DOI: 10.1002/chem.201000102

Synthesis and Characterization of Tetramethylammonium Trifluorosulfate

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Abstract: $[Me_4N]^+[SO_2F_3]^-$, the first example of a $[SO_2F_3]^-$ salt, has been prepared from Me_4NF and SO_2F_2. The colorless, microcrystalline solid was characterized by its infrared and Raman spectra. The trigonal bipyramidal structure of C_{2v} symmetry of the $[SO_2F_3]^-$ anion is predicted by ab initio calculations. Two oxygen atoms with $d(\mathrm{SO}) = 143.2$ pm and one fluorine atom with $d(\mathrm{SF}) = 157.9$ pm occupy the equatorial plane. The two fluorine atoms in the axial position with $d(\mathrm{SF}) = 168.5$ pm are repulsed by the two oxygen atoms forming a bent axis with $\measuredangle(F_{ax}SF_{ax}) = 165.2°$.

Keywords: ab initio calculations · NMR spectroscopy · Raman spectroscopy · trifluorosulfate · vibrational spectroscopy

Introduction

In the family of formally fluorine-substituted sulfuric acid derivatives, fluorosulfuric acid and the corresponding salts are well known and are important basic chemicals in industrial processes.[1] Far less is known about other fluoro derivatives.

Pentafluorosulfuric acid was prepared by Seppelt in 1976. It is only stable kept in dry ice and decomposes with the formation of SOF_4 and HF.[2,3] Its cesium and trisdimethylaminosulfonium (TAS) salts are stable at room temperature. They are prepared by the reaction of CsF and TASF, respectively, with SOF_4 [Eq. (1)].[4–8]

$$X^+F^- + SOF_4 \rightarrow X^+SOF_5^- \quad (X = \mathrm{Cs, TAS}) \tag{1}$$

To the best of our knowledge, no evidence for the existence of trifluorosulfuric acid has been reported in the literature. The free trifluorosulfate ion has been observed in ion cyclotron resonance experiments.[9–11] Garber and Ault reported, in 1983, the isolation of a $Cs^+[SO_2F_3]^-$ ion pair by co-deposition of CsF vapor and SO_2F_2 in an argon matrix.[13] Their evidence for the formation of such an ion pair is weak, since only five infrared bands were observed, and their frequencies do not correspond well to those found in this study. There is no further mention in the literature of an isolated $[SO_2F_3]^-$ salt formed through fluoride ion addition to SO_2F_2.

The syntheses of several missing anions such as $[FCO_2]^-$, $[PF_4]^-$, $[ClF_6]^-$, $[POF_4]^-$, and $[SOF_3]^-$ have been achieved by using "naked" fluoride (Me_4NF) as the fluoride ion source.[14–19] Trends in the tendency to form yet unknown anionic species by fluoride addition can be predicted on the basis of F^- affinities available from ion cyclotron measurements or theoretical calculations.[10–12] Considering a simple thermochemical cycle, the uncertainty of such general predictions lies in the change of the lattice energy between the fluorinating salt and the resulting salt, which can be estimated only roughly.[20] If the F^- affinity is less than 40 kcal mol^{-1} the uncertainty of the latter term becomes dominant and the predictions are vague.

The fluoride affinity of SO_2F_2 in the gas phase (35.8 kcal mol^{-1})[10] is comparatively small and, therefore, it was of interest to us to see whether $[SO_2F_3]^-$ salts could be prepared using "naked" fluoride.

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Results and Discussion

Synthesis of $[Me_4N]^+[SO_2F_3]^-$: The trifluorosulfate salt is formed slowly by treating an excess of SO_2F_2 with Me_4NF and acetonitrile as the solvent at room temperature according to Equation (2). The presence of acetonitrile as the solvent is important, since attempts to complete the reaction without acetonitrile resulted in very low yields below 10%. Furthermore, the use of an ultrasonic bath shortened the reaction time to a few hours. Without an ultrasonic bath the reaction is not complete within 24 h and then the formation of byproducts from the reaction between acetonitrile and Me_4NF is observable. Attempts to prepare the cesium salt from CsF under similar conditions have shown that within 2 days no significant reaction was observed.

