text{N}(\text{SO}_3)_2] \cdot 3\text{H}_2\text{O}$ and $\text{CaNa}[\text{P}(\text{SO}_3)_2] \cdot 3\text{H}_2\text{O}$ at the HF/6-311+G** level. The calculated normal modes for $[\text{N}(\text{SO}_3)_2]^{3-}$ and $\text{CaNa}[\text{N}(\text{SO}_3)_2] \cdot 3\text{H}_2\text{O}$ are used to assign the experimental spectra.

2. RESULTS AND DISCUSSION

2.1. Ion $[\text{NH}(\text{SO}_3)_2]^{2-}$. The crystal structure of potassium aminodisulphonate, $\text{K}_2[\text{NH}(\text{SO}_3)_2]$, has been studied experimentally by other authors.^{8,10,11} The S–N bond lengths range from 1.655⁸ to 1.674 Å.¹¹ In refs 8–10, the location of the H atom could not be determined, but it was suggested that the geometry around the N atom is trigonal planar, suggesting a sp^2 hybridization of nitrogen. The results by Hodgson et al.¹¹ and by Barbier et al.¹² indicated that the N atom is sp^3 -hybridized.

The geometry of $[\text{NH}(\text{SO}_3)_2]^{2-}$ has been optimized at the MP2/6-311+G** level. The molecule was initially built with S1–N1–H1–S2 in a plane.

Figure 1 shows the optimized structure of $[\text{NH}(\text{SO}_3)_2]^{2-}$. The total energy for $[\text{NH}(\text{SO}_3)_2]^{2-}$ is -1300.95739 au.

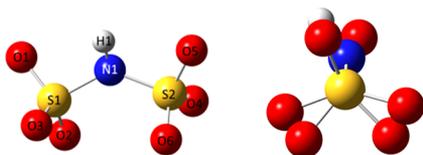


Figure 1. Structure of $[\text{NH}(\text{SO}_3)_2]^{2-}$ (C_1) determined at the MP2/6-311+G** level.

The optimized structure of $[\text{NH}(\text{SO}_3)_2]^{2-}$ has C_1 symmetry. The hydrogen atom is no longer in the plane containing S1–N1–S2, and nitrogen can be regarded as sp^3 -hybridized. The structural parameters obtained in the MP2/6-311+G** calculations for $[\text{NH}(\text{SO}_3)_2]^{2-}$ are listed in Table 1 together with the electrostatic charges determined for each atom.

The calculated average S–N bond length, 1.738 Å, is larger than the experimentally determined values from refs 8, 10, 11 by a magnitude ranging from 0.064 to 0.083 Å. The average S–O bond length, 1.478 Å, derived in the present work is larger than that from refs 8, 10, 11 by 0.025–0.036 Å. These discrepancies are presumably related to the exclusion of the cations in the model. The H1–N1–S1 and H1–N1–S2 angles are reasonably close to the tetrahedral angle, 109.47°, expected for a sp^3 -hybridized N atom, whereas the S1–N1–S2 angle, 127.82°, is significantly larger than the tetrahedral angle. This is probably due to the bulky SO_3 groups. The dihedral angle O1–S1–S2–O5 is 33.27°. Thus, the results derived in the present work clearly show that the arrangement around the N atom is not planar. The N atom must be considered sp^3 -hybridized.

Table 1. Geometrical Parameters and Electrostatic Charges on Each Atom in $[\text{NH}(\text{SO}_3)_2]^{2-}$ Determined Using the MP2/6-311+G Calculations**

bond distances (Å)		angles (deg)		electrostatic charges (<i>e</i>)	
S1–N1	1.735	S1–N1–S2	127.82	N1	−0.79
S2–N1	1.741	O1–S1–O2	114.73	S1	+1.68
S1–O1	1.485	O1–S1–O3	111.95	S2	+1.66
S1–O2	1.470	O2–S1–O3	114.48	O1	−0.86
S1–O3	1.480	N1–S1–O1	100.45	O2	−0.76
S2–O4	1.472	N1–S1–O2	105.19	O3	−0.81
S2–O5	1.488	N1–S1–O3	108.65	O4	−0.78
S2–O6	1.475	N1–S1–H1	106.54	O5	−0.85
N1–H1	1.017	O4–S2–O5	113.84	O6	−0.78
		O4–S2–O6	113.88	H1	+0.30
		N1–S2–O4	105.59		
		N1–S2–O5	99.29		
		N1–S2–O6	109.57		
		N1–S2–H1	105.59		

The molecular orbitals for $[\text{NH}(\text{SO}_3)_2]^{2-}$ were calculated at the HF/6-311+G** level. The highest-lying occupied molecular orbital (HOMO) is the lone-pair orbital on nitrogen. One of the lower-lying orbitals shows some π character between nitrogen and sulfur. Two orbitals, HOMO(−20) and HOMO(−21), show σ bonds between nitrogen and sulfur. The bonds between the sulfur and oxygen atoms have both σ and π characters.

2.2. Ions $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$. The nitrogen and phosphorus atoms bonded to only two ligands are unusual structures.

Figure 2 shows the Lewis structures obeying the octet rules for ions $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$.

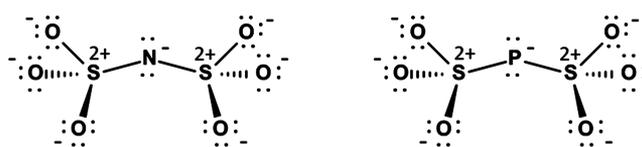


Figure 2. Lewis structures of $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$.

