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Vibration assignment of carbon–sulfur bond in 2-thione-1,3-dithiole-4,5-dithiolate derivatives

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Abstract

The higher frequency peak near 1050 cm^{-1} of the doublet in the infrared and Raman spectra of 2-thione-1,3-dithiole-4,5-dithiolate (DMIT) derivatives corresponds mainly to the stretching vibration of carbon–sulfur double bond in the terminal $S{=}CS_2$ fragments of DMIT skeletons while the lower one corresponds mainly to the Fermi resonance peak between overtones of symmetric stretching vibration of two carbon–sulfur single bond in the $S{=}CS_2$ fragment of DMIT skeletons and the higher frequency. On the other hand, the higher frequency near 500 cm^{-1} corresponds mainly to the symmetric stretching vibration of two carbon–sulfur single bond in the $S{=}CS_2$ fragments of DMIT skeletons while the lower one corresponds mainly to the symmetric stretching vibration of the four carbon–sulfur single bond in the $S_2C{=}CS_2$ fragments of DMIT skeletons.

Keywords: 2-Thione-1,3-dithiole-4,5-dithiolate; Carbon–sulfur bond; Infrared and Raman spectra; Fermi resonance; Molecular orbital

1. Introduction

2-Thione-1,3-dithiole-4,5-dithiolate (DMIT or dmit) derivatives (series 1 and 3 in Scheme 1) are essential precursors for building molecular conductors and superconductors. Generally the DMIT skeleton, i.e. Na_2DMIT (for this abbreviation, please refer to Table 1 and Scheme 1 and hereafter the abbreviations follow these references too), is synthesized by reduction of carbon disulfide with metal sodium in the *N*,*N*-dimethyl formamide solvent. Since Na_2DMIT is not air-stable [1] $(PhCO)_2$DMIT [3,4] and $TBA_2[Zn(dmit)_2]$ [5,6]/$TEA_2[Zn(dmit)_2]$ [7] are in practical use for providing DMIT skeletons. Using either $TEA_2[Zn(dmit)_2]$ [7] or $(PhCO)_2$DMIT [3] as starting material people can obtain EDT-DTT, which can, after two well-developed steps [3], provide 4,5-bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF), the famous donor molecule for producing most of organic molecular conductors and superconductors [8]. While using $(PhCO)_2$DMIT as starting material researchers can also obtain molecular conductors and superconductors based on metal–dmit complexes (series 3 in Scheme 1) [4].

Since compounds of series 1 in Scheme 1 are considered only precursors for organic molecular conductors, to our knowledge, their infrared (IR) spectra received only a little attention. On the initial synthesis of the DMIT derivatives Steimecke et al. [9] have recorded the IR spectra of compounds of series 1 in Scheme 1. Doublets of the S=C stretching vibration were given unambiguously for the IR spectra of BMT-DTT (1064/strong and 1039/medium) and EDT-DTT (1068/strong and 1050/medium) etc. In their considerations the two peaks in the doublets were both assigned as S=C fundamental vibration. Kozlov et al. [10] have performed fundamental vibration assignment on compounds EDT-DTT, EDT-DTO (thiocarbonyl group in EDT-DTT replaced by carbonyl group) and their deuterated forms. However, for the IR and Raman spectra of EDT-DTT they did not mention the doublet peaks near 1050 cm^{-1} and only assigned 1061 cm^{-1} peak to S=C fundamental stretching vibration. Studied IR and Raman spectra of dmit-complex are mainly confined to the transition metal nickel [9,11–14], palladium [12] and platinum [11]. Moreover, these papers [12–14] mainly concentrate their attention on the eight A_g

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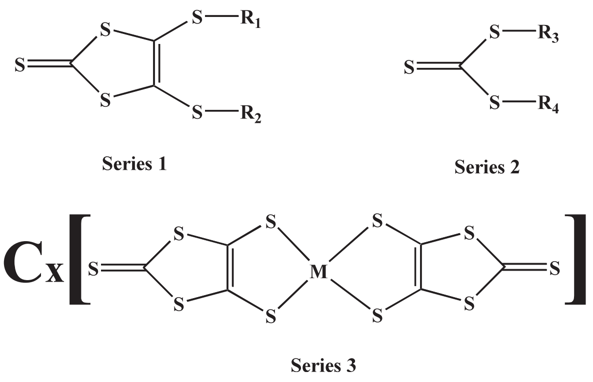

Scheme 1. Chemical structure of DMIT derivatives (series 1 and 2) and trithiocarbonate derivatives (series 2).

modes of nickel–dmit complexes, for it is considered that these A_g modes are relevant to the electron-molecular vibration coupling, the parameters of which are believed to be very important for the development of the superconductivity theory in molecular solids. Steimecke et al. [9] also considered that in the IR spectra of $TBA_2[Ni(dmit)_2]$, $TBA[Ni(dmit)_2]$ and $[Ni(dmit)_2]^0$ the two peaks in the doublets near 1050 cm^{-1} both should be assigned as S=C vibrations. On the other hand Pokhodnya et al. [12] have also been convinced of the splitting, called doublet in this paper, of S=C A_g (2) stretching vibrational mode and considered the splitting is “apparently due to deviation from perfect D_{2h} symmetry”. In addition they also pointed out “the appearance (splitting or doublet) in the spectra of very intensive B_{1u} modes (i.e. IR active)”. These experimental descriptions are in accordance with those of ours and confirm the existence and generality of the doublets near 1050 cm^{-1} while the reasons for the doublets will need more consideration. In this paper the generality of the doublet phenomena will be further described in detail and the possible reasons for leading to this doublet will be analyzed.