$$[Me_4N]^+F^- + SO_2F_2 \rightarrow [Me_4N]^+[SO_2F_3]^- \qquad (2)$$

The $[SO_2F_3]^-$ salt is a colorless microcrystalline solid, which rapidly hydrolyzes on contact with moisture according to Equation (3). An excess of water does not lead to further hydrolysis.

$$\begin{aligned}&3[Me_4N]^+ \cdot [SO_2F_3]^- + H_2O \rightarrow \\ &[Me_4N]^+[SO_3F]^- + 2[Me_4N]^+HF_2^- + 2\,SO_2F_2\end{aligned} \qquad (3)$$

The trifluorosulfate salt is insoluble in nonpolar solvents and slightly soluble in polar solvents such as acetonitrile. In acetonitrile solutions slow decomposition of the $[SO_2F_3]^-$ anion was observed. Attempts to obtain single crystals for X-ray diffraction were not successful due to the absence of a suitable solvent.

Scheme 1 shows a summary of the simplest sulfur oxides, oxofluorides and fluorides, and their fluoride affinities in the gas phase. Sulfur hexafluoride has not been considered for further discussion, since it does not form an $[SF_7]^-$ ion in the gas phase. Sulfur monoxide and sulfur difluoride are both unstable molecules and no successful synthesis of the corresponding fluoride anions is reported in literature. Among the sulfur(IV) and sulfur(VI) compounds in Scheme 1, SO_2F_2 and SOF_2 have the lowest fluoride affinities and do not react with alkali metal fluorides, whereas the other molecules form the corresponding anions. For SOF_2, radiotracer experiments have ruled out a reaction with CsF and in the case of SO_2F_2 our experiments show no reaction with CsF.[21] Therefore, the synthesis of the $[SO_2F_3]^-$ anion can be counted as another example of missing anions that can be prepared by using Me_4NF.

$SO \xrightarrow{?} SOF^-$	$SF_2 \xrightarrow{?} SF_3^-$		
$SO_2 \xrightarrow{44} SO_2F^-$	$SOF_2 \xrightarrow{37} SOF_3^-$	$SF_4 \xrightarrow{44} SF_5^-$	
$SO_3 \xrightarrow{78} SO_3F^-$	$SO_2F_2 \xrightarrow{36} SO_2F_3^-$	$SOF_4 \xrightarrow{58} SOF_5^-$	$SF_6 \xrightarrow{<0} SF_7^-$

Scheme 1. Fluoride affinities [kcal mol^{-1}] of sulfur fluorides, oxides, and oxofluorides; data from ref. [10].

^{19}F NMR spectra: The ^{19}F NMR spectrum of a freshly prepared sample of $[Me_4N]^+\cdot[SO_2F_3]^-$ in acetonitrile at room temperature shows a broad singlet at $\delta = 79$ ppm and in addition a small doublet at $\delta = -148.5$ ppm ($J = 120$ Hz) and a singlet at $\delta = 46$ ppm. The latter two resonances are attributable to HF_2^- ($\delta = -145$ to -148 ppm, J(HF) = 121 Hz for $[Me_4N]^+HF_2^-$ in acetonitrile)[22,23] and $[SO_3F]^-$ ($\delta = 43$ ppm).[24] Both anions have arisen from the hydrolysis of the $[SO_2F_3]^-$ anion during synthesis or sample preparation. The HF_2^- anion is also formed by a slow reaction of acetonitrile with the fluoride ion.[22] The broad singlet at $\delta = 79$ ppm was assigned to the $[SO_2F_3]^-$ anion. The expected fine structure for a rigid pentacoordinated anion comprising a doublet and a triplet for the axial and equatorial fluorine atoms, respectively, was not resolved. This indicates that the $[SO_2F_3]^-$ anion undergoes a fast inter- or intramolecular ligand exchange, as was observed in the case of the $[SOF_3]^-$ anion.[16] To suppress a possible intermolecular exchange, a sample with an excess (ca. 50%) of Me_4NF was measured, but no significant changes occurred for the singlet at $\delta = 79$ ppm. Also spectra measured above the melting point of acetonitrile (−40 °C) did not show the expected fine structure.

