Contribution from the Department of Chemistry,
Clarkson College of Technology, Potsdam, New York 13676

Raman and Resonance Raman Studies of Bis(3,5-dimethyl-1,2-dithiolylium) Tetrachloroferrate(II) and -manganate(II)

R. CALLAGHAN and O. SIIMAN*

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Raman and resonance Raman spectra of the title compounds, $(C_5H_7S_2)_2MCl_4$, M = Fe(II), Mn(II), have been measured with laser excitation lines between 350 and 650 nm. The sulfur–sulfur stretching mode of the cyclic disulfide ring was reassigned to a band at 525 cm^{-1}. The relatively high $\nu(\mathrm{S}\overset{-}{\cdot\cdot}\mathrm{S})$ frequency indicates considerable double-bond character in the S–S bond. With the addition to previous infrared spectral data and normal mode analysis, reassignment of some other vibrational bands was also made. Electronic absorption spectra of KBr pellets of both Fe(II) and Mn(II) salts at 77 K showed a major band maximum at 500 nm and weak shoulders between 600 and 900 nm. Excitation into the 500-nm absorption band of $(C_5H_7S_2)_2FeCl_4$ produced a slight enhancement of all Raman bands that involve the sulfur atom. No metal–chloride modes, however, were detected. The visible absorption band has been assigned to an anion → cation, metal → sulfur charge-transfer electronic transition. Unexpectedly strong enhancement of some Raman bands was also observed with 647.1-nm excitation, possibly due to the presence of a previously undetected $n(S) \rightarrow \sigma^*(S)$ electronic absorption band in the 600–700-nm region.

Introduction

Ever since the synthesis[1,2] of the title iron compound, the chemistry of dithiolylium halometalates has been an active area[3] of research. Nevertheless, several unanswered questions remain. Direct metal–sulfur covalent bonding, responsible for the intense charge-transfer absorption spectra of many metal–sulfur complexes, has not been found in these salts. X-ray studies[4–6] show that the bis(3,5-dimethyl-1,2-dithiolylium) tetrachloroferrate(II) (I) in the solid state is composed of discrete dithiolylium and tetrachloroferrate(II) ions (yellow and pale cream in aqueous solution, respectively) with no direct metal–sulfur interaction. Yet, the solid is deep red in color and exhibits an electronic absorption band at 500 nm, a region in which neither $Fe^{II}Cl_4^{2-}$ nor the cyclic disulfide cation absorb intensely. Although it was postulated[7] that this band arises from a charge-transfer transition from the anion to the cation, the nature of the transfer has not been established. In addition, π delocalization within the five-membered dithiolylium ring is expected to be extensive; however, the degree of multiple-bond character within the disulfide bond has not been substantiated.

In order to obtain further information on inter- and intramolecular bonding within these salts, we have measured Raman and resonance Raman (RR) spectra of I and its Mn(II) analogue, II, with several visible and ultraviolet excitation wavelengths. RR spectra can be used in conjunction with normal Raman and infrared spectra to obtain information on the vibrational as well as electronic states of metal–sulfur ligand complexes.[8]

Experimental Section

I and II were prepared by previously described methods.[1,2,7]

Table I. Raman Band Frequencies (cm^{-1}) and Depolarization Ratios of I and II in Aqueous Solution (pH 2)

I	ρ (350.7 nm)	ρ (514.5 nm)	II	ρ (488.0 nm)
270			260	0.18
440			440	0.72
530	0.24	0.17	530	0.15
580	0.35		580	0.32
714	0.20	0.41	715	0.13
1210	0.13	0.0	1214	0.0
1380	0.32		1380	0.41
1490	0.69		1490	0.76