Another issue is how to distinguish the origins of the two peaks near 500 cm^{-1} in the IR and Raman spectra of the DMIT derivatives. As we know, one of them originates from the symmetric stretching vibration of two carbon–sulfur single bond in the $S{=}CS_2$ fragments of the DMIT skeletons (hereafter abbreviated as $\nu_s S_2C{=}S$) and the other originates from the symmetric stretching vibration of the four

Table 1
Corresponding relationship between chemical structures and abbreviations of compounds in Scheme 1

R_1	R_2	Abbreviation	
(*a*) *Series 1*			
Sodium	Sodium	Na_2DMIT	
Benzoyl	Benzoyl	$(PhCO)_2DMIT$	
Ethylene	EDT-DTT		
Methyl	Methyl	BMT-DTT	
Acetyl	Acetyl	BAT-DTT	
Carboxymethyl	Carboxymethyl	BCMT-DTT	
p-Bromobenzyl	*p*-Bromobenzyl	BBBT-DTT	
Benzyl	Benzyl	BBT-DTT	
2′-Cyanoethyl	2′-Cyanoethyl	BCNET-DTT	
C	x	M	Abbreviation
(*b*) *Series 3*			
Tetrabutyl ammonium	2	Zinc	$TBA_2[Zn(dmit)_2]$
Tetraethyl ammonium	2	Zinc	$TEA_2[Zn(dmit)_2]$
Tetrabutyl ammonium	2	Nickel	$TBA_2[Ni(dmit)_2]$
Tetrabutyl ammonium	1	Nickel	$TBA[Ni(dmit)_2]$
	0	Nickel	$[Ni(dmit)_2]$
Tetrabutyl ammonium	0.25	Nickel	$TBA_{0.25}[Ni(dmit)_2]$
Tetrabutyl ammonium	0.29	Nickel	$TBA_{0.29}[Ni(dmit)_2]$
Benzyl trimethyl ammonium	2	Nickel	$BTMA_2[Ni(dmit)_2]$
Tetrabutyl ammonium	2	Copper	$TBA_2[Cu(dmit)_2]$
Benzyl trimethyl ammonium	2	Copper	$BTMA_2[Cu(dmit)_2]$
N-methyl pyridine	2	Copper	$NMP_2[Cu(dmit)_2]$
N-ethyl pyridine	2	Copper	$NEP_2[Cu(dmit)_2]$
N-*n*-octyl pyridine	2	Copper	$NOP_2[Cu(dmit)_2]$
Cobaltocenium	1	Nickel	$(CoCp_2)[Ni(dmit)_2]$
Cobaltocenium	2	Nickel	$(CoCp_2)_2[Ni(dmit)_2]$
Cobaltocenium	2	Palladium	$(CoCp_2)_2[Pd(dmit)_2]$
Cobaltocenium	1	Palladium	$(CoCp_2)[Pd(dmit)_2]$
	0	Palladium	$[Pd(dmit)_2]$
Tetrabutyl ammonium	1	Palladium	$TBA[Pd(dmit)_2]$
Tetrabutyl ammonium	2	Palladium	$TBA_2[Pd(dmit)_2]$
Tetrabutyl ammonium	1	Platinum	$TBA[Pt(dmit)_2]$
Tetrabutyl ammonium	0.2	Platinum	$TBA_{0.2}[Pt(dmit)_2]$

carbon–sulfur single bond in the $S_2C{=}CS_2$ fragments of the DMIT skeletons (hereafter abbreviated as $\nu_s S_2C{=}CS_2$). Ramakumar et al. [14] have assigned the higher frequency near 500 cm^{-1} mainly to $\nu_s S_2C{=}S$ and lower frequency near 500 cm^{-1} mainly to $\nu_s S_2C{=}CS_2$ while Pokhodnya et al. [12] gave a contrary conclusion for "the positive sign of its frequency shift due to reduction" of the latter group. Thus a detailed molecular orbital analysis, such as bonding or antibonding character between atoms, of the lowest unoccupied molecular orbital (LUMO) of the neutral [Ni(dmit)$_2$] molecule is performed because of the existence of such opposite arguments.

2. Experimental and theoretical methods

2.1. Compounds synthesis

TBA$_2$[Zn(dmit)$_2$] was synthesized according to literature [5,2]. (PhCO)$_2$DMIT was synthesized by adding benzoyl chloride dropwise into the acetone solution of TBA$_2$[Zn(dmit)$_2$] with stirring [9]. EDT-DTT was synthesized by treating 1,2-dibromoethane with TBA$_2$[Zn(dmit)$_2$] in acetone with stirring for several days at room temperature [3]. BCNET-DTT was synthesized according to literature [15] and BBBT-DTT was synthesized with similar procedure as that for the preparation of BCNET-DTT. TBA$_2$[Ni(dmit)$_2$], TBA$_2$[Pd(dmit)$_2$], BTMA$_2$[Ni(dmit)$_2$], BTMA$_2$[Cu(dmit)$_2$], NMP$_2$[Cu(dmit)$_2$] and NOP$_2$-[Cu(dmit)$_2$] were synthesized by deprotecting (PhCO)$_2$-DMIT with sodium ethoxide in ethanol at nitrogen atmosphere followed by adding methanol solution of corresponding metal chlorides with stirring and after that adding methanol solution of corresponding cation chlorides to precipitate these complexes [9,4]. (CoCp$_2$)$_2$[Ni(dmit)$_2$] was synthesized by mixing the TBA$_2$[Ni(dmit)$_2$] and (CoCp$_2$)PF$_6$ in acetonitrile under the Ar atmosphere. (CoCp$_2$)$_2$[Pd(dmit)$_2$] was synthesized with the similar procedure as that for (CoCp$_2$)$_2$[Ni(dmit)$_2$]. TBA[Ni(dmit)$_2$] and TBA[Pd(dmit)$_2$] were synthesized according literature [9]. (CoCp$_2$)[Ni(dmit)$_2$] was synthesized by mixing the TBA[Ni(dmit)$_2$] and (CoCp$_2$)PF$_6$ in acetonitrile and (CoCp$_2$)[Pd(dmit)$_2$] was synthesized with similar procedure. [Ni(dmit)$_2$] was synthesized by slow diffusing of TBA[Ni(dmit)$_2$] and (FeCp$_2$)BF$_4$ in the newly distilled acetonitrile with diffusion cell [4] and [Pd(dmit)$_2$] was synthesized with similar procedure.

2.2. Measurements of IR and Raman spectra

The IR spectra of all compounds studied except those mentioned otherwise were recorded in the solid state in potassium bromide pellets on a Nicolet 20SX FT-IR infrared spectrometer at room temperature in the region of 400–4000 cm^{-1}. And the Raman spectra measurement were carried out on a SPEX-1430 Laser Raman spectrometer with Ar$^+$ lasers for excitation in the potassium bromide pellets.

