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Trifluoromethanesulfonato Complexes of Nickel and Cobalt

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Nickel(II) and cobalt(II) compounds of general formula $[ML_4(CF_3SO_3)_2]$ *are reported (L = pyridine, 3-methylpyridine, 4-methylpyridine, 3,5-lutidine, 4-ethylpyridine, and 4-isopropylpyridine). Infrared and electronic spectra and magnetic susceptibility measurements indicate that all are high-spin six coordinate complexes. Upon evaluation of crystal field paramaters, Ds and Dt, it was found that the trifluoromethanesulfonate anion coordinates more strongly than perchlorate and tetrafluoroborate, but less strongly than perrhenate, chloride, and bromide.*

1. Introduction

The coordinating properties of anions of strong acids have been the subject of several studies. In particular, the anions of perchloric, tetrafluoroboric, hexafluorophosphoric, and fluorosulfonic acid have generated much interest. A review of the coordinating tendencies of anions of strong acids has been presented by Rosenthal [1].

Although trifluoromethanesulfonic acid has been shown by conductivity measurements [2] to be comparable in strength to perchloric acid in the solvent acetic acid, the ligational properties of the trifluoromethanesulfonate anion have received little attention. Yeats [3, 4] and coworkers have prepared tin (IV) compounds containing covalently bound trifluoromethanesulfonate. These workers indicated, on the basis of infrared spectroscopy, that the CF_3SO_3 group is acting as a bidentate ligand with coordination through the oxygens. Schmeisser [5] has described the preparation of a number of heavy metal complexes. The complexing tendency of CF_3SO_3 group toward chromium(III) has been investigated by Scott [6]. Based on aquation rates of the 1:1 complexes, the trifluoromethanesulfonate anion was found to be more nucleophilic than the perchlorate ion toward chromium(III). This paper describes the preparation and characterization of some cobalt(II) and nickel(II) complexes containing the coordinated CF_3SO_3 group.

Experimental

Reagents

The nickel and cobalt trifluoromethanesulfonates were prepared in the same manner. A slurry of the metal carbonate (Baker) was treated with trifluoromethanesulfonic acid (Willow Brook) until the reaction ceased. The solution was evaporated on a hot plate until crystals began to form. The solution was then cooled in an ice bath, and the metal trifluoromethanesulfonate collected by filtration. The hydrated salts were dried in an oven between 60–70 °C for several days. Pyridine (Baker Analyzed) was used as received. 3-methylpyridine (3-mepy) and 4-methylpyridine (4-mepy) were obtained from Eastman Organic Chemical Corporation. Reilly Tar and Chemical Corporation was the source of the 3,5-lutidine (3,5-lut), 4-ethylpyridine (4-etpy), and 4-isopropylpyridine (4-ippy). The 3,5-lutidine (b.p. 172 °C), 3-methylpyridine (b.p. 144 °C) and 4-methylpyridine (b.p. 145 °C) were distilled once from barium oxide. The 4-ethylpyridine (b.p. 168 °C) and 4-isopropylpyridine (b.p. 182 °C) were distilled from KOH pellets. Practical grade 2,2-dimethoxypropane and ligroine (Eastman), methanol and diethyl ether (Fisher) and benzene (Baker) were used as received.

Synthesis

The trifluoromethanesulfonate coordination compounds were prepared by dissolving the hydrated metal trifluoromethanesulfonates in a suitable solvent, dehydrating the solution with 2,2-dimethoxypropane [7] and adding a slight excess of the pyridine base. In most cases the solutions were kept at room temperature or below before filtration. All of the compounds were observed to be stable in air and showed no decomposition upon storage at 60 °C. None of the compounds showed a definite melting point, decomposing over a 20–30 °C range above 170 °C.

