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Article

New Series of Asymmetrically Substituted Bis(1,2-dithiolato)-Nickel(III) Complexes Exhibiting Near IR Absorption and Structural Diversity[†]

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The synthesis, structural characterization, and properties of a new series of asymmetrically substituted bis(dithiolene) nickel(III) compounds $[Bu_4N][Ni(Phdt)_2]$ (**1**) (Phdt = 2-Phenyl-1,2-dithiolate), $[Bu_4N][Ni(NO_2Phdt)_2]$ (**2**) (NO_2Phdt = 2-(*p*-nitrophenyl)-1,2-dithiolate), $[Bu_4N][Ni(FPhdt)_2]$ (**3**) (FPhdt = 2-(*p*-fluorophenyl)-1,2-dithiolate), $[Bu_4N][Ni(ClPhdt)_2]$ (**4**) (ClPhdt = 2-(*p*-chlorophenyl)-1,2-dithiolate), and $[Bu_4N][Ni(BrPhdt)_2]$ (**5**) (BrPhdt = 2-(*p*-bromophenyl)-1,2-dithiolate) have been described. All complexes **1**−**5** exhibit absorptions in the near-infrared region; the shift of these absorption bands can be tuned by the choice of the substituents on the relevant dithiolene moieties. The substituents on the dithiolene moiety are also responsible for their structural diversities. The nature of the substituents on the dithiolene moiety play an important role in tuning the redox potentials along this series. The nitro derivative (compound **2**) exhibits several redox couples in its cyclic voltammogram in contrast to the other compounds in this series. The synthesis and characterization of two asymmetrically halogen substituted tetrathiafulvalene (TTF) derivatives 4,4′-bis(4-chlorophenyl)-tetrathiafulvalene ClPhTTF (**6**) and 4,4′-bis(4-bromophenyl)-tetrathiafulvalene (BrPhTTF) (**7**) have been described. One of these compounds has been structurally characterized. Iodine treatment of the monoanionic Ni(III) compound $[Bu_4N][Ni(ClPhdt)_2]$ (**4**) results in the formation of a neutral Ni(IV) complex $[Ni(ClPhdt)_2]$ (**8**). All monoanionic compounds **1**−**5** are Ni(III) complexes, as evidenced by electron spin resonance spectroscopy. Interestingly, strong Cl···Cl interactions are observed in the solid state structures of the chlorinated compounds **6** and **8**. Finally, the structural features of compound $[Ni(ClPhdt)_2]$ (**8**) and the TTF derivative ClPhTTF (**6**) are compared based on their enormous structural similarities, and the neutral compound $[Ni(ClPhdt)_2]$ (**8**) is classed as the "an inorganic counterpart of TTF".

Introduction

The synthesis of asymmetrically substituted metal bis-dithiolene complexes with more conjugated systems is fascinating because of their unusual optical,[1] electronic,[2] near-infrared (NIR) absorption,[3] magnetic,[4] and electrochemical properties.[5] These properties are often related to the different substitutions or the modulation of the dithiolene part, as well as the mode of the conjugations. The scope of metal-dithiolene complexes has expanded to heteroleptic metal dithiolene complexes in the context of organometallic compounds.[6] To date, many of the symmetrically substituted metal bis-dithiolene complexes[7] have been investigated extensively, but studies based on asymmetrical dithiolene metal complexes are still limited. Mueller-Westerhoff and co-workers reported nickel complexes of asymmetrically substituted dithiolenes describing their electrochemical properties and NIR spectroscopy.[8] Fourmigué and Bertran described an interesting paramagnetic nickel-asymmetric-

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[†] Dedicated to Professor Sabyasachi Sarkar on the occasion of his 60th birthday.

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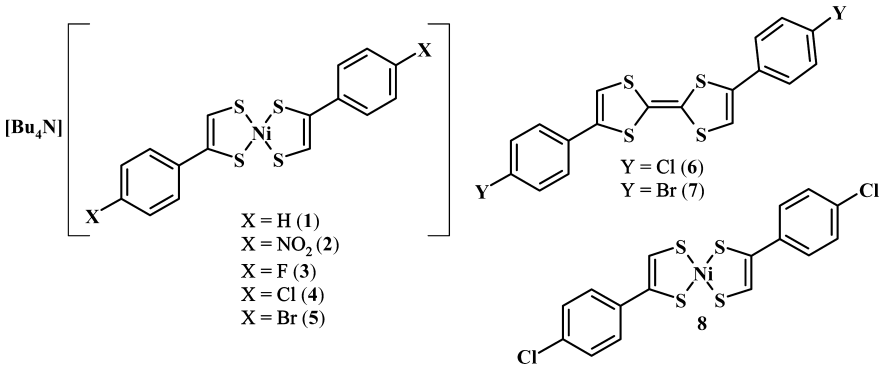
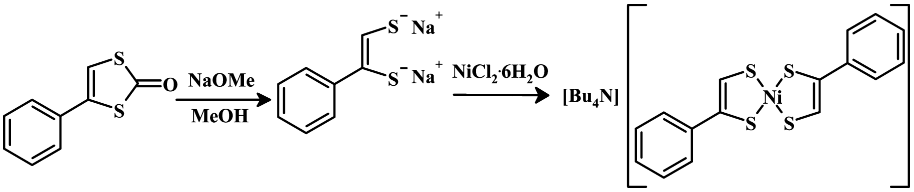
10.1021/ic701408m CCC: $40.75

Scheme 1



Scheme 2. Synthesis of $[Bu_4N][Ni(Phdt)_2]$ (**1**) (Phdt = 2-Phenyl-1,2-dithiolate)



dithiolene complex analog $[Ni(edt-CN)_2]^{2-}$ (edt = 1,2-ethanedithiolate) of $Ni(mnt)_2^-$ (mnt = maleonitrile dithiolate) with two cyano groups only for both oxidation states, together with the singlet−triplet behavior.[9]The asymmetrically substituted dithiolene complex bis(2-cyano-1,2-ethanedithiolato), nickelate(III) has been stabilized with (meso-tetraphenylporphinato)manganese(III) resulting in an interesting magnetic material $[MnTPP]\{Ni[S_2C_2H(CN)]_2\}$.[10] The unsymmetrical character of the dithiolate ligand 2-(trifluoromethyl)acrylonitrile-1,2-dithiolate (tfadt) makes it possible for the first time to evaluate experimentally the inversion barrier for cis−trans isomerization of the complex $[Ni(tfadt)_2]$.[11] Synthesis and structural characterization of gold(III) complexes$[Au(dithiolene)_2]^-$, each involving two asymmetrically substituted dithiolene ligands (SC(H)C(R)S; R = phenyl, pyridin-2-yl, pyridin-3-yl, or pyridin-4-yl) have been reported with interesting electrochemical properties.[12] The rational synthesis of transition metal (Ni, Pd, and Pt)-asymmetrically substituted dithiolene complexes has been described with mesomorphic properties.[13] The effect of bulky substituents adjacent to the dithiolene ring has been addressed by studying Ni(II)-asymmetrically substituted dithiolenes $[Ni(SCR' = CR''S)_2]$ ($R' = Ph$; $R'' = {}^{n}Bu$, cyclopentylmethyl, or 4-pentylcyclohexyl).[14] The addition of bulky groups to the phenyl ring may affect the ability of the ring to rotate and thus limits the conjugation between the ring and the dithiolene core. This can result in a decrease in the width of the absorption band.[14] Laguna and co-workers have chosen an asymmetrically substituted phenyl group on dithiolene-transition metal complexes, in which the phenyl group contains the −CN group as substituent, and studied the resulting optoelectronic properties.[15] Drexhage and co-workers discovered that transition metal dithiolene complexes, especially those of Nickel, are particularly suitable for Q-switching lasers-dyes for Nd:YAG lasers operating at 1064 nm.[8c,d] The NIR absorption maxima, observed in nickel dithiolenes system, is a function of both extensive electron delocalization within the dithiolene ring system, and the interaction of this delocalized system with available d-orbitals on the central metal.[16] Thus, the rational design and development of NIR absorbing dyes are a challenging task because of their technological significances. Indeed, some liquid crystalline (LC) display systems are known to use a

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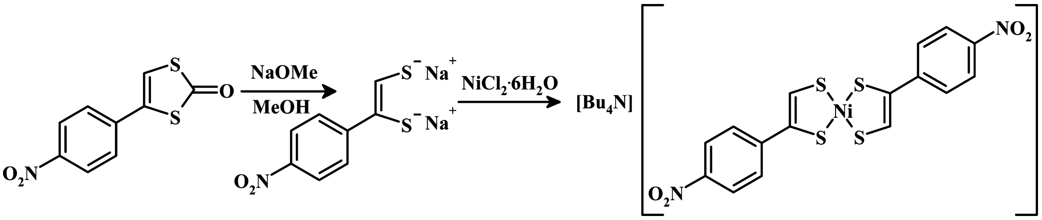
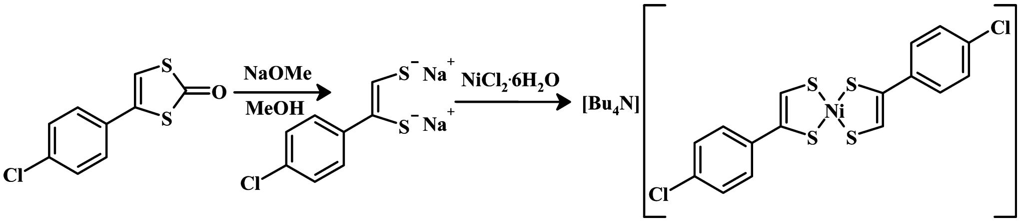
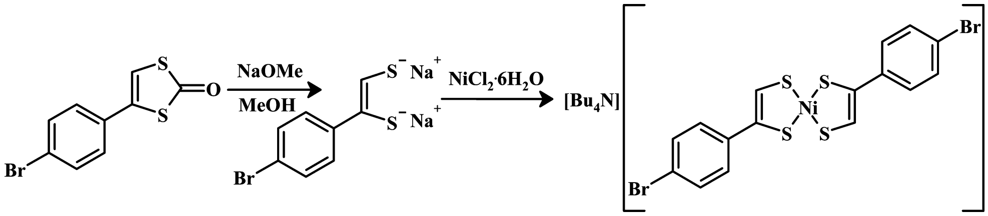
Scheme 3. Synthesis of $[Bu_4N][Ni(NO_2Phdt)_2]$ (**2**) (NO_2Phdt = 2-(*p*-nitrophenyl)-1,2-dithiolate)



Scheme 4. Synthesis of $[Bu_4N][Ni(ClPhdt)_2]$ (**4**) (ClPhdt = 2-(*p*-chlorophenyl)-1,2-dithiolate)



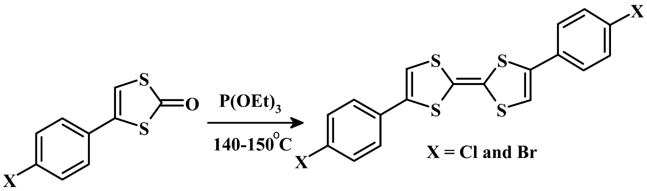
Scheme 5. Synthesis of $[Bu_4N][Ni(BrPhdt)_2]$ (**5**) (BrPhdt = 2-(*p*-bromophenyl)-1,2-dithiolate)



nickel dithiolene complex as the NIR absorbing dye.[17] This is because the guest nickel bis(dithiolene) dyes possess a number of important criteria such as high solubility in the liquid crystal host to maximize contrast, excellent chemical and thermal stability, and low impact on the long-range molecular ordering in the LC host, besides its strong absorbance maximum at or near the wavelength of incident laser radiation. Most of the commercially available NIR dyes of organic compounds are ionic or highly polar and accordingly show poor solubility in hydrocarbon-like liquid crystal hosts.[17] Thus, the inorganic nickel dithiolenes are of special interest for their high solubilities (up to 10 wt %) in LC hosts. It is important to note that nickel-dithiolene dyes themselves can possess LC properties[18] if appropriate terminal functional groups are selected on the relevant dithiolene moiety.