It is noted that the formal charge on nitrogen and phosphorus is -1 , whereas that on the neighboring sulfur atoms is $+2$. Furthermore, the Lewis structures indicate that both nitrogen and phosphorus are divalent. Divalent nitrogen and phosphorus with two lone pairs are known from organometallic coordination chemistry, and such compounds are commonly used in the design of new ligands.^{16–18}

The structures of $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$ were optimized using MP2/6-311+G** calculations. The total energy for $[\text{N}(\text{SO}_3)_2]^{3-}$ is -1300.09633 au, and for $[\text{P}(\text{SO}_3)_2]^{3-}$, -1586.35125 au. Figure 3 shows the optimized structures of $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$. It is noted that the symmetry of $[\text{N}(\text{SO}_3)_2]^{3-}$ is C_{2v} whereas that of $[\text{P}(\text{SO}_3)_2]^{3-}$ is C_{2v} . Imposing the C_{2v} symmetry on $[\text{N}(\text{SO}_3)_2]^{3-}$ results in a slightly higher energy and one imaginary vibrational frequency of 33 cm^{-1} . Therefore, this structure is not a stable conformation and the molecule in the C_{2v} symmetry should be considered as a transition state leading to the C_2 geometry.

Structural parameters obtained using MP2/6-311+G** calculations for $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$ are shown in Table 2.

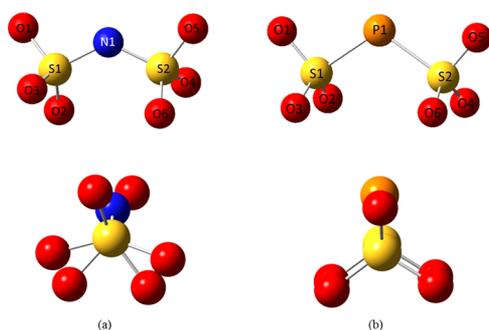


Figure 3. Molecular structure of $[\text{N}(\text{SO}_3)_2]^{3-}$ (C_2) (a) and $[\text{P}(\text{SO}_3)_2]^{3-}$ (C_{2v}) (b) determined at the MP2/6-311+G** level.

In $[\text{N}(\text{SO}_3)_2]^{3-}$, the S–N bond lengths are 1.640 Å and the average S–O bond length is 1.510 Å. For $[\text{P}(\text{SO}_3)_2]^{3-}$, the S–P bond lengths are 2.245 Å and the average S–O bond length is 1.507 Å. The S–N–S angle is 127.53° for $[\text{N}(\text{SO}_3)_2]^{3-}$, and the S–P–S angle for $[\text{P}(\text{SO}_3)_2]^{3-}$ is 112.77° . The dihedral angle O1–S1–S2–O5 is derived to be 42.79° for $[\text{N}(\text{SO}_3)_2]^{3-}$ and 0.00° for $[\text{P}(\text{SO}_3)_2]^{3-}$. This reveals that the two SO_3 groups are twisted considerably in $[\text{N}(\text{SO}_3)_2]^{3-}$, whereas $[\text{P}(\text{SO}_3)_2]^{3-}$ retains the C_{2v} geometry with the two SO_3 groups eclipsed to one another. This difference between the nitrogen and phosphorus compounds is presumably due to the longer S–P bonds, 2.245 Å, relative to the S–N bonds, 1.640 Å.

Table 3 shows the electrostatic charges for the atoms in $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$. It is noted that the calculated electrostatic charge is $-1.09e$ and $-0.92e$ on nitrogen and phosphorus, respectively. For sulfur, the electrostatic charges are $+1.99e$ and $+1.74e$, respectively, for $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$. The average value of the charges on the oxygen atoms amounts to $-0.98e$ for $[\text{N}(\text{SO}_3)_2]^{3-}$ and $-0.93e$ for $[\text{P}(\text{SO}_3)_2]^{3-}$.

It is noted that the values of the electrostatic charges are very much in line with the formal charges presented in the Lewis structures in Figure 2.

For $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$, the molecular orbitals were analyzed to elucidate the bonding properties. In Figure 4, selected molecular orbitals are shown for $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$. The molecular orbitals are derived using HF/6-311+G** calculations. The chosen orbitals for both ions are the highest occupied molecular orbital (HOMO) and the lower-

Table 3. Electrostatic Charges (e) on the Atoms in the $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$ Ions As Derived by the MP2/6-311+G** Calculations Using SPARTAN'14¹⁹

$[\text{N}(\text{SO}_3)_2]^{3-}$ (C_2)		$[\text{P}(\text{SO}_3)_2]^{3-}$ (C_{2v})	
atom	electrostatic charge	atom	electrostatic charge
N1	−1.09	P1	−0.92
S1	+1.99	S1	+1.74
S2	+1.99	S2	+1.74
O1	−1.01	O1	−0.93
O2	−0.96	O2	−0.92
O3	−0.98	O3	−0.92
O4	−0.96	O4	−0.92
O5	−1.01	O5	−0.93
O6	−0.98	O6	−0.92

lying molecular orbitals HOMO(−1), HOMO(−20), and HOMO(−21), respectively. The HOMO orbitals are π -type lone-pair orbitals for both ions. HOMO(−1) is a σ -type lone-pair orbital on the nitrogen and phosphorus atoms. HOMO(−20) and HOMO(−21) show σ bonds between the nitrogen or phosphorus and the sulfur atoms. A closer examination of all of the valence orbitals reveals that no π character is present between the nitrogen and sulfur atoms. The same applies for the bonds between phosphorus and sulfur.

Thus, the molecular orbital analyses of $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$ show that both ions are characterized by two lone pairs of electrons on the central nitrogen and phosphorus atoms. These lone pairs on the nitrogen and phosphorus atoms occupy the two highest-lying molecular orbitals, HOMO and HOMO(−1). The electrostatic charges associated with N in $[\text{N}(\text{SO}_3)_2]^{3-}$ and with P in $[\text{P}(\text{SO}_3)_2]^{3-}$ are close to $-1e$, whereas the sulfur atoms in both ions have charges close to $+2e$. Surprisingly, no delocalization of electrons belonging to the negatively charged atoms is observed.