2.3. Theoretical details

The geometry optimizations and frequency calculations are preformed with the package GAUSSIAN 98 [16]. Initial guess of the geometry of neutral [Ni(dmit)$_2$] is derived from the literature [17]. The process of transformation from Crystallographic Information File (CIF) to Gaussian Job File (GJF) is as following. The CIF file of the crystal [Ni(dmit)$_2$] was opened with the package MERCURY 1.1 [18] and then saved as Protein Database Bank (PDB) file *.ent. The *.ent file was transformed into GJF file using *NewZMat* option in the *Utilities* of Gaussian 98. The following was specified in the Route Section of the GJF file of this molecule: *opt freq = raman b3lyp/6-31 + g(d) nosymm*. The normal vibrational modes of nickel–dmit complex skeleton and their corresponding frequencies were assigned with the package GAUSSVIEW 2.1 [19]. The atom displacements corresponding specific normal vibration modes are retrieved from the *.out file. The LUMO of [Ni(dmit)$_2$] is displayed in GAUSSVIEW with the corresponding Checkpoint file.

3. Results and discussions

3.1. Issue of doublet peaks near 1050 cm^{-1}

3.1.1. Generality of this doublet phenomena

3.1.1.1. Doublet in TBA$_2$[Zn(dmit)$_2$] compound. TBA$_2$-[Zn(dmit)$_2$] is nearly the first starting material for providing dmit skeletons and plays fundamental role in the research fields concerning dmit fragments [1]. Thus its IR spectra are the first imagination and choice. In the crystal structure of TBA$_2$[Zn(dmit)$_2$] (space group: $C2/c$, $Z' = 4$, where Z' is the number of Zn(dmit)$_2$ unit in each Bravais space cell. The same meaning follows in the following sections) the four sulfurs coordinate to the central zinc cation tetragonally [20], i.e. the two dmit skeleton planes are nearly perpendicular with each other and in the ideal condition the point group of the [Zn(dmit)$_2$]$^{2-}$ dianion is D_{2d}. In the packing diagram of TBA$_2$[Zn(dmit)$_2$] no short contacts between different [Zn(dmit)$_2$]$^{2-}$ dianions are observed using MERCURY 1.1. And the two dmit fragments in the dianion [Zn(dmit)$_2$]$^{2-}$ have two $S{=}CS_2$ groups with the same environment. However, our six samples of IR spectra show clear doublets at 1056 and 1033 cm^{-1}, respectively, although their relative intensity is different with different samples (different solvents (acetone or acetonitrile) for crystallizing as well as different condensed matter (power or crystal or mixture between them)). The intensity of the former changes from medium, medium strong to strong in the IR spectra but is always weaker than the latter.

3.1.1.2. Doublet in the IR and Raman spectra of nickel–dmit complexes. DMIT complexes of nickel, palladium and platinum have similar preparation process, crystal structure and electrical conductive properties [4]. Also they have similar IR and Raman spectroscopy properties. They receive predominant attention in the field of dmit–transition metal complexes for producing molecular conductors and superconductors [4]. This is especially the case for nickel–dmit complexes. No matter in the dianion, anion or neutral compounds most of the $[Ni(dmit)_2]$ skeletons always have a good planar configuration. On the other hand for the same compound it will be possible to have several polymorphs. For example $TBA[Ni(dmit)_2]$ at least has four polymorphs with the space group being $P\bar{1}$ (two, one of is $Z'=2$), $P2_1/c$ ($Z'=4$) and $C2/c$ ($Z'=4$), respectively [6]. Furthermore, even in the specific polymorph of the same compound the $[Ni(dmit)_2]$ skeletons may have different geometry parameters (corresponding bond lengths). The crystal structure of $TBA_2[Ni(dmit)_2]_7{\cdot}2CH_3CN$ ($P\bar{1}$, $Z'=14$) (or $TBA_{0.29}[Ni(dmit)_2]$ ignoring the solvent molecules) [5] is an extreme example of such type. As displayed in MERCURY 1.1 with no packing there are eight $[Ni(dmit)_2]$ skeletons with the geometry parameters (corresponding bond lengths) of one different with those of another. Thus the $S{=}CS_2$ fragments in these complexes have great diversity. And this is contrary to the case in compound $TBA_2[Zn(dmit)_2]$.

The IR spectrum of $TBA_2[Ni(dmit)_2]$ shows doublet at 1025 and 1047 cm^{-1} (Table 2), respectively, and the intensity of the former is strong while that of the latter is medium strong. This is nearly the same case as that of $TBA_2[Zn(dmit)_2]$. While the intensities of the doublet of the IR spectrum of $(CoCp_2)[Ni(dmit)_2]$ are both strong and on the contrary the intensity of the higher frequency is slightly stronger than that of the lower one. In the IR spectrum of neutral $[Ni(dmit)_2]$ the doublet locates at 1053 and 1077 cm^{-1}, respectively, and the intensity difference between them is relatively large. One is strong and the other is medium. Interestingly, the Raman spectra of nickel- [12] (this work), palladium- (this work) and platinum- [11] complexes also show clear doublets. The locations of the doublets in the Raman spectra of $TBA_2[Ni(dmit)_2]$, $TBA[Pt(dmit)_2]$ and $[Ni(dmit)_2]$ are 1046 and 1025, 1052 and 1025 as well as 1070 and 1058 cm^{-1}, respectively. Their intensities change from weak to medium in the Raman spectra and the relative intensity of the two peaks in the doublet change too from one to another.

3.1.1.3. Doublet in the IR spectra of copper–dmit complexes. Other transition metal–dmit complexes come into being another type except $TBA_2[Zn(dmit)_2]$ and nickel–dmit complexes. For the sake of experiment only copper complexes are concerned. Crystal structures of copper–dmit complexes are only a few while the following two both have representative significance. One is $TBA_2[Cu(dmit)_2]$ ($P21/c$, $Z'=2$) [20] and the other is $NEP_2[Cu(dmit)_2]$ ($C2/m$, $Z'=4$) [21]. In the crystal structure of $TBA_2[Cu(dmit)_2]$ the $[Cu(dmit)_2]$ dianion skeleton form a relatively good planar configuration, which is special for copper–dmit complexes, and no short contacts were observed with MERCURY 1.1. The bond length of S=C in $TBA_2[Cu(dmit)_2]$ (1.67 Å) [20] is between that in $TBA_2[Zn(dmit)_2]$ (1.65 Å) [20] and that in $TBA_2[Ni(dmit)_2]$ (1.68 Å) [22] but approaches more closer to the latter. While the bond length of S=C in $NEP_2[Cu(dmit)_2]$, in the crystal of which the $[Cu(dmit)_2]$ dianion skeleton has a distorted tetragonal configuration for the CuS_4 fragment and many short contacts concerning the terminal S=C group are observed, is 1.65 Å too. This change of bond lengths, i.e. from 1.65 to 1.67 Å for $NEP_2[Cu(dmit)_2]$ and $TBA_2[Cu(dmit)_2]$, respectively, shows that the planarity of the $[M(dmit)_2]$ (M, transition metals) skeleton plays some role in determining the geometry parameters of $[M(dmit)_2]$ skeleton. Doublets of concerned compounds are listed in Table 2.

