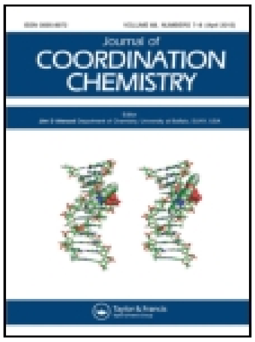

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Structural and spectroscopic analyses of a ternary supramolecular complex [(o-C_6F_4Hg)$_3$(o-Me_2TTF)·CH_3CN]: elucidating and validating non-covalent interactions in the solid state

STEVEN P. FISHER†, RYAN H. GROENEMAN‡ and ERIC W. REINHEIMER*†

†Department of Chemistry and Biochemistry and the W.M. Keck Foundation Center for Molecular Structure, California State University San Marcos, San Marcos, CA, USA
‡Department of Biological Sciences, Webster University, St. Louis, MO, USA

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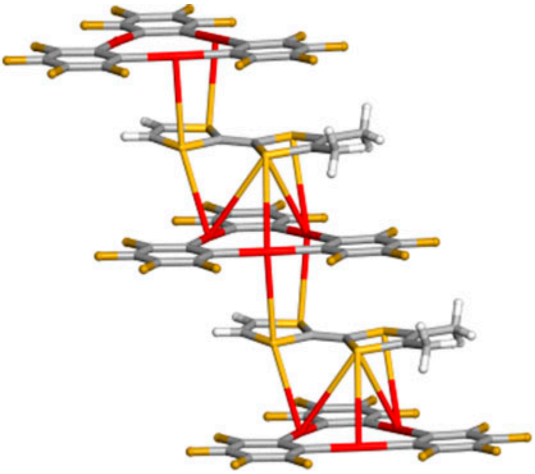

Given the presence of Hg(II) ions, heightened electron-withdrawing properties, and the presence of readily accessible electrophilic sites on its molecular surface, trimeric perfluoro-*ortho*-phenylene mercury (o-C_6F_4Hg)$_3$ has been classified throughout the literature as one of the most powerful Lewis acids. Due to this fact, numerous supramolecular complexes containing both neutral and anionic substrates have been synthesized. In this paper, we highlight the structural and spectroscopic properties of a complex containing (o-C_6F_4Hg)$_3$ and o-3,4-dimethyltetrathiafulvalene (o-Me_2TTF). The supramolecular complex [(o-C_6F_4Hg)$_3$(o-Me_2TTF)·CH_3CN] (**1**) is based upon an alternating stack structure of the two compounds held together by non-covalent Hg···S interactions. Fluorine atoms are found accepting C–H···F hydrogen bonds from hydrogens bonded to both sp^2- and sp^3-hybridized carbons, producing a 3-D supramolecular assembly. Infrared spectroscopic measurements confirmed the presence of both Hg···S and Hg···N supramolecular interactions within **1** due to a shift in respective vibrational frequencies.

Keywords: Supramolecular chemistry; Trimeric perfluoro-*ortho*-phenylene mercury; Hg···S Interactions, C–H···F Hydrogen bonds

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*Corresponding author. Emails: ereinhei@csusm.edu, eric.reinheimer@gmail.com

1. Introduction

Multidentate Lewis acids capable of complexing various substrates endure as an attractive field of research in supramolecular chemistry [1]. Among the Lewis acids investigated are polyfunctional organomercurials containing mercury ions bridged by an organic framework. These mercury containing molecules have been identified as promising candidates that are suitable for complexing a wide array of neutral and anionic substrates. As a direct result of the highly unsaturated nature of Hg(II), several different classes of these organomercurials have exhibited a predilection to function as acceptors for a variety of electron-rich substrates [2]. Among the fluorinated genre of these acceptors, trimeric perfluoro-*ortho*-phenylene mercury (o-$C_6F_4Hg)_3$ [figure 1(a)] remains a benchmark with which to conduct supramolecular studies due to its planarity, electrophilic nature of its constituent Hg(II) ions, and heightened electron-withdrawing properties. To date, (o-$C_6F_4Hg)_3$ has served as a receptor for aromatic substrates [3], metallocenes [4], anions [5], nitriles [6], sulfoxides [7], formamides [8], carbonyls [9], ethers [10], and nitronyl nitroxides [11].

