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Methylation of Tetrakis(fod) Europate NMR Shift Reagent by *S*-Methyldibenzothiophenium Ion

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ABSTRACT: NMR and luminescence spectroscopy were combined to study *S*-methyldibenzothiophenium ion in the presence of the anionic shift reagent $Eu(fod)_4^-$, where fod is 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione. The NMR resonances of the methyl hydrogens are observed to shift from 3.4 ppm for the fluoroborate salt to 25.4 ppm for the $Eu(fod)_4^-$ salt at 0.1 M concentration in chloroform-*d*. The thiophenium ion is observed to methylate $Eu(fod)_4^-$ anion at 25 °C resulting in the formation of $Eu(fod)_3$, CH_3fod and dibenzothiophene. The reaction is >95% complete in about 4 h. Evidence for the formation of dibenzothiophene and CH_3fod is revealed by ^1H NMR spectroscopy. The fod enolate anion is both *C*- and *O*-methylated in nearly equal amounts. *C*-Methylated fod exists almost entirely in the keto form with no evidence of enol formation, consistent with semi-empirical AM1 calculations. Additional evidence supporting the methylation of $Eu(fod)_4^-$ is observed in the luminescence spectrum of the Eu(III) ion. By monitoring changes in the luminescence spectrum as a function of time, the transformation of $Eu(fod)_4^-$ into $Eu(fod)_3$ is observed. *S*-Methylbenzothiophenium ion also methylates $Eu(fod)_4^-$ but more rapidly than *S*-methyldibenzothiophenium cation. © 1998 John Wiley and Sons, Ltd.

KEYWORDS: NMR; ^1H NMR; ^{13}C NMR; NMR shift reagents; tetrakis(fod) europate; thiophenium ions; methylation

INTRODUCTION

Wenzel and Zaia[1,2] have shown that the ^1H NMR spectra of ammonium, sulfonium and isothiouronium cations are effectively shifted by the lanthanide tetrakis chelate anion $Eu(fod)_4^-$, where fod is 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione. The observed shifts of the cations are significantly larger than those observed with $Eu(fod)_3$. The superior effectiveness of $Eu(fod)_4^-$ is attributed to the formation of an ion pair between the cation and shift reagent. Ion pair formation is accomplished by reacting the organic salt with either $K[Eu(fod)_4]$ or $Ag[Eu(fod)_4]$, with the choice of binuclear shift reagent depending on the counter anion of the organic salt. For example, sulfonium tetrafluoroborate salts are reacted with $K[Eu(fod)_4]$ in chloroform to form the ion pair and the precipitate KBF_4:

$$\mathrm{R{-}\overset{+}{S}(R'')R'\ BF_4^-} + \mathrm{Eu(fod)_3} \rightarrow \mathrm{R{-}\overset{+}{S}(R'')R'\ Eu(fod)_4^-} + \mathrm{KBF_4}\downarrow \quad (1)$$

The formation of the precipitate forces the association of the organic cation with the shift reagent and accounts for the enhanced NMR shifts observed with this reagent. $Ag[Eu(fod)_4]$ is the preferred reagent when halide is the counter anion of the organic salt.

Most sulfonium or thiophenium ions studied by Wenzel and Zaia are apparently stable in the presence of shift reagent at room temperature.[1] However, we have observed *S*-methyl benzothiophenium, an ion examined in their study, to demethylate rapidly to benzothiophene in about 30 min near room temperature. *S*-Methyldibenzothiophenium ion also demethylates but at a slower rate. This demethylation chemistry in the presence of $Eu(fod)_3$ has not been reported previously. We therefore chose to investigate this reaction using ^1H and ^{13}C NMR spectroscopy and luminescence spectroscopy.

RESULTS AND DISCUSSION

S-Methyldibenzothiophenium Ion

The unshifted ^1H NMR spectra of *S*-methyldibenzothiophenium tetrafluoroborate salts in acetonitrile-d_3 are consistent with assignments made earlier by Acheson and Harrison.[3] The *S*-methyl resonance appears as a singlet at 3.4 ppm. The shifted spectrum, shown in Fig. 1, shows the *S*-methyl resonance of this ion as a broad singlet at 25.4 ppm. Thus a shift of 22.0 ppm is achieved. The signal at 13.7 ppm is most probably attributed to the hydrogens *ortho* to the sulfur atom (H-a), since Wenzel and Zaia[1] have suggested that the shift reagent associates more closely with the sulfur atom. Accordingly the resonance at 9.8 ppm is attributed to H-b and the resonances at 9.1 ppm to H-c and H-d.