3.1.1.4. Doublets in the IR spectra of compounds of series 1 in Scheme 1. EDT-DTT and its analogues are precursors for synthesizing BEDT-TTF and its analogues, which are organic donors for organic molecular conductors and superconductors [8]. Kozlov et al. [10] have performed detailed fundamental vibration assignment to EDT-DTT and its deuterated form. However, they did not mention the doublet around 1050 cm^{-1}. In the region 1000–1100 cm^{-1} the only assigned vibration except 1061 cm^{-1}, which is considered to be S=C stretching vibrational frequency, is 1014 cm^{-1}. This peak appears also in our three samples of EDT-DTT IR spectra (1013 cm^{-1}, medium strong). And in the IR spectrum of BBBT-DTT it also appears a peak at 1010 cm^{-1} with medium strong intensity. On the other hand both in the IR spectrum of EDT-DTT and BBBT-DTT there still appears a peak around 1034 cm^{-1} with medium strong intensity between the peak around 1059 cm^{-1} and the peak around 1013 cm^{-1}. In addition Steimecke et al. [9] also listed two peaks around 1050 cm^{-1}, i.e. 1068 and 1050 cm^{-1}, respectively, both of which were assigned as S=C vibration. Thus Kozlov et al. did not consider that the lower frequency (around 1034 cm^{-1}) near 1050 cm^{-1} originates from a fundamental vibration even if this peak exists indeed in their IR spectrum of EDT-DTT. Table 2 lists the doublets in the IR spectra of compounds of series 1.

3.1.1.5. Doublets in the IR and Raman spectra of compounds of series 2 in Scheme 1. As a reference, doublets in the IR and Raman spectra of compounds of series 2 in Scheme 1 are also listed in Table 2. Compounds of series 2 are not dmit-derivatives but trithiocarbonate derivatives. The similarity between them is the trithiocabonate (CS_3) fragment included in both of them. Ethylene trithiocarbonate ($-R_3-R_4-=-CH_2-CH_2-$ group in series 2 of Scheme 1, ETTC) has two peaks at 1064 and 1029 cm^{-1}, respectively, in its IR spectrum [23]. One remarkable point in this spectrum is the peak 1006 cm^{-1}, which is assigned to $2\nu_{10}(A)$, while the 1029 cm^{-1} is assigned to $\nu_8+\nu_{24}(B)$

Table 2
General phenomena of doublet in compounds containing DMIT skeleton

Compounds	Type[a]	Higher (cm^{-1})/Int.[b]	Lower (cm^{-1})/Int.	Compound[c]	$\nu_s S_2C{=}S$ (cm^{-1})/Int.	Reference
BMT-DTT	IR	1064/s	1039/m	H > L		9
EDT-DTT	IR	1068/s	1050/m	H > L		9
EDT-DTT	IR	1060/s	1035/s	H > L	522/m	This work
$TBA_2[Zn(dmit)_2]$	IR	1056/m-s	1033/s	H < L	519-525/w	This work
$TBA_2[Ni(dmit)_2]$	IR	1065/s	1034/s			9
$TBA_2[Ni(dmit)_2]$	IR	1047/ms	1025/s	H < L	522/w	This work
$(CoCp_2)_2[Ni(dmit)_2]$	IR	1043/s	1022/ms	H > L		This work
$(CoCp_2)_2[Ni(dmit)_2]$	R	1045/w	1024/w	H > L	516/s	This work
$TBA_2[Ni(dmit)_2]$	R				518/s	This work
$TBA_2[Ni(dmit)_2]$	R	1046/w	1025/w	H < L	521/vs	12
$TBA[Ni(dmit)_2]$	IR	1063/s	1030/m	H > L		9
$[NHBu_3][Ni(dmit)_2]$	IR	1049/s	1029/s	H > L		17
$(CoCp_2)[Ni(dmit)_2]$	IR	1056/s	1045/s	H > L		This work
$(CoCp_2)[Ni(dmit)_2]$	R	1058/m	1043/m	H > L	514/ms	This work
$[Ni(dmit)_2]$	IR	1077/m	1053/s	H < L		This work
$[Ni(dmit)_2]$	IR	1088/m	1064/s	H < L		9
$[Ni(dmit)_2]$	R	1070/w	1058/m	H < L	500/m	This work
$BTMA_2[Ni(dmit)_2]$	IR	1048/s	1024/s	H > L	517/m	This work
$TBA_{0.25}[Ni(dmit)_2]$	R	1075/s	1061/s	H < L		11
$TBA_2[Pd(dmit)_2]$	IR	1052/ms	1028/s	H < L		This work
$TBA_2[Pd(dmit)_2]$	R				524/ms	This work
$TBA[Pd(dmit)_2]$	R	1067/w	1056/m	H < L	516/m	This work
$(CoCp_2)_2[Pd(dmit)_2]$	IR	1046/s	1025/ms	H > L		This work
$(CoCp_2)_2[Pd(dmit)_2]$	R	1055/w	1036/w	H < L	520/s	This work
$(CoCp_2)[Pd(dmit)_2]$	IR	1056/s	1021/ms	H > L		This work
$(CoCp_2)[Pd(dmit)_2]$	R	1068/m	1053/m	H > L	516/s	This work
$[Pd(dmit)_2]$	R	1088/m	1068/w	H > L	528/m	This work
$TBA[Pt(dmit)_2]$	R	1052/m	1025/m	H > L	513/vs	11
$TBA_{0.2}[Pt(dmit)_2]$	IR	1070/s	1060/s	H < L	500/w	11
$TBA_{0.2}[Pt(dmit)_2]$	R	1087/s	1065/s	H > L	503/s	11
$BTMA_2[Cu(dmit)_2]$	IR	1048/ms	1024/s	H < L	516/w	This work
$NOP_2[Cu(dmit)_2]$	IR	1051/ms	1027/s	H < L	522/m	This work
$NMP_2[Cu(dmit)_2]$	IR	1048/ms	1017/s	H < L	521/m	This work
BAT-DTT	IR	1060/s	1030/w	H > L	516/m	9
BCMT-DTT	IR	1068/s	1040/sh	H > L		9
BBBT-DTT	IR	1059/s	1034/ms	H > L	510/m	This work
BBT-DTT	IR	1058/s	1042/s		528/w	9
$(PhCO)_2DMIT$	IR	1059/s	1030/w	H > L	512/w	This work
$(PhCO)_2DMIT$	IR	1064/s	1037/w	H > L	521/m	9
$(PhCO)_2DMIT$	IR	1062/s	1033/w	H > L	520/w	24
BCNET-DTT	IR	1069/vs	1034/m	H > L	516/m	This work
ETTC	IR	1064/vs	1029/m	H > L	505/m	23
ETTC	R	1062/vs	1036/w	H > L	503/vs	23
DMTTC	IR	1072/vs	1050/vs	H > L	505/vw	24
MTTTC	IR	1072/s	1050/vs	H < L	508/ms	24