Raman spectra with the 457.9-, 488.0-, 514.5-nm Ar^+ and 647.1-nm Kr^+ lines of Spectra-Physics model 164 lasers were measured with a Jarrell-Ash 25-100 double monochromator employing an RCA C31034 phototube for detection. Raman spectra with the 350.7-nm Kr^+ line of a Coherent model CR-3000K laser were measured with a Spex 1301 0.5-m double monochromator using a Gencom picoammeter for DC detection. Solid-state spectra were obtained by pressing a thin layer of material, in some cases mixed 50% by weight with anhydrous sodium sulfate as an internal standard, into a circular groove of a rotating stainless-steel cell. Spectra of solutions were measured in either a stationary rectangular or a rotating cylindrical quartz cell. So that photodecomposition could be avoided in UV work, solutions were recirculated with a peristaltic pump through a quartz capillary at right angles to the incident beam. Scattered light was collected at 90° to the incident beam.

Electronic absorption spectra were measured with a Cary 14 spectrophotometer. Potassium bromide pellets were prepared, soaked in Nujol, and dried prior to use. A Dewar flask with suprasil quartz windows and an insertable copper block assembly was used to obtain liquid-N_2-temperature (77 K) spectra of the pellets.

Results

The electonic absorption spectra of solids I and II between 350 and 1000 nm are shown in Figure 1. Both salts exhibit band maxima near 500 nm, although the band intensity for the tetrachloromanganate(II) salt (30 mg in 300 mg of KBr), $\epsilon \sim 60$ M^{-1} cm^{-1}, is weaker than that for the tetrachloroferrate(II) salt (~ 3 mg in 300 mg of KBr), $\epsilon \sim 1000$ M^{-1} cm^{-1}. The spectrum of I agrees with previous results of reflectance spectral measurements by Heath et al.[7] Furuhashi et al.[2] reported spectra of I and II which differ from those reported here and elsewhere;[7] however, their samples were diluted with magnesium carbonate which is believed to cause decomposition of the dithiolylium salts. Since I decomposes in aqueous solution, its solution spectrum is due mainly to the dithiolylium cation. Two intense bands below 300 nm, also

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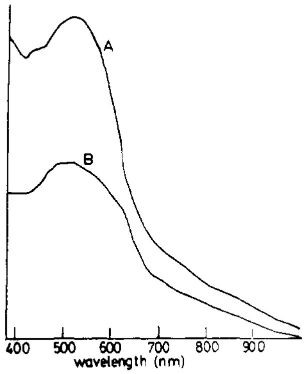

Figure 1. Electronic absorption spectra of I (0.99% by weight), A, and II (9.1%), B, in potassium bromide matrix at 77 K.

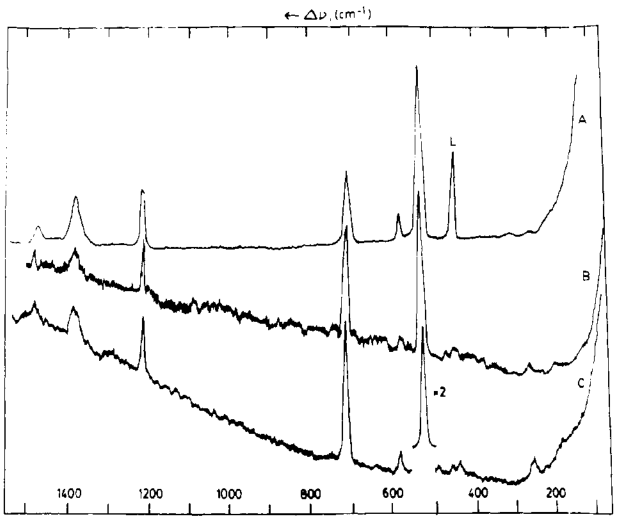

Figure 2. Raman spectra of aqueous solutions (pH 2): A, $(C_5H_7S_2)_2FeCl_4$, 0.1 M; B, $(C_5H_7S_2)_2FeCl_4$, 0.5 M; C, $(C_5H_7S_2)_2MnCl_4$, 0.25 M. Experimental conditions [excitation wavelength (nm), laser power (mW), sensitivity, spectral slit width (cm^{-1}), time constant (s), scan speed (cm^{-1}/s)]: A, 350.7 Kr^+, 45, 1 μA, 8.0, 4.4, 0.75; B, 514.5 Ar^+, 200, 20000 counts/s, 6.0, 2, 0.5; C, 488.0 Ar^+, 50, 2000 counts/s, 6.0, 2, 1.0.