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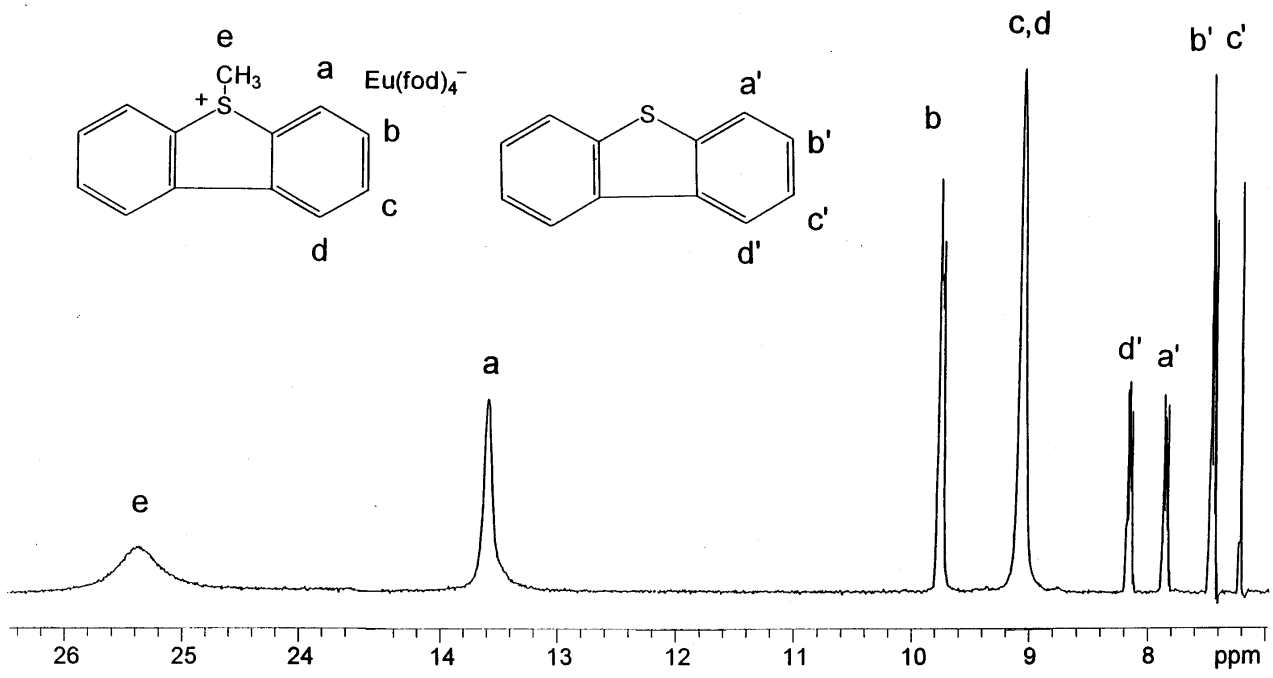


Figure 1. ^{1}H NMR spectrum of S-methyldibenzothiophenium Eu(fod)$_4^-$ salt (0.1 M) in chloroform-d after 30 min. The spectrum shows the dibenzothiophene product from the demethylation reaction.

The ^{1}H resonances of the shifted *S*-methyldibenzothiophenium ion decreased with time. At the same time, the resonances attributed to dibenzothiophene, also shown in Fig. 1, increased. The spectrum of the product dibenzothiophene is essentially identical with that of dibenzothiophene in the absence of shift reagent, consistent with the finding that the related benzothiophene exhibits no shift in the presence of Eu(fod)$_3$,[1] also a product of this reaction (see above).

^{13}C NMR spectra were also acquired as function of time. The chemical shifts of the *S*-methyldibenzothiophenium ion, both as the fluoroborate and tetrakiseuropate(III) salts, are shown in Table 1. The tetrakiseuropate(III) ion clearly causes a downfield shift of the carbon resonances, with the methyl resonance shifted the most as expected. As the reaction proceeded, the intensity of these peaks decreased, with a corresponding increase in the intensity of the dibenzothiophene resonances, also shown in Table 1. The dibenzothiophene resonances are very close to those of dibenzothiophene in the absence of shift reagent, consistent with the ^{1}H NMR spectrum above. The conversion of methyldibenzothiophenium ion into dibenzothiophene was 95% complete in about 4 h at 25 °C.

Table 1. ^{13}C NMR chemical shifts

Carbon	*S*-Methyldibenzothiophenium ion	
	BF_4^- salt[a]	Eu(fod)$_4^-$ salt[b]
S-CH_3	34.9	52.2
a, f	131.6, 140.3	136.7, 142.3
b, c, d, e	125.2, 128.6	125.8, 132.7
	132.1, 135.0	133.5, 135.8
	Dibenzothiophene[c]	Dibenzothiophene[d]
a′, f′	135.8, 139.4	135.5, 139.1
b′, c′, d′, e′	121.6, 122.8	121.5, 122.8
	124.2, 126.7	124.3, 126.7

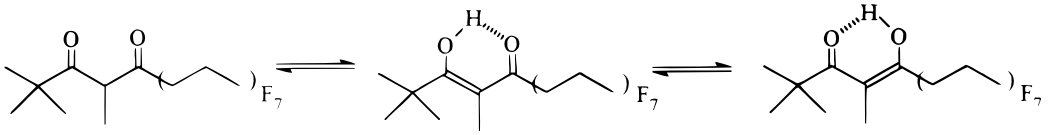
[a] Acetonitrile-d_3 as solvent.
[b] $CDCl_3$ as solvent.
[c] Dibenzothiophene spectrum obtained at completion of reaction in $CDCl_3$.
[d] Dibenzothiophene spectrum in $CDCl_3$, no shift reagent.

^{1}H NMR spectroscopy also revealed the formation of the *O*- and *C*-methylated forms of the fod anion. All possible methylated products are shown in Scheme 1. There are three possible *C*-methylated products which are in potential equilibrium, including one keto form (**1**) and two enol forms (**2** and **3**). There are two possible *O*-methylated products due to the unsymmetrical nature of the fod anion (**4** and **5**).