We wish to report herein the synthesis, structural characterization, and properties of a new series of asymmetrically substituted Ni(III)-dithiolene complexes **1**−**5** as shown in Scheme 1. We have demonstrated how the nature of substituents on the dithiolene moiety in **1**−**5** influences the position of the NIR band maxima in their electronic absorption spectra and the overall packing of the molecules in the solid state. While working with this system (compounds **1**−**5**), two "sulfur" containing organic compounds **6** and **7**, known as tetrathiafulvalenes (TTFs) as shown in Scheme 1, have been prepared based on a structural analogy of **6** and **7** from the anions of compounds **1**−**5**. They are analogues in the sense that if the nickel ion (in the anions of compounds **1**−**5**) is replaced by a C═C bond, an organic TTF will be obtained. We have also reported a neutral Ni(IV) compound **8** (Scheme 1), which can be described as the inorganic counterpart to an organic TTF molecule as far as the structural analogies between compounds **8** and **6**/**7** (Scheme 1) are concerned.

Scheme 6. Synthesis of 4,4′-Bis(4-chlorophenyl)-tetrathiafulvalene (ClPhTTF) (**6**)



Experimental Details

General Consideration. All chemicals were purchased from commercial sources and used without further purification. Microanalytical (C, H, N, S) data were obtained with a FLASH EA 1112 Series CHNS Analyzer. The IR spectra (with KBr pellets) were recorded in the range of 400−4000 cm^{-1} on a JASCO FT/IR-5300 spectrometer. UV−vis−NIR spectra were recorded using a 3101 PC/UV/vis−NIR Philips spectrometer equipped with a diffuse reflectance accessory. The electron spin resonance (ESR) spectra were recorded on a (JEOL) JESFA200 ESR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DRX-400 spectrometer using $Si(CH_3)_4$ (TMS) as an internal standard. Solution mass spectra (LCMS) were obtained on a LCMS-2010A Shimadzu spectrometer. A Cypress model CS-1090/CS-1087 elec-

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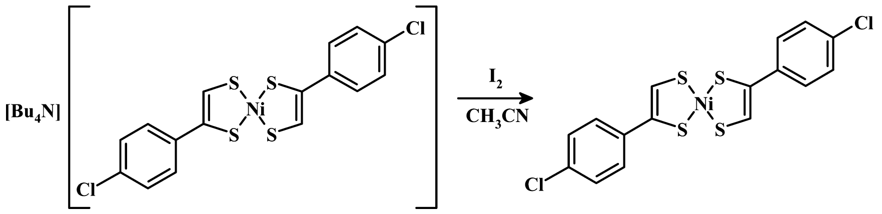
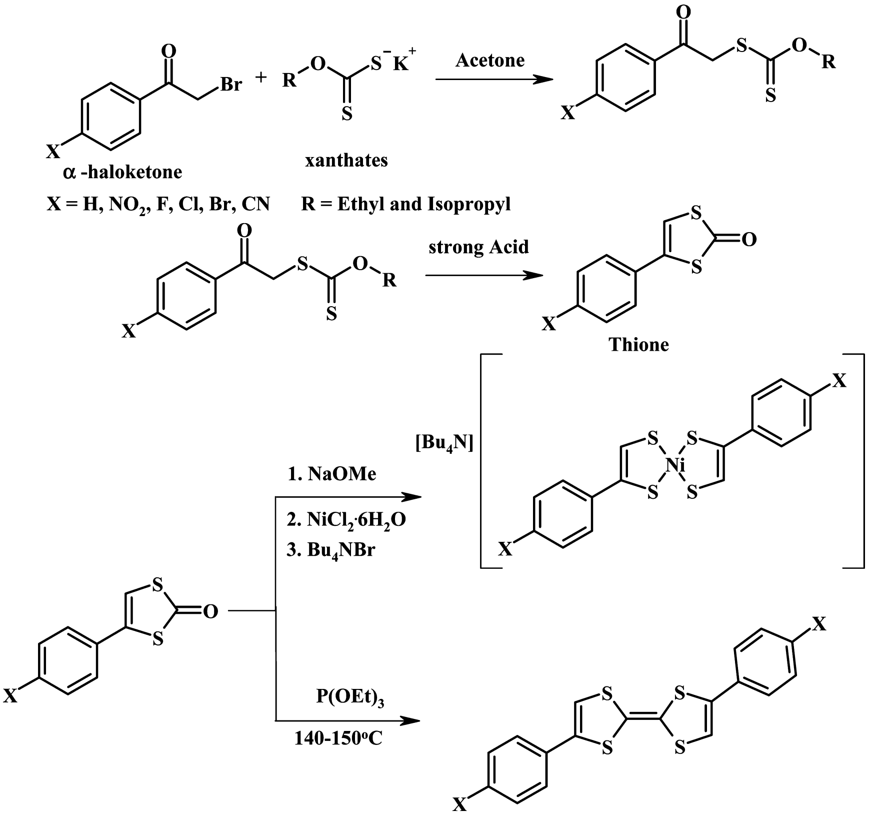
Scheme 7. Synthesis of Neutral [Ni(ClPhdt)$_2$] (**8**) (ClPhdt = 2-(*p*-chlorophenyl)-1,2-dithiolate)



Scheme 8. Synthetic Route for Preparation of Asymmetrically Substituted Anionic Ni(III) Bis-(dithiolene) Complexes and Asymmetrically Substituted Tetrathiafulvalenes



troanalytical system was used for cyclic voltammetric experiments. The electrochemical experiments were measured in acetonitrile solvent containing Bu_4NClO_4 as a supporting electrolyte, using a conventional cell consisting of two platinum wires as working and counter electrodes and a saturated calomel electrode(SCE) as reference. The potentials reported here are uncorrected for junction contributions.

Synthetic Procedures[19] for the 1,3-Dithiol-2-one Derivatives. (4-Phenyl-1,3-dithiol-2-one, 4-(*p*-nitrophenyl)-1,3-dithiol-2-one, 4-(*p*-fluorophenyl)-1,3-dithiol-2-one, 4-(*p*-chlorophenyl)-1,3-dithiol-2-one, 4-(*p*-bromophenyl)-1,3-dithiol-2-one), which have been used as starting precursors for the preparation of compounds **1** through **5** respectively, are presented in the Supporting Information, section S1.

Synthesis of [Bu$_4$N][Ni(Phdt)$_2$]. A 0.2 g (1 mmol) quantity of 4-phenyl-1,3-dithiol-2-one was suspended in 10 mL of absolute EtOH; to this reaction mixture was added sodium (0.06 g, 2.6 mmol) under a dry N_2 atmosphere, and the color of the reaction mixture turned from yellow to orange. Then, the solution of $NiCl_2 \cdot 6H_2O$ (0.12 g, 0.5 mmol) in absolute EtOH (10 mL) was added dropwise to the orange solution. After complete addition of the $NiCl_2 \cdot 6H_2O$ solution, it was continuously stirred for 20−25 min followed by the addition of absolute EtOH solution of [Bu$_4$N]Br (0.322 g, 1 mmol). This immediately resulted in the precipitation of **1** as a red solid. This product was then recrystallized from a 1:1 mixture of acetone and 2-propanol. Yield 0.165 g (52%). Anal. Calcd for $C_{32}H_{48}NNiS_4$: C, 60.65; H, 7.63; N, 2.21; S, 20.237. Found: C, 60.37; H, 7.11; N, 2.39; S, 19.81. IR (KBr pellet): (ν/cm^{-1}) = 2959, 2866, 1588, 1477, 1452, 1429, 1373, 1206, 1024, 931, 877, 835, 750, 690, 613, 449. LCMS mass spectrum (neg ion mode; CH_3CN solution): m/z = 390 [Ni(Phdt)$_2$]$^-$. UV−vis (CH_3CN): λ_{max}, nm (ε, M^{-1} cm^{-1}) = 383 (2898), 514 (1920), 623 (455), 837 (2987). CV (in CH_3CN vs SCE): $E^1_{1/2}$ = 0.26, E^2 = −0.63 V (irrev.) (Scheme 2).

Table 1. Cyclic Voltammetry Data[a]

compound	reduction wave $E_{1/2}$, V (ΔEp, mV)	oxidation wave $E_{1/2}$, V (ΔEp, mV)
[Bu$_4$N][Ni(Phdt)$_2$] (**1**)	−0.63	0.26 (70)
[Bu$_4$N][Ni(NO$_2$Phdt)$_2$] (**2**)	−0.31 (90), −0.56 (170), −0.98 (170)	0.42 (130)
[Bu$_4$N][Ni(ClPhdt)$_2$] (**4**)	−0.44 (60)	0.36 (120)
[Bu$_4$N][Ni(BrPhdt)$_2$] (**5**)	−0.43 (60)	0.37 (130)

[a] Cyclic voltammogram of compounds **1**,**2**, **4**, and **5** (10^{-3} M) in CH_3CN.

Synthesis of [Bu$_4$N][Ni(NO$_2$Phdt)$_2$] (2). A 0.13 g (0.54 mmol) quantity of 4-(*p*-nitrophenyl)-1,3-dithiol-2-one was suspended in

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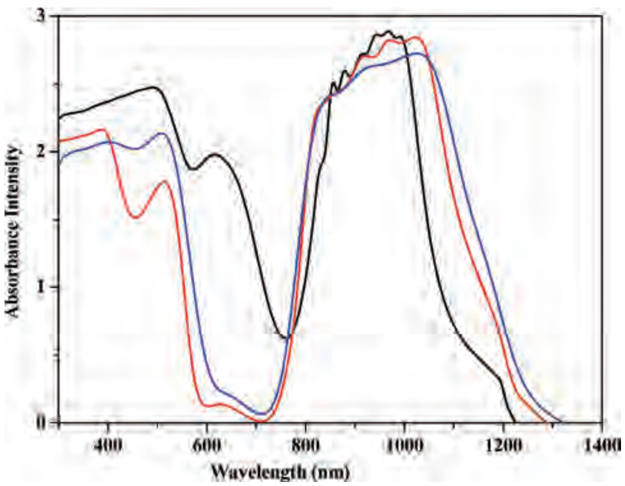

Figure 1. Electronic absorption spectra of NO_2-substituted Ni(III) bis(dithiolene) complex **2** (black line), F-substituted Ni(III) bis(dithiolene) compound **3** (red line), and Cl-substituted Ni(III) bis(dithiolene) compound **4** (blue line; 1×10^{-3} M, CH_3CN).