In addition to those substrates outlined above, the organosulfur donor tetrathiafulvalene (TTF) was also successfully coupled with (o-$C_6F_4Hg)_3$ [12]. A survey of solid-state materials has shown that TTF and derivatives are crucial for the observation of several unusual physical phenomena such as metallic conductivity [13], superconductivity [14], neutral-to-ionic phase transitions [15], and as components in multifunctional hybrid molecular materials [16]. Recently, the hemi-methylated TTF derivative o-3,4-dimethyltetrathiafulvalene (o-Me_2TTF) [figure 1(b)] has seen increased usage in the preparation of new charge transfer complexes, hybrid materials, and organic metals [17]. Additionally, o-Me_2TTF serves as a starting material for the synthesis of the redox-active chelating diphosphine o-P2, a ligand employed in the preparation of various homoleptic transition metal coordination compounds [18].

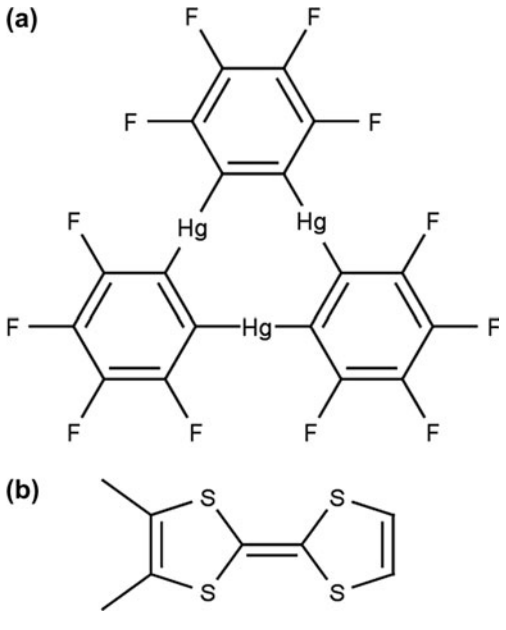

Figure 1. Renderings of (o-$C_6F_4Hg)_3$ (**a**) and o-Me_2TTF (**b**), the constituent molecules within **1**.

As (o-C_6F_4Hg)$_3$ has already demonstrated a capacity in forming a supramolecular adduct with TTF, we were curious if o-Me_2TTF could also successfully function as a substrate. As a result, a study was undertaken to determine the overall structure of a complex based upon (o-C_6F_4Hg)$_3$ and o-Me_2TTF. In this contribution, the synthesis, crystal structure, and spectroscopic properties of a new supramolecular adduct, [(o-C_6F_4Hg)$_3$(o-Me_2TTF)·CH_3CN] (**1**), was determined. Solid **1** is comprised of alternating stacks of (o-C_6F_4Hg)$_3$ and o-Me_2TTF that produce an infinite array based upon Hg···S interactions. Analysis of the resulting infrared (IR) spectroscopic data showed a slight shift of selected vibrational frequencies for o-Me_2TTF which is indicative of non-covalent interactions between divalent mercury and sulfur. The addition of the methyl groups on TTF caused a dramatic change from the related complex [((o-C_6F_4Hg)$_3$)$_2$(TTF)] (**2**), not only in the formula of the material but also in the overall crystal packing of the groups [12]. The overall crystal structure of **1** will be discussed with special attention to all of the different types of non-covalent interactions observed that produce a 3-D supramolecular material.

2. Experimental

2.1. *Materials*

The solvents dichloromethane (99.8% anhydrous), acetonitrile (99.8% anhydrous), and hexanes (99% mixture of isomers) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without additional purification. During preparation of the ternary complex, the solvents were not dried prior to their use.