The ^{1}H NMR spectra as function of time showed the emergence of a quartet at 4.7 ppm and a doublet at 1.6 ppm (relative integration 1:3), consistent with the coupled CH and CH_3 groups of keto form **1**, respectively. Surprisingly, there is no evidence for either enol form of the *C*-methylated product, **2** or **3**, in the spectrum, which should exhibit a singlet in the 15–16 ppm range for the intramolecularly hydrogen-bonded OH hydrogen. Two singlets observed at 6.2 and 4.1 ppm (relative integrations 1:3) are consistent with the vinyl H and *O*-CH_3 hydrogens, respectively, of one of the *O*-methylated fod molecules, **4** or **5**, but a distinction of isomers cannot be made. Integration of these respective resonances revealed that *O*-methylation (55%) is slightly favored over *C*-methylation (45%).

For comparison purposes, *S*-methyldibenzothiophenium tetrafluoroborate was

C-methylated Product

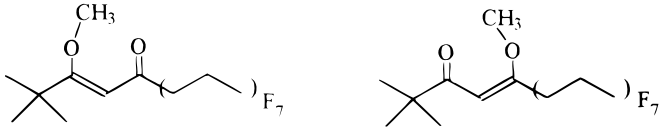


Keto Form — **Hf = -424.77 kcal/mol** — **1**

Enol 1 — **Hf = -422.21 kcal/mol** — **2**

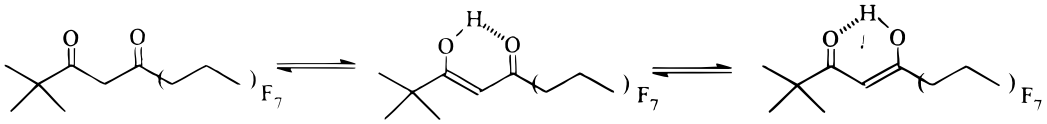
Enol 2 — **Hf = -421.69 kcal/mol** — **3**

O-Methylated fod



4 **5**

Hfod



Keto Form — **Hf = -421.39 kcal/mol** — **6**

Enol 1 — **Hf = -423.80 kcal/mol** — **7**

Enol 2 — **Hf = -421.15 kcal/mo** — **8**

Scheme 1

reacted in chloroform-*d* with Kfod at room temperature (no shift reagent). Methylation readily occurred with reaction complete in less than 30 min. Thus the reaction of fod^- anion is clearly faster with K^+ as the cation than with Eu^{3+}. The ^1H NMR spectrum of the resulting reaction mixture showed a predominance of *O*-methylation (*ca.* 90%) with two singlets observed at 6.20 and 3.82 ppm (relative integrations 1:3). A quartet at 4.50 ppm and doublet at 1.42 ppm (relative integrations 1:3) were consistent with a minor amount of *C*-alkylation. As in the case when shift reagent was present, there was no evidence of the enol form of the *C*-alkylated product.

The absence of an enol form for the *C*-methylated product was surprising. This observation was in distinct contrast to our observation that protonated fod (Hfod) exists predominantly in the enol form (>99%) in chloroform-*d*, as evidenced by the resonance of the intramolecularly hydrogen-bonded hydroxyl hydrogen at 15.1 ppm in its ^1H NMR spectrum in chloroform-*d*. To investigate this apparent inconsistency, AM1 semi-empirical calculations were carried out to determine heats of formation for the keto and enol forms for both the methylated and protonated fod molecules. The results of these calculations are shown in Scheme 1.

The results reveal that for Hfod, one of the two possible enol forms (**7**) is favored by 2.4 kcal mol^{-1} over the keto form. Hence, Hfod should exist predominantly in the enol form at equilibrium, consistent with the observed ^1H NMR spectrum. For the *C*-methylated fod the keto form (**1**) is favored by 2.5 kcal mol^{-1} over the most stable enol form. Hence CH_3fod should exist predominantly in the keto form at equilibrium, again consistent with our observations. The presence of the methyl group probably destabilizes the enol form by creating steric interactions between the methyl group and the bulky *tert*-butyl groups. Others have observed that alkyl substitution on the central carbon of β-dicarbonyl compounds results in a large reduction of the percentage of enol at equilibrium.[4,5] The AM1 calculations presented here ignore solvent effects but nevertheless help to explain why the enol form of the *C*-methylated fod species is not observed as a methylation product.