For further examination of the bond properties between nitrogen and sulfur or phosphorus and sulfur, SPARTAN'14¹⁹ was used to determine the rotational barrier around the S–N and S–P bonds calculated at the MP2/6-311+G** level. During these calculations, the dihedral angles of S1–N1–S2–O5 and S1–P1–S2–O5 were changed from 0 to 360° in steps of 6° , while optimizing everything else. This resulted in a rotational barrier of 2.89 kJ/mol for $[\text{N}(\text{SO}_3)_2]^{3-}$ and 9.95 kJ/

Table 2. Geometrical Parameters of $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$ Determined by the MP2/6-311+G** Calculations

$[\text{N}(\text{SO}_3)_2]^{3-}$				$[\text{P}(\text{SO}_3)_2]^{3-}$			
bond distances (Å)		angles (deg)		bond distances (Å)		angles (deg)	
S1–N1	1.640	S1–N1–S2	127.53	S1–P1	2.245	S1–P1–S2	112.77
S2–N1	1.640	O1–S1–O2	110.21	S2–P1	2.245	O1–S1–O2	110.54
S1–O1	1.513	O1–S1–O3	109.00	S1–O1	1.514	O1–S1–O3	110.54
S1–O2	1.506	O2–S1–O3	109.96	S1–O2	1.503	O2–S1–O3	110.49
S1–O3	1.511	N1–S1–O1	103.36	S1–O3	1.503	P1–S1–O1	98.15
S2–O4	1.511	N1–S1–O2	112.96	S2–O4	1.503	P1–S1–O2	113.27
S2–O5	1.513	N1–S1–O3	111.12	S2–O5	1.514	P1–S1–O3	113.27
S2–O6	1.506	O4–S2–O5	109.00	S2–O6	1.503	O4–S2–O5	110.54
		O4–S2–O6	109.96			O4–S2–O6	110.49
		O5–S2–O6	110.21			O5–S2–O6	110.54
		N1–S2–O4	111.12			P1–S2–O4	113.27
		N1–S2–O5	103.36			P1–S2–O5	98.15
		N1–S2–O6	112.96			P1–S2–O6	113.27

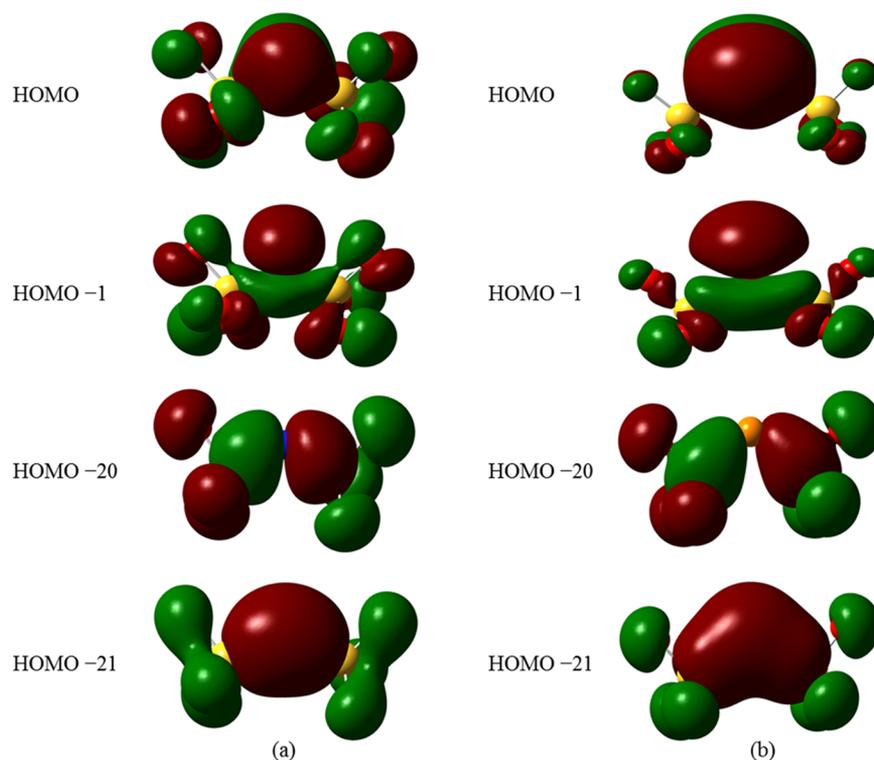


Figure 4. Selected molecular orbitals for $[\text{N}(\text{SO}_3)_2]^{3-}$ (a) and $[\text{P}(\text{SO}_3)_2]^{3-}$ (b) as derived by HF/6-311+G** calculations.

mol for $[\text{P}(\text{SO}_3)_2]^{3-}$. These barrier heights do not indicate any significant π bonding.

In view of these results, there is no evidence of the double-bond character between nitrogen and sulfur in $[\text{N}(\text{SO}_3)_2]^{3-}$ and the insignificant double-bond character between phosphorus and sulfur in $[\text{P}(\text{SO}_3)_2]^{3-}$.

Natural bond orbital (NBO) analyses have been carried out on both ions. The results revealed that the S atoms are basically sp^3 -hybridized with little contributions from the d polarization functions. The d contributions in all sp^3 hybrids of S in $[\text{N}(\text{SO}_3)_2]^{3-}$ are 0.10. In the corresponding $[\text{P}(\text{SO}_3)_2]^{3-}$ ion, the d orbital contributions amount to 0.09–0.10. Thus, the NBO analyses are consistent with single σ bonds between S and N, S and P, and also between all S and O atoms.

Altogether, the analyses of the molecular orbitals and of the electrostatic charges on the atoms in the ions indicate that the Lewis structures of $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$ shown in Figure 2 provide adequate representations of the two ions.