[a] The type refers to whether it is an infrared (IR) spectrum or a Raman (R) spectrum.

[b] This intensity (Int.) refers to the relative intensity of the peak in the IR or Raman spectrum. s, strong; vs, very strong; m, medium; ms, medium strong; w, weak; vw, very weak; sh, shoulder.

[c] This comparison (Comp.) refers to the relative intensity of the two peaks in the doublet. H represents the intensity of the higher one while L does for that of the lower one.

and 1064 cm^{-1} is assigned mainly to S=C stretching vibration. However, the standard IR spectrum of ETTC [24] basically has a broad very strong band centered at 1050 cm^{-1}. Dimethyl trithiocarbonate ($R_3 = R_4 = –CH_3$ group in series 2 of Scheme 1, DMTTC) and methyl *p*-tolyl trithiocarbonate (R_3 = methyl R_4 = *p*-tolyl group in series 2 of Scheme 1, MTTTC) both have two very strong peaks at 1072 and 1050 cm^{-1}, respectively [24] while the relative intensity of the two peaks is contrary in the two compounds.

3.1.2. Possibilities for leading to these doublets

S=C stretching vibration is one of the most characteristic vibration in the IR spectra of DMIT derivatives. This is especially the case in the transition metal–dmit complexes, in which eight are molecular superconductors [4]. In these electrical conductive complex compounds the metal–dmit complex anions play the critical role for the conductivity. For the sake of composition of the metal–dmit complex anion a very convenient empirical method for identifying the electrical conductivity of a synthesized compound is the analysis of its IR spectra. Carbon–carbon double bond in the $S_2C{=}CS_2$ group receives more attention for its large vibrational frequency shift on oxidation while the frequency shift of the terminal S=C stretching vibration upon oxidation is complex [12]. Thus the existence of the doublet will disturb the right judgment of the frequency shift and it is necessary to distinguish this doublet from different arguments.

3.1.2.1. Whether it is appropriate to identify the S=C stretching vibration in the IR spectra with the intensity. As mentioned above and listed in Table 2, the doublet near 1050 cm^{-1} in the IR spectra of dmit derivatives are general and the relative intensity of the two peaks in the doublet changes from compounds to compounds and from samples to samples. S=C stretching vibration shows very strong intensity in the IR spectra. Thus is it appropriate to assign the S=C stretching vibration with intensity? According to this consideration the stronger peak near 1050 cm^{-1} will be the peak for S=C stretching vibration and the other one will be else. The problem appears when both peaks are strong. For example this is the case in the spectra of both $BTMA_2[Ni(dmit)_2]$ and $(CoCp_2)[Ni(dmit)_2]$. The intensity of the higher frequency near 1050 cm^{-1} is only a little stronger than that of the lower one. On the other hand the intensity of the higher one is stronger than that of the lower one in most IR spectra of compounds of series 1 in Scheme 1 while on the contrary the intensity of the higher one is weaker than that of the lower one in most IR spectra of compounds of series 3 in Scheme 1 with $x = 2$. For example in the IR spectrum of $TBA_2[Zn(dmit)_2]$ the doublet locates at 1057 and 1033 cm^{-1}, respectively, and in the IR spectrum of BBBT-DTT the doublet locates at 1059 and 1034 cm^{-1}, respectively. The relative intensity of the two peaks in the doublet almost change oppositely from the IR spectra of $TBA_2[Zn(dmit)_2]$ to those of BBBT-DTT. Thus, in our consideration, the intensity can not be a good choice for identifying the S=C fundamental stretching vibration in the IR and Raman spectra and this choice will make confusions in the assignment except that the relative intensity of the two peaks in the doublet show a too much large difference.

3.1.2.2. Whether one of the peaks in the doublet originates from the vibration irrelevant to the dmit skeleton. In the IR spectrum of tetrabutyl ammonium bromide (TBABr) [24], there are two weak peaks around 1050 cm^{-1} located at 1025 and 1060 cm^{-1}, respectively. Is it possible that one of the peaks in the IR spectra of $TBA_2[Zn(dmit)_2]$ originates from the vibration relevant to the TBA cation? This is impossible based on the current experimental spectra. Firstly, the doublet is almost always strong in the IR spectra even relative to the strongest peaks in the spectrum of TBABr while the above two peaks in the IR spectrum of TBABr are weak. Secondly, if it originated from the cation TBABr, the locations of the doublet should not change much from $TBA_2[Zn(dmit)_2]$ to $TBA_2[Ni(dmit)_2]$. This is also the case in the Raman spectra of $TBA_2[Ni(dmit)_2]$ and $TBA[Ni(dmit)_2]$. Thirdly, in the IR and Raman spectra of neutral $[Ni(dmit)_2]$ complex the doublet still exists. Finally, according to Pokhodnya et al. [12] no vibration modes were observed in the region near 1050 cm^{-1} in the IR spectra of $[M(dmio)_2]$ (S=C changes to O=C in series 3 of Scheme 1) compounds. So the doublet can definitely originate from the dmit skeleton.