Vibrational spectra: The infrared and Raman spectra of $[Me_4N]^+\cdot[SO_2F_3]^-$ are shown in Figure 1, and the observed frequencies are summarized in Table 1. The assignments for the Me_4N^+ cation were made according to well-known literature data.[23,25] The assignments for the $[SO_2F_3]^-$ were made by comparison with the isoelectronic compounds ClO_2F_3,

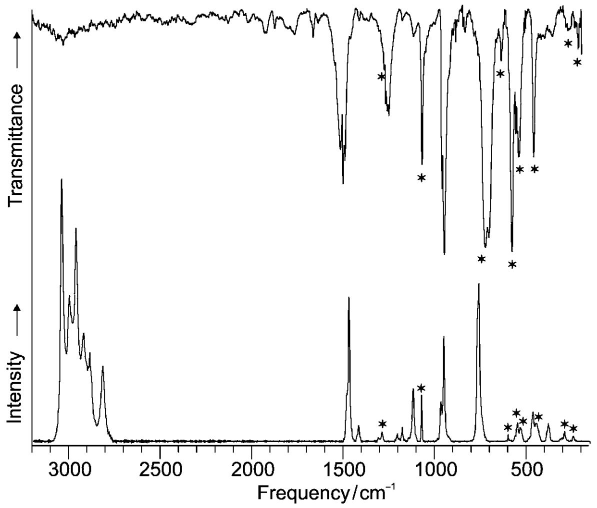

Figure 1. Infrared (top) and Raman spectra (bottom) of $[Me_4N]^+[SO_2F_3]^-$. Vibrations of the $[SO_2F_3]^-$ anion are marked with an asterisk (*).

Table 1. Vibrational frequencies [cm^{-1}] of tetramethylammonium trifluorosulfate.

IR	Raman	Assignment $[SO_2F_3]^-$	$[Me_4N]^+$
3030 (vw)	3045 (100)		$\nu(CH_3)$
	3004 (55)		
	2967 (21)		$\nu(CH_3)$
	2927 (8)		
	2883 (6)		
	2812 (11)		$2\delta_s(CH_3)$
1498 (m)			$\delta_{as}(CH_3)$
1488 (m)	1474 (14)		
	1420 (3)		$\delta_s(CH_3)$
1275 (m)	1289 (2)	$\nu_{as}(SO_2)$	
1255 (m)			$\delta_{rocking}$ (CH_3)
	1174 (3)		$\delta_{rocking}(CH_3)$
1118 (vw)	1123 (9)		
1072 (s)	1076 (6)	$\nu_s(SO_2)$	
969 (s)	970 (4)		$\nu_{as}(C_4N)$
953 (vs)	954 (10)		
752 (vs)	767 (15)	$\nu(SF_{eq})$	$\nu_s(C_4N)$
742 (vs)			$\nu_s(C_4N)$
644 (m)		$\nu_{as}(SF_{ax2})$	
582 (vs)	599 (2)	$\delta_{wag}(F_{eq}SO_2)$	
547 (s)	551 (3)	$\nu_s(SF_{ax2})$	
531 (m)	528 (2)	$\delta(SO_2/SF_{ax2})$	
463 (s)	466 (3)		$\delta_{as}(C_4N)$
	452 (2)	$\delta_{twist}(SO_2/SF_{ax2})$	
375 (w)	384 (3)		$\delta_s(C_4N)$
283 (w)	294 (2)	$\delta(SO_2/SF_{ax2})$	
230 (w)	247 (6)	$\delta_{wag}(F_{ax}SF_{ax})$	

SOF_4, and POF_4^- (Figure 2) and ab initio calculated frequencies listed in Table 2.[18,26,27] An ab initio investigation, which is discussed later, gives the expected structure of symmetry C_{2v}, in accordance with the isoelectronic ClO_2F_3 molecule. Consequently, 12 fundamentals ($5A_1+A_2+3B_1+3B_2$) that should all be active in the Raman spectrum are expected for $[SO_2F_3]^-$. All fundamentals, with exception of species A_2, should be active in the infrared spectrum.

The sulfur–oxygen stretching modes of the $[SO_2F_3]^-$ anion are observed at 1282 and 1074 cm^{-1} in a region typical for S=O double and single bonds, respectively. The three sulfur–fluorine stretching modes occur in the region above 500 cm^{-1}. In accordance with a trigonal bipyramidal arrangement of the ligands, the $\nu(SF_{eq})$ is observed at 760 cm^{-1}, whereas the S−F_{ax} stretching modes appear at lower frequencies (644 and 549 cm^{-1}). These differences reflect the different bonding situations of the axial and equatorial fluorine ligands. The same trend is observed in the case of isolelectronic molecules and ions.

