

Direct Observation of the Electron-Donating Property of the 5,6-Dihydro-1,4-dithiin-2,3-dithiolate (ddd) Ligands in Square Planar $M(\text{ddd})_2$ Complexes ($M = \text{Ni}, \text{Pd}, \text{Pt}, \text{and Au}$)

H. Hau Wang* and Shannon B. Fox

Chemistry and Materials Science Divisions
Argonne National Laboratory
Argonne, Illinois 60439

Eduard B. Yagubskii, Lyudmila A. Kushch, and
Alexander I. Kotov

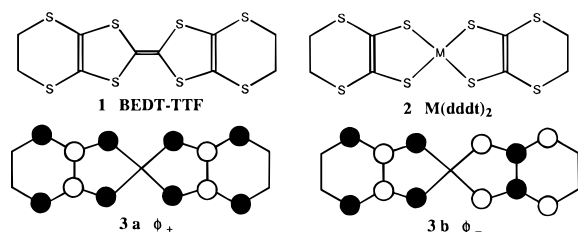
Institute of Chemical Physics in Chernogolovka
Russian Academy of Sciences
Chernogolovka MD, 142432 Russia

Myung-Hwan Whangbo

Department of Chemistry
North Carolina State University
Raleigh, North Carolina 27695-8204

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The donor molecule bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, **1**) forms radical cations of varying charges between +0.5 and +2. Many salts of BEDT-TTF are metallic, and some are superconductors with critical temperatures ranging from 1 to 13 K.^{1–3} The 5,6-dihydro-1,4-dithiin-2,3-dithiolate dianions, ddd^{2-} , generated *in situ* from a precursor 2,5,7,9-tetrathiabicyclo[4.3.0]non-1(6)-en-8-one (TTBEO), form stable square planar metal complexes $[M(\text{ddd})_2]^-$ ($M = \text{Ni}, \text{Pd}, \text{Pt}, \text{and Au}$).^{4,5} The $[M(\text{ddd})_2]^-$ anions are easily oxidized by



chemical oxidants to neutral species $[M(\text{ddd})_2]$ (**2**), which can be used as a starting material to form conducting salts $[M(\text{ddd})_2]_m X_n$ with monovalent anion X^- (e.g., $m = 2, n = 1$; $m = 3, n = 2$) with use of electrocrystallization techniques.^{6–13} More than 20 such salts have been synthesized, and a few of them are metallic from room temperature to 1.3 K.^{6,11} In describing the electron-donating properties of the $[M(\text{ddd})_2]$ ($M = \text{Ni}, \text{Pd}, \text{Pt}, \text{and Au}$) complexes, one faces a similar problem as that found for metal bis(dithiene) complexes $[M(\text{S}_2\text{C}_2\text{R}_2)_2]^q$ ($M = \text{Ni}, \text{Pd}, \text{Pt}; \text{R} = \text{CN}, \text{Ph}, \text{CF}_3; q = 0, -1, -2$).^{14,15} In principle, the ddd ligand can carry a charge from 0 in the dithioketone form to -2 in the dithiolato dianion form, and the metal M can also take on various oxidation states. For $[\text{Ni}(\text{ddd})_2]^-$, both $\text{Ni}^{3+}(\text{d}^7)$ and $\text{Ni}^{2+}(\text{d}^8)$ electronic configura-

tions have been proposed.^{4,5,16} So far, there has been no direct experimental proof.

The HOMO (ϕ) of a ddd^{2-} ion is a π orbital. When two ddd^{2-} ligands are brought together to form a $[M(\text{ddd})_2]^-$ ($M = \text{Ni}, \text{Pd}, \text{Pt}$) complex, their HOMOs lead to bonding and antibonding orbitals, ϕ_+ and ϕ_- (see **3a** and **3b**), respectively.^{5,16} In the orbitals ϕ_+ and ϕ_- , the C=C bond regions of ddd are bonding. Consequently, the strength of the C=C bond, and hence the C=C stretching frequency, should increase as the total number of electrons in the ϕ_+ and ϕ_- orbitals increases. This prediction can be easily tested by studying the C=C stretching vibrations of ddd complexes. For this purpose, Raman scattering is preferred over infrared spectroscopy because it is active to symmetric C=C stretchings and, in addition, it is not strongly coupled to conduction electrons. Infrared reflectance spectra of highly conducting complexes show that the electron-phonon coupling causes large peak shifts and significant line broadening of infrared peaks associated with the C=C stretching vibrations.¹⁷ Past attempts to use the Raman techniques for this purpose are incomplete, presumably due to low scattering intensities and sample decompositions under high incident laser intensities. These difficulties have been largely overcome with the recent development of Raman microscope spectrometer.