3.1.2.3. Whether the doublet originates from the vibrations of different groups in dmit skeleton. $S{=}CS_2$ and $S_2C{=}CS_2$ are two characteristic groups in the DMIT skeleton. Is it possible that one of the peaks in the doublet originates from $S{=}CS_2$ while the other one originate from $S_2C{=}CS_2$ (i.e. the asymmetric stretching vibration of the four carbon–sulfur bond in the $S_2C{=}CS_2$ group)? This is impossible based on the existing experimental spectra. Firstly, the doublets still exist in the IR spectra of compounds of series 2 in Scheme 1 while $S_2C{=}CS_2$ group does not exist in these compounds. Secondly, again according to Pokhodnya et al. [12], no vibration modes were observed in the region near 1050 cm^{-1} in the IR spectra of $[M(dmio)_2]$. If the doublet originates from different groups the two peaks in the doublet should not disappear together and the intensity as well as location of one peak should not change much with the disappearance of the other, which is not the case for the IR spectra of EDT-DTT and EDT-DTO, BBBT-DTT and BBBT-DTO (S=C changes to O=C in BBBT-DTT) as well as BCNET-DTT and BCNET-DTO (S=C changes to O=C in BCNET-DTT). Thus generally the doublet can not originate from the vibrations of different groups in dmit skeleton.

3.1.2.4. Whether the doublet originates from the deviation of the dmit skeletons from its idealized symmetry. Pokhodnya et al. [12] considered that the doublet is due to the deviation of $[Ni(dmit)_2]$ skeleton from its perfect D_{2h} symmetry. Unfortunately, they did not explain this relationship in detail. In the transition metal–dmit complexes mentioned above there are two dmit skeletons in one $M(dmit)_2$ unit. As mentioned in Section 3.1.1 in the crystal structure of some compounds there exist indeed dmit skeletons with different geometry parameters. However, there also exist dmit skeletons with the same geometric parameters such as those in the crystal structure of $TBA_2[Zn(dmit)_2]$, in the IR spectra of which the doublet is obvious. Frequency calculations on $[Zn(dmit)_2]^{2-}$ skeleton were performed with the geometry parameters derived from the crystal structure of $TBA_2[Zn(dmit)_2]$ [20] without optimization using *rb3lyp/6-31g(d) freq = raman* in the route section with GAUSSIAN 98. According to the calculated results deviation from the ideal D_{2d} symmetry can indeed lead to doublet (1149 and 1151 cm^{-1}, respectively) because of transformation of Raman active only in the ideal symmetry to both Raman and IR active in the deviated symmetry of the peak 1151 cm^{-1} while this splitting (2 cm^{-1}) is too small relative to the experimental value (23 cm^{-1}). Thus, in our consideration, deviations from the ideal symmetry can account well for the broadening of the peak derived from S=C stretching vibration while accounting for the doublet will need further considerations. On the other hand frequency calculations on EDT-DTT (*rb3lyp/6-31 + g(d) opt freq = noraman*) do not show the splitting derived from S=C stretching vibration although the optimized geometry obviously has no C_{2v} symmetry. Special attentions must be paid to the methods used in the route section of GJF file for calculating the vibrational frequency. With *B3LYP/sto-3g* or *B3LYP/6-31g** in the route section the calculated frequency of the stretching vibration concerning the S=C group is larger than that of the asymmetric stretching vibration of the carbon–sulfur bond concerning the $S_2C{=}CS_2$ group. While with *HF/sto-3g* or *HF/6-31g** in the route section the former is smaller than the latter on the contrary. And the basis set used for the methods can not change the relative locations of this two fundamental vibrations.

3.1.2.5. The doublet may originate from the Fermi resonance between S=C fundamental stretching vibration and the overtones of $\nu_s S_2C{=}S$. The peak of S=C fundamental stretching vibration in the doublet should be identified before a reasonable explanation can be given to the appearance of the doublet. The higher frequency in the IR spectra of compounds of series 1, 2 and 3 in Scheme 1 is assigned to the fundamental stretching vibration of S=C group. And this argument agrees with that of Pokhodnya et al. [12]. The reasons are as follows. Firstly, in the IR spectra of ETTC and its deuterated form [23] as well as in those of EDT-DTT and of its deuterated form [10] the higher frequency (1064, 1060, 1061 and 1064 cm^{-1}, respectively) was assigned to such fundamental vibration. Furthermore, as listed above, this peak almost shows no change from ETTC to EDT-DTT although the skeletons of them change considerably. Secondly, as shown in Table 2 the relative intensity of the higher one to the lower one in both $(PhCO)_2$DMIT and BCNET-DTT is too large, which is hard to accepted that the weaker (lower one) one is the characteristic fundamental vibration of the S=C group. Thirdly, although in most of the IR spectra of compounds of series 3 with x = 2 in Scheme 1 the lower peak has stronger intensity than the higher one the higher frequency peak is still a strong one relative to other peaks in the spectra. In addition the locations of the higher frequency peak and the lower one as well as their relative locations in the doublet have only a little change in some spectra while in some others they have almost no change relative to the doublets in the IR spectra of compounds of series 1 and 2 in Scheme 1. However, on the other hand, compounds of series 1 and 3 in Scheme 1 both have the dmit skeletons. Thus the higher frequency peak in the IR spectra of compounds of series 3 with x = 2 in Scheme 1 is still considered as the fundamental vibration of S=C group although its intensity is not stronger than that of the lower one. A counterexample for supporting this argument is that the intensity of the higher frequency peak is slightly stronger than that of the lower one in the IR spectrum of $BTMA_2[Ni(dmit)_2]$. Thus, in our consideration, the lower frequency near 1050 cm^{-1} will be the Fermi resonance peak derived from interactions between S=C fundamental vibration and the overtones of $\nu_s S_2C{=}S$. The reasons are as follows. Firstly, this doublet phenomena spans all the three series in Scheme 1 and other explanations such as concerned above can not be satisfactory based on the existing experimental spectra. Secondly, the three series in Scheme 1 contain the same fragment, i.e. trithiocarbonate ($S{=}CS_2$) skeleton. This confirms the first choice of this fragment in interacting with the S=C group to arouse Fermi resonance although other groups may also take part in the resonance. As pointed out by Borch et al. [23], one of the above two fundamentals in ETTC is the out-of-phase combination of νS=C (stretching vibration of S=C) and ν_sSCS (symmetric stretching vibration of S–CS–S, i.e. $\nu_s S_2C{=}S$ in this paper) coupled to δCSS (angle bending vibration of S=C–S). While in the dmit skeleton this fundamental also involves the stretching vibration of C=C. The other is the in-phase combination of νS=C and ν_sSCS coupled with a small amount of δ_sCSC (symmetric angle bending vibration of C–S–C). Thus these two fundamentals are both mainly concerned with the trithiocarbonate skeleton. And this implies that the interactions between these two vibrational modes will be more easily and directly. Thus the overtones of the latter modes will be easy to “steal” intensity from the former modes in the Fermi resonance process [25]. Thirdly, chemical structures of the three series in Scheme 1 are very similar with those (Fig. 1) that the doublets in the IR or Raman spectra of which have been identified firmly [25–27] as from Fermi resonance. All the four chemical structures in Fig. 1 have the same functional group O=C and in corresponding to this chemical structures in Scheme 1 all have the same functional group S=C, which is very similar to O=C. In addition the five-membered ring skeleton of dmit is also very similar to that of cyclopentanone and ethylene carbonate [27]. As discussed in the literature [25,26], overtones of the symmetrical breathing (mainly concerning the $-CH_2-CO-CH_2-$ group) vibration of the ring (889 cm^{-1}) in the IR and Raman spectra of cyclopentanone will be possible