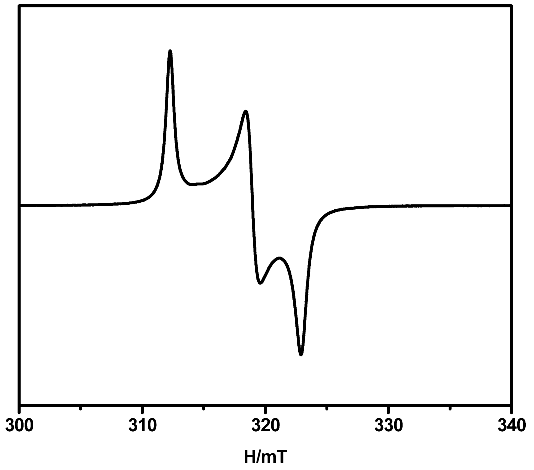

Figure 2. ESR spectrum of the powder form of compound $[Bu_4N][Ni(Phdt)_2]$ (**1**) at liquid nitrogen temperature.

10 mL of MeOH. This mixture was then stirred until complete dissolution, resulting in an orange solution. To this mixture was added 0.03 g (1.3 mmol) of sodium metal, and the color of the reaction mixture became dark. It was then stirred for 10 min at room temperature under a dry N_2 atmosphere. Subsequently, 5 mL MeOH solution of $NiCl_2 \cdot 6H_2O$ (0.070 g, 0.295 mmol) was added to the above reaction mixture, and the resulting reaction mixture was additionally stirred for 10 min followed by the addition MeOH solution (5 mL) of $[Bu_4N]Br$ (0.2 g, 0.62 mmol). The resulting red precipitate was separated out by adding of 7 mL of H_2O. This red precipitate was then crystallized from a (1:1) mixture of acetone/2-propanol. The thin-plate shaped crystals of **2** were washed with MeOH and dried in vacuum. Yield 0.110 g (51%). Anal. Calcd for $C_{32}H_{46}N_3O_4NiS_4$: C, 53.11; H, 6.41; N, 5.80; S, 17.72. Found: C, 53.76; H, 5.98; N, 5.59; S, 17.32. IR (KBr pellet): (ν/cm^{-1}) = 2955, 2874, 1643, 1584, 1504, 1334, 1209, 1103, 850, 748, 690. LCMS mass spectrum (neg ion mode; CH_3CN solution): *m*/*z* = 479 $[Ni(NO_2Phdt)_2]^-$. UV−vis (CH_3CN): λ_{max}, nm (ε, M^{-1} cm^{-1}) = 483 (2480), 616 (1980), 970 (2910). CV (in CH_3CN vs SCE): $E^1{}_{1/2} = 0.42$, $E^2{}_{1/2} = -0.31$ V, $E^3{}_{1/2} = -0.56$, $E^4{}_{1/2} = -0.98$ V (Scheme 3).

Synthesis of $[Bu_4N][Ni(FPhdt)_2]$ (3) (FPhdt = 2-(*p*-fluorophenyl)-1,2-dithiolate). A 0.15 g (0.71 mmol) quantity of 4-(*p*-fluorophenyl)-1,3-dithiol-2-one was suspended in 10 mL of MeOH. This mixture was stirred until its complete dissolution, resulting in an orange solution. To this mixture was added 0.03 g (1.3 mmol) of sodium metal, and the reaction mixture color became dark It was then stirred for 10 min at room temperature under a dry N_2 atmosphere. Subsequently, 5 mL of a MeOH solution of $NiCl_2 \cdot 6H_2O$ (0.070 g, 0.3 mmol) was added to above reaction mixture, and it was additionally stirred for 10 min followed by the addition of 5 mL of a MeOH solution of $[Bu_4N]Br$ (0.2 g, 0.62 mmol). The red precipitate was separated out by adding of 7 mL of H_2O. Compound **3** was then washed with MeOH and dried in vacuum. Single crystals, suitable for X-ray structure analysis, were grown from a (1:1) mixture of acetone and 2-propanol mixed solvent. Yield 0.122 g (60%). Anal. Calcd for $C_{32}H_{46}F_2NNiS_4$: C, 57.39; H, 6.92; N, 2.092; S, 19.15. Found: C, 57.12; H, 6.11; N, 2.39; S, 20.01. IR (KBr pellet): (ν/ cm^{-1}) = 2955, 2868, 1583, 1476, 1443, 1378, 1204, 1070, 1009, 879, 813, 784, 698, 473, 421. UV−vis (CH_3CN): λ_{max}, nm (ε, M^{-1} cm^{-1}) = 390 (2190), 515 (1790), 628 (130), 1020 (2850).

Synthesis of $[Bu_4N][Ni(ClPhdt)_2]$ (4). A 0.38 g (1.66 mmol) quantity of 4-(*p*-chlorophenyl)-1,3-dithiol-2-one was dissolved in 15 mL of MeOH. This reaction mixture was stirred until its complete dissolution resulting in an orange solution. To this mixture was added 0.07 g (3 mmol) of sodium metal. The ensuing dark reaction mixture was then stirred for 10 min at room temperature under dry N_2 atmosphere. A 5 mL MeOH solution of $NiCl_2 \cdot 6H_2O$ (0.17 g, 0.71 mmol) was added and the resulting reaction mixture was further stirred for 10 min followed by the addition of a 5 mL MeOH solution of $[Bu_4N]Br$ (0.5 g, 1.55 mmol). The red precipitate, thus obtained, was washed with MeOH and dried in vacuum. Single crystals, suitable for X-ray structure analysis, were grown from CH_2Cl_2-hexane (1:1) mixed solvents. Yield 0.22 g (44%). Anal. Calcd for $C_{32}H_{46}Cl_2NNiS_4$: C, 54.70; H, 6.59; N, 1.994; S, 18.25. Found: C, 54.43; H, 6.10; N, 1.69; S, 19.02. IR (KBr pellet): (ν/cm^{-1}) = 2957, 2866, 1585, 1481, 1444, 1377, 1207, 1087, 1008, 879, 815, 779, 709, 474. LCMS mass spectrum (neg ion mode; CH_3CN solution): *m*/*z* = 460 $[Ni(ClPhdt)_2]^-$. UV−vis (CH_3CN): λ_{max}, nm (ε, M^{-1}cm^{-1}) = 401 (2000), 510 (2180), 651 (230), 1033 (2760). CV (in CH_3CN vs SCE): $E^1{}_{1/2} = 0.36$, $E^2{}_{1/2} = -0.44$ V (Scheme 4).

Synthesis of $[Bu_4N][Ni(BrPhdt)_2]$ (5). A 0.2 g (0.73 mmol) quantity of 4-(*p*-bromophenyl)-1,3-dithiol-2-one was suspended in 15 mL of MeOH. This reaction mixture was then stirred until complete dissolution, resulting in an orange solution. To this mixture was added 0.04 g (1.73 mmol) of sodium metal. The dark reaction mixture, thus obtained, was stirred for 10 min at room temperature under a dry N_2 atmosphere. Subsequently, a 5 mL MeOH solution of $NiCl_2 \cdot 6H_2O$ (0.1 g, 0.42 mmol) was added to the above reaction mixture, and it was then stirred for 10 min followed by the addition of 5 mL MeOH solution of $[Bu_4N]Br$ (0.23 g, 0.71 mmol). The red precipitate, thus obtained, was washed with MeOH and dried in vacuum. Single crystals, good enough for X-ray structure analysis, were grown from an acetone-isopropyl alcohol solvent mixture. Yield 0.13 g (40%). Anal. Calcd for $C_{32}H_{46}Br_2NNiS_4$: C, 48.56; H, 5.86; N, 1.77; S, 16.20. Found: C, 47.97; H, 5.58; N, 1.63; S, 16.32. IR (KBr pellet): (ν/cm^{-1}) = 2957, 2870, 1580, 1478, 1379, 1206, 1068, 1005, 927, 879, 814, 783, 692, 466, 412. LCMS mass spectrum (neg ion mode; CH_3CN solution): *m*/*z* = 547 $[Ni(BrPhdt)_2]^-$. UV−vis (CH_3CN): λ_{max}, nm (ε, M^{-1} cm^{-1}) = 400 (1990), 510 (2100), 648 (220), 1037 (2800). CV (in CH_3CN vs SCE): $E^1{}_{1/2} = 0.37$, $E^2{}_{1/2} = -0.43$ V (Scheme 5).

Synthesis of 4,4′-Bis(4-chlorophenyl)-tetrathiafulvalene (ClPhTTF) (6). A 0.33 g (1.44 mmol) quantity of 4-(*p*-chlorophenyl)-1,3-dithiol-2-one was suspended in a 20 mL round-bottom flask under a dry N_2 atmosphere. To this mixture was added 5 mL of