2.2. *Formation of the ternary complex*

Given the extreme toxicity of organomercurials, all synthetic procedures were completed in a well-ventilated hood and extreme care was exercised to avoid exposure to solids and solutions known to contain mercury. The synthesis of (o-C_6F_4Hg)$_3$ was achieved in a similar manner as first reported by Sartori and Golloch [19]. Solutions of (o-C_6F_4Hg)$_3$ (0.0200 g, 1.91×10^{-5} mol) and o-Me_2TTF (0.0200 g, 8.99×10^{-5} mol) were prepared each from 20.0 mL of CH_2Cl_2, yielding an orange microcrystalline precipitate immediately upon their combination. The vial containing the combined solutions was sealed and placed in a freezer at −10 °C for one hour. After this period, the precipitate was filtered, washed with 20.0 mL of cold CH_2Cl_2 to remove unreacted starting reagents, and allowed to dry in air. Despite being used initially to prepare the complex, even boiling CH_2Cl_2, was unable to dissolve the precipitate in order to grow single crystals. Other solvents were investigated, such as diethyl ether and hexane, but neither was able to dissolve the insoluble product. Benzene and toluene were not tested due to the formation of strong adducts with (o-C_6F_4Hg)$_3$. Finally, despite its propensity to weakly complex with (o-C_6F_4Hg)$_3$, CH_3CN was considered due to the numerous reported results as an effective solvent for o-Me_2TTF. Ultimately, the material was recrystallized using warm CH_3CN where, after one hour in the freezer, orange block-like crystals were realized. After sitting overnight at −10 °C, the crystals were filtered, washed with a cold isomeric mixture of hexanes, and allowed to dry in air; yield of 0.0152 g (62%) was based upon the mass of (o-C_6F_4Hg)$_3$. We note that crystals of **1** stored in the dark and at ambient conditions became opaque and brittle after a few weeks when exposed to the atmosphere. The loss of crystallinity is attributed to loss of interstitial acetonitrile from the crystal.

2.3. *Single-crystal X-ray crystallography*

X-ray diffraction data for a small orange block-like crystal of **1** with the dimensions 0.10 × 0.09 × 0.08 mm^3 were collected using graphite-monochromated Mo $K_{\alpha 1}$ radiation ($\lambda = 0.71073$ Å) on a Bruker SMART 1K CCD detector system at 293(2) K. SMART was used for data collection, indexing of reflections, and determination of cell parameters [20]. SAINT was used for the integration of reflection intensities and multiscan absorption corrections were performed using SADABS [21]. The structure was solved using direct methods and difference Fourier techniques via SHELXS-97 [22]. The hydrogens from *o*-Me_2TTF were fixed using the HFIX 43 and 137 commands and refined using SHELXL-97 [23]. The final structure refinement included anisotropic temperature factors on all non-hydrogen atoms. The space group of the complex was unambiguously verified using PLATON [24]. The crystallographic data for **1** are listed in table 1.

2.4. *Infrared spectroscopy*

The IR absorption spectrum for **1** was recorded at room temperature on a solid crystalline sample on a glass surface using a Thermo Nicolet iS10 spectrophotometer with attached Thermo Scientific Smart iTR ATR (Attenuated Total Reflectance) sampling accessory from 500 to 4000 cm^{-1}. Utilizing published values for the C–S vibrations within *o*-Me_2TTF as well as those for the nitrile group of CH_3CN, it was possible to ascertain if any non-covalent supramolecular interactions occurred within **1** [25].