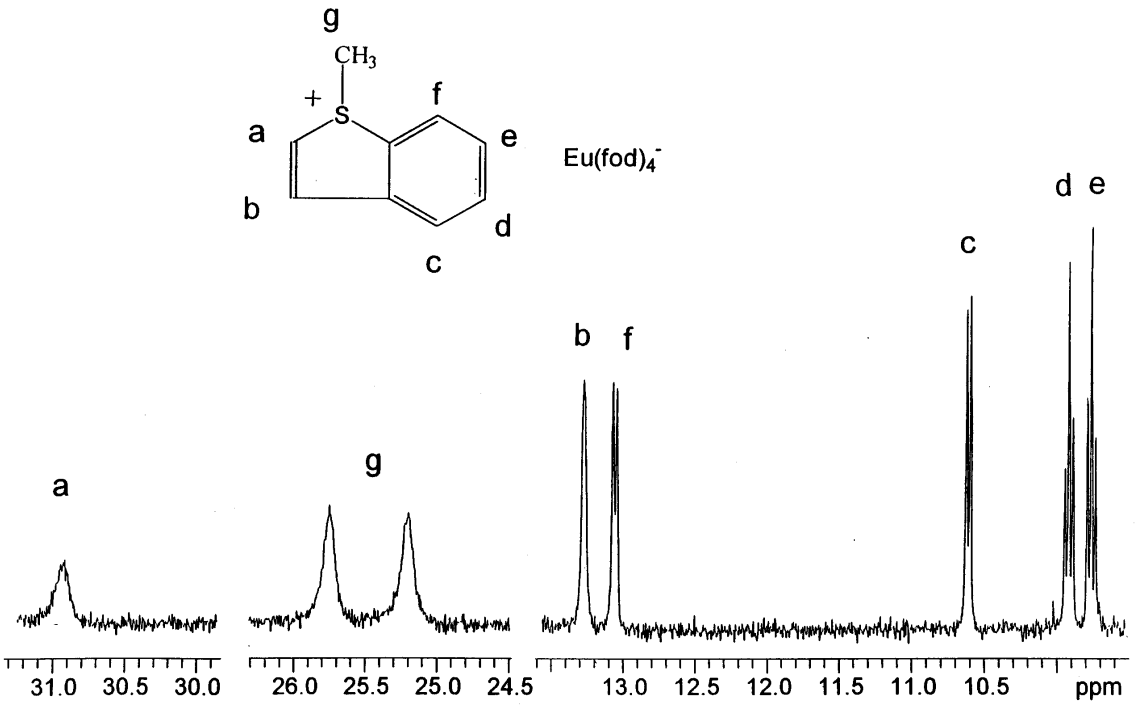


Figure 2. ^{1}H NMR spectrum of S-methylbenzothiophenium Eu(fod)$_4^-$ salt (0.1 M) in chloroform-d after 15 min.

S-Methylbenzothiophenium Ion

S-Methylbenzothiophenium ion was also ion paired with Eu(fod)$_4^-$. The unshifted ^{1}H NMR spectrum of *S*-methylbenzothiophenium fluoroborate in acetonitrile-d_3 is consistent with assignments made according to Acheson and Harrison.[3] The methyl hydrogens appear at 3.3 ppm. The shifted spectrum using Eu(fod)$_4^-$ as the anion, shown in Fig. 2, reveals that the *S*-methyl hydrogens are shifted to 25.5 ppm. The *S*-methyl hydrogens are split into a doublet in this case due to the ^{13}C-enriched methyl group which was incorporated into the molecule during synthesis. This was done, in part, in order to detect more easily the ^{13}C NMR resonances of this methyl group in the product CH_3fod molecule. The H-a hydrogen, α to the sulfur atom, is dramatically shifted downfield at 31.0 ppm and appears as a singlet, probably because it is broadened by the strong interaction with the shift reagent. All six non-equivalent ring hydrogens are clearly resolved in the shifted spectrum. The two upfield triplets near 10 ppm are more logically attributed to H-d and H-e. The doublets at 10.6 and 13.2 ppm are probably H-c and H-f, respectively, since H-f is significantly closer to the sulfur atom. The broadened singlet at 13.3 is probably H-b, similar to the broadened singlet at 31.0 ppm for H-a.

This ion also demethylates as evidenced by the appearance of the unshifted spectrum of benzothiophene in the region of 7–8 ppm (not shown). Again, evidence for both *O*- and *C*-methylated fod was obtained. A singlet at 6.2 ppm is attributed to the vinyl H of the *O*-methylated product. In this case, *O*-CH_3 hydrogens do not give rise to a singlet at 4.1 ppm but rather as a pair of doublets centered at 3.9 and 4.0 ppm, as shown in Fig. 3. The doublets are attributed to coupling with the ^{13}C isotope of the methyl group and both have J values of 149 Hz, typical of ^{13}C–^{1}H coupling constants.[6] The appearance of two doublets and not one in this region are indicative of the formation of both *O*-methylated fod molecules (**4** and **5**) shown in Fig. 4. The minor, more deshielded, doublet is probably compound **5** since its methyl group is closer to the more electronegative perfluorinated propyl group. A quartet observed at 4.6 ppm (not shown) is consistent with the *C*-methylated product. Again, integration reveals nearly equal amounts of *O*- and *C*-methylated products, with

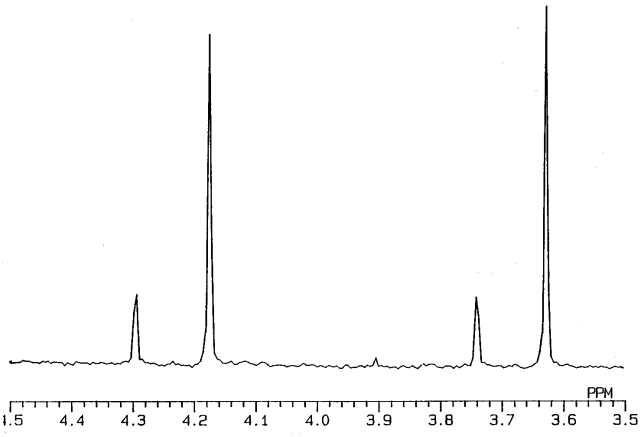


Figure 3. ^{1}H NMR spectrum of product from S-methylbenzothiophenium Eu(fod)$_4^-$ salt (0.1 M) in chloroform-d after 15 min. Resonances are attributed to methyl hydrogens of O-methylated fod molecules, **4** and **5**. See text for explanation.