2.3. Compounds $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ and $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$. In the investigation of the structure of $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ and $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, the positioning of the cations, calcium and sodium, are based on the crystal data derived from Fogh et al.¹ With respect to water, various placements of the water molecules have been attempted in relation to minimizing the total energy. The structures of $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ and $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ are optimized by MP2/6-311G** calculations. Figure 5 shows the resulting structures for $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ and $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$. The total energy is -2368.30795 and -2654.53101 au for $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ and $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, respectively.

Table 4 shows the structural results obtained for $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ in the MP2/6-311+G** calculations. The experimental values from Fogh et al.¹ are also included. Table

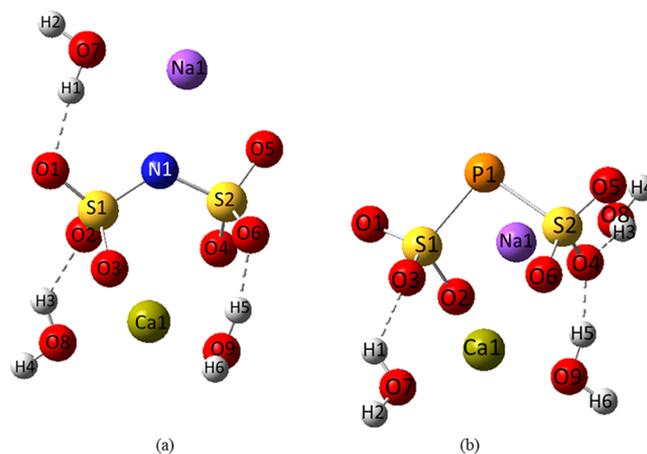


Figure 5. Lowest-energy structure for $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ (a) and $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ (b) determined by MP2/6-311+G** calculations. Hydrogen bonds are indicated by the dotted lines.

5 shows the corresponding data obtained for $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$.

For $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, the S1–N1 bond length obtained is 1.611 Å, whereas the S2–N1 bond length is slightly longer, 1.644 Å. The S–N bond lengths in the work of Fogh et al.¹ are determined to be 1.602 and 1.604 Å, respectively, which are slightly shorter than the calculated S–N bond lengths. The S1–O1 and S2–O5 bond lengths are derived to be 1.465 and 1.479 Å, respectively. The average S–O bond length is 1.501 Å. The experimentally obtained¹ S1–O1 and S2–O5 bond lengths are 1.470 and 1.467 Å, respectively, which are in reasonable agreement with the calculated values. The remaining calculated S–O bonds are slightly longer than the ones obtained experimentally.¹ The S–N–S angle is derived to be 120.10°, whereas the experimental value of the

Table 4. Geometrical Parameters for $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ Determined by the MP2/6-311+G Calculations and Compared with the Corresponding Experimental Values by Fogh et al.¹**

bond distances (Å)		ref 1	angles (deg)		ref 1	distances (Å)	
S1–N1	1.611	1.602(1)	S1–N1–S2	120.10	118.10(7)	Na ⁺ ...N1	2.326
S2–N1	1.644	1.604(1)	O1–S1–O2	113.05	111.49(7)	Na ⁺ ...O5	2.468
S1–O1	1.465	1.470(1)	O1–S1–O3	115.98	109.75(7)	Na ⁺ ...O7	2.324
S1–O2	1.529	1.463(1)	O2–S1–O3	102.70	110.67(6)	Ca ²⁺ ...O2	2.414
S1–O3	1.517	1.464(1)	O1–S1–N1	105.88	109.57(6)	Ca ²⁺ ...O3	2.336
S2–O4	1.525	1.465(1)	O2–S1–N1	109.60	104.75(7)	Ca ²⁺ ...O4	2.251
S2–O5	1.479	1.467(1)	O3–S1–N1	109.59	110.51(7)	Ca ²⁺ ...O8	2.375
S2–O6	1.490	1.465(1)	O4–S2–O5	113.40	109.97(7)	Ca ²⁺ ...O9	2.371
			O4–S2–O6	107.19	110.81(7)		
			O5–S2–O6	113.96	111.80(7)		
			O4–S2–N1	108.28	111.74(6)		
			O5–S2–N1	102.32	110.81(7)		
			O6–S2–N1	111.61	101.49(7)		
hydrogen bonds (Å)							
O _{molecule} ...H _{water}			O _{molecule} ...O _{water}			angles, water-anion (deg)	
O1...H1	1.823		O1...O7	2.795		O1...H1–O7	171.29
O2...H3	1.864		O2...O8	2.614		O2...H3–O8	131.06
O6...H5	1.686		O6...O9	2.663		O6...H5–O9	165.04

Table 5. Geometrical Parameters for $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ Determined by MP2/6-311+G Calculations**

bond distances (Å)		angles (deg)		angles (deg)		distances (Å)	
S1–P1	2.163	S1–P1–S2	96.34	O4–S2–O5	111.50	Na ⁺ ...O2	2.330
S2–P1	2.180	O1–S1–O2	112.83	O4–S2–O6	104.13	Na ⁺ ...O4	2.388
S1–O1	1.457	O1–S1–O3	114.59	O5–S2–O6	114.80	Na ⁺ ...O8	2.342
S1–O2	1.552	O2–S1–O3	101.49	O4–S2–P1	110.07	Ca ²⁺ ...O2	2.322
S1–O3	1.519	O1–S1–P1	107.22	O5–S2–P1	106.42	Ca ²⁺ ...O3	2.353
S2–O4	1.546	O2–S1–P1	106.58	O6–S2–P1	109.93	Ca ²⁺ ...O6	2.235
S2–O5	1.456	O3–S1–P1	113.90			Ca ²⁺ ...O7	2.369
S2–O6	1.515					Ca ²⁺ ...O9	2.363
hydrogen bonds (Å)							
O _{molecule} ...H _{water}			O _{molecule} ...O _{water}			angles, water-anion (deg)	
O3...H1	1.984		O3...O7	2.641		O3...H1–O7	123.27
O4...H3	1.827		O4...O8	2.650		O4...H3–O8	139.99
O4...H5	1.615		O4...O9	2.594		O4...H5–O9	163.61