3. Results and discussion

The molecular complex **1** crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with single molecules of (o-C_6F_4Hg)$_3$, *o*-Me_2TTF, and CH_3CN within the asymmetric unit. As expected, the included *o*-Me_2TTF molecule crystallizes with the ternary complex in its neutral form as illustrated by the length of both the central C=C and ancillary C–S bonds [26]. Similar to **2**, the crystal structure of **1** demonstrates non-covalent Hg···S interactions since the corresponding interatomic distances are below the sum of their corresponding van der Waals radii. Each mercury and sulfur within **1** engage in non-covalent interactions in the solid state. The non-methylated ring sulfurs have different non-covalent interactions where one bonds with two mercury ions (Hg···S (Å): 3.446(2) and 3.495(2)) while the other bonds to only a single mercury (Hg···S (Å): 3.336(2)) producing an extended structure (figure 2).

Turning attention to the methylated ring, each sulfur is found interacting in a distinct manner. The first sulfur interacts with a single mercury (Hg···S (Å): 3.783(4)) within **1** (figure 2). A second unique set of Hg···S interactions were observed for the other sulfur which interacts with three mercury ions (Hg···S (Å): 3.708(2), 3.818(2), and 3.919(3)) on the same (o-C_6F_4Hg)$_3$ [figures 2 and 3(a) and (b)]. The interaction pattern is reminiscent of other (o-C_6F_4Hg)$_3$ complexes with both carbonyl [9] and nitrile [6] moieties. More specifically, the location of the sulfur is nearly perpendicular to the centroid defined by the three

Table 1. X-ray crystallographic and refinement data for **1**.

Formula	$C_{28}H_{11}F_{12}Hg_3N_1S_4$
FW (g/mol)	1319.39
CCDC code	941165
Wavelength (Å)	0.71073
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	*P-1*
a (Å)	8.1093(2)
b (Å)	10.7145(3)
c (Å)	19.3932(5)
α (°)	90.896(2)
β (°)	98.537(2)
γ (°)	105.714(2)
Volume $(Å)^3$	1601.31(7)
Z	2
r (calcd) (g/cm^3)	2.736
Abs (mm^{-1})	14.700
$F(0\ 0\ 0)$	1196
Crystal size (mm^3)	0.10 × 0.09 × 0.08
Theta range (°)	2.30–23.26
Refl./uniq.	4468/3661
R (int)	0.0322
Abs. correction	Multiscan
Max./min.	0.357/0.254
Ref. method	Full matrix least squares on F^2
Data/restraints/parameters	4468/0/436
GOF on F^2	1.012
R_1 indices ($I > 2\sigma$)	0.0271
wR_2	0.0549
Peak/hole ($e^-/Å^3$)	1.0 and −0.80

mercury ions with angles of 86.48°, 90.45°, and 93.04°, respectively [figure 3(a) and (b)]. As a result of the supramolecular interactions, an infinite alternating stacking column of (o-$C_6F_4Hg)_3$ and o-Me_2TTF molecules was realized. In addition to the Hg···S interactions, the interstitial acetonitrile molecule also interacts with a mercury ion within **1** by means of a Hg···N contact (Hg···N (Å): 3.079(2)).

Literature related to structures containing TTF and its derivatives has shown that when these molecules are crystallized in the neutral state, the molecules are often non-planar displaying bends up to 30° along dithiol or diseleno hinges [27]. Within **1**, the o-Me_2TTF substrate appears to deviate slightly from planarity based on an angle measured by calculated centroids within the substrate's three C=C bonds. To be considered planar along the dithiol bridges, the angle between these points would be approximately 180°. Analysis of the structure of **1** revealed an angle of 174.98° between the three C=C bonds. While it can be speculated that the greater number of Hg···S interactions from the sulfur atoms near the methyl groups might be responsible for the substrate's lack of planarity, it cannot be overlooked that this dithiol bridge is closer to the more sterically encumbering methyl groups of o-Me_2TTF. Given the steric bulk of the van der Waals surface of the Lewis acid, a slight deviation of the substrate from planarity seems necessary in order to facilitate complex formation between the constituent molecules in **1** and maximize the number of Hg···S interactions.