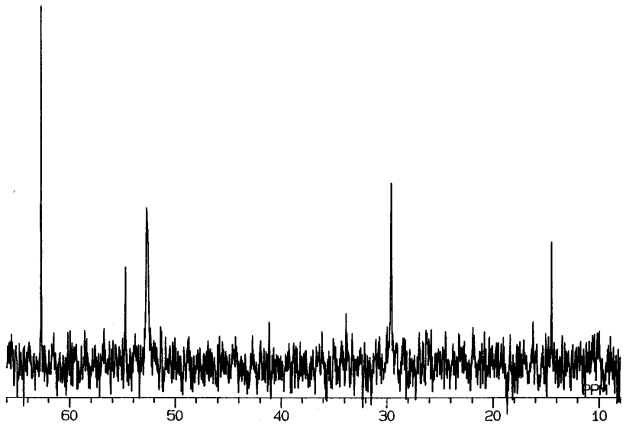


Figure 4. ^{13}C NMR spectrum of product from S-methylbenzothiophenium $Eu(fod)_4^-$ salt (0.1 M) in chloroform-d after 15 min. The methyl group was 99 at% ^{13}C-enriched to enhance signal of the methyl carbon. Assignments: S-methyl carbon of shifted thiophenium, 52.6 ppm; tert-butyl methyl carbons of shift reagent, 29.6 ppm; C-methyl carbon of **1**, 14.5 ppm; O-methyl carbons of **4** and **5**, 54.8 and 62.7 ppm.

no evidence of the enol form of the *C*-methylated product.

The use of a ^{13}C-enriched methyl group in this cation allowed us easily to follow the methyl group by ^{13}C NMR spectroscopy during the reaction. A ^{13}C NMR spectrum after a 15 min. reaction time revealed five major resonances as shown in Fig. 4. A broadened resonance at 52.6 ppm is attributed to the methyl resonance of *S*-methylbenzothiophenium, shifted from 31.7 ppm. This resonance was observed to disappear with time. The resonance at 29.6 ppm is attributed to the *tert*-butyl methyl carbons of $Eu(fod)_3$ or $Eu(fod)_4^-$. This resonance was routinely observed in all our spectra with its intensity remaining relatively constant with time. The resonance at 14.5 ppm increased with time and is attributed to the methyl resonance of the *C*-methylated fod molecule, **1**. The resonances at 54.8 and 62.7 ppm are attributed to the two *O*-methylated products, **4**, and **5**. Their relative intensities are consistent with the ^1H NMR signals of the methyl hydrogens of these two products.

Eu(III) Ion Luminescence

The use of lanthanide luminescence spectroscopy to monitor changes in the chemical environment in the first and second coordination sphere surrounding the lanthanide ion is well documented.[7–10] Within the luminescence spectrum of the Eu(III) ion, one manifold is of particular interest, the $^5D_0$ to $^7F_2$ transition manifold. The $^5D_0$ to $^7F_2$ transition manifold is referred to as a 'hypersensitive' transition due to the unique sensitivity of the manifold to changes in the chemical environment.[11] Changes in the chemical environment are reflected as shifts in peak positions and splitting patterns.

The luminescence spectra of $Eu(fod)_3$ (bottom) and $Eu(fod)_4^-$ (top) in $CHCl_3$ are shown in Fig. 5. The peaks observed in the 16 500–16 000 cm^{-1} region are due to transitions within the $^5D_0$ to $^7F_2$ manifold. For