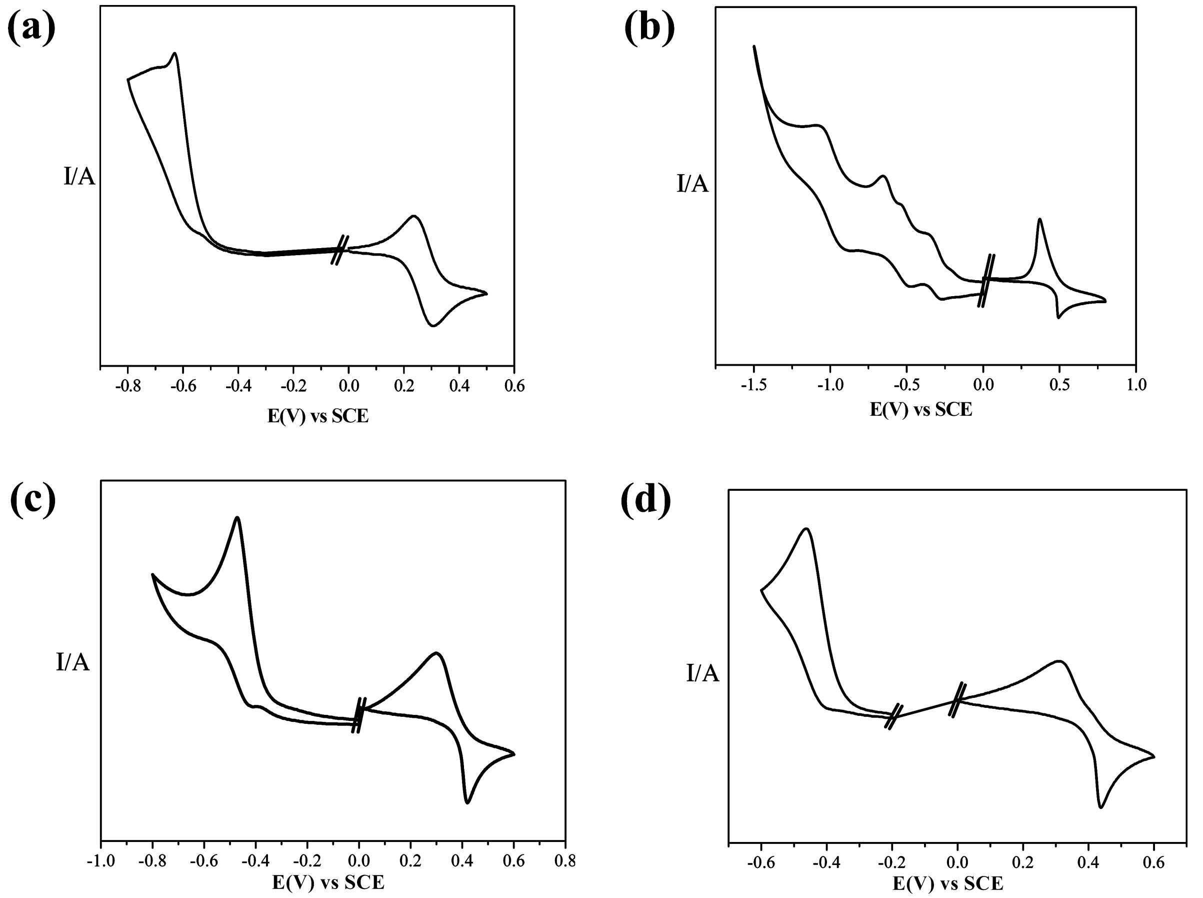

Figure 3. Cyclic voltammograms of unsymmetrical dithiolene complexes in acetonitrile. (a) $[Bu_4N][Ni(Phdt)_2]$ (**1**), (b) $[Bu_4N][Ni(NO_2Phdt)_2]$ (**2**), (c) $[Bu_4N][Ni(ClPhdt)_2]$ (**4**), and (d) $[Bu_4N][Ni(BrPhdt)_2]$ (**5**). All compounds peak potential were recorded vs SCE at 298 K.

freshly distilled $P(OEt)_3$, it was continuously heated for 2 h at 140−150 °C, and the color of the reaction mixture became dark. It was then cooled to room temperature, after which time 10 mL of MeOH was added resulting in the formation of an orange precipitate. Single crystals, suitable for X-ray analysis, were grown by slow evaporation of $CHCl_3$ solution. Yield 0.52 g (85%). Anal. Calcd for $C_{18}H_{10}Cl_2S_4$: C, 50.82; H, 2.37; S, 30.15. Found: C, 50.43; H, 2.41; S, 29.86. ^1H NMR (d_6-DMSO): (δ/ppm) = 6.67 (s, 2H), 7.30 (d, 4H), 7.50 (d, 4H). IR (KBr pellet): (ν/cm^{-1}) = 1651, 1541, 1473, 1394, 1072, 1005, 918, 817, 761, 457 (Scheme 6).

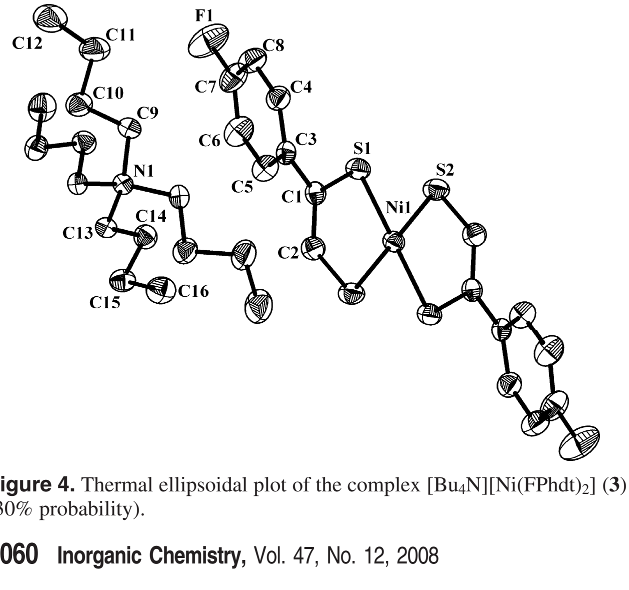

Figure 4. Thermal ellipsoidal plot of the complex $[Bu_4N][Ni(FPhdt)_2]$ (**3**) (30% probability).

Table 2. Crystal Data and Structural Refinement for Compounds **3** and **4**

	3	4
empirical formula	$C_{32}H_{46}F_2NNiS_4$	$C_{32}H_{46}Cl_2NNiS_4$
formula weight	669.65	702.55
T [K]	298(2)	298(2)
λ [Å]	0.71073	0.71073 A
crystal system	monoclinic	monoclinic
space group	$C2/c$	$P2(1)/c$
a [Å]	20.410(5)	9.6059(16)
b [Å]	8.949(2)	40.727(7)
c [Å]	19.574(4)	9.0719(15)
α [deg]	90	90
β [deg]	109.772(3)	91.483(3)
γ [deg]	90	90
V [Å^3]	3364.2(13)	3547.9(10)
Z	4	4
D_{calc} [Mg m^{-3}]	1.322	1.315
μ [mm^{-1}]	0.858	0.955
F [000]	1420	1484
crystal size [mm^3]	0.35 × 0.34 × 0.12	0.20 × 0.14 × 0.06
θ range for data collection [deg]	2.12 to 25.00	2.00 to 25.00
reflections collected/unique	15593/2964	33998/6255
R (int)	0.0522	0.0666
refinement method	full-matrix least-squares on F^2	
data/restraints/parameters	2964/0/185	6255/0/365
goodness-of-fit on F^2	1.100	0.918
R_1, wR_2 [I > 2σ(I)]	0.0356/0.1027	0.0419/0.0855
R_1, wR_2 (all data)	0.0407/0.1057	0.0658/0.0921
largest diff. peak/hole [e Å^3]	0.473/−0.291	0.455/−0.214

Synthesis of 4,4′-Bis(4-bromophenyl)-tetrathiafulvalene (Br-PhTTF) (7). Ten milliliters of freshly distilled $P(OEt)_3$ was added to 0.5 g (1.83 mmol) of 4-(p-bromophenyl)-1,3-dithiol-2-one, taken

Table 3. Selected Bond Lengths [Å] and Angles [°] for Compound **3**[a]

C(1)−C(2)	1.349(3)	C(1)−C(3)	1.477(3)
C(1)−S(1)	1.739(2)	C(2)−S(2)#1	1.713(2)
C(7)−F(1)	1.352(3)	C(9)−N(1)	1.516(2)
C(10)−C(11)	1.518(3)	C(13)−N(1)	1.515(2)
N(1)−C(13)#2	1.515(2)	N(1)−C(9)#2	1.516(2)
Ni(1)−S(2)	2.1384(6)	Ni(1)−S(2)#1	2.1384(6)
Ni(1)−S(1)	2.1478(7)		
C(2)−C(1)−S(1)	117.09(17)	C(3)−C(1)−S(1)	119.03(15)
C(1)−C(2)−S(2)#1	122.57(17)	S(2)#1−C(2)−H(2)	118.7
F(1)−C(7)−C(8)	119.6(3)	F(1)−C(7)−C(6)	118.4(3)
C(10)−C(9)−N(1)	117.47(18)	C(14)−C(13)−N(1)	116.72(17)
C(14)−C(13)−H(13A)	108.1	C(13)#2−N(1)−C(13)	106.1(2)
C(13)#2−N(1)−C(9)#2	110.92(11)	C(13)−N(1)−C(9)#2	111.68(11)
C(13)#2−N(1)−C(9)	111.68(11)	C(13)−N(1)−C(9)	110.92(11)
C(9)#2−N(1)−C(9)	105.6(2)	S(2)−Ni(1)−S(2)#1	180.0
S(2)−Ni(1)−S(1)	88.70(2)	S(2)#1−Ni(1)−S(1)	91.30(2)
S(2)#1−Ni(1)−S(1)#1	88.70(2)	S(1)−Ni(1)−S(1)#1	179.999(1)
C(1)−S(1)−Ni(1)	105.16(7)	C(2)#1−S(2)−Ni(1)	103.83(8)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 2, -y, -z$; #2, $-x + 2, y, -z + 1/2$.

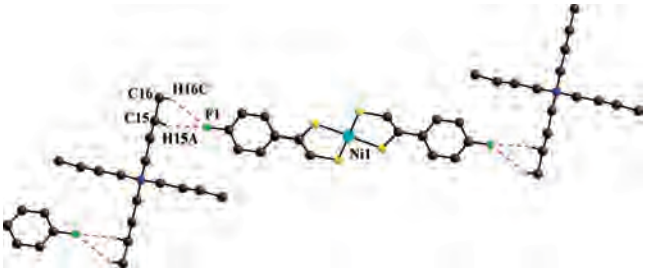

Figure 5. C−H···F hydrogen bonding interactions (purple dotted lines) between $[Bu_4N]^+$cation and $[Ni(FPhdt)_2]^-$ anion in the compound **3**. Color code: F, green; C, gray; S, yellow; Ni, cyan; N, blue.

in a 20 mL round-bottom flask, under a dry N_2 atmosphere. This mixture was continuously heated for 1 h at 140−150 °C after which time the reaction mixture became red. The reaction mixture was then cooled to room temperature affording an orange crystalline product over a period of 24 h. Single crystals, suitable for X-ray analysis, were grown by slow evaporation of a $CHCl_3$ solution. Yield 0.76 g (81%). Anal. Calcd for $C_{18}H_{10}Br_2S_4$: C, 42.03; H, 1.96; S, 24.93. Found: C, 41.86; H, 2.01; S, 24.48. ^1H NMR (d_6-DMSO): (δ/ppm) = 6.52 (s, 2H), 7.28 (d, 4H), 7.47 (d, 4H). IR (KBr pellet): (ν/cm^{-1}) = 1651, 1541, 1473, 1394, 1072, 1005, 918, 817, 761, 457. LCMS mass spectrum (pos ion mode; CH_3CN solution): $m/z = 514$ (Scheme 6).

Synthesis of [Ni(ClPhdt)$_2$] (8). A 0.14 g (0.2 mmol) quantity of $[Bu_4N][Ni(ClPhdt)_2]$(**4**) was dissolved in 10 mL of dry acetonitrile. To this solution was added 0.05 g (0.197 mmol) of I_2 in dry acetonitrile (5 mL). The reaction mixture was then continuously stirred for 30 min resulting in the formation of a bluish green precipitate. The single crystals, suitable for X-ray analysis, were grown via vapor diffusion of diethyl ether into a THF solution of the precipitate. Yield 0.08 g (84%). Anal. Calcd for $C_{16}H_{10}Cl_2NiS_4$: C, 41.77; H, 2.19; S, 27.88. Found: C, 41.78; H, 2.32; S, 27.15. IR (KBr pellet): (ν/cm^{-1}) = 1478, 1440, 1334, 993, 815, 785, 693, 461 (Scheme 7).