Table 6. Electrostatic Charges (*e*) on the Atoms of $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ and $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ Based on the Structures Derived Using the MP2/6-311+G Calculations**

$\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$				$\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$			
atom	electrostatic charge	atom	electrostatic charge	atom	electrostatic charge	atom	electrostatic charge
N1	−1.02	O1	−0.68	P1	−0.45	O1	−0.57
S1	+1.65	O2	−0.88	S1	+1.22	O2	−0.82
S2	+1.59	O3	−0.86	S2	+1.13	O3	−0.78
Ca1	+1.69	O4	−0.83	Ca1	+1.69	O4	−0.75
Na1	+0.90	O5	−0.73	Na1	+0.75	O5	−0.50
		O6	−0.72			O6	−0.82

S–N–S angle is 118.10°. The dihedral angle O1–S1–S2–O5 is 38.25°. Thus, the O1–S1–N1–S2–O5 atoms are far from being in plane, as was assumed in the experimental work.^{1,12,13}

The present work represents the first theoretical investigations on $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ and the $[\text{P}(\text{SO}_3)_2]^{3-}$ ion. In addition, no experimental work has been done on these phosphorus systems.

For $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, the calculated P1–S1 and P1–S2 bond lengths are 2.163 and 2.180 Å, respectively. These bond lengths are shorter than the ones derived for $[\text{P}(\text{SO}_3)_2]^{3-}$, 2.245 Å. The S1–O1 and S2–O5 bond lengths are 1.457 and

1.456 Å, respectively, which are shorter than those of the corresponding bonds derived for $[\text{P}(\text{SO}_3)_2]^{3-}$, 1.514 Å. The average S–O bond length is 1.508 Å. The S–P–S angle is 96.343°, which is remarkably smaller than that identified for $[\text{P}(\text{SO}_3)_2]^{3-}$, 112.77°. The dihedral angle O1–S1–S2–O5 is 49.63° for $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$. This shows that $[\text{P}(\text{SO}_3)_2]^{3-}$ in the $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ system no longer possesses the C_{2v} symmetry.

Tables 4 and 5 include the shortest distances between the cations, calcium and sodium, and the oxygen atoms of the anions.

For both $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ and $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, three hydrogen bonds are observed, similar to the results obtained in the diffraction experiment of $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$.¹ The calculated structural data obtained using MP2/6-311+G** calculations for $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ resulted in overall good agreement with the experimental data.

The $\text{O}_{\text{water}}-\text{H}_{\text{water}}\cdots\text{O}_{\text{molecule}}$ angle in the work by Fogh et al.¹ ranges from 166 to 177°. The $\text{O}_{\text{molecule}}\cdots\text{O}_{\text{water}}$ distances range from 2.731 to 2.898 Å, and the $\text{H}_{\text{water}}\cdots\text{O}_{\text{molecule}}$ distances range from 1.79 to 2.10 Å.¹ These values compare reasonably with the calculated values. According to the definition of Jeffrey, referenced by Steiner,²⁰ the hydrogen bonds in $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ and $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ are all of moderate strength.

Table 6 lists the electrostatic charges derived, on basis of the structures obtained by the MP2/6-311+G** calculations, for each of the atoms in $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ and $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$.

For the systems containing nitrogen, $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ and $[\text{N}(\text{SO}_3)_2]^{3-}$, the electrostatic charge of nitrogen in the bare ion, $-1.09e$, is numerically slightly larger than that of nitrogen, $-1.02e$, in $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$. The electrostatic charges of the sulfur atoms in $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, $+1.65e$ and $+1.59e$, respectively, are remarkably smaller than those of $[\text{N}(\text{SO}_3)_2]^{3-}$, $+1.99e$. For the oxygen atoms, the most significant changes occur for O1 and O5. In $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, the charges are $-0.68e$ and $-0.73e$, respectively, whereas both of the corresponding charges in $[\text{N}(\text{SO}_3)_2]^{3-}$ are $-1.01e$. Thus, in $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, relative to $[\text{N}(\text{SO}_3)_2]^{3-}$, the charge is transferred from the oxygen atoms to the sulfur atoms and to the metal atoms, whereas the charge on nitrogen is almost unchanged.

For the systems containing phosphorus, $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$, there are significant changes in the electrostatic charges. The electrostatic charge on phosphorus changes from $-0.92e$ in $[\text{P}(\text{SO}_3)_2]^{3-}$ to $-0.45e$ in $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$. For the sulfur atoms, the electrostatic charges in $[\text{P}(\text{SO}_3)_2]^{3-}$ are $+1.74e$, and in $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, S1 and S2 have electrostatic charges of $+1.22e$ and $+1.13e$, respectively. For both O1 and O5 in $[\text{P}(\text{SO}_3)_2]^{3-}$, the charges are $-0.93e$. These charges are reduced to $-0.57e$ and $-0.50e$, respectively, in $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$. The charges on the remaining O atoms are numerically slightly reduced, that is, from $-0.92e$ to approximately $-0.80e$. In $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, relative to $[\text{P}(\text{SO}_3)_2]^{3-}$, the charge is transferred from the oxygen atoms to the sulfur atoms and to the metal atoms, whereas the charge on phosphorus is reduced from -0.92 to -0.45 . This is presumably because the valence electrons of phosphorus are loosely bound relative to the valence electrons of nitrogen.