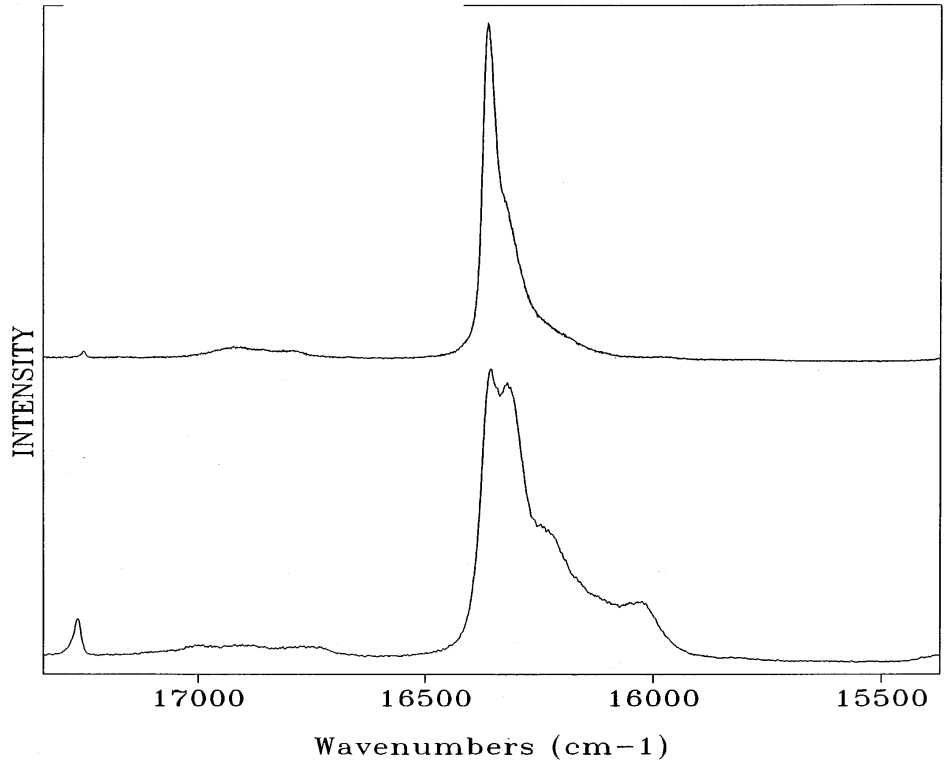


Figure 5. Luminescence spectrum of Eu(III) ion in $Eu(fod)_3$ (bottom) and $Eu(fod)_4^-$ (top). The spectral range includes transitions from the $^5D_0$ excited state to the $^7F_{0,1,2}$ states.

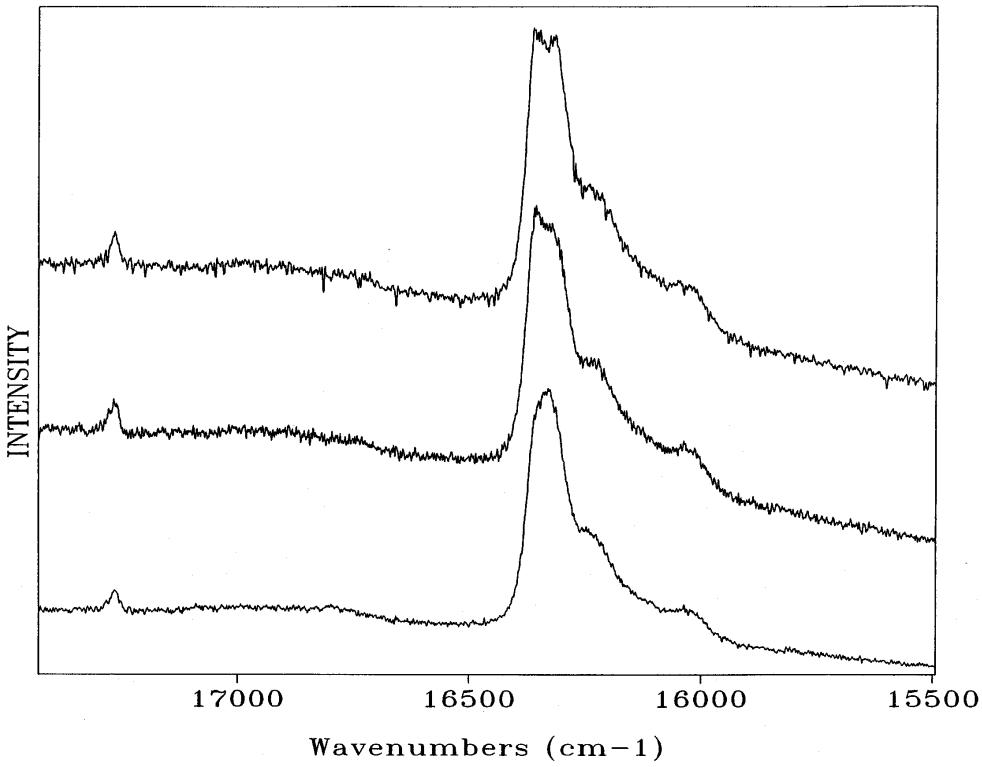


Figure 6. Luminescence spectrum of Eu(III) ion in $Eu(fod)_4^-$ anion–thiophenium cation mixture as a function of time, 30 (bottom), 60 (middle) and 150 min (top) after mixing. The spectral range includes transitions from the $^5D_0$ excited state to the $^7F_{0,1,2}$ states.

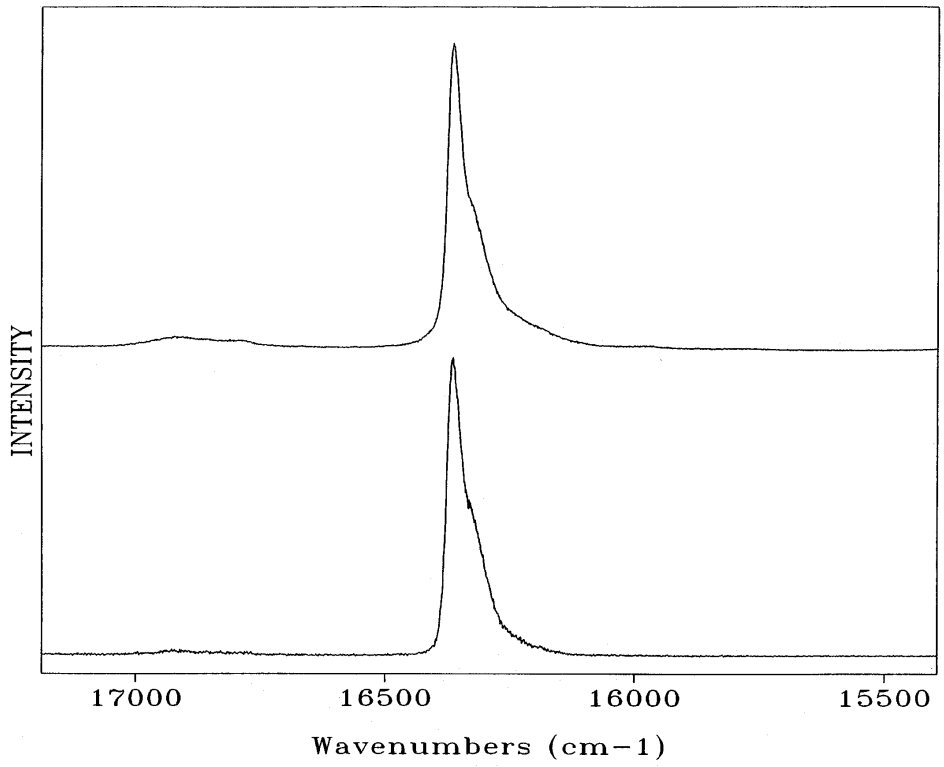
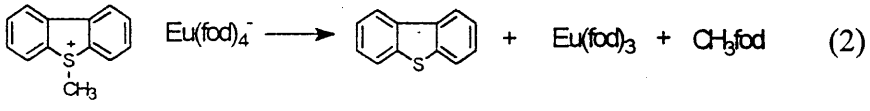