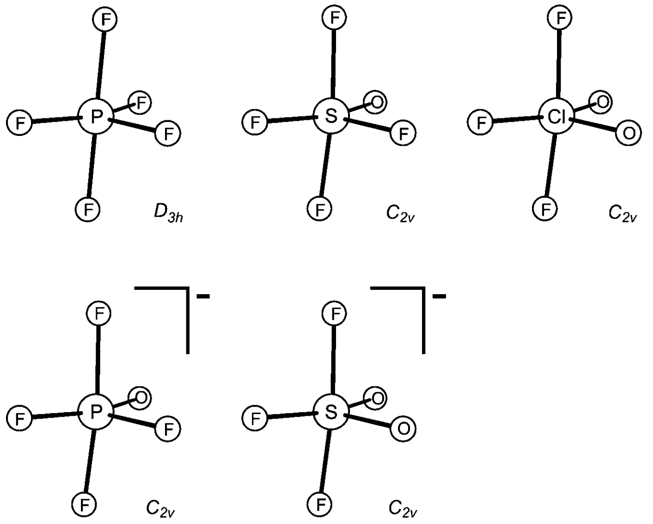

Figure 2. Trifluorosulfate and its isoelectronic ions and molecules.

The seven deformation modes occur below 600 cm^{-1}. The mode descriptions, listed in Table 2, were made by inspection of the calculated displacement coordinates. In most cases the physical meaning of the deformation mode is best described as a mixing of symmetry coordinates.

The frequencies for a $Cs^+[SO_2F_3]^-$ ion pair found by Garber and Ault in matrices of CsF co-deposited with SO_2F_2 do not correspond well to those found in this study. Similar discrepancies were noted by us between $Me_4N^+SOF_3^-$ and a reported $Cs^+SOF_3^-$ ion pair isolated in an argon matrix.[16] Another example is given by Christe et al. who found large

Table 2. Comparison of observed and calculated frequencies [cm^{-1}] of $[SO_2F_3]^-$ with isoelectronic molecules and ions.

obs.[a]	$[SO_2F_3]^-$ calcd[b]	matrix[c]	ClO_2F_3 exptl[d]	Assignment XO_2F_3[e]		SOF_4 exptl[f]	$[POF_4]^-$ calcd[g]	Assignment XOF_4	
1282 (m/2)	1281 (463/1.93)	1408	1327	ν_{10} (B_2)	$\nu_{as}(XO_2)$	924	833	ν_{10} (B_2)	$\nu_{as}(XF_{eq2})$
1074 (s/6)	1073 (231/13.9)	1130	1093	ν_1 (A_1)	$\nu_s(XO_2)$	1380	1267	ν_1 (A_1)	$\nu(XO)$
760 (vs/15)	776 (179/13.3)	810	683	ν_2 (A_1)	$\nu(XF_{eq})$	796	741	ν_2 (A_1)	$\nu_s(XF_{eq2})$
644 (m/–)	637 (520/0.03)	925	695	ν_7 (B_1)	$\nu_{as}(XF_{ax2})$	819	708	ν_7 (B_1)	$\nu_{as}(XF_{ax})$
591 (vs/2)	582 (348/0.60)		592	ν_8 (B_1)	$\delta_{wag}(F_{eq}XO_2)$	639	570	ν_8 (B_1)	$\delta_{wag}(F_{eq}XO_2)$
549 (s/3)	541 (26.0/3.28)		520	ν_3 (A_1)	$\nu_s(XF_{ax2})$	593	481	ν_3 (A_1)	$\nu_s(XF_{ax2})$
–	536 (45.7/1.69)		531	ν_{11} (B_2)	$\delta(XF_3)$	558	514	ν_{11} (B_2)	$\delta(XF_{ax2}/XF_{eq2})$
529 (m/2)	514 (0/1.85)	649	487	ν_4 (A_1)	$\delta(XO_2/XF_{ax2})$	565	521	ν_4 (A_1)	$\delta(XF_{eq2}/XF_{ax2})$
–	505 (6.43/0.92)		372	ν_9 (B_1)	δ_{as} $(F_{eq}XF_{ax})$	566	484	ν_9 (B_1)	$\delta_{wag}(OXF_{eq2})$
452 (–/2)	460 (1.44/4.97)		402	ν_6 (A_2)	$\delta_{twist}(XO_2/XF_{ax2})$	566	493	ν_6 (A_2)	τ
289 (w/2)	281 (0.19/0.82)		287	ν_5 (A_1)	$\delta(XO_2/XF_{ax2})$	174	169	ν_5 (A_1)	$\delta(XF_{eq2}/XF_{ax2})$
239 (w/6)	233 (0.05/0.36)		222	ν_{12} (B_2)	$\delta_{wag}(F_{ax}XF_{ax})$	270	245	ν_{12} (B_2)	$\delta(XF_{eq2}/XF_{ax2})$