Bistrifluoromethanesulfonatotetrapyridinecobalt(II)

To approximately 2.3 grams (5×10^{-3} mol) of the hydrated $Co(CF_3SO_3)_2$ was added 20 ml of 2,2-

dimethoxypropane In another beaker, approximately 2.0 grams (2 5 X 10^{-2} mol) of pyridine was added to 20 ml of 2,2-dimethoxypropane The solutions were stirred for about one hour and combined slowly A pink solid formed immediately and the slurry was stirred for about two hours The solid was collected by suction filtration, washed with ether, and bottled wet The material was dried at 78 ℃ and at reduced pressure over $CaSO_4$ for several hours *Anal* Calcd for $[Co(C_5H_5N)_4(CF_3SO_3)_2]$ 39 25% C, 2 99% H, 8 32% N Found 38 21% C, 3 10% H, 8 26% N

Bistrifluoromethanesulfonatotetrakis(3-methylpyridine)cobalt(II)

To 20 ml of 2,2-dimethoxypropane was added approximately 2 3 grams (5 X 10^{-3} mol) of the hydrated $Co(CF_3SO_3)_2$ This solution was stirred for about one hour A second solution containing approximately 2 3 grams (2 5 X 10^{-2} mol) of 3-methylpyridine in 20 ml of 2,2-dimethoxypropane was added dropwise to the $Co(CF_3SO_3)_2$ solution A pink solid formed immediately The slurry was stirred for two hours and the solid was collected by suction filtration The material was washed with ether and bottled wet The solid was dried at 78 ℃ at low pressure over $CaSO_4$ for several hours *Anal* Calcd for $[Co(C_6H_7N)_4(CF_3SO_3)_2]$ 42 82% C, 3 87% H, 7 68% N Found 41 92% C, 4 13% H, 7 57% N

Bistrifluoromethanesulfonatotetrakis(4-methylpyridine)cobalt(II)

Approximately 2 3 grams (5 X 10^{-3} mol) of the hydrated $Co(CF_3SO_3)_2$ was added to 20 ml of 2,2-dimethoxypropane and stirred for about one hour To another 20 ml portion of 2,2-dimethoxypropane was added approximately 2 3 grams (2 5 X 10^{-2} mol) of 4-methylpyridine The solution was stirred for about one hour then combined with the $Co(CF_3SO_3)_2$ solution A pink solid formed in a few minutes and the resultant slurry was stirred for two hours The solid was collected by suction filtration, washed with 2,2-dimethoxypropane, and bottled wet The material was dried at 78 ℃ at reduced pressure over $CaSO_4$ *Anal* Calcd for $[Co(C_6H_7N)_4(CF_3SO_3)_2]$ 42 82% C, 3 87% H, 7 68% N Found 41 66% C, 3 87% H, 7 68% N

Bistrifluoromethanesulfonatotetrakis(3,5-lutidine) cobalt(II)

To 5 ml of methanol and 20 ml of 2,2-dimethoxypropane was added approximately 2 3 grams (5 X 10^{-3} mol) of hydrated $Co(CF_3SO_3)_2$ The solution was stirred for one hour and a second solution containing approximately 2 7 grams (2 5 X 10^{-2} mol) of 3,5-lutidine in 20 ml of 2,2-dimethoxypropane was added dropwise The resulting deep red solution was stirred for about two hours and cooled in an ice bath Dropwise addition of ether resulted in the formation of a viscous red oil Ten milliliters of benzene was added to the oil and upon adding ligroine, a pink solid was formed The solid was collected by suction filtration and washed with several small portions of ligroine The material was bottled wet and dried at 78 ℃ at reduced pressure over $CaSO_4$ *Anal* Calcd for $[Co(C_7H_9N)_4(CF_3SO_3)_2]$ 45 88% C, 4 62% H, 7 13% N Found 45 05% C, 4 62% H, 6 68% N

Bistrifluoromethanesulfonatotetrakis(4-ethylpyridine)cobalt(II)

Approximately 2 3 grams (5 X 10^{-3} mol) of the hydrated $Co(CF_3SO_3)_2$ was added to 20 ml of 2,2-dimethoxypropane and stirred for about one hour A solution containing approximately 2 7 grams (2 5 X 10^{-2} mol) of 4-ethylpyridine in 20 ml of 2,2-dimethoxypropane was added dropwise to the $Co(CF_3SO_3)_2$ solution A pink solid formed as the solution was cooled in an ice bath The slurry was stirred for another hour and the solid isolated by suction filtration The solid was washed with ether and bottled wet The material was dried over $CaSO_4$ at 78 ℃ at reduced pressure for several hours *Anal* Calcd for $[Co(C_7H_9N)_4(CF_3SO_3)_2]$ 45 88% C, 4 62% H, 7 13% N Found 45 79% C, 4 66% H, 7 13% N

Bistrifluoromethanesulfonatotetrapyridinenickel(II)