Table II. Frequency Dependence of Relative Raman Band Intensities of Solid I

	λ_0,[a] nm			
Δν, cm^{-1}	457.9	488.0	514.5	647.1
425			0.16	
444			0.22	
464			0.38	
525	0.57	0.51	0.72	4.64
550	0.31	0.27	0.18	4.17
576	0.08	0.10	0.10	2.50
704	0.50	0.49	0.68	4.39
724	0.32	0.30	0.24	2.88
1210	0.12	0.15	0.10	

[a] Relative Intensity with respect to Na_2SO_4 sulfate band at 995 cm^{-1}.

observed in simple $(C_5H_7S_2)X$ (X = halide) salts, and two lower energy (1000 times less intense) bands at 420 and 520 nm were observed for I.

Raman spectra of aqueous solutions of I and II (adjusted to pH 2 with hydrochloric acid) are shown in Figure 2. The spectra were very nearly identical and independent of the excitation wavelength. Depolarization ratios, ρ_l, were measured for the more intense bands and are tabulated with the band frequencies in Table I.

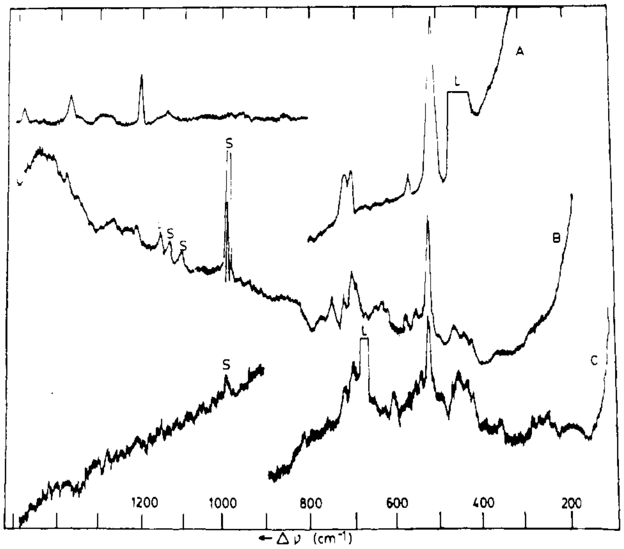

Figure 3. Raman spectra of solid I in Na_2SO_4 (50% by weight) for B and C. Experimental conditions [excitation wavelength (nm), laser power (mW), sensitivity, spectral slit width (cm^{-1}), time constant (s), scan speed (cm^{-1}/s)]: A, 350.7 Kr^+, 35, 300 nA, 8.0, 4.4, 0.75; B, 514.5 Ar^+, 200, 2000 counts/s, 8.3, 5, 0.5; C, 647.1 Kr^+, 80, 1000 counts/s, 8.0, 5, 0.5.