[a] Average values from infrared and Raman spectra; relative infrared and Raman intensities in brackets. [b] RHF/6-31+G*; frequencies scaled by an empirical factor of 0.9. Infrared intensities are reported in $km\,mol^{-1}$ and Raman activities in $Å^4/\mu$ in brackets. [c] From ref. [13]. [d] From ref. [26]. [e] X=S, Cl, or S, P, respectively. [f] From ref. [27]. [g] From ref. [18].

discrepancies between $Me_4N^+PF_4^-$ and a reported $Cs^+PF_4^-$ ion pair isolated in an argon matrix.[15,28] The differences between the frequencies for these three examples of ion pairs isolated in matrices and the calculated gas-phase frequencies cannot be explained in terms of regular matrix effects only. It seems more likely that the structures of the anions in the ion pairs are strongly affected by the adjacent cation. Also covalent bonding between cations and anions might exist in the alleged ion pairs, as it is known for alkali metal halides trapped in matrices.[29] Notably, in case of $Cs^+SO_2F^-$ isolated in argon matrices by the same technique as described above such discrepancies do not exist. The frequencies of the matrix-isolated ion pair agree well with calculated gas-phase frequencies, as well as experimental data.[13,20] Finally, more thorough matrix experiments together with theoretical calculations are required to get a deeper insight into the nature of these ion pairs.

Ab initio calculations: The ab initio RHF/6-31+G* calculated harmonic frequencies for the $[SO_2F_3]^-$ anion are given in Table 2 and compared with the observed frequencies. We find reasonable agreement for all vibrational modes. The calculated geometry for $[SO_2F_3]^-$ is shown in Figure 3 and listed together with literature data for the isoelectronic SOF_4, POF_4^-, and PF_5 in Table 3.[18,30,31]

The energy minimum is found for a trigonal bipyramidal arrangement of C_{2v} symmetry. The oxygen atoms in the equatorial positions cause a bending of the F_{ax}-S-F_{ax} axis (165.2°) and a compression of the F_{eq}-S-O angle (115.4°) from the ideal value of 120°. The S–O bond length of 143.2 pm is in the range of regular sulfur–oxygen double bonds in similar anions, such as SO_2F^- (calcd: 145.8 pm; exptl: 147.8(1) pm)[20,32], SOF_3^- (calcd: 143.3 pm)[16], and SO_3F^- (exptl: 142.4(4)–145.5 pm)[33], and as expected longer than in SO_2F_2 (138.6(2) pm), because the negative charge increases the ionic character of the bond.[34]

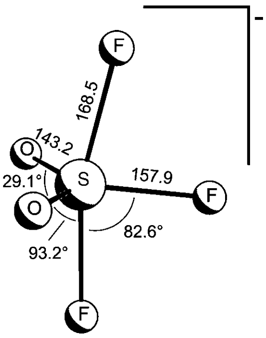

Figure 3. Calculated (RHF/6-31+G*) structure of the $[SO_2F_3]^-$ anion; bond lengths in pm.

Table 3. Geometry of $[SO_2F_3]^-$ (calcd) compared to those of isoelectronic ions and molecules.