Approximately 2 3 grams (5 X 10^{-3} mol of the hydrated $Ni(CF_3SO_3)_2$ was added to 20 ml of 2,2-dimethoxypropane The solution was stirred with a magnetic stirrer for one hour A solution containing approximately 2 0 grams (2 5 X 10^{-2} mol) of pyridine in 20 ml of 2,2-dimethoxypropane was added dropwise to the nickel solution The solution turned a deep blue and upon cooling in an ice bath a blue solid formed The slurry was stirred for another two hours maintaining the temperature near 0 ℃ The solid was collected by suction filtration, washed with ether and bottled wet The sample was then dried at 78 ℃ at reduced pressure over $CaSO_4$ for several hours *Anal* Calcd for $[Ni(C_5H_5N)_4(CF_3SO_3)_2]$ 39 25% C, 2 99% H, 8 32% N Found 38 58% C, 3 18% H, 8 23% N

Bistrifluoromethanesulfonatotetrakis(3-methylpyridine)nickel(II)

To 20 ml of 2,2-dimethoxypropane was added approximately 2 3 grams (5 X 10^{-3} mol) of hydrated $Ni(CF_3SO_3)_2$ The solution was stirred about one hour and combined with a solution containing approximately 2 3 grams (2 5 X 10^{-2} mol) of 3-methylpyridine in 2,2-dimethoxypropane A deep blue solution formed which gave a blue solid upon cooling in an ice bath The solid was collected by suction filtration, washed with ether, and bottled wet The material was dried at 78 ℃ at reduced pressure over $CaSO_4$ *Anal* Calcd for $[Ni(C_6H_7N)_4(CF_3$-

TABLE I. Magnetic Susceptibilities.

Compound	$\chi_m \times 10^6$	Molar Diamagnetic Correction $\times 10^6$	$\chi_m^{corr} \times 10^6$	μ_{eff} BM
$[Co(py)_4(CF_3SO_3)_2]$	11,372	292	11,664	5.28
$[Co(3\text{-}mepy)_4(CF_3SO_3)_2]$	11,088	340	11,428	5.22
$[Co(4\text{-}mepy)_4(CF_3SO_3)_2]$	10,640	340	10,980	5.12
$[Co(3,5\text{-}lut)_4(CF_3SO_3)_2]$	11,438	387	11,825	5.31
$[Co(4\text{-}etpy)_4(CF_3SO_3)_2]$	10,510	387	10.897	5.10
$[Ni(py)_4(CF_3SO_3)_2]$	4,061	292	4,353	3.22
$[Ni(3\text{-}mepy)_4(CF_3SO_3)_2]$	4,207	340	4,547	3,29
$[Ni(4\text{-}mepy)_4(CF_3SO_3)_2]$	3,934	340	4,274	3.19
$[Ni(3,5\text{-}lut)_4(CF_3SO_3)_2]$	3,973	387	4.360	3.23
$[Ni(4\text{-}etpy)_4(CF_3SO_3)_2]$	4,261	387	4,648	3.33
$[Ni(4\text{-}ippy)_4(CF_3SO_3)_2]$	4,281	435	4,716	3.36

$SO_3)_2]$: 42.82% C; 3.87% H; 7.68% N. Found: 41.94% C; 4.06% H; 7.59% N.

Bistrifluoromethanesulfonatotetrakis(4-methylpyridine)nickel(II).

Approximately 2.3 grams (5×10^{-3} mol) of the hydrated $Ni(CF_3SO_3)_2$ was added to 20 ml of 2,2-dimethoxypropane and magnetically stirred for one hour. A solution containig 2.7 grams (approximately 2.5×10^{-2} mol) of 4-methylpyridine in 2,3-dimethoxypropane was added slowly to the nickel solution. A deep blue solution formed which yielded a blue solid upon cooling in an ice bath. The solid was collected by suction filtration, washed with ether, and bottled wet. The solid was dried at 78 °C at reduced pressure over $CaSO_4$. *Anal.* Calcd. for $[Ni(C_6H_7N)_4(CF_3SO_3)_2]$: 42.82% C; 3.87% H; 7.68% N. Found: 42.28% C; 3.83% H; 7.90% N.

Bistrifluoromethanesulfonatotetrakis(3,5-lutidine)nickel(II).