NBO analyses have been carried out for $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ and $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$. For both compounds, the results revealed that the S atoms in the S–N, S–P, and S–O σ bonds are basically sp^3 -hybridized with little contributions from the d polarization functions. The d contributions in all sp^3 hybrids of S in $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ are in the range of 0.09–0.12. In $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, the corresponding d orbital contributions amount to 0.07–0.12. Thus, same as for the $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$ ions, the NBO analyses are consistent with single σ bonds between S and N, S and P, and also between all S and O atoms.

2.4. Raman Spectra. A $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ crystal was placed directly under a microscope, and a clear spot was used for recording. The provided crystal was brown and clear; the

brown areas were assigned to impurities, and it was proved to be important to record the spectrum through a clear crystal area. The recorded spectrum was obtained according to the specifications given in the Materials and Methods section. The recorded spectrum is corrected for the background and for the N_2 band at 2331 cm^{-1} .

Figure 6 shows the experimentally obtained and calculated spectra of $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$.

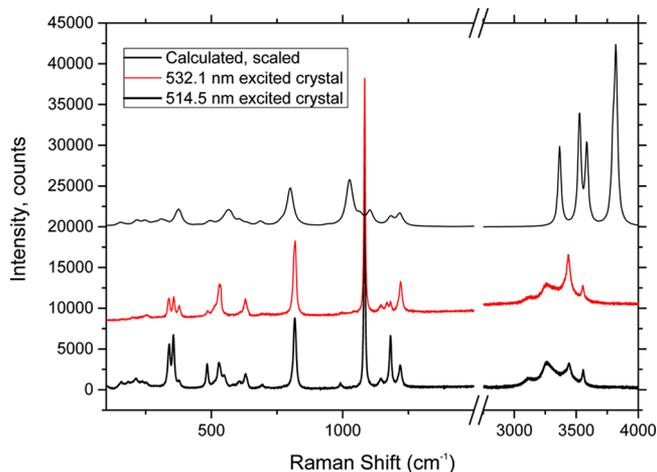


Figure 6. Raman spectra of two crystals of $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, obtained at room temperature. The spectrum obtained with 532.15 nm excitation is shifted for ease of comparison to the spectrum obtained with 514.5 nm excitation. The top spectrum shows the scaled spectrum of $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, based on the HF/6-311+G** calculation and assuming Gaussian band shapes of half-height at half-width of 16 cm^{-1} .

The 0–1200 cm^{-1} range is mostly associated with the $\text{CaNa}[\text{N}(\text{SO}_3)_2]$ moiety, whereas the 3000–4000 cm^{-1} range is associated with the three crystal water molecules.

Theoretical Raman spectra for $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ and $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ were obtained by the HF/6-311+G** calculations using Gaussian'09.²¹ As suggested in the work of Merrick et al.,²² an empirical scale factor of 0.9059 was used to correct the frequencies derived by the HF/6-311+G** calculations. The scaled frequencies are used to assign the bands obtained in the experimental spectra. The bending modes of the three water molecules in the salt were calculated to be at a scaled value at around 1750 cm^{-1} , but these modes were not observed experimentally, probably because of weakness. Table 7 lists the derived frequencies for $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ with assignments of the characteristic peaks.

The S–N and S–O stretchings associated with the $[\text{N}(\text{SO}_3)_2]^{3-}$ moiety are assigned to the bands in the 800–1350 cm^{-1} range. Several authors^{13,23,24} have measured the Raman spectra of $\text{K}_3[\text{N}(\text{SO}_3)_2]\cdot \text{H}_2\text{O}$. Their assignments of the symmetric S–N and S–O stretchings at 794 and 1046 cm^{-1} are in good agreement with the scaled frequencies presented in Table 7.

Figure 7 shows the spectra derived for $[\text{P}(\text{SO}_3)_2]^{3-}$ and $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ based on the HF/6-311+G** calculations. The water bending modes in the spectrum, Figure 7b, are found between 1500 and 1750 cm^{-1} .

Table 8 lists the frequencies derived for the $[\text{P}(\text{SO}_3)_2]^{3-}$ ion, as well as the frequencies for $[\text{P}(\text{SO}_3)_2]^{3-}$ as part of

Table 7. Experimentally Observed Spectral Bands for $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ (in cm^{-1}) Compared with the Frequencies Obtained by the HF/6-311+G Calculations (800–1250 cm^{-1})^a**

experimental	calculated frequencies	scaled frequencies	assignments
817	883	800	sym. stretch (S–N)
991	1041	943	sym. stretch (S–O)
1083	1141	1034	sym. stretch (S–O)
1145	1177	1066	asym. stretch (S–N)
1181	1305	1182	asym. stretch (S–N)
1218	1344	1218	asym. stretch (S–O)

^aAlso included are the scaled frequencies (cm^{-1}).

$\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ with assignments of the characteristic peaks.

2.5. IR Spectra. Figure 8a shows two experimental IR absorption spectra obtained for $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, dispersed in KBr powder and pressed under evacuation into rather clear disks.

As for the Raman spectra, the range from approximately 400 to 1500 cm^{-1} is mostly associated with the $\text{CaNa}[\text{N}(\text{SO}_3)_2]$ moiety itself and the range 1500–4000 cm^{-1} is mostly associated with the three molecules of crystal water, the low modes being due to bendings, the higher ones due to OH stretchings, the symmetric ones at lower values, and the asymmetric ones at somewhat higher wavenumbers. The calculated spectrum in Figure 8b is scaled by a factor of 0.9059. This spectrum corresponds rather well with the experimentally obtained spectra for $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, even though they probably also contain weak bands due to the occurrence of overtone and combination transitions.

3. CONCLUSIONS

The results of the MP2/6-311+G** calculations on $[\text{N}(\text{SO}_3)_2]^{3-}$ show that the arrangement around nitrogen is not planar; therefore, nitrogen must be considered to be sp^3 -hybridized.