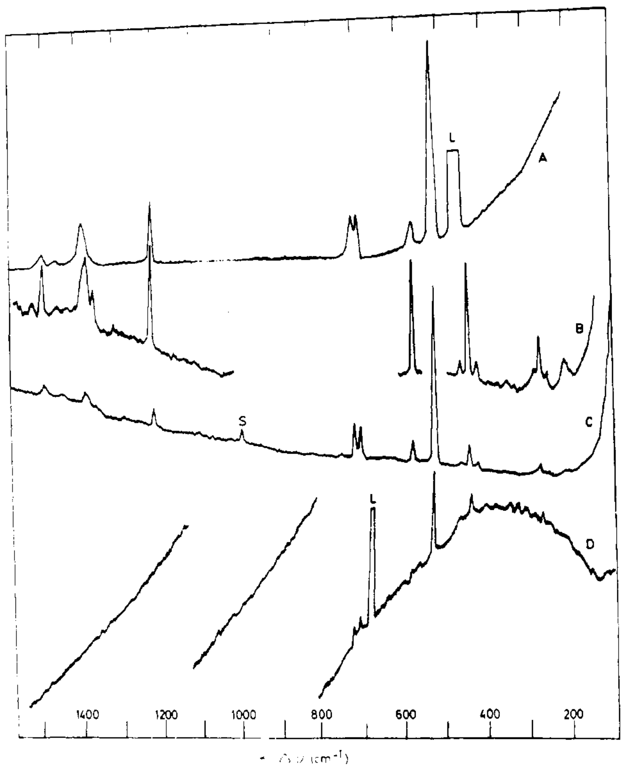

Figure 4. Raman spectra of solid II in Na_2SO_4 (50%) for C and D. Experimental conditions [excitation wavelength (nm), laser power (mW), sensitivity, spectral slit width (cm^{-1}), time constant (s), scan speed (cm^{-1}/s)]: A, 350.7 Kr^+, 35, 1 μA, 8.0, 4.4, 0.75; B, 488.0 Ar^+, 150, 10000 counts/s, 5.0, 2, 1.0; C, 488.0 Ar^+, 200, 40000 counts/s, 6.0, 2, 0.5; D, 647.1 Kr^+, 100, 8000 counts/s, 5.0, 2, 1.0.

Raman spectra of solid I, obtained with the 350.7-nm Kr^+, 514.5-nm Ar^+, and 647.1-nm Kr^+ laser lines are shown in Figure 3. The intensities of the bands below 800 cm^{-1} increase relative to the intensities of those above 800 cm^{-1} as the excitation wavelength increases. Other spectra, obtained with 457.9- and 488.0-nm Ar^+ laser lines, were similar to the one with 514.5-nm Ar^+ excitation. Band frequencies and relative

Table III. Infrared and Raman Band Frequencies (cm^{-1}) of the 3,5-Dimethyl-1,2-dithiolylium Cation

solid $(C_5H_7S_2)_2FeCl_4$		solid $(C_5H_7S_2)_2MnCl_4$		predominant modes
IR	R	IR	R	
		a. In-Plane Modes		
		A_1 Species		
1370 w	1380	1374 w	1377	$\nu(\mathrm{C}\overline{\cdot\cdot}\mathrm{C})$
1204 s	1210	1208 s	1214	$\nu(\mathrm{C{-}CH_3})$
712 vw	724	717 vw	718	$\nu(\mathrm{C}\overline{\cdot\cdot}\mathrm{S})$
573 vw	576	573	574	ring def
525 w	525	523	525	$\nu(\mathrm{S{-}S})$
348 vw		340 vw		$\delta(\mathrm{C{-}CH_3})$
		B_2 Species		
1476 vs	1480	1477 vs	1483	$\nu(\mathrm{C}\overline{\cdot\cdot}\mathrm{C})$
1232 m		1232 m		$\delta(\mathrm{C{-}H})$
1092 vw		1095 vw		$\nu(\mathrm{C{-}CH_3})$
697 m	704	700 m	704	$\nu(\mathrm{C}\overline{\cdot\cdot}\mathrm{S})$
457 w	464	460 w	460	$\delta(\mathrm{C{-}CH_3})$
435 m	440	433 m	441	ring def
		b. Out-of-Plane and Methyl Group Modes		
1426 w 1399 w		1425 w 1395 w	1400	CH_3 deg def
1351 w		1353 w	1356	CH_3 sym def
1019 w 1006 m 995 w 980 w		1020 w 1007 m 1000 w 1000 w 985 w		$\rho(\mathrm{CH_3})$
861 s		862 s		$\pi(\mathrm{C{-}H})$
557 s	557	556 s	560	$\pi\left(\mathrm{S{-}C}\genfrac{}{}{0pt}{}{\diagup\mathrm{C}}{\diagdown\mathrm{C}}\right)$

intensities measured with respect to the sodium sulfate band at 995 cm^{-1} are given in Table II.