To 5 ml of methanol and 20 ml of 2,2-dimethoxypropane was added approximately 2.3 grams (5×10^{-3} mol) of the hydrated $Ni(CF_3SO_3)_2$. The solution was stirred for about one hour and a second solution containing approximately 2.7 grams (2.5×10^{-2} mol) of 3,5-lutidine in 2,2-dimethoxypropane was added slowly to the first. The resulting deep blue solution was stirred about two hours in an ice bath. Dropwise addition of ether caused a viscous blue oil to separate from the solution. The oil was dissolved in benzene and upon addition of ligroine to the solution, a blue solid was formed. The solid was collected by suction filtration, washed with several small portions of ligroine and bottled wet. The sample was dried over $CaSO_4$ at 78 °C at reduced pressure for several hours. *Anal.* Calcd. for $[Ni(C_7H_9N)_4(CF_3SO_3)_2]$: 45.88% C; 4.62% H; 7.13% N. Found: 45.16% C; 4.50% H; 6.91% N.

Bistrifluoromethanesulfonatotetrakis(4-ethylpyridine)nickel(II).

Approximately 2.3 grams (5×10^{-3} mol) of the hydrated $Ni(CF_3SO_3)_2$ was added to 20 ml of 2,2-dimethoxypropane. The solution was stirred for one hour. A second solution containing 2.7 grams (approximately 2.5×10^{-2} mol) of 4-ethylpyridine in 2,2-dimethoxypropane was added to the first solution. Upon cooling in an ice bath, a blue solid formed. The slurry was stirred about two hours and the solid collected by suction filtration. The sample was washed with ether and bottled wet. The solid was dried at 78 °C at reduced pressure over $CaSO_4$. *Anal.* Calcd. for $[Ni(C_7H_9N)_4(CF_3SO_3)_2]$: 45.88% C; 4.62% H; 7.13% N. Found: 46.10% C; 4.59% H; 7.15% N.

Physical Measurements

Infrared spectra were obtained on the solid samples as Nujol mulls. A Perkin–Elmer model 257 recording spectrophotometer utilizing sodium chloride plates was used in the 1650–900 cm^{-1} range. The 900–400 cm^{-1} spectra were obtained with a Perkin–Elmer model 337 spectrophotometer utilizing silver chloride plates. The spectra were calibrated using polystyrene film.

Magnetic susceptibilities of the compounds were measured using a Gouy balance, consisting of an electromagnet, power supply, and current regulator (Alpha Scientific Laboratories) and a semi-micro balance (Mettler). $HgCo(SCN)_4$ was used as a calibrant [8]. All measurements were made at 23 ± 2 °C. Spectra of the complexes in the visible and near-infrared region were obtained using a Cary model 171 recording spectrophotometer manufactured by the

TABLE II. Vibrational Frequencies (cm^{-1}) for CF_3SO_3 in $NaCF_3SO_3$ and $[Copy_4(CF_3SO_3)_2]$[a].

$NaCF_3SO_3$	Tentative Assignments (local symmetries, C_{3v})	$[Copy_4(CF_3SO_3)_2]$	Tentative Assignments (local symmetries: CF_3, C_{3v}; $O-SO_2$, C_s)
		1310	$A''\nu_{as}$ (S–O)
1280	E ν_{as} (SO_3)	1240	A' ν_s (S–O)
1230	A_1 ν_s (CF_3)	1230	A_1 ν_s (CF_3)
1168	E ν_{as} (CF_3)	1170	E ν_{as} (CF_3)
1035	A' ν_s (SO_3)	1040	A' ν_s (S–O)
770	A_1 δ_s (CF_3)	770	A_1 δ_s(CF_3)
585	E δ_{as} (SO_3)	590	A'' δ_{as} ($O-SO_2$)
		575	A' δ_s ($O-SO_2$)
515	E δ_{as} (CF_3)	515	E δ_{as} (CF_3)

[a] Symbols are: A, non-degenerate; E, doubly degenerate; s, symmetric; as, asymmetric; ν, stretch; δ, bending.

Applied Physics Corporation. The spectra were obtained as Nujol mulls placed on strips of filter paper. Filter paper saturated with Nujol was placed in the reference beam to help compensate for light scattering.

Results and Discussion

The results of the magnetic susceptibility measurements on the new compounds are summarized in Table I. The magnetic moments of the compounds are typical of cobalt(II) and nickel(II) in high-spin octahedral complexes [8].