Single Crystal Structure Determination. Data were measured at room temperature for compounds **3**, **4**, **6**, and **7** on a Bruker SMART APEX CCD area detector system [λ (Mo Kα) = 0.7103 Å], graphite monochromator; 2400 frames were recorded with an ω scan width of 0.3°, each for 8 s, crystal-detector distance 60 mm, collimator 0.5 mm. Data reduction was performed with the SAINTPLUS software,[20] absorption correction using an empirical method SADABS,[21] structure solution using the SHELXS-97 program,[22] and refined using the SHELXL-97 program.[23] Hydrogen atoms on the aromatic rings were introduced on the calculated positions and included in the refinement riding on their respective parent atoms.

Results and Discussion

Synthesis. We have synthesized the asymmetrically substituted anionic nickel bis-1,2-dithiolene complexes **1**−**5** (Scheme 1) from the corresponding 1,3-dithiol-2-one derivatives; the 1,3-dithiol-2-one derivatives were synthesized by the reaction of the respective α-haloketones and alkylxanthates following previously reported procedures,[13,19,24] Scheme 8.

Like the preparation of other substituted nickel bis(1,2-dithiolene) complexes,[13,25] 1,3-dithiol-2-one is needed as the starting precursor for the preparation of both metal-asymmetric-dithiolene complexes and tetrathiafulvalene derivatives. Even though the Ni(II) salt has been used during the preparation of compounds **1**−**5**, we obtained monoanionic Ni(III)-dithiolene complexes as evidenced by electron paramagnetic resonance (EPR) spectroscopy (vide infra). Molecular oxygen from air is the possible oxidant in this oxidation from Ni(II) to Ni(III). The neutral nickel(IV) complex $[Ni(ClPhdt)_2]$ (**8**) was synthesized by the chemical oxidation of the anionic nickel(III) dithiolene complex $[Bu_4N][Ni(ClPhdt)_2]$ (**4**) using molecular iodine (oxidant) in acetonitrile as shown in Scheme 7.

As shown in Scheme 8, we have succeeded in preparing a number of dithiolene derivatives with a range of substituents, X = H(**1**), NO_2(**2**), F(**3**), Cl(**4**), and Br(**5**), leading to compounds **1**−**5**, respectively. We also intended to use −CN (an electron withdrawing group) as one of the substituents because of their importance of the derivatives as optoelectronic materials.[15] The significance of cyano-substituted dithiolene complexes are evidenced by the fact that a platinum dithiolene complex with cyano substituents gives a $\chi^{(3)}$ (= third order non linearity) value of 4.2×10^{-12} esu compared to 1.4×10^{-13} esu exhibited by a CF_3 analogue.[14] In this context, the synthesis of heteroleptic Ni(II) and Pd(II)-dithiolenes with asymmetrically substituted cyanide group has recently been reported.[26] However, in our synthesis (Scheme 8), we could not isolate the cyano-substituted

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(20) *Software for the CCD Detector System*; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1998.

(21) Sheldrick, G. M., *SADABS, Program for Absorption Correction with the Siemens SMART Area-Detector System*; University of Göttingen: Göttingen, Germany, 1996.

(22) Sheldrick, G. M. *SHELXS-97, Program for Solution of Crystal Structures*. University of Göttingen: Göttingen, Germany. 1997.

(23) Sheldrick, G. M. *SHELXS-97, Program for Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(24) (a) Svenstrup, N.; Becher, J. *Synthesis* **1995**, 215. (b) Clausen, R. P.; Becher, J. *Tetrahedron* **1996**, *52*, 3171. (c) Cerrada, E.; Garrido, J.; Laguna, M.; Lardies, N.; Romeo, I. *Synth. Met.* **1999**, *102*, 1709. (d) Gorgues, A.; Hudhomme, P.; Salle, M *Chem. Rev.* **2004**, *104*, 5151. (e) Fabre, J. M *Chem. Rev.* **2004**, *104*, 5133. (f) Kobayashi, A.; Fujiwara, E.; Kobayashi, H. *Chem. Rev.* **2004**, *104*, 5243.

(25) Keefer, C. E.; Purrington, S. T.; Bereman, R. D.; Boyle, P. D. *Inorg. Chem.* **1999**, *38*, 5437.

(26) Lardies, N.; Cerrada, E.; Laguna, M. *Polyhedron* **2006**, *25*, 2785.

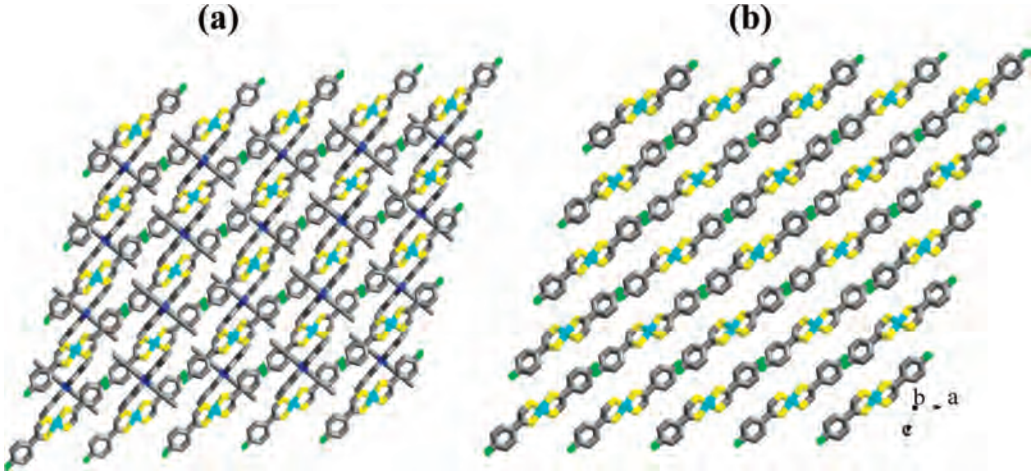

Figure 6. View (wire-frame representation) of the crystal packing of **3** in (2 × 2) cells looking down to the crystallographic *b* axis: (a) packing diagram of $[Bu_4N][Ni(FPhdt)_2]$ and (b) packing diagram of the same without $[Bu_4N]^+$ cation. Color code: F, green; C, gray; S, yellow; Ni, cyan; N, blue.

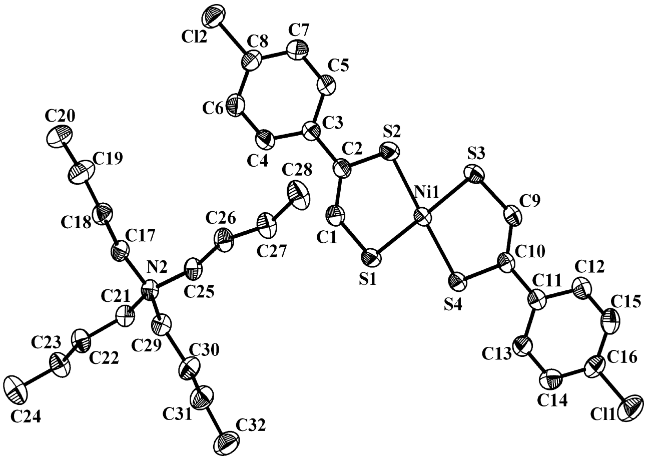

Figure 7. Thermal ellipsoidal plot of the compound $[Bu_4N][Ni(ClPhdt)_2]$ (**4**) (30% probability).

Table 4. Selected Bond Lengths [Å] and Angles [°] for Compound **4**

C(1)−C(2)	1.337(4)	C(9)−C(10)	1.338(4)
C(9)−S(3)	1.712(3)	C(17)−N(2)	1.514(3)
C(17)−C(18)	1.516(4)	C(29)−N(2)	1.520(3)
Ni(1)−S(1)	2.1374(9)	Ni(1)−S(2)	2.1411(9)
Ni(1)−S(3	2.1433(8)	Ni(1)−S(4)	2.1515(9)
C(8)−Cl(2)	1.745(3)		
C(2)−C(1)−S(1)	122.6(2)	C(1)−C(2)−S(2)	17.2(2)
C(3)−C(2)−S(2)	118.8(2)	C(14)−C(16)−Cl(1)	119.8(3)
N(2)−C(17)−C(18)	116.1(2)	C(30)−C(29)−N(2)	116.0(2)
C(17)−N(2)−C(25)	110.6(2)	C(17)−N(2)−C(21)	110.5(2)
C(25)−N(2)−C(21)	106.59(19)	S(1)−Ni(1)−S(4)	89.49(3)
S(2)−Ni(1)−S(4)	178.48(4)	S(3)−Ni(1)−S(4)	91.58(3)
C(1)−S(1)−Ni(1)	103.74(11)	C(2)−S(2)−Ni(1)	105.49(11)
C(9)−S(3)−Ni(1)	103.48(10)		

derivative and obtained an insoluble product in the second step (by the use of 80% H_2SO_4, cyclization purpose). We believe that, this insoluble product is most likely the result of acid hydrolysis of the −CN group to the corresponding carboxylic acid. This is consistent with the IR data. The relevant IR spectrum does not show the characteristic IR bands for the −CN group. The insolubility of this product precludes us from synthesizing and characterizing further −CN substituted asymmetrical 1,2-dithiolene complexes following our reaction Scheme 8. In the synthesis of asymmetrically substituted tetrathiafulvalenes **6** and **7** (Scheme 8), a 1,3-dithiol-2-one derivative has been shown to react with triethylphosphite ($P(OEt)_3$) at 140−150 °C. This methodology is well-established in literature.[27]

Compounds **1**−**8** were characterized by elemental analyses and routine spectral studies including cyclic voltammetry studies for compounds **1**, **2**, **4**, and **5**. Whereas compounds **3**, **4**, **6** and **8** were unambiguously characterized by single crystal X-ray structure determinations, compounds **1**, **2**, **5**, and **7** could not be studied by single crystal X-ray structural studies because of their poor crystal quality.

Spectroscopic and Electronic Characterization. Nickel based transition metal unsymmetrical dithiolene complexes $[Bu_4N][Ni(XPhdt)_2]$ (X = H, F, Cl, Br, and NO_2) exhibit strong absorbance bands in the region of 850−1000 nm. Interestingly, these compounds are extremely soluble in nonpolar organic solvents. The functional groups attached to the nickel dithiolene core have a large effect on both the position of the electronic absorbance maxima and the solubility of the relevant dye. We found that the NO_2-substituted unsymmetrical metal dithiolene complex of Ni^{2+} (compound **2**) shows the absorption band at 970 nm in CH_3CN solution (ε = 2910 M^{-1} cm^{-1}), whereas for the F and Cl substituted Ni^{2+} dithiolene complexes, the absorption maxima are red-shifted by 50 and 60 nm, respectively. This low energy NIR broad feature in the region of 800 to 1000 nm (for compounds **1**−**5**) as shown in the electronic absorption spectra (Figure 1) is a characteristic of bis(dithiolene)nickel complexes and is generally assigned to $\pi \rightarrow \pi^*$ transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). It usually appears as a broad but intense band with ε = 15000−40000 M^{-1} cm^{-1} which is important in connection with its use as NIR dyes[3a,28] and in turn its

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[27] (a) Svenstrup, N.; Rasmussen, K. M.; Hansen, T. K.; Becher, J. *Synthesis* **1994**, 809. (b) Becher, J.; Lau, J.; Leriche, P.; Mørk, P.; Svenstrup, N *J. Chem. Soc., Chem. Commun.* **1994**, 2715. (c) Lau, J.; Simonsen, O.; Becher, J. *Synthesis* **1995**, 521. (d) Simonsen, K. B.; Svenstrup, N.; Lau, J.; Simonsen, O.; Mørk, P.; Kristensen, G. J.; Becher, J. *Synthesis* **1996**, 407.