The synthesis of the ddd compounds studied in our work has been described elsewhere.^{4–11} All specimens were crystalline samples, and the chemical compositions for majority of the samples were based on X-ray structure determination (see Table 1). All Raman measurements were carried out at room temperature with a Raman microscope spectrometer (Renishaw, Ltd.) equipped with a He–Ne laser ($\lambda_0 = 6328 \text{ \AA}$). Typical spectrum was collected overnight between 50 and 2500 cm^{-1} with a 1 cm^{-1} resolution and averaged over 20–40 scans. The scattering peaks were calibrated against a Si standard (520 cm^{-1}).

As a representative example, Figure 1 shows the Raman spectrum of a needle-like crystal of $\text{NBu}_4[\text{Ni}(\text{ddd})_2]$ recorded with laser polarization parallel (dashed line) and perpendicular (solid line) to the needle axis (i.e., a axis).⁵ Three prominent peaks $\nu_1, \nu_3,$ and ν_5 are readily identified as totally symmetric A_g modes for three reasons: (1) the peak intensities are very strong, (2) the peak intensities are smaller for the perpendicular than for the parallel orientation,¹⁸ and (3) the three weak combination peaks, $\nu_1 + \nu_3, \nu_1 + \nu_5,$ and $\nu_3 + \nu_5,$ are clearly identified; suggesting that the three peaks $\nu_1, \nu_3,$ and ν_5 have the same symmetry.¹⁹ The $\nu_1, \nu_3,$ and ν_5 vibrations are associated with the symmetric stretching of the C=C, C–S, and M–S bonds, respectively.^{14,20–23}

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Table 1. Raman Scattering Frequencies of $[M(\text{dddt})_2]$ Complexes^a

complexes	$\nu_1 + \nu_3$	$\nu_1 + \nu_5$	$\nu_1 A_g$ (C=C)	$\nu_3 A_g$ (C-S)	$\nu_5 A_g$ (M-S)
NBu ₄ Au(dddtd) ₂ ⁵		1915w	1526m		382vs
NBu ₄ Ni(dddtd) ₂ ^{b,5}	2316w	1804w	1435vs	877vs	365m
NBu ₄ Pd(dddtd) ₂	2306w	1814w	1436vs	867s	374m
NBu ₄ Pt(dddtd) ₂ ⁷			1442s	867m	376w
Au(dddtd) ₂ ^{b,5}			1436m		388vs
[Au(dddtd) ₂] ₂ HgBr ₃			1384m, 1375sh		387m
Ni(dddtd) ₂ ^{b,12}		1724w	1348m	896m	374vs
Pd(dddtd) ₂ ^b	2245w	1728s	1350vs	896m	378s
Pt(dddtd) ₂ ^{b,13}	2248w	1728s	1350vs	898m (br)	378s
[Pd(dddtd) ₂] ₂ PF ₆ ^{b,c,6}			1309s	915m, 875s	378vs
[Pd(dddtd) ₂] ₂ SbF ₆ ^{b,c,6}			1309m	914m, 875s	379m
[Pd(dddtd) ₂] ₂ AuBr ₂ ^{b,c,6}			1306s	913m, 877s	379s
[Pd(dddtd) ₂] ₂ Ag _{1.54} Br _{3.50} ^{b,11}			1301s	909m	382s
[Pt(dddtd) ₂] ₂ IBr ₂ ^{b,9}			1309s	907m, 878s	367m
[Ni(dddtd) ₂] ₃ (HSO ₄) ₂ ^{b,8}			1302s	911m	373vs
[Ni(dddtd) ₂] ₃ (ClO ₄) ₂ ^{b,9}			1306m	913m	368s

^a Key: vs (very strong), s (strong), m (medium), w (weak), sh (shoulder), and br (broad). ^b Chemical stoichiometry is based on single-crystal X-ray structure determination. ^c Structures to be published by R. P. Shibaeva et al.

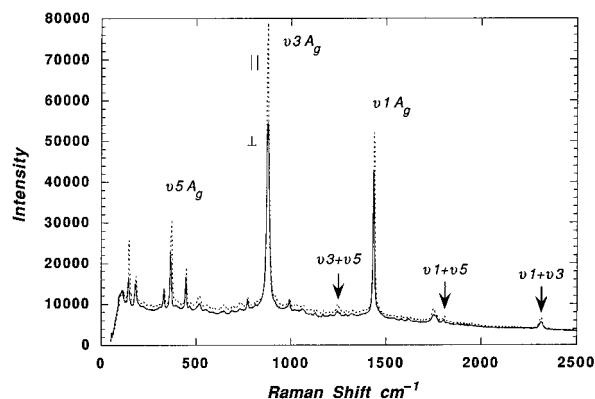


Figure 1. The Raman spectra of a needle crystal of NBu₄[Ni(dddtd)₂] with laser polarization parallel (dashed line) and perpendicular (solid line) to the needle axis (*a* axis).⁵