The infrared spectral frequencies associated with the trifluoromethanesulfonate ion, $NaCF_3SO_3$, and those associated with a typical complex in which the ion is coordinated, $[Copy_4(CF_3SO_3)_2]$, are listed in Table II. Spectral features of the other complexes prepared in this study were identical to within our ability to assess them. The pyridine and substituted pyridine absorption bands were typical of previously reported coordination compounds containing these nitrogen bases [9–11].

The sulfonate unit of the trifluoromethanesulfonate ion can be considered as belonging to the C_{3v} point group [3]. If we consider the anion as $X\text{-}SO_3$ ($x = CF_3$), there are nine internal modes of vibration, three of which are degenerate. All six fundamental vibrations are active in the infrared. Upon coordination of the CF_3SO_3 group in which an oxygen is the donor atom, the CF_3 group can be considered to retain local C_{3v} symmetry while the $O-SO_2$ will be reduced to local C_s symmetry, giving rise to nine active fundamental modes of vibration.

Because of the extensive coupling of the SO_3 and CF_3 vibrations which have identical symmetries (A_1 and E), assignments for the $CF_3SO_3^-$ ion have been difficult and conflicting [13–16]. Our assignments in the stretching regions (Table II) differ from those of previous workers in that the two C–F stretching bands are assigned with the frequency of the mode of E symmetry at a lower value than the mode of A_1 symmetry. This reversal of assignments is necessary to account for the observed splitting of the band at 1280 cm^{-1} upon coordination of the CF_3SO_3 group indicating that its absorption must be associated with SO_3 group. It then follows that the 1230 cm^{-1} band must be of A_1 symmetry (ν_sCF_3) and the 1168 cm^{-1} band of E symmetry ($\nu_{as}CF_3$) to be consistent with the Raman polarization and intensity observations of Tobias [13]. The assignment of the A_1 mode at an energy greater than the E mode for CF_3 stretching is not unique to this study [17].

The expected splitting of a band in the deformation region of the spectrum upon coordination is observed with the 585 cm^{-1} band. Thus, based on these observations, it is concluded that the CF_3SO_3 group is coordinated in all of the complexes with one oxygen atom acting as the donor.

The visible and near infrared spectra of the nickel complexes and the cobalt complexes are given in Table III. The assignments are consistent with those in the literature for $[NiL_4X_2]$ type compounds and cobalt(II) compounds of O_h symmetry. All spectra of the nickel(II) compounds are characterized by four main absorption areas. In the near-infrared there is a very broad, low intensity band having a maximum near 1200 nm. Near 870 nm there is a very broad band which has a broad shoulder on the low energy side. The band near 590 nm is nearly symmetrical and of intermediate intensity. The highest intensity band has a maximum near 380 nm and has slight assymmetry indicating another band near 400 nm. The band near 400 nm was not well enough resolved in any of the compounds to be given a value.

TABLE III. Visible and Near-Infrared Spectral Data for $[NiL_4(CF_3SO_3)_2]$ and $[CoL_4(CF_3SO_3)_2]$.

Compound	Absorption Maxima[a,b] (cm^{-1}) and Assignments					
	$^3B_{1g} \to {}^3E_g$	$\to {}^3B_{2g}$	$\to {}^3A_{2g}$	$\to {}^3Eg$	$\to {}^3A_{2g}$	$\to {}^3Eg$
$[Ni(py)_4(CF_3SO_3)_2]$	8,400	11,900	13,700 (14,200)	17,000	(26,000)	27,400
$[Ni(3\text{-mepy})_4(CF_3SO_3)_2]$	8,400	11,900	13,500 (14,000)	17,000	(25,700)	27,000
$[Ni(4\text{-mepy})_4(CF_3SO_3)_2]$	8,333	12,000	13,500 (14,200)	17,000	(26,000)	27,400
$[Ni(3,5\text{-lut})_4(CF_3SO_3)_2]$	8,400	11,900	13,600 (14,000)	17,000	(25,700)	27,000
$[Ni(4\text{-etpy})_4(CF_3SO_3)_2]$	8,333	12,050	13,500 (14,300)	17,000	(25,900)	27,400
$[Ni(4\text{-ippy})_4(CF_3SO_3)_2]$	8,400	12,000	13,500 (14,300)	17,000	(26,000)	27,400