The results of MP2/6-311+G** calculations for $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$ reveal that the central atom, that is, N or P, is singly bonded to the S atoms in both ions. The N atom has a negative charge of $-1.09e$, whereas that of P is $-0.92e$. It is shown that N and P each has two lone pairs. In addition, nitrogen and phosphorus can be considered sp^2 -hybridized.

NBO analyses show that the chemical bonds between N and S as well as between P and S are single σ bonds and that both the S and O atoms are sp^3 -hybridized with only a slight contribution from the polarization d orbitals. All bonds between the S and O atoms are single σ bonds.

Thus, the calculated structures of both ions are consistent with the simple Lewis structures in which the nitrogen and phosphorus atoms are divalent, each with a negative charge and two lone pairs.

The geometry of the isolated $[\text{N}(\text{SO}_3)_2]^{3-}$ ion is not significantly different from that of the ion in $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$. The geometry of $[\text{P}(\text{SO}_3)_2]^{3-}$ changes significantly when the ion becomes part of $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, going from the C_{2v} symmetry to the C_1 symmetry.

When the anions, $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$, become part of $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ and $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, the charge is transferred from the oxygen atoms to the sulfur atoms and to the metal atoms. Whereas the charge on nitrogen hardly changes, the charge on phosphorus is reduced significantly. This is presumably due to the valence electrons of phosphorus being loosely bound relative to the valence electrons of nitrogen.

The measured Raman and IR spectra associated with $[\text{N}(\text{SO}_3)_2]^{3-}$ in $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ have been assigned by comparison with the calculated spectra. The vibrational bands observed above 1500 cm^{-1} are mostly due to the water molecules incorporated in the crystal structure, but other bands are also observed probably due to the overtone and combination transitions. In addition, the characteristic bands associated with the bare ion, $[\text{P}(\text{SO}_3)_2]^{3-}$, and with the ion in a $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ crystal have been predicted and assigned.

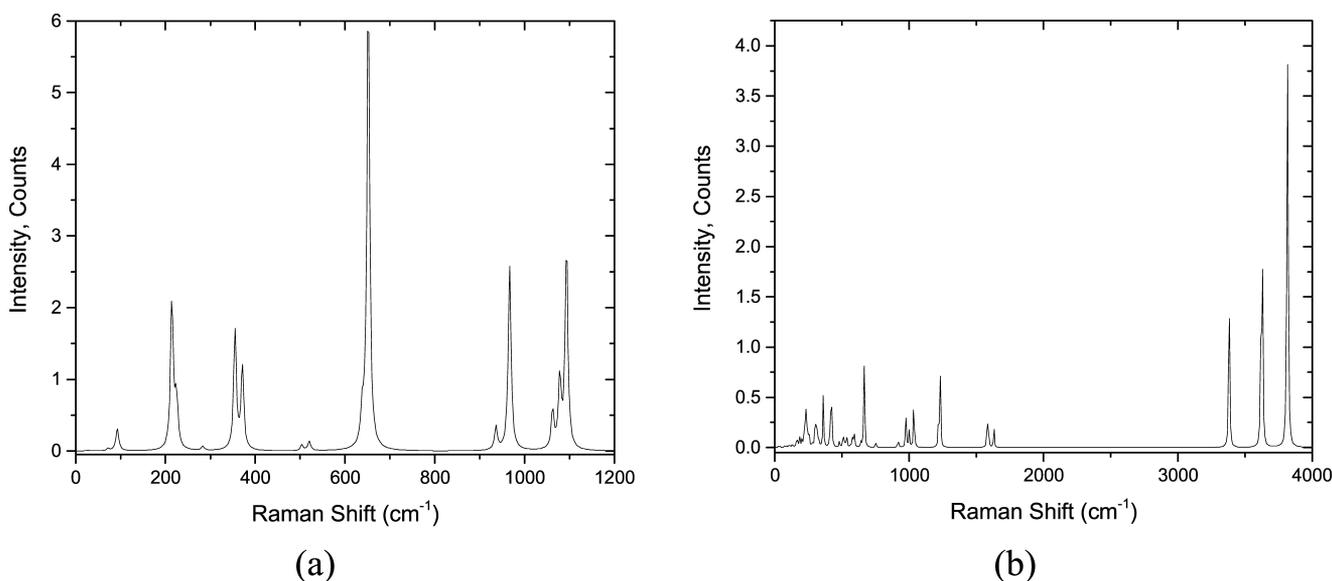


Figure 7. (a) Scaled Raman spectrum of $[\text{P}(\text{SO}_3)_2]^{3-}$ based on the HF/6-311+G** calculation. (b) Scaled Raman spectrum of $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ based on the HF/6-311+G** calculations. Gaussian band shapes of half-height at half-width of 4 cm^{-1} have been assumed.

Table 8. Vibrational Frequencies of $[\text{P}(\text{SO}_3)_2]^{3-}$ and $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ Derived by the HF/6-311+G Calculation (in cm^{-1})^a**

$[\text{P}(\text{SO}_3)_2]^{3-}$		$\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$		assignments
calculated frequencies	scaled frequencies	calculated frequencies	scaled frequencies	
704	638	708	641	asym. stretch (S–P)
719	651	734	665	sym. stretch (S–P)
1033	936	1012	917	sym. stretch (S–O)
1067	967	1076	975	sym. stretch (S–O)
1173	1063	1103	999	asym. stretch (S–O)
1190	1078	1142	1035	asym. stretch (S–O)
1207	1093	1344	1218	asym. stretch (S–O)

^aAlso included are the scaled frequencies.