The Raman spectra of solid II with 350.7-nm Kr^+, 488.0-nm Ar^+, and 647.1-nm Kr^+ excitation are depicted in Figure 4. The vibrational bands occur at nearly the same energies as in I and their relative intensities vary with excitation wavelength in a similar way, but absolute band intensities are much higher for the Mn(II) salt. Low-intensity bands are more resolved in spectrum B of Figure 4, measured at a 4-fold lower photon count rate. A steep base line attributable to fluorescence emission[9] from the ligand field states of $\mathrm{Mn^{II}Cl_4}^{2-}$ was observed with excitation in the red (spectrum D, Figure 4).

Discussion

Initial attempts[2] at making vibrational assignments of infrared bands of the dithiolylium salts were unsuccessful since incorrect structures (covalent metal–sulfur bonds) were assumed. Since the metalate anion has little effect on the infrared spectrum above 300 cm^{-1}, the results of a normal coordinate analysis[10] on the 3,5-dimethyl-1,2-dithiolylium cation alone were used to assign IR bands of I. The Raman spectra reported herein indicate that several revisions in band assignments should be made. Infrared and Raman band frequencies and predominant mode assignments are summarized in Table III.

The extent of double bonding between the sulfur atoms has been under dispute.[3] The symmetric S–S stretch was previously[10] assigned to the strong IR band at 435 cm^{-1}. However, Raman spectra show that ν(S–S) occurs as a very intense polarized ($\rho_l = 0.17$) band at 530 cm^{-1} in aqueous solution and at 525 cm^{-1} in the solid state. In a recent comprehensive study[11] the factors affecting disulfide stretching frequencies were analyzed. An increase in the dihedral angle between the carbon–sulfur bonds from 0 to 90° causes an increase of 30 cm^{-1} in the S–S stretching frequency. For a planar aliphatic disulfide, ν(S–S) occurs near 480 cm^{-1}. The aromatic disulfides, on the other hand, all showed stretching frequencies at about 515 cm^{-1} in the solid state and 525 cm^{-1} in solution. It is thus apparent that the dithiolylium cation ring has considerable aromatic character. This is consistent both with the X-ray structures,[4-6] which show that the bond distances in the ring are all midway between double-bond and single-bond values, and with MO calculations which predict considerable aromatic character for the ring.[3]