[28] Bigoli, F.; Chen, C.-T.; Wu, W.-C.; Deplano, P.; Mercuri, M. L.; Pellinghelli, M. A.; Pilia, L.; Pintus, G.; Serpe, A.; Trogu, E. F. *Chem. Commun.* **2001**, 2246–2247.

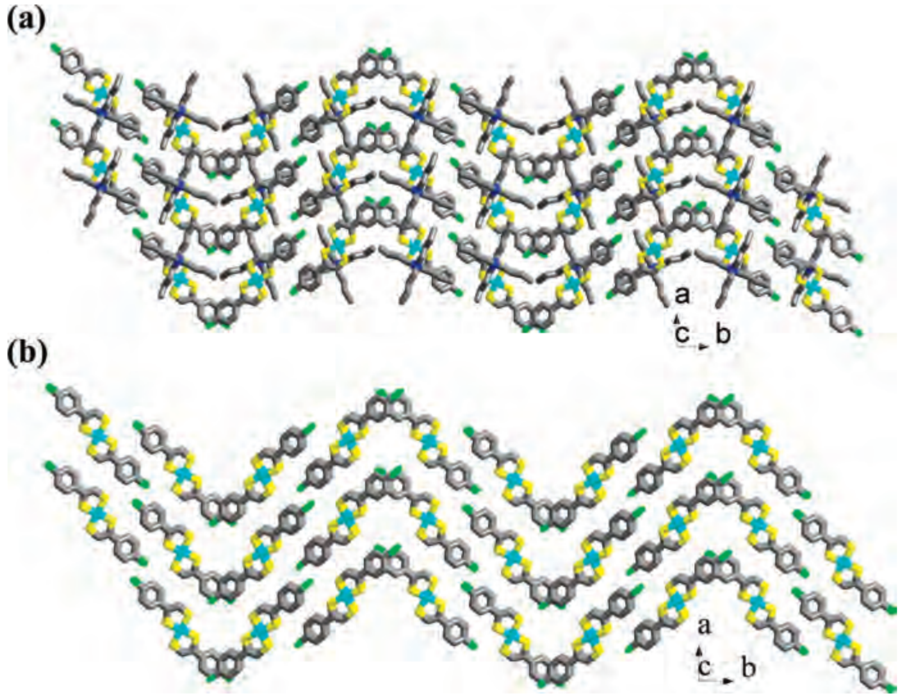

Figure 8. View (wire-frame representation) of the crystal packing of **4** in (2 × 2) cells viewed down to the crystallographic *c* axis: (a) packing diagram of $[Bu_4N][Ni(ClPhdt)_2]$ and (b) packing diagram of the same without $[Bu_4N]^+$ cation.

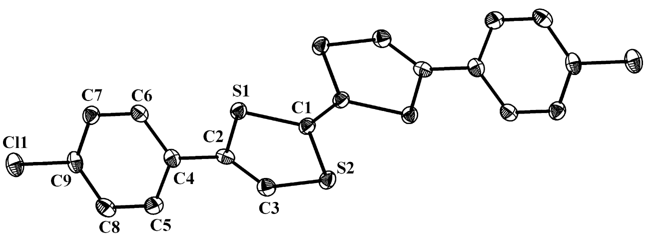

Figure 9. Thermal ellipsoidal plot of the molecule ClPhTTF (**6**) (30% probability).

Table 5. Crystal Data and Structural Refinement for Compounds **8** and **6**

	8	**6**
empirical formula	$C_{16}H_{10}Cl_2NiS_4$	$C_{18}H_{10}Cl_2S_4$
formula weight	474.10	425.40
T [K]	298(2)	298(2)
λ [Å]	0.71073	0.71073
crystal system	monoclinic	monoclinic
space group	$P2(1)/c$	$P2(1)/c$
a [Å]	10.790(3)	10.5339(6)
b [Å]	9.143(2)	9.0891(5)
c [Å]	8.849(2)	8.8956(5)
α [deg]	90	90
β [deg]	90.965(4)	92.8190(10)
γ [deg]	90	90
V [Å^3]	872.9(4)	850.67(8)
Z	2	2
D_{calc} [Mg m^{-3}]	1.804	1.661
μ [mm^{-1}]	1.893	0.869
F[000]	478	432
crystal size [mm^3]	0.36 × 0.32 × 0.10	0.20 × 0.10 × 0.06
θ range for data collection [deg]	1.89 to 24.99	1.94 to 25.00
reflections collected/unique	7926/1539	7900/1497
R (int)	0.0826	0.0323
refinement method	full-matrix least-squares on F^2	
data/restraints/parameters	1539/0/107	1497/0/109
goodness-of-fit on F^2	1.115	1.085
R_1, wR_2 [$I > 2\sigma(I)$]	0.0295/0.0724	0.0242/0.0635
R_1/wR_2 (all data)	0.0309/0.0736	0.0269/0.0647
largest diff. peak/hole [e Å^3]	0.281/−0.432	0.286/−0.239

application in Q-switching infrared lasers.[8c,d] However, in the present system, even though the $\pi \rightarrow \pi^*$ transition appears in the NIR region (Figure 1), it is not as intense a transition (ε values are around 3000 M^{-1} cm^{-1}) in comparison with that of bis(dithiolene)nickel complexes that are used as NIR dyes.[28] One of the major conditions in obtaining high ε values is coplanarity of the ligand moieties around the nickel ion. In the present study, the outer two phenyl rings (substituents on dithiolenes) are found to be twisted out of the plane defined by the dithiolene moiety (vide infra). This probably affects the intensity of the $\pi \rightarrow \pi^*$ transition in the NIR region by perturbing the symmetry of the frontier orbitals.

The absorption maxima shift toward the NIR region in the order of the nature of the substituents NO_2 < F < Cl (Figure 1). Thus, tuning of the NIR absorption bands is attributed to the substituents on dithiolene ligands. In this series, the $-NO_2$ group, being the most electron withdrawing substituent, decreases the electron density of the dithiolene moiety and thereby increases the gap of HOMO and LUMO (the $\pi \rightarrow \pi^*$ transition). This results in the blue-shift of the NIR absorption maximum of the nitro-substituted compound **2** compared to the absorption maxima of fluoro-, chloro- and bromo-substituted compounds **3**, **4**, and **5**, respectively. The present system (unsymmetrical nickel(III) dithiolene complexes, $[Bu_4N][Ni(XPhdt)_2]$ (X = H, F, Cl, Br, and NO_2)) is of great attraction in the sense that further work can be put forward by the substitution of more electron donating substituents in the place of halogens or by the reduction of the electron withdrawing $-NO_2$ group to an electron donating $-NR_2$(R = H, alkyl) group.

The ESR spectra of solid samples for compounds **1**−**5** were recorded at room temperature and at liquid nitrogen

Table 6. Selected bond Lengths [Å] and Angles [°] for Compound **6**[a]

C(1)−C(1)#1	1.346(4)	C(2)−C(3)	1.340(3)
C(1)−S(2)	1.7591(18)	C(1)−S(1)	1.7649(18)
C(2)−S(1)	1.7707(18)	C(3)−S(2)	1.7342(18)
C(9)−Cl(1)	1.7404(18)		
C(1)#1−C(1)−S(2)	122.12(19)	C(1)#1−C(1)−S(1)	123.30(19)
S(2)−C(1)−S(1)	114.55(10)	C(3)−C(2)−S(1)	115.63(14)
C(4)−C(2)−S(1)	119.81(13)	C(2)−C(3)−S(2)	119.63(14)
C(7)−C(9)−Cl(1)	119.76(14)	C(8)−C(9)−Cl(1)	119.03(14)
C(1)−S(1)−C(2)	95.06(8)	C(3)−S(2)−C(1)	94.64(8)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 2, -y + 1, -z$.

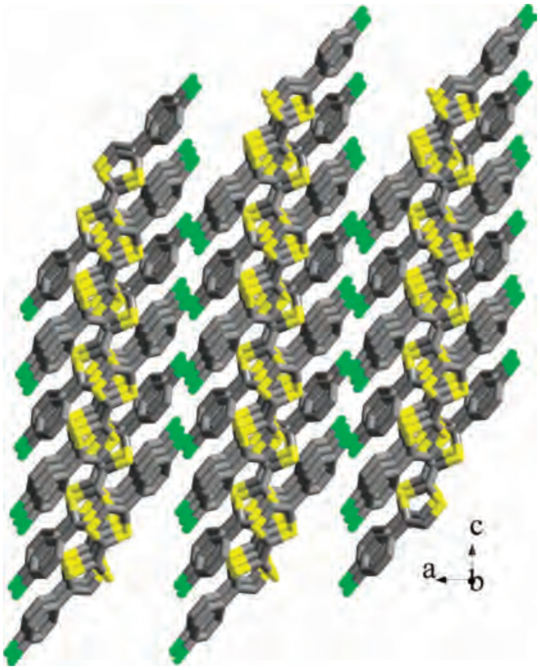

Figure 10. Packing diagram (wire frame representation) of compound ClPhTTF (**6**) viewed down to the crystallographic *b* axis. Color code: C, gray; S, yellow; Cl, green.

temperature. All exhibit a rhombic type signal ($g_x = 2.095$, $g_y = 2.053$, and $g_z = 2.026$ for compound **1**; $g_x = 2.096$, $g_y = 2.062$, and $g_z = 2.004$ for compound **4**; $g_x = 2.089$, $g_y = 2.061$, and $g_z = 2.008$ for compound **5** at liquid nitrogen temperature) indicating that compounds **1**−**5** are formally Ni(III) complexes. A representative ESR spectrum (compound **1**) is shown in Figure 2 (see Supporting Information, section S2 for ESR spectra of compounds **4** and **5**). The anisotropy in the ESR spectra implies some contribution of the d orbital of nickel in the total spin density, which is usually, in this class of materials,[29] distributed 40% on nickel and 60% on the ligands. The similarity of the ESR parameters of our systems and similar compounds, reported earlier,[29] suggests this spin distribution for our compounds too.

Such rhombic feature is not unusual for square-planar Ni(III) complexes that arises because of a distortion from square-planar geometry.[30] This distortion is indeed realized in our present system from crystal structure analysis (vide infra). Thus, ESR studies are consistent with electronic absorption studies, where we have argued that this type of twist or distortion (with square planar geometry) might diminish the intensity of the $\pi \rightarrow \pi^*$ NIR transition as described in the preceding section. A similar Ni(III) rhombic type ESR signal has been shown earlier for the dithiolene complex, $[Ni(DDDT)_2]^-$ (DDDT = 5,6-dihydro-1,4-dithin-2,3-dithiolate).[31] Considering all the EPR features and comparing these data with already known mononuclear square-planar Ni(III) complexes,[30−32] it is logical to describe the present compounds **1**−**5** as a formal Ni(III) system.