Figure 7. Luminescence spectrum of Eu(III) ion in 'regenerated' $Eu(fod)_4^-$ (bottom) and 'non-ion-paired' $Eu(fod)_4^-$ (top). The spectral range includes transitions from the $^5D_0$ excited state to the $^7F_{0,1,2}$ states.



the $Eu(fod)_4^-$ species, the $^5D_0$ to $^7F_2$ manifold consists of a primary peak (16 363 cm^{-1}) with a shoulder (16 316 cm^{-1}). The $^5D_0$ to $^7F_2$ manifold for the $Eu(fod)_3$ species contains two slightly split peaks (16 355, 16 319 cm^{-1}) and two weaker intensity broad peaks (16 232, 16 029 cm^{-1}). Additional differences in the spectra are seen in the $^5D_0$ to $^7F_0$ manifold region around 17 300–17 200 cm^{-1}. In the $Eu(fod)_4^-$ species only a minor peak (17 252 cm^{-1}) is observed (indicative of a high symmetry complex), whereas in the $Eu(fod)_3$ species a distinct peak (17 263 cm^{-1}) is seen (indicative of a low-symmetry complex). These differences in the luminescence spectra indicate a distinct difference in the chemical environment surrounding the Eu(III) ion in each species, as would be expected since the species differ in the number of coordinated fod ligands (four vs three).

After mixing equal molar amounts of $Eu(fod)_4^-$ and *S*-methyldibenzothiophenium in $CHCl_3$, the luminescence spectrum of the Eu(III) ion was monitored as a function of time. The resulting spectra, 30, 60 and 150 min after mixing, are shown in Fig. 6. In the initial scan (bottom), an intense broad peak (16 332 cm^{-1}) with two weaker peaks (16 235, 16 038 cm^{-1}) are observed in the $^5D_0$ to $^7F_2$ manifold. These changes in the $^5D_0$ to $^7F_2$ manifold between the $Eu(fod)_4^-$ chloroform solution (Fig. 5, top) and the $Eu(fod)_4^-$–thiophenium mixture are expected owing to the formation of an ion pair between the $Eu(fod)_4^-$ and the thiophenium cation. The association of the thiophenium cation with the $Eu(fod)_4^-$ anion perturbs the otherwise symmetrical distribution of four fod ligands surrounding the Eu(III) ion. As the luminescence spectrum is recorded over time, the initial broad peak (16 332 cm^{-1}) can be seen to split slightly into two peaks (16 355, 16 320 cm^{-1}) corresponding to the two peaks observed in the original $Eu(fod)_3$ spectrum. This splitting into two peaks was reproducible and is not the product of noise in the spectra. Hence the luminescence spectra indicate that the $Eu(fod)_4^-$ species has reacted with the thiophenium cation, resulting in the formation of $Eu(fod)_3$. This is consistent with the NMR spectra which indicate that a fod anion is methylated by the thiophenium cation. The methylated fod species, being uncharged, would have less tendency to coordinate the Eu(III) ion, leaving $Eu(fod)_3$ as the major Eu(III) species in solution.

If $Eu(fod)_3$ is the major Eu(III) species present after completion of the methylation reaction, it should be possible to regenerate the $Eu(fod)_4^-$ species by adding an equimolar amount of Kfod to the reacted solution. An equimolar amount of Kfod was added to the reacted solution and the luminescence spectrum recorded. As expected, comparison of the luminescence spectra of the 'regenerated' $Eu(fod)_4^-$ anion (Fig. 7, bottom) and the 'non-ion-paired' $Eu(fod)_4^-$ anion (Fig. 7, top) reveals that the two spectra are identical in the $^5D_0$ to $^7F_{0,1,2}$ regions.

The luminescence and NMR spectra, taken together, indicate the overall reaction shown opposite in equation (2).