In addition to the non-covalent Hg···S interactions within **1**, an array of C–H···F hydrogen bonds were observed, producing a 2-D sheet. The hydrogen bond donors are based upon both sp^2- and sp^3-hybridized carbons [figure 4(a)]. Two methyl hydrogens interact

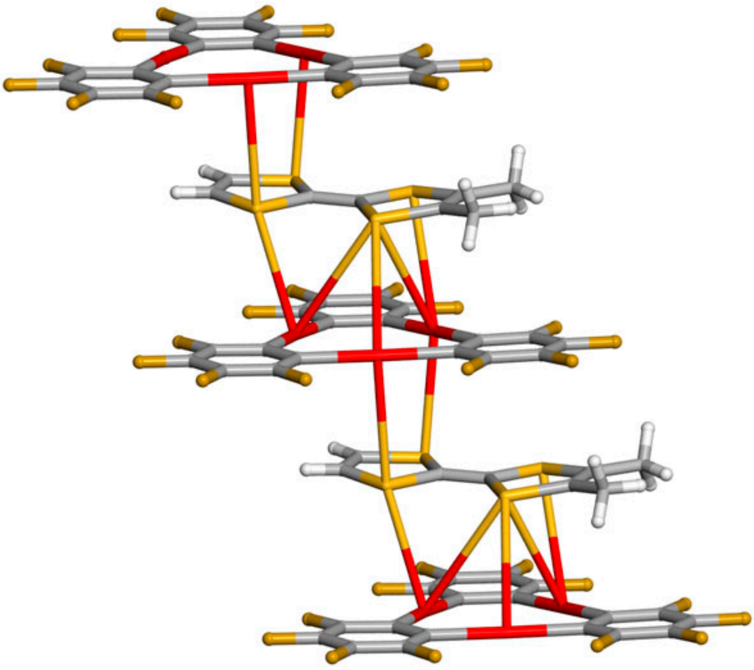

Figure 2. View of the extended supramolecular array based upon Hg···S interactions within **1** that produce the infinite column.

with a single fluorine in an accepting bifurcated hydrogen bond pattern (C···F (Å): 3.323 (5), 3.716(5)). The aromatic hydrogens form C–H···F hydrogen bonds; however, this type of hydrogen bond is based upon a donating bifurcated interaction as each hydrogen interacts with two different fluorines (C···F (Å): 3.187(8), 3.421(2), 3.475(6), 3.588(2)) on two neighboring ($(o\text{-}C_6F_4Hg)_3$) molecules. The 2-D hydrogen bonded sheet produces alternating columns of $(o\text{-}C_6F_4Hg)_3$ and o-Me_2TTF where the CH_3CN molecules are found within the voids in the o-Me_2TTF column [figure 4(b)].

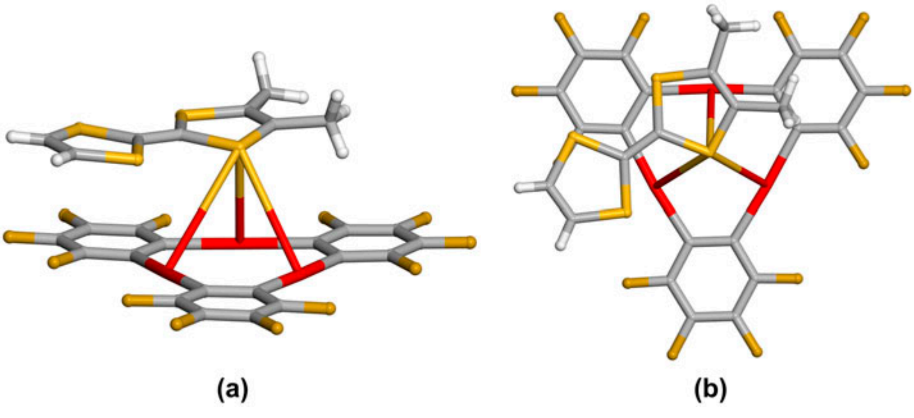

Figure 3. (**a**) Side view of the secondary set of Hg···S interactions involving the three mercury atoms of $(o\text{-}C_6F_4Hg)_3$. (**b**) Top view of the Hg···S interactions illustrating the near superposition of the sulfur atom from o-Me_2TTF that engages in the three Hg···S interactions.