The ^{1}H NMR spectra for the Ni(III) monoanionic complexes were measured in DMSO-d_6. We have already confirmed that the compounds **1**−**5** are paramagnetic (vide supra). The presence of unpaired electron in the same molecule gives rise to large isotropic shifts (up to several hundred ppm) and severely broadened resonances, which usually make integration of signals difficult.[33] For a paramagnetic chromium complex, protons attached to carbon atoms directly bonded to Cr(III) (e.g., methyl groups) are typically unobservable.[33] Any report/discussion on ^{1}H NMR spectrum of Ni(III) coordination complex is hardly known.[34] In the ^{1}H NMR spectra for compounds **1**−**5**, only the signals corresponding to the $[n\text{-}Bu_4N]^+$ cations were observed; very weak broad features are detected in the shifted aromatic region (see the Supporting Information, section S3 for the relevant ^{1}H NMR spectra). The severely low solubility of the neutral compound **8** precluded us from studying its ^{1}H NMR spectra. The organic compounds **6** and **7** exhibited the expected ^{1}H NMR signals (see Supporting Information, section S3 for the NMR spectrum of compound **7**).

The LCMS for the monoanionic Ni(III) complexes show the parent complex anion in all cases. The organic compounds (**6** and **7**) also exhibited the expected molecular mass (see Supporting Information, section S4 for relevant mass spectra).

The redox behavior of the unsymmetrical substituted nickel bis(dithiolene) complexes $[Bu_4N][Ni(Phdt)_2]$ (**1**), $[Bu_4N][Ni(NO_2Phdt)_2]$ (**2**), $[Bu_4N][Ni(ClPhdt)_2]$ (**4**), and $[Bu_4N][Ni(BrPhdt)_2]$ (**5**) in acetonitrile solutions, each containing 0.10 M $[Bu_4N]ClO_4$ as supporting electrolyte, was investigated by cyclic voltammetry versus SCE. The results are summarized in Table 1. As shown in Figure 3, the cyclic voltammograms of compounds **1**, **4**, and **5** exhibit an oxidative response and a reductive response (irreversible for compound **1** and quasi-reversible for compounds **4** and **5**). Initial developments on electrochemistry of transition metal dithi-

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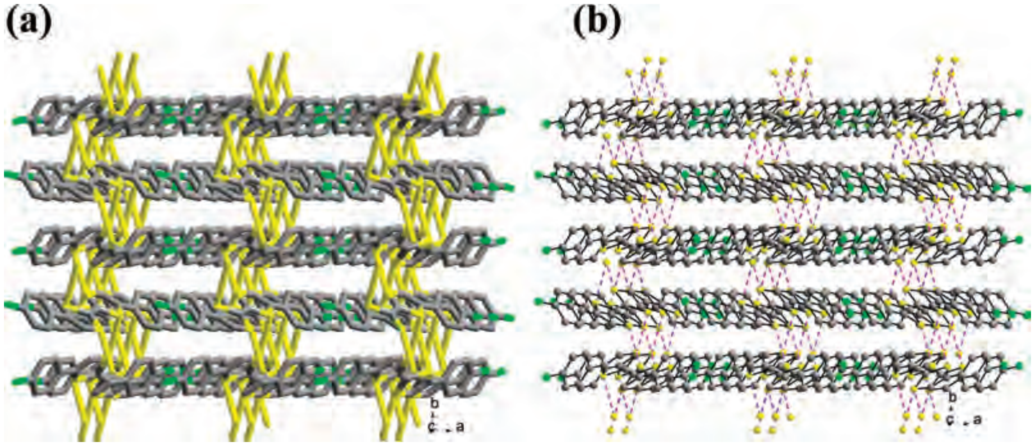

Figure 11. Packing diagram of ClPhTTF (**6**): (a) view of the wire frame representation, solid yellow lines indicate intermolecular S···S contacts, and (b) view of the ball and stick representation, purple dotted lines indicate intermolecular S···S contacts, viewed down to the crystallographic *c* axis.

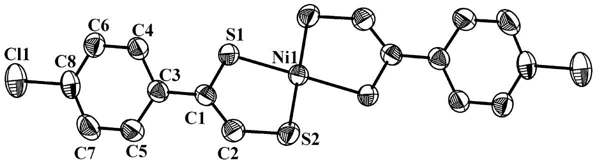

Figure 12. Thermal ellipsoidal plot of the neutral compound [Ni(ClPhdt)$_2$] (**8**) (30% probability).

Table 7. Selected Bond Lengths [Å] and Angles [°] for Compound **8**[a]

C(1)−C(2)	1.373(3)	C(1)−S(1)	0.712(2)
C(2)−S(2)	1.680(2)	C(8)−Cl(1)	1.737(2)
Ni(1)−S(2)	2.1146(6)	Ni(1)−S(2)#1	2.1146(6)
Ni(1)−S(1)#1	2.1381(6)	Ni(1)−S(1)	2.1382(6)
C(2)−C(1)−C(3)	122.29(19)	C(2)−C(1)−S(1)	117.09(16)
C(3)−C(1)−S(1)	120.61(16)	C(1)−C(2)−S(2)	122.22(17)
C(8)−C(7)−C(5)	118.9(2)	C(5)−C(7)−H(7)	120.6
C(7)−C(8)−Cl(1)	119.20(18)	S(2)−Ni(1)−S(2)#1	180.0
S(2)−Ni(1)−S(1)#1	88.33(2)	S(2)#1−Ni(1)−S(1)#1	91.67(2)
S(2)−Ni(1)−S(1)	91.67(2)	S(2)#1−Ni(1)−S(1)	88.33(2)
S(1)#1−Ni(1)−S(1)	180.0	C(1)−S(1)−Ni(1)	104.81(8)
C(2)−S(2)−Ni(1)	104.18(8)		

[a] Symmetry transformations used to generate equivalent atoms: #1, −*x* + 2, −*y* + 2, −*z*.

Scheme 9

$$[ML_2]^0 \underset{-e}{\overset{e}{\rightleftharpoons}} [ML_2]^{1-} \underset{-e}{\overset{e}{\rightleftharpoons}} [ML_2]^{2-}$$

olene complexes, that have been summarized by McCleverty,[35] led to recognition and experimental realization of the three-membered, planar series {ML$_2$} with M = Ni, Pd, or Pt as presented in Scheme 9, in which the neutral and dianionic members are diamagnetic and the monoanion is paramagnetic with a $S = 1/2$ ground state. On the basis of Scheme 9 and comparing the present electrochemical data with other similar systems reported earlier,[29c,35,36] the oxidative response for compounds **1**, **4**, and **5** is attributed to the [Ni^{IV}L$_2$]^0/[Ni^{III}L$_2$]$^{1-}$ couple, and the reductive response at negative potentials is assigned as being due to the [Ni^{III}L$_2$]$^{1-}$/[Ni^{II}L$_2$]$^{2-}$ couple. Similarly, the cyclic voltammogram (Figure 3b) of compound [Bu$_4$N][Ni(NO$_2$Phdt)$_2$] (**2**) shows a quasi-reversible oxidative response at +0.42 V because of the [Ni^{IV}(NO$_2$Phdt)$_2$]^0/[Ni^{III}(NO$_2$Phdt)$_2$]$^{1-}$ couple and a reversible reductive response at −0.31 V that can be assigned to the [Ni^{III}(NO$_2$Phdt)$_2$]$^{1-}$/[Ni^{II}(NO$_2$Phdt)$_2$]$^{2-}$ couple. Compound **2** displays two more quasi-reversible reductive responses at −0.98 V and −0.56 V, most probably because of the participation of the nitro groups. Similar electrochemical behavior of 5-(nitrophenyl)-1,2-dithiole-3-thiones has been reported.[37]

Thus, electrochemical studies indicate that the small variation in the electron withdrawing substituents on the dithiolene moiety can tune the redox potentials (Table 1) of the metal dithiolene complexes. It is noteworthy that the metal centered oxidation process (for example, from Ni^{3+} to Ni^{4+}) is easier in the case of the chloro- and bromo-substituted complexes (**4** and **5**, respectively) compared with nitro-derivative (compound **2**), showing that the reaction proceeds more easily as the electron density on the dithiolene moiety is less decreased in the chloro- and bromo-substituted complexes than in nitro-derivative (nitro group is more electron withdrawing, more positive $E_{1/2}$, see Table 1).

On the basis of the same logic, the nitro-derivative (compound **2**) is more easily reduced (−0.31 V) compared with the chloro- and bromo-derivatives (−0.44 V and −0.43 V, respectively; Table 1). We see the metal centered reduction of a metal dithiolene complex very rarely. In the present study, compounds **2**, **4**, and **5**, having nitro, chloro, and bromo groups, respectively, on each dithiolene ligand, can be stabilized in their (formally) +4, +3, and +2 oxidation states, as suggested by the electrochemical studies.

X-ray Crystallographic Studies.

Crystal Structure Description of Compound [Bu$_4$N][Ni(FPhdt)$_2$] (3). Red crystals of the complex [Bu$_4$N][Ni(FPhdt)$_2$] (**3**), suitable for X-ray structure analysis, could be grown from acetone-isopropyl alcohol (1:1) mixture. The crystal structure shows that the relevant crystals belong to the monoclinic system with a *C*2/*c* space group. The

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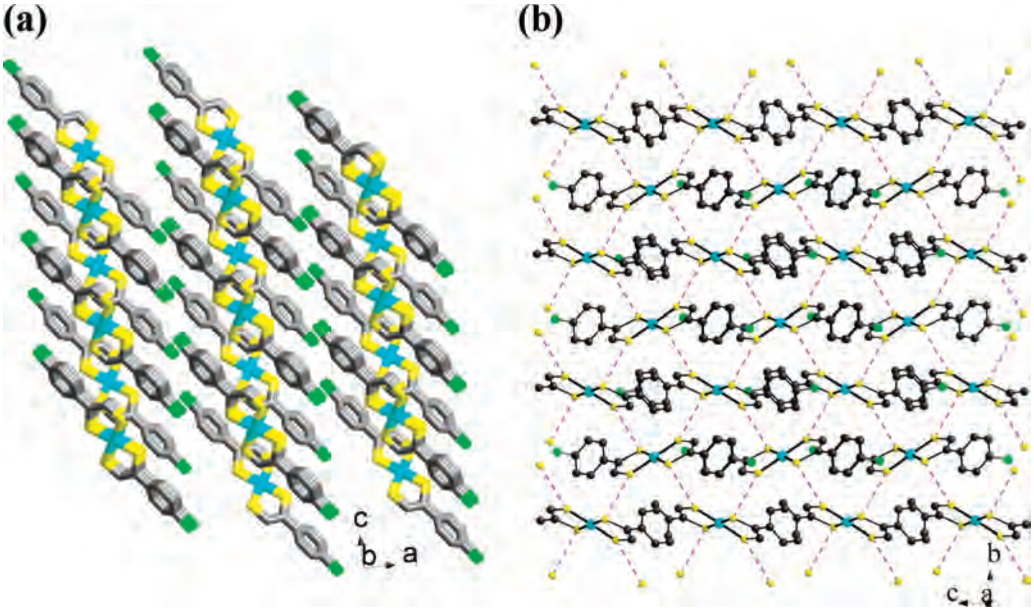

Figure 13. (a) Packing diagram of the [Ni(ClPhdt)$_2$] (**8**) looking down to the crystallographic *b* axis and (b) packing diagram of the same looking down to the crystallographic *a* axis in which the purple dotted lines (···) indicates the S···S intermolecular interactions. Color code: Cl, green; C, gray; S, yellow; Ni, cyan.