As summarized in Table 1, the Raman spectra of various ddt complexes are quite similar. If [Ni(dddtd)₂]⁴⁻ is described as Ni^{III}(dddtd)₂⁴⁻, the $\nu_{C=C}$ is expected to be similar to that of the [Au(dddtd)₂]⁻, Au^{III}(dddtd)₂⁴⁻, and if [Ni(dddtd)₂]⁻ is described as Ni^{II}(dddtd)₂³⁻, the C=C frequency is expected to be similar to the [Au(dddtd)₂]⁰, i.e., Au^{III}(dddtd)₂³⁻. The most striking to note from Table 1 is that the frequency of the ν_1 (C=C) mode decreases in the order [Au(dddtd)₂]⁻ > [M(dddtd)₂]⁻ (M = Ni, Pd, Pt) \approx [Au(dddtd)₂]⁰ > [M(dddtd)₂]⁰ > [Pd(dddtd)₂]^{0.5+} > [Ni(dddtd)₂]^{2/3+}. The ν_1 frequency decreases gradually with decreasing number of valence electrons in the [M(dddtd)₂] (M = Ni, Pd, Pt, Au) complexes. This finding shows that in the charge transfer compounds of these complexes, the oxidation and reduction take place primarily on the ddt ligands. In essence, therefore, [Au(dddtd)₂]⁻ is characterized by the valence configuration (d⁸)(ϕ_+)²(ϕ_-)²; [M(dddtd)₂]⁻ (M = Ni, Pd, Pt) and [Au(dddtd)₂]⁰ by (d⁸)(ϕ_+)²(ϕ_-)¹; [M(dddtd)₂]⁰ (M = Ni, Pd, Pt) by (d⁸)(ϕ_+)²; [Pd(dddtd)₂]₂⁺ by [(d⁸)(ϕ_+)²][(d⁸)(ϕ_+)¹], and so on. The average charge on each ddt ligand ($-n$) (where n is positive), is related to the total number (N) of electrons in the two orbitals ϕ_+ and ϕ_- by $N = 2n$. As shown in Figure 2, the

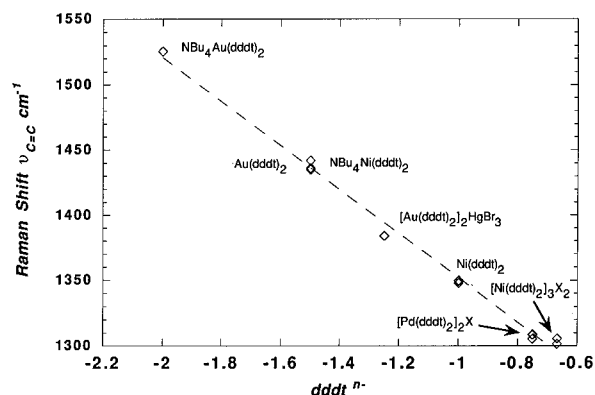


Figure 2. The totally symmetric C=C vibration frequency ($\nu_1 A_g$) against the charge ($-n$) of the dddt^{n-} ligand based on Au³⁺(d⁸) and M²⁺(d⁸) (M = Ni, Pd, and Pt) formalism showing a linear correlation.

frequency ν_1 decreases linearly with decreasing n , and the frequency vs charge plot is well described by the equation, ν_1 (cm⁻¹) = 1183 + 169 n . The frequency decreases with decreasing n since the number of electrons in the ϕ_+ and ϕ_- orbitals decreases, thereby reducing the extent of bonding in the C=C bonds. As an example of the utility of the relationship, consider the [Pd(dddtd)₂]₂Ag_{1.54}Br_{3.50} salt which is metallic to 1.3 K.¹¹ The study of its electronic band structure led to the conclusion that the oxidation state of Ag is +2.¹¹ This is nicely supported by the ν_1 vs $-n$ relationship, i.e., the ν_1 frequency (1301 cm⁻¹) of this salt corresponds to $n = 0.70$, which gives the charge of +1.88 on Ag.

The C-S bond regions are antibonding in the ϕ_+ and ϕ_- orbitals (see **3a** and **3b**). Therefore, with decreasing number of valence electrons in ϕ_+ and ϕ_- , the extent of antibonding in the C-S bonds decreases so that the ν_3 frequency should increase. For [Pd(dddtd)₂]₂X (X = PF₆, SbF₆, AuBr₂) and [Pt(dddtd)₂]₂IBr₂ complexes, two sets of peaks were observed in the ν_3 region due to the dimer crystal-packing arrangements which can further split the ν_3 peak. When the frequencies of the first set of peaks (corresponding to higher oxidation of the ligands) were plotted in the ν_3 vs $-n$ plot, the trend for the ν_3 frequency indeed increases with decreasing number of electrons in ϕ_+ and ϕ_- , and the correlation is well described by the equation, ν_3 (cm⁻¹) = 950 - 53 n (n is positive). A plot of $\nu_3 A_g$ vs $-n$ is deposited in the supplementary material.

To summarize, in these complexes, the metal cations are unambiguously described as d⁸ ions and the ddt ligands are involved in oxidation and reduction.

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Supporting Information Available: One figure of vibration frequency versus charge (2 pages). See any current masthead page for ordering and Internet access instructions.

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