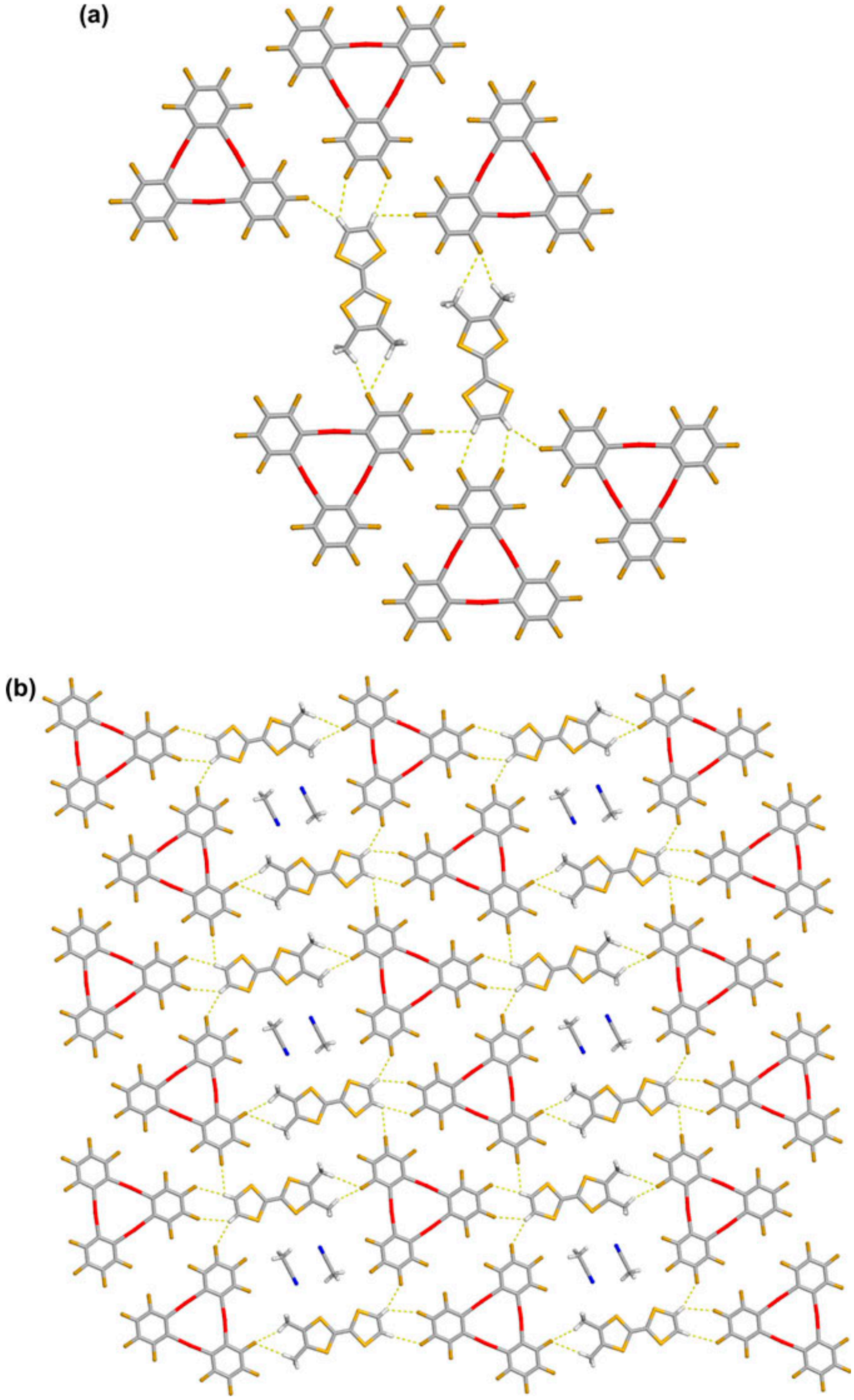

Figure 4. (**a**) View of the C–H···F hydrogen bonding interactions within **1** that are based upon both accepting and donating bifurcated interactions. (**b**) View of the columns of both (o-$C_6F_4Hg)_3$ and o-Me_2TTF that form due to the hydrogen bonding pattern. In addition, the locations of the CH_3CN molecules are shown in the voids relative to the o-Me_2TTF column.

Coupling of a substrate with (o-C_6F_4Hg)$_3$ via non-covalent interactions shifts the frequency of specific bands based upon the atoms involved in this interaction [6, 9]. Work by Jankowski and coworkers on the spectroscopic behavior of o-Me_2TTF allowed for a more in-depth analysis of selected vibrational bands for this substrate within **1** [25]. Utilizing these published results, modes for interactions containing sulfurs could be identified which suggest the presence of non-covalent Hg···S interactions. Upon inspection of the IR spectrum for **1**, bands at 816 cm^{-1} (ν_{28}; C–S stretch), 770 cm^{-1} (ν_{30}; C–S stretch) and 732 cm^{-1} (ν_{32}; C–S stretch within the ring) were observed at frequencies lower than those found for the free molecule.

Substrates containing carbonyl groups that engage in similar non-covalent Hg···O interactions also display a shift to lower frequencies in the IR spectrum [9]. The combination of lower frequency shifts for the C–S stretches coupled with favorable interatomic distances is indicative of Hg···S supramolecular interactions observed within **1**.

Continued inspection of the IR spectrum for **1** revealed a band corresponding to the cyanide stretching frequency at 2250 cm^{-1}. Similar to the change in stretching frequencies for o-Me_2TTF, the peak corresponding to CH_3CN shifted to a lower value when compared to the free form which has a value of 2254 cm^{-1} [6]. The frequency shift in **1** to a lower frequency for the nitrile band mirrors that seen for carbonyl substrates, illustrating non-covalent Hg···N interactions between CH_3CN and (o-C_6F_4Hg)$_3$ [9].