	$^4T_{1g} \to {}^4T_{2g}$		$^4T_{1g} \to {}^4T_{1g}(^4P)$	
$[Co(py)_4(CF_3SO_3)_2]$	9500 w	18,900 sh;	20,000 vs;	21,700 s
$[Co(3\text{-mepy})_4(CF_3SO_3)_2]$	9400 w	18,500 sh;	19,600 vs;	22,200 s
$[Co(4\text{-mepy})_4(CF_3SO_3)_2]$	9600 w	18,500 sh;	19,600 vs;	22,400 s
$[Co(3,5\text{-lut})_4(CF_3SO_3)_2]$	9600 w	18,500 sh;	19,600 vs;	21,900 s
$[Co(4\text{-etpy})_4(CF_3SO_3)_2]$	9600 w	18,400 sh;	19,600 vs;	22,200 s

[a] Calculated values in parentheses. [b] w, weak; s, strong; vs, very strong; sh, shoulder.

TABLE IV. Visible Spectral Parameters for $[NiL_4(CF_3SO_3)_2]$ (cm^{-1}).

Parameter[a]	L = py	3-mepy	4-mepy	3,5-lut	4-etpy	4-ippy
Dq_{xy}	1190	1190	1200	1190	1205	1200
Dq_z	574	581	549	581	553	566
Ds	817	845	806	845	781	766
Dt	353	349	371	349	378	367
B′	880	847	880	847	880	879
$d\sigma$	−1890	−1920	−1900	−1970	−1880	−1840
$d\pi$	− 343	− 395	− 281	− 395	− 227	− 232

[a] All values include configurational interaction.

Expressions [17] relating the observed transition energies to the parameters Ds, Dt, Dq_{zy}, and Dq_z and the Racah B′ term (where B′ corresponds to the complex ion) have been developed for the nickel(II) ion. The parameters as well as values for the two $^3B_{1g} \to {}^3A_{2g}$ transitions were evaluated using a least-squares computer program and are listed in Table IV.

The calculated values for the transitions show some variation from the observed energies in some cases but a reasonable B′ value (near 880 cm^{-1} was found for each compound.

McClure [18] has given expressions which relate the crystal field parameters to molecular orbital parameters. These expressions are applicable only to high-spin *trans*-$[M(L)_4(X)_2]$ complexes derived from O_h $M(L)_6$ compounds [19]. The quantity $d\sigma$ is defined as $d\sigma = \sigma_z - \sigma_{xy}$. Here σ_z and σ_{xy} represent the sigma antibonding ability of ligands along the z-axis and the ligands in the xy-plane. A large positive $d\sigma$-value represents strong σ-donor strength of the axial ligands when compared to the equatorial ligands. The quantity $d\pi$ represents the π-antibonding character and is defined as $d\pi = d\pi_z - d\pi_{xy}$. Thus, the quantities $d\sigma$ and $d\pi$ give a quantitative comparison of differences in bonding strength of the CF_3SO_3 group and the pyridine or substituted pyridine bases.

Referring to Table IV, it is seen that in all the nickel(II) compounds the pyridine or substituted pyridines are stronger σ-donors than the trifluoromethanesulfonate ion. It is also evident from the sign of dπ that the π-antibonding interaction is greater in the xy-plane than along the z-axis. Compared with values calculated for $[Ni(py)_4(X)_2]$ [9, 20] compounds where X represents the chloride, bromide, perchlorate, tetrafluoroborate, and perrhenate ion, the trifluoromethanesulfonate ion is ranked in the following series of decreasing dσ and dπ values:

$$d\sigma: Cl^- > Br^- > CF_3SO_3^- > ReO_4^- > ClO_4^- > BF_4^-$$

$$d\pi: Cl^- > Br^- > ClO_4^- > CF_3SO_3^- > BF_4^- > ReO_4^-$$

It has been shown that in $Co(L)_4(X)_2$ complexes [21] two peaks are frequently observed in the visible region. In addition, the separation of these two peaks in *trans* compounds should be much greater than in those with *cis* structures. The *cis* compounds normally have a very broad band while *trans* compounds have a distinct separation in the two bands. Since at least two peaks are evident in the visible band, it seems that the CF_3SO_3 groups occupy the *trans* positions. This further supports a D_{4h} assignment to the compounds.

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