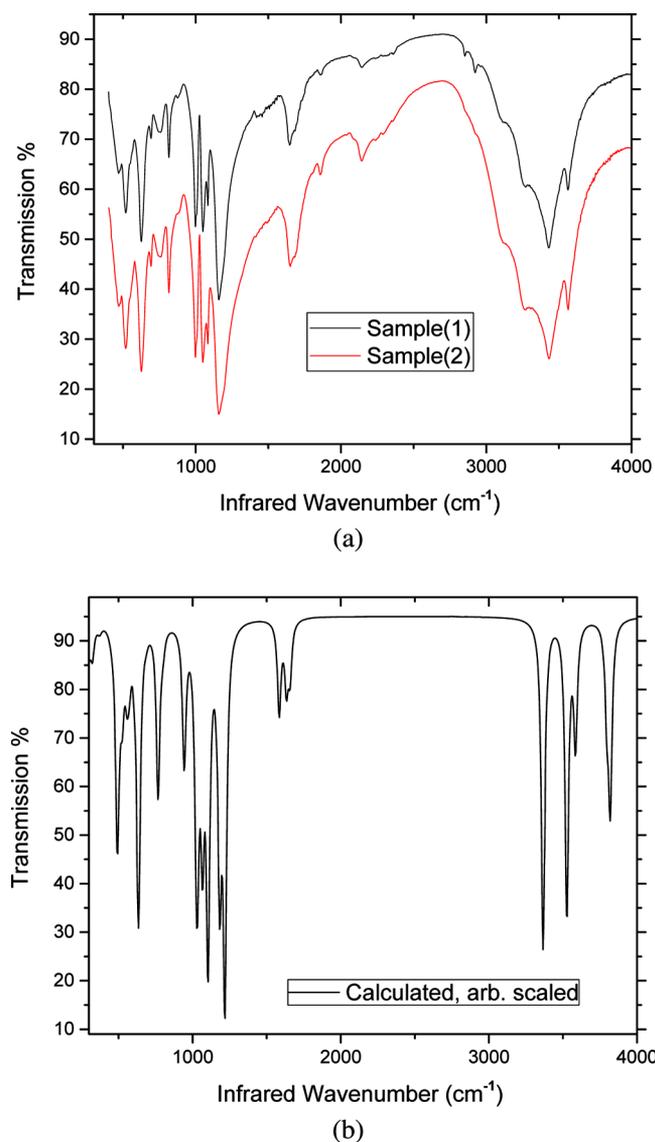


Figure 8. (a) IR absorption spectra of two different KBr disks containing $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, at room temperature. (b) Absorption spectrum calculated based on the HF/6-311+G** results and using a Gaussian profile of half-width at half-height of 16 cm^{-1} . The y axis values are obtained by calculating the percentage of the epsilon absorption values, followed by conversion to percent transmission.

4. MATERIALS AND METHODS

4.1. Experimental Methods. The $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ crystals were received directly from the Enstedvaerk power plant, Denmark. The Raman spectra of $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ were obtained using a DILOR XY 800 mm focal length multichannel spectrometer with microentrance, laser excitation (532.15 and 514.5 nm, 400 mW) and cooled CCD detection. Filtration of Rayleigh scattering was done with notch filters, and calibration was done with argon lines and Raman lines of cyclohexane.²⁵ Slits were set to $500\text{ }\mu\text{m}$ corresponding to a spectral resolution of approximately 6 cm^{-1} . The spectra were obtained by recording 12 frames in 120 s, two times.

The spectra were not corrected for the small changes in the instrument response versus wavenumber.

IR absorption spectra were obtained from microcrystalline samples dispersed in KBr on a PerkinElmer 1720 Fourier transform instrument with a liquid-nitrogen-cooled Ge-diode detector. The crystals were intensively mixed with KBr by grinding in agate mortar and pressing the resulting powder into disks under vacuum. The spectra were recorded in transmission mode at $25\text{ }^\circ\text{C}$ against a similar empty reference disk. The spectral resolution was around 4 cm^{-1} .

4.2. Computational Methods. All of the molecules studied were initially built using SPARTAN'14.¹⁹ For all of the calculations, Gaussian'09 was used.²¹ To obtain adequate convergence, the optimization criteria in all calculations performed were chosen as tight, that is, with the maximum force less than 0.000015 au and the maximum displacement less than 0.000060 au . The geometries of $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ and $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ were optimized using restricted MP2/6-311+G** calculations with the frozen core approximation. The molecular geometries of $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$ were optimized imposing both C_2 and C_{2v} point group symmetries. To ensure that the optimized energies are local minima on the potential energy surfaces, the vibrational frequencies were derived by diagonalization of the Hessian matrix. The optimized structures of all investigated compounds were identified as true minima because the Hessian matrices revealed only positive eigenvalues. Furthermore, the Raman spectra of $[\text{N}(\text{SO}_3)_2]^{3-}$ and $[\text{P}(\text{SO}_3)_2]^{3-}$ as well as of $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ and $\text{CaNa}[\text{P}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$ were calculated from the optimized structures determined using HF/6-311+G** calculations. The resulting frequencies were scaled by the empirical factor of 0.9059.²² For $\text{CaNa}[\text{N}(\text{SO}_3)_2]\cdot 3\text{H}_2\text{O}$, compared to that from the experimental data, the scaling consisted in multiplication of the intensity values in $\text{\AA}^4/\text{AMU}$ by 20 000, shifting by +20 000, and putting on a guessed Gaussian profile of half-width at half-height of 16 cm^{-1} . For

$[P(SO_3)_2]^{3-}$ and $CaNa[P(SO_3)_2] \cdot 3H_2O$ bands, half-height at half-width of 4 cm^{-1} has been assumed.

The electrostatic charges on the atoms are defined as the partial charges associated with each atom giving rise to an electrostatic potential map that is identical within a chosen threshold to that derived from the wave functions. Such electrostatic charges have been derived for all of the compounds investigated using SPARTAN'14.¹⁹

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Notes

The authors declare no competing financial interest.

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