4. Conclusion

Herein, the synthesis, structure, and spectroscopic properties of the supramolecular complex coupling the Lewis acid (o-C_6F_4Hg)$_3$ with the organosulfur donor o-Me_2TTF are reported. The complex is dominated by alternating, integrated stacks of the acid and substrate which produce an extended structure. Non-covalent Hg···S interactions are found within the stacks based upon the small intermolecular distances as well as the lower frequency of the bonding groups within the IR spectrum. In a similar manner, Hg···N interactions were observed between the nitrogen of an interstitial acetonitrile and one of the divalent mercury ions which was also confirmed by the shift of the vibrational peaks in the IR spectrum. Concurrently, a network of C–H···F hydrogen bonds was observed in **1** where hydrogens attached to both sp^2- and sp^3-hybridized carbons are hydrogen bond donors. Both accepting and donating bifurcated hydrogen bonds were observed within **1** producing a 3-D supramolecular adduct in the solid state. Currently, other supramolecular complexes with (o-C_6F_4Hg)$_3$ are being investigated in order to better understand the nature of these non-covalent interactions and the overall structures of the complexes. In addition, other crystal forms of (o-C_6F_4Hg)$_3$ and o-Me_2TTF will be investigated by varying the solvent used during crystallization. Recently in this area, the ability to produce polymorphic forms of molecular complexes containing (o-C_6F_4Hg)$_3$ and TTF have been realized due to varying the crystallizing solvent [28].

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Disclosure statement

No potential conflict of interest was reported by the authors.

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