The behavior of the two bands near 700 cm^{-1} is interesting. In the Raman spectra of both solid I and II, the two bands have nearly equal intensity, whereas in the solution spectra (Figure 2) only one band at 718 cm^{-1} is observed. The infrared spectrum of solid I shows a weak band at 712 cm^{-1} and a medium band at 697 cm^{-1}. X-ray studies[4-6] have shown that the two sulfur atoms of the dithiolylium ring are not in equivalent positions in the crystalline state. One sulfur atom is 0.10 Å further away from the nearest chlorine atom. This may be sufficient to cause a slight splitting of the carbon–sulfur symmetric stretching band in the solid state. In solution only one $\nu_s(\mathrm{C}\overline{\cdot\cdot}\mathrm{S})$ band is expected to appear. Normal-coordinate analysis[10] suggested that both the asymmetric and the symmetric $\mathrm{C}\overline{\cdot\cdot}\mathrm{S}$ stretching modes occur in the region around 700 cm^{-1}. In the IR the $\nu_{as}(\mathrm{C}\overline{\cdot\cdot}\mathrm{S})$ band is expected to be more intense than the $\nu_s(\mathrm{C}\overline{\cdot\cdot}\mathrm{S})$ band, while the opposite intensity relationship is anticipated in the Raman spectrum. If the crystal-splitting hypothesis is valid, then some of the intensity of the infrared band at 697 cm^{-1} may be due to the fortuitous superposition of the asymmetric $\mathrm{C}\overline{\cdot\cdot}\mathrm{S}$ stretching band onto the lower frequency symmetric $\mathrm{C}\overline{\cdot\cdot}\mathrm{S}$ stretching band. In 3,5-dimethyl-1,2-dithiolylium iodide, the sulfur atoms are in equivalent positions and the IR band at 697 cm^{-1} is lower in intensity relative to other bands while the weak band occurs at 704 cm^{-1}, a shift of about 10 cm^{-1} from the band in the halometalate salts. Alternatively, in the Raman spectrum the asymmetric stretch may borrow intensity from another mode. In either case the Raman band at 724 cm^{-1} is assigned to $\nu_s(\mathrm{C}\overline{\cdot\cdot}\mathrm{S})$ while the band at 704 cm^{-1} is assigned to either $\nu_{as}(\mathrm{C}\overline{\cdot\cdot}\mathrm{S})$ or a combination of $\nu_{as}(\mathrm{C}\overline{\cdot\cdot}\mathrm{S})$ and $\nu_s(\mathrm{C}\overline{\cdot\cdot}\mathrm{S})$.

The asymmetric $\mathrm{C}\overline{\cdot\cdot}\mathrm{C}$ stretching mode was correctly assigned[10] to an IR band at 1477 cm^{-1}. It is a very strong, broad band in the infrared spectrum and a medium band in the Raman spectrum of the solid ferrate salt. The symmetric counterpart, previously assigned to an IR band at 1318 cm^{-1}, has been reassigned to a 1377-cm^{-1} Raman band, which is the most intense one in the 1250–1600 cm^{-1}-region. A very weak IR band at 1374 cm^{-1} may originate from $\nu_s(\mathrm{C}\overline{\cdot\cdot}\mathrm{C})$.

Three Raman bands of II at 1400, 1356, and 1310 cm^{-1} in Figure 4 (spectrum B) are too weak to be observed in the other spectra. There are weak infrared counterparts at 1395, 1353, and 1318 cm^{-1}, which are assigned to methyl group deformations. A strong, sharp Raman band at 1210 cm^{-1}, found at 1208 cm^{-1} in the infrared, was correctly assigned[10] to the carbon–methyl group symmetric C–C stretch.

The Raman band at 576 cm^{-1} in solids and 580 cm^{-1} in solutions has a depolarization ratio of 0.30 which indicates its assignment to a totally symmetric mode. Normal coordinate calculations predicted a sulfur–sulfur symmetric stretch in this region and assigned[10] a strong infrared band at 557 cm^{-1} to it. The former mode might be better characterized as a totally symmetric ring deformation with substantial $\nu_s(\mathrm{S}\overline{\cdot\cdot}\mathrm{S})$ character and is reassigned to the Raman band at 576 cm^{-1}. The

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557-cm^{-1} band is then reassigned to an out-of-plane ring deformation mode previously associated with the IR band at 525 cm^{-1}.

There are three bands in the 400–500-cm^{-1} region. In Raman spectra two are very weak and tend to overlap with the third band unless high-resolution spectra are measured. The medium-intensity infrared and Raman band at 441 cm^{-1} has a measured depolarization ratio of 0.72, which is close to the maximum theoretical value, $\rho_l = {}^3/_4$ in solution. Assignment of this band to a non-totally symmetric mode is thus indicated. The 441-cm^{-1} band intensity is resonance enhanced with 647.1-nm excitation. Since the other modes that are enhanced involve the sulfur atoms, this leads to its assignment as an in-plane ring deformation mode of B_2 symmetry. This mode was previously assigned in I to an infrared band[10] at 370 cm^{-1}, which disappears when I is recrystallized from ethanolic solution saturated with HCl gas and purged with nitrogen gas. The band at 460 cm^{-1} is weak in both infrared and Raman spectra and is assigned to the asymmetric carbon–methyl group bending mode. The assignment for the weak band at 420 cm^{-1} is uncertain.