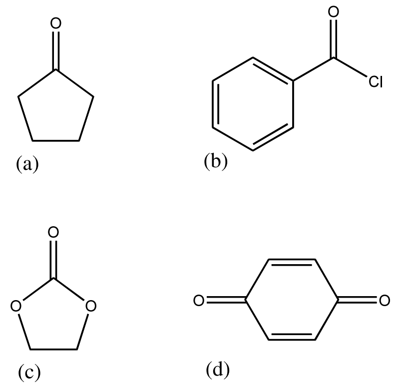

Fig. 1. Chemical structures of which the doublets have been firmly identified. (a) cyclopentanone (b) benzoyl chloride (c) ethylene carbonate (d) *p*-benzoquinone.

to act with the O=C fundamental to arouse Fermi resonance. And according to Bertran et al. [26] the interacting levels for leading to the doublet in the IR spectra of benzoyl chloride are most probably the first excited carbonyl stretching ($\nu_a = 1777$ cm^{-1}; a') and the first harmonic of the C–Cl stretching ($\nu_b = 873$ cm^{-1}; a'; $2\nu_b = 1746$ cm^{-1}; a'). Thus the chemical structure of S–CS–S group in dmit skeletons is similar to that of the –CH$_2$–CO–CH$_2$– group in cyclopentanone and to that of –CO–Cl in benzoyl chloride. On the other hand chemical structures of series 1 and 3 in Scheme 1 are not ideal structure (C$_{2v}$, D$_{2d}$ or D$_{2h}$) in their crystal structures; application of selection rules may be difficult to ensure that only the overtones take part in the Fermi resonance and the combination band may also contribute to the doublet [25–27]. Fourthly, as listed in Table 2 the doublet phenomena appears in both the IR and Raman spectra of series 3, not only confined to the IR spectra. Correspondingly, the doublets also appear in both the IR and Raman spectra of cyclopentanone [27]. Such similarities enable us more confidently to consider that the doublet can attribute to the Fermi resonance. Finally, as listed in Table 2 the ν_sS$_2$C=S peak in the range from 500 to 530 cm^{-1} in the IR and Raman spectra of the compounds of series 1 and 3 supports this argument experimentally.

3.2. Assignment of ν_sS$_2$C=S and ν_sS$_2$C=CS$_2$ in the fundamental vibrations of dmit skeletons

Both ν_sS$_2$C=S and ν_sS$_2$C=CS$_2$ are intensive characteristic vibrations in the Raman spectra of compounds containing dmit skeletons. As discussed in Section 1 there exist two completely opposite arguments in the assignment of these two vibrations. Ramakumar et al. [14] have assigned the higher frequency near 500 cm^{-1} to ν_sS$_2$C=S while the lower one is assigned to ν_sS$_2$C=CS$_2$ according to their theoretical calculations. According to the Raman spectra measured by Pokhodnya et al. [12] they concluded that the higher one should be the ν_sS$_2$C=CS$_2$ because they considered that the frequency of this vibration increases with the increase of the reduction as listed in Table 3. In the following theoretical bases considered by Pokhodnya et al. are repeated and analyzed in detail with molecular orbital theory.

Fig. 2 shows the orbital composition of the LUMO of neutral [Ni(dmit)$_2$] molecule. In this LUMO two carbon–sulfur single bond in the group of S–CS–S are bonding while four carbon–sulfur single bond in the group of S$_2$C=CS$_2$ are antibonding. As far as the double bond is concerned, the carbon–carbon double bond in the S$_2$C=CS$_2$ group is bonding while the carbon–sulfur double bond in the terminal S=CS$_2$ group of dmit skeleton is antibonding. The bonding condition of all above mentioned bond, including the two carbon–sulfur single bond in the group of S=CS$_2$, is the same as those described by Canadell et al. [28] for [Ni(dmit)$_2$] skeleton. Thus the following two descriptions by Pokhodnya et al. [12] will be suspectable. One is “In the M(dmit)$_2$ anion, this orbital is bonding with respect to the C=C bond but antibonding with respect to the C–S and S–M bond”. The other is “On the contrary, the frequencies of all modes, containing S–C or Ni–S bond stretching components (A$_g$(3, 5–8)), decrease with increasing *n*, demonstrating a negative ionization shift”. Furthermore, according to their discussion, the A$_g$(5) mode is assigned to the “S–C stretching mode of the terminal thione fragments”. In conclusion they seem to consider that the two carbon–sulfur single bond in the S=CS$_2$ group are antibonding in the LUMO of neutral Ni(dmit)$_2$] molecule. While this consideration is not consistent with what expressed in Fig. 1 of the paper of Canadell et al. [28]. So the frequency of ν_sS$_2$C=S increases with the increased reduction from [Ni(dmit)$_2$]^0, [Ni(dmit)$_2$]$^{1-}$ to [Ni(dmit)$_2$]$^{2-}$, which is consistent with the experimental value listed in Table 3.