	$[SO_2F_3]^-$ calcd[b]	SOF_4 exptl[c]	PF_5 exptl[d]
$r(X{-}F_{ax})$[a] [pm]	168.5	159.6	157.7
$r(X{-}F_{eq})$ [pm]	157.9	153.9	153.4
$r(X{-}O)$ [pm]	143.2	140.9	–
∡(F_{ax}-X-F_{ax}) [°]	165.2	164.6	180
∡(O-X-F_{eq}) [°]	115.4	123.6	–
∡(O-X-O) [°]	129.1	–	–
∡(F_{eq}-X-F_{eq}) [°]	–	112.8	120
∡(F_{ax}-X-F_{eq}) [°]	82.6		90
∡(F_{ax}-X-O) [°]	93.2	97.7	–

[a] X = S, P. [b] RHF/6-31+G*. [c] From ref. [30]. [d] From ref. [31].

The calculated S–F bonds of 168.5 and 157.9 are both longer than in SO_2F_2 (151.4(2) pm)[34] and reveal the different kinds of bonds in the trigonal bipyramidal ion, which can be rationalized in terms of semi-ionic three-center four-electron bonding for the axial fluorine ligands and a mainly covalent S–F_{eq} bond. The difference in S–F bond lengths of 10.6 pm is comparable to molecules, such as SF_4, where differences between S–F_{eq} and S–F_{ax} of 10.1 pm have been observed.[35] Comparing molecules and isoelectronic molecules, the formal negative charges in anions clearly enhance the formation of semi-ionic, three-center four-electron bonds, thereby causing their unusual lengths.

Conclusion

The first example of a $[SO_2F_3]^-$ salt has been prepared from Me_4NF and SO_2F_2 The successful synthesis of the $[SO_2F_3]^-$ anion can be ascribed to the high reactivity of "naked fluoride", since alkali metal fluorides do not react with SO_2F_2. The vibrational spectra agree well with ab initio calculations, which predict a trigonal bipyramidal structure of C_{2v} symmetry.

Experimental Section

Apparatus and materials: All synthetic work and sample handling were performed employing standard Schlenk techniques and a standard vacuum line. Me_4NF was prepared by the literature method.[23] The preparation and purification of SO_2F_2 from SO_2Cl_2 and NaF is described elsewhere.[36] **Caution**: SO_2F_2 is an odorless, poisonous gas.

The infrared spectra were recorded on a Bruker ifs 113v spectrophotometer. Spectra of dry powders were obtained by using a CsBr plate coated with the neat sample. The Raman spectra were recorded with an ISA T64000 spectrometer using an argon ion laser at 514.5 nm from Spectra Physics. The ^{19}F NMR spectra were recorded with a Bruker DPX 300 spectrometer. The spectra were referenced to external samples of neat $CFCl_3$. The IUPAC chemical shift convention was used.

Synthesis of $[Me_4N]^+[SO_2F_3]^-$: A sample of dry Me_4NF (210 mg, 2.26 mmol) was placed into a dried 5 mL quartz ampoule, and SO_2F_2 (2.04 g, 20 mmol)and acetonitrile (2 mL) were condensed in at −196 °C. The sealed ampoule was warmed to room temperature. The reaction proceeds in a few hours in an ultrasonic bath. The excess of SO_2F_2 and the acetonitrile were pumped off first at dry ice temperature and then at room temperature. The weight (430 mg; calcd: 441 mg for quantitative yield) of the colorless solid indicated almost quantitative yield of $[Me_4N]^+$ $[SO_2F_3]^-$. Further characterization of the obtained compound was carried out by vibrational and ^{19}F NMR spectroscopy. The trifluorosulfate salt is extremely sensitive to moisture. The salt decomposes at about 90 °C with the formation of sulfuryl fluoride, trimethylamine, methylfluoride, and traces of other unidentified products.

Computational methods: The ab initio calculations for $[SO_2F_3]^-$ were performed at the restricted Hartree–Fock level of theory using the Gaussian 94 program.[37] All calculations were carried out at the 6-31+G* basis level, which augments the standard double-ζ plus polarization treatment (6-31G*) with a diffuse set of s,p functions (+) on each heavy atom and is known to describe anionic systems in an appropriate way. Harmonic vibrational frequencies were computed for the minimum-energy structure and scaled by the empirical factor 0.90 to maximize their fit with the experimentally observed frequencies.[38,39]

Acknowledgements

This work has been supported by the Deutsche Forschungsgemeinschaft.

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Received: January 15, 2010
Revised: August 10, 2010