There are four bands in the Raman spectrum of solid II at 287, 270, 252, and 214 cm^{-1}, none of which are resolved in its infrared spectrum. The medium band at 270 cm^{-1} has a measured depolarization ratio of 0.18 and is therefore assigned to ν_s(Mn–Cl). The other three bands in this region are probably also metal–chlorine stretching modes since no dithiolylium modes are expected below 300 cm^{-1}.

In resonance Raman spectra those vibrations which occur in the same region of the molecule as the orbitals involved in the electronic transition are expected to be most strongly enhanced when the exciting wavelength lies within the electronic absorption band. This can be explained by Franck–Condon factors. The intensity of a given Raman band depends on the product of an electronic overlap integral and the sum of the overlap integrals of the vibrational levels of the ground and excited electronic states.[12] These Franck–Condon vibrational overlap integrals are large when either the equilibrium distance or the force constant of a given mode is considerably different in its ground and excited electronic states. Changing the occupancy of a molecular orbital is likely to have the greatest effect on those modes in the same region of the molecule so that as a general rule these modes are expected to show the greatest enhancement.

Previously published[7] electronic spectra of I showed that the absorption maximum in the visible occurred at about 500 nm and was thought to originate from a charge-transfer transition. Since iron(II) in tetrachloroferrate is readily oxidizable and the dithiolylium cation is readily reducible, this band assignment seems reasonable. The electronic absorption spectrum of II also shows a band in this region, but it is much weaker since manganese(II) is less easily oxidized. The X-ray structure[4–6] of I showed that the sulfur–iron distances were longer than the sum of the van der Waals radii, while the sulfur–chlorine distances were shorter; therefore, any charge-transfer mechanism would be expected to occur through the chlorine atoms. On this basis, we would expect the ν(Fe–Cl) and ν(S–S) bands to be most strongly enhanced in intensity.

The spectra (Figures 3 and 4) of solids I and II taken with 350.7-nm excitation are similar to each other and to the solution spectra with respect to relative band intensities. As the frequency of excitation is moved within the 500-nm absorption band of I, the intensities of the Raman bands at 724, 704, 576, 557, 525, and 440 cm^{-1} increase with respect to the Raman bands above 1000 cm^{-1}. All these enhanced bands are assigned to vibrations involving the sulfur atoms. Compound II exhibits similar behavior but the enhancement is less pronounced. Surprisingly neither compound shows an enhancement of the metal–chlorine vibrations. It therefore seems likely that the charge transfer does not involved the chlorine atoms at all but occurs directly from d_π(Fe) orbitals into a ring π^* orbital of predominantly S–S character.

The relative intensities of Raman bands in I and II with 647.1-nm excitation was unexpected (Figure 3, spectrum C, and Figure 4, spectrum B). Both compounds showed considerable enhancement of the bands at 440, 525, 576, 704, and 724 cm^{-1}. None of the bands above 1000 cm^{-1} were detected above the background noise, and the 995-cm^{-1} band of the sodium sulfate internal standard was barely detected in the spectrum of I and not observed at all in the spectrum of II. No electronic absorption band was observed for either solid compound in the 600-nm region; however, absorption spectra of methanolic solutions of I and of 3,5-dimethyl-1,2-dithiolylium iodide[3] showed a very weak band at 600 nm originating from the dithiolylium cation alone. This band has a molar extinction coefficient of about 20 so that it would be overshadowed in the solid state by the much stronger charge-transfer band at 500 nm. Since only vibrations involving sulfur atoms are enhanced, the probable assignment for this electronic band is n(S) to σ^*(S–S). Similar absorption bands have been observed in the visible spectra of other cyclic disulfides.[13]

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