CONCLUSIONS

The ^1H NMR spectra of *S*-methyldibenzothiophenium and *S*-methylbenzothiophenium ions are strongly downfield shifted in the presence of $Eu(fod)_4^-$ using chloroform-*d* as solvent. The downfield shift is attributed to ion pair formation between the thiophenium cation and the tetrakis(fod) europate anion. However, the thiophenium cation is unstable and readily methylates fod anion associated with europium, resulting in the formation of the $Eu(fod)_3$ as observed by luminescence spectroscopy. Acheson and Harrison[3] observed that *S*-methylbenzothiophenium ion was a powerful methylating agent which readily methylates pyridine and DMSO at room temperature. In addition, optically active methyl- and ethylsulfonium ions have been used in the asymmetric alkylation of enolates derived from β-keto esters.[12] Hence methylation of the nucleophilic fod anion by *S*-methylthiophenium ions is not surprising in this case. We suspect that other reactive *S*-methylsulfonium or *S*-methylthiophenium ions may behave similarly and therefore interpretation of shifted spectra should take into account this possibility.

EXPERIMENTAL

Synthesis of *S*-Methylbenzothiophenium and *S*-Methyldibenzothiophenium Tetrafluoroborate

A procedure similar to that of Acheson and Harrison[3] was employed. Dibenzothiophene or benzothiophene (1 mmol) and iodomethane (1.2 mmol) were dissolved in 2 ml of 1,2-dichloroethane (DCE). After stirring at room temperature for 30 min, a DCE solution of $AgBF_4$ (1.2 mmol) was added dropwise slowly (30 min). In the case of benzothiophene, ^{13}C-enriched methyl iodide (99 at%) was used. An immediate yellow precipitate (AgI) formed. After stirring at room temperature under nitrogen for 12 h, the mixture was centrifuged and the supernatant was removed. After washing the precipitate twice with 3 ml of acetonitrile, the combined supernatants were placed in a 25 ml round-bottomed flask and rotovaporized. The solid product was recrystallized by first dissolving it in a minimum amount of acetonitrile and then adding diethyl ether until a cloudiness persisted. The product was then cooled in a dry-ice–acetone bath, filtered and dried. *S*-Methylbenzothiophenium tetrafluoroborate: 68% yield, m.p. 69–70 °C (lit.[3] m.p. 72–72 °C). ^1H NMR (270 MHz, acetone-d_6), δ 3.33 (s, 3H), 7.71 (d, 1H), 7.83 (t, 1H), 7.92 (t, 1H), 8.14 (d, 1H), 8.17 (d, 1H), 8.50 (d, 1H). *S*-Methyldibenzothiophenium tetrafluoroborate: 78% yield, m.p. 149–151 °C (lit.[3] m.p. 149–151 °C). ^1H NMR (270 MHz, acetone-d_6), δ 3.42 (s, 3H), 7.82 (t, 2H), 8.00 (t, 2H), 8.48 (d, 2H), 8.54 (d, 2H).

Synthesis of K(fod)[13]

6,6,7,7,8,8,8-Heptafluoro-2,2-dimethyloctane-3,5-dione (1 mmol) was mixed with 2 ml of 50% KOH. The white solid that formed immediately was filtered and washed with 1 ml of cold water. The product was dried under vacuum overnight.

Preparation of *S*-Methyldibenzothiophenium and *S*-Methylbenzothiophenium Tetrakis(fod) Europate(III) Ion Pair

The procedure of Wenzel and Zaia[1] was used. *S*-Methylbenzothiophenium tetrafluoroborate, Kfod and $Eu(fod)_3$ (0.1 mmol of

each) were added to 1 ml of dry chloroform-*d* in a vial under a dry nitrogen atmosphere. A magnetic stir bar was added and the vial was capped and stirred for 10 min. The mixture was then centrifuged to remove solid KBF_4 and the supernatant was removed by pipet and placed in an NMR tube for analysis.

NMR Spectra

The ^1H and ^{13}C NMR spectra were recorded on a JEOL 270 MHz FT-NMR instrument using chloroform-*d* as solvent and TMS as a standard at concentrations of 0.1 mmol ml^{-1} of thiophenium ion and shift reagent. The probe temperature was 20 °C. For the ^1H NMR of the shifted spectra, the experimental conditions were a pulse width of 5.2 μs, and a spectral width of 20 000 Hz with 32K points for digital resolution of 1.22 Hz per point.

AM1 Calculations

Calculations were carried out using the Spartan AM1 semi-empirical program with geometry optimization.

Luminescence Spectra of Europium

Luminescence spectra were obtained using a 6 W Innova 300 argon ion laser (Coherent Radiation) and an HG.2S 1 m double monochromator (Jobin–Yvon Instruments) with a resolution of 0.5 cm^{-1} at 514.5 nm as an emission monochromator. The emission monochromator was equipped with a cooled red-sensitive Type 636 PMT (Hamammatsu) as a detector. The PMT pulses were preamplified and sent to a Model 1121 amplifier discriminator (PAR). The resulting pulses were recorded with an 1170 Series Signal Average multichannel analyzer (Nicolet).

The samples were typically sealed in glass capillaries. The luminescence was collected at an angle 90° to the path of the excitation beam and focused on to the entrance slit of the monochromator.

All luminescence spectra were obtained by mixing equal volumes of 0.1 mM chloroform solutions of *S*-methyldibenzothiophenium fluoroborate and $K[Eu(fod)_4]$. The mixtures were shaken for 10 min before measuring the spectra.

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