On the other hand frequency of ν_sS$_2$C=CS$_2$ should not increase either with the increase of reduction of the [Ni(dmit)$_2$] skeleton even only the group S$_2$C=CS$_2$ is concerned. As shown in Fig. 2 in the LUMO of neutral [Ni(dmit)$_2$] four carbon–sulfur single bond in the group of S$_2$C=CS$_2$ are antibonding and the carbon–carbon double bond in the S$_2$C=CS$_2$ group is bonding. Upon reduction of the [Ni(dmit)$_2$] skeleton they have opposite effect on the peak near 500 cm^{-1} and thus the compound effect is hard to predict. Furthermore, it is possible that in the complex vibrations, which are in charge of the peak near 500 cm^{-1} and composed of two vibrations, of the S$_2$C=CS$_2$ group one may be positive and dominating and the other may be subordinative. Thus change of the frequency of the complex vibration will depend on the change of the dominating vibration but not the subordinative one. In the case of the complex vibration in charge of the peak near 500 cm^{-1} in S$_2$C=CS$_2$ group the dominating vibration is the symmetric vibration of C–S but not the symmetric vibration of C=C, for the frequency of the C=C stretching vibration can not be so low. Thus be-

Table 3
ν_sS$_2$C=S and ν_sS$_2$C=CS$_2$ (cm^{-1}) in the Raman spectra of [Ni(dmit)$_2$]$^{2-/1-/0}$ series

	TBA$_2$-[Ni(dmit)$_2$]	TBA-[Ni(dmit)$_2$]	[Ni(dmit)$_2$]	Reference
ν_sS$_2$C=S	521	507	496	[12]
ν_sS$_2$C=CS$_2$	466	478	488	[12]
ν_sS$_2$C=S	518	512	500	This work
ν_sS$_2$C=CS$_2$	470	484	492	This work

The assignment of ν_sS$_2$C=S and ν_sS$_2$C=CS$_2$ in [12] is opposite from that of listed in this table.

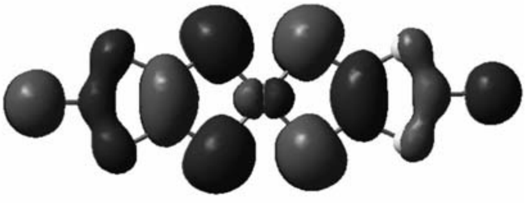

Fig. 2. Orbital composition of LUMO for neutral [Ni(dmit)$_2$].

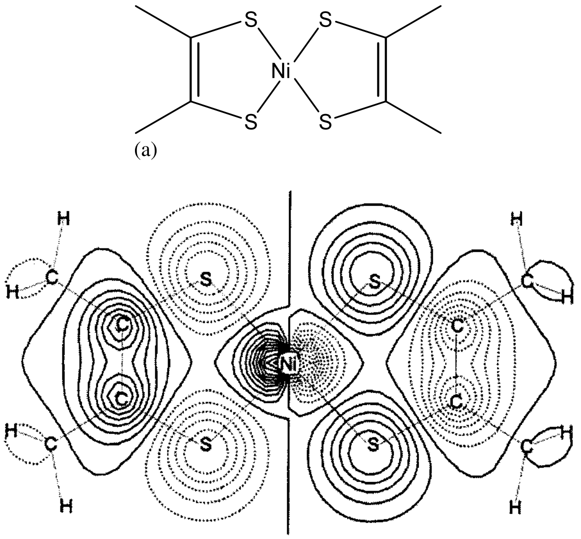

Fig. 3. Chemical structure (a) and orbital composition (b) of LUMO of $[Ni(S_2C_2Me_2)_2]$.

cause four C–S bond in the $S_2C{=}CS_2$ group are antibonding in the LUMO of $[Ni(dmit)_2]^0$ the stretching frequency of them should decrease with the increase of reduction, which is consistent with the experimental spectra listed in Table 3. This is consistent with results from Lim et al. [29] for the chemical structure of $[Ni(S_2C_2Me_2)_2]$ (Me = methyl) shown in Fig. 3(a) and its orbital composition of the LUMO is shown in Fig. 3(b), which is the Figure 6 in the paper of Lim et al. [29]. Upon reduction the infrared frequency of C–S stretching vibration changes from 799 (neutral) cm^{-1}, 769 (anion) cm^{-1} to 744 (dianion) cm^{-1} for the series $[Ni(S_2C_2Me_2)_2]^{0/1-/2-}$.

4. Conclusions

Firstly, the doublet phenomena near 1050 cm^{-1} in the IR and Raman spectra of series 1 and 3 in Scheme 1 are general. Both of the peaks in the doublets of the IR spectra show strong intensity while those of the Raman spectra show weak intensity. The locations of the doublets may change a little for different association and oxidation state of the dmit skeletons. Relative intensity of the two peaks in the doublets of the IR spectra is generally opposite for series 1 and 3 with x = 2 in Scheme 1 and changes from sample to sample even for the same compound.

Secondly, possibilities of the doublets due to the fragments or constituents other than the dmit skeleton of the compounds are very small. Also it is impossible that the doublets originate from different groups of the dmit skeleton. The explanation that deviations from the idealized geometry contribute to the doublets also can not be satisfactory for the existence of the generality of the doublets and of the strong intensity of the doublets. After the comparisons between the compounds of which the Fermi resonance are definitely identified and those in Scheme 1 are performed in the similarities of the IR and Raman spectra and of the chemical structure the lower frequency near 1050 cm^{-1} in the doublet is tentatively mainly assigned to the Fermi resonance peak between fundamental of stretching vibration of S=C and the overtones of the $\nu_s S_2C{=}S$ for series 1 and 3 in Scheme 1. However, this can not exclude the possibility of participance in the Fermi resonance of the combination bands. Finally, to some compounds where special crystal structures, special oxidation state, special cations and special relative intensity of the doublet of the dmit derivatives may exist, the doublet could be a compound effect and all the possible factors mentioned above should be given full considerations so that the doublet can not be assigned erroneously.

Thirdly, the higher frequency near 500 cm^{-1} in the IR or Raman spectra of dmit derivatives is definitely assigned to the $\nu_s S_2C{=}S$ while the lower one is assigned to $\nu_s S_2C{=}CS_2$.

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