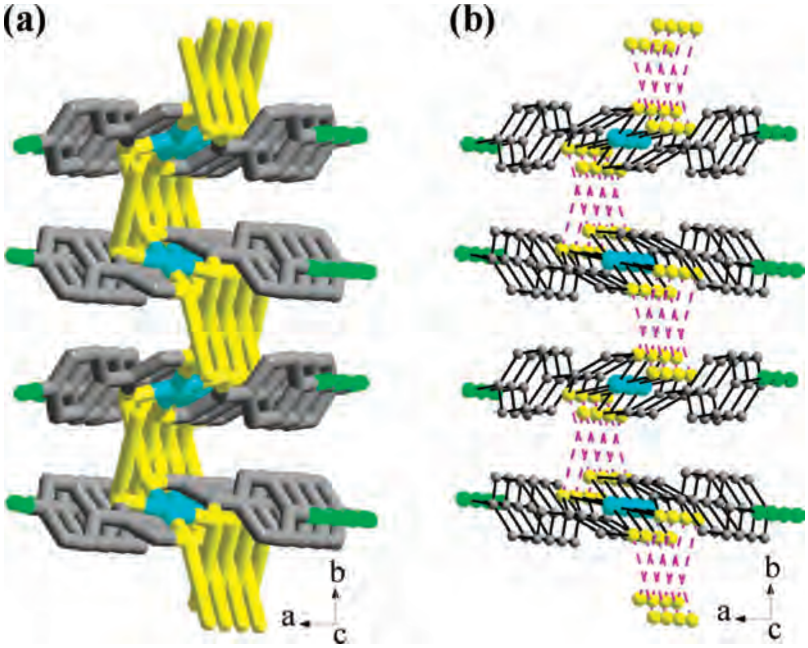

Figure 14. (a) View of the wire-frame representation of [Ni(ClPhdt)$_2$] (**8**) looking down to the crystallographic *c* axis, yellow solid lines show the S···S intermolecular interactions, and (b) view of the same in ball and stick representation.

Figure 15. π-π stacking interactions in the compound [Ni(ClPhdt)$_2$] (**8**); blue colored six membered rings indicate that these are directly involved in π-π stacking interactions.

Figure 16. Cl···Cl interactions in compound [Ni(ClPhdt)$_2$](**8**). Color code: Cl, green; C, gray; S, yellow; Ni, cyan.

asymmetric unit contains half of the molecule. Figure 4 shows the full molecule with the atom labeling scheme. The basic crystallographic data (compound **3**) are presented in Table 2, and the selected interatomic distances and bond angles are given in Table 3. The four sulfur atoms surrounding the nickel ion yield the square planar geometry with S−Ni−S angles of 91.30(2)°. The tetra-coordinated nickel ion is deviated by 0.0147(8) Å out of the S_4 square-plane of two dithiolate ligands. In the five member chelate ring, the average Ni−S, C−S, and C═C bond lengths are 2.143, 1.726, and 1.348 Å, respectively. The overall charge of this Ni(III) complex anion $[Ni(FPhdt)_2]^{1-}$ in compound **3** as expected is −1, and this anionic charge is compensated by a $[Bu_4N]^+$ cation as observed in the crystal structure (Figure 4).

In this complex, the outer phenyl rings are skewed with a dihedral angle of 17.29(0.12)° with the least-squares plane

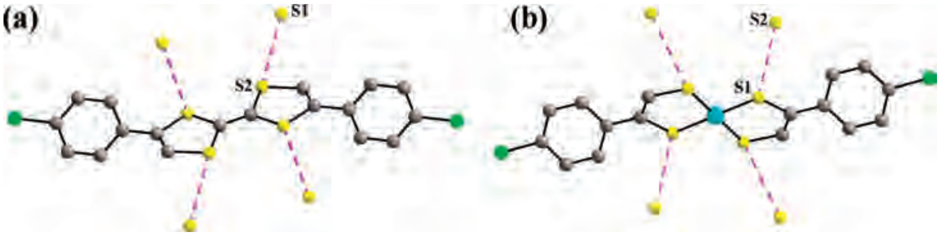

Figure 17. Molecular structures of compound ClPhTTF (**6**) (shown in a) and compound [Ni(ClPhdt)$_2$] (**8**) (shown in b) showing the intermolecular S•••S interactions.

formed by the rest of the molecule. This accounts for both the reduced intensity of the NIR absorption maximum and the rhombic-shape of the ESR spectrum (vide supra).

In the present series of compounds, the organic fluorine atom in compound [Bu$_4$N][Ni(FPhdt)$_2$] (**3**) plays some important role in the supramolecular aspect of its solid-state structure. Fluorine can accept a hydrogen bond involving C−H•••F hydrogen bonding interactions.[38] The C−H•••F hydrogen bond is very unique in the sense that it is very weak but a soft donor-hard acceptor interaction of unusual kind. Even though fluorine is the most electronegative element in the periodic table, organic fluorine accepts a hydrogen bond with great difficulty because of its lack of polarizability and therefore reports on C−H•••F hydrogen bonds are very scarce in literature.[39] In the present system (compound **3**), the existence of C−H•••F hydrogen bonding interactions, that involve the [Bu$_4$N]$^+$cation and the [Ni(FPhdt)$_2$]$^-$ anion, lead to the formation of a chainlike structure as depicted in Figure 5. As shown in Figure 5, the fluorine (F1) undergoes bifurcated hydrogen bonding interactions with C15 and C16 of the cation. The hydrogen bonding parameters for these C−H•••F interactions (C15−H15A•••F1: 0.97, 2.62, 3.201(3), 118.9; C16−H16C•••F1: 0.96, 2.76, 3.339(3), 119.7) are comparable with previously reported C−H•••F hydrogen bonds.[39]

The packing diagram of compound [Bu$_4$N][Ni(FPhdt)$_2$] (**3**) (viewed down to the crystallographic *b* axis) shows that the [Ni(FPhdt)$_2$]$^-$ molecules pack in the form of a layered structure that includes the aggregation of linearly arranged complex molecules on the *ac* plane as shown in Figure 6. The closest Ni•••Ni contact is of 8.949(2) Å. The large separation between stacks of complexes (in each linear arrangement) is probably due to the external substitution of a phenyl ring on the dithiolene moiety, in which the phenyl ring slightly deviates from the molecular plane. Notably, this compound shows no short S•••S or F•••F interactions within its crystal structure.

Crystal Structure Description of Compound [Bu$_4$N][Ni(ClPhdt)$_2$] (4). Crystals of compound [Bu$_4$N][Ni(ClPhdt)$_2$] (**4**), suitable for X-ray structure analysis, were grown from a CH$_2$Cl$_2$/hexane (1:1) mixture and crystallized in the monoclinic space group *P*2(1)/*c*. The molecular structure with the appropriate label scheme is shown in Figure 7. The basic crystallographic data are presented in Table 2, and the selected interatomic distances and bond angles are given in Table 4. The four sulfur atoms that surround the nickel ion provide the square planar coordination with average S−Ni−S angle of 90.5°, with the deviation of nickel ion of 0.0160(4) Å from the square plane. In the five membered chelate ring containing the nickel atom, the average Ni−S, C−S, and C═C bond lengths are consistent with those in the crystal structure of compound [Bu$_4$N][Ni(FPhdt)$_2$] (**3**).

The outer two phenyl rings deviate from the planarity of the dithiolene moiety, as observed in the crystal of compound **3**. In compound **4**, the dihedral angles between the least-squares planes of Ni-dithiolene chelate rings {(Ni1, S1, S2, C1, C2) and (Ni1, S3, S4, C9, C10)} and external phenyl rings {(C3, C4, C5, C6, C7, C8) and (C11, C12, C13, C14, C15, C16)} are 29.57° and 22.02°, respectively. Interestingly, in compound [Bu$_4$N][Ni(FPhdt)$_2$] (**3**), both external phenyl rings deviate in the same fashion with a dihedral angle of 17.29 (0.12)° from the least-squares plane of the rest of the Ni-dithiolene chelate ring, but in the compound [Bu$_4$N][Ni(ClPhdt)$_2$] (**4**), both external rings deviate inconsistently with two different dihedral angles of 29.57° and 22.02°, respectively (from the least-squares planes of Ni-dithiolene chelate ring). We believe that these differences might be due to the difference in substitution of the halogen atoms namely, F and Cl on the *p*-position of the external phenyl ring. In compound **3**, the fluorine atom is involved in hydrogen bonding interactions (namely C−H•••F), whereas in compound **4**, the substituted chlorine atom is not involved in such hydrogen bond formation. Thus, it can be argued that in similar mononuclear metal-asymmetric-dithiolene complexes, the molecular arrangement can be altered by varying the substituents on the dithiolene moiety: fluorine substitution (compound **3**) gives a layer of simple chain-like arrangement (Figure 6); on the other hand, chlorine substitution (compound **4**) affords layers of wave-like zigzag chains of complex anions as shown in Figure 8.

The closest Ni•••Ni separation is found to be 9.072(2) Å, and the large separation between the molecular stacks (in a zigzag wave-like arrangement, Figure 8) is due to the external substitution of the phenyl ring on the dithiolene moiety, as was described for the complex **3**. The Ni•••Ni separation in the compound **4** is 0.123 Å larger than that in compound **3**. We have not observed any Cl•••Cl interactions in the crystals

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of compound [Bu_4N][Ni($ClPhdt)_2$] (**4**), despite the presence of a chlorine atom as a substituent on the outer phenyl ring.

Crystal Structure Description of 4,4′-Bis(4-chlorophenyl)-tetrathiafulvalene (ClPhTTF) (6). Orange crystals of compound **6** can easily be grown from $CHCl_3$ solvent by slow evaporation. Compound **6** crystallizes in the monoclinic system with space group *P*2(1)/*c*. The asymmetric unit of compound **6** contains half of the molecule.The molecular structure of **6** is presented in Figure 9 with the atom labeling description. The crystallographic data are presented in Table 5, and the selected distances and bond angles are described in Table 6. The TTF skeleton is almost planar, and both external phenyl rings (C4, C5, C6, C7, C8, C9) are considerably tilted, with a dihedral angle of 28.28 (0.08)°. In the five membered dithiolate ring, the average C−S, C═C, and S−C bond distances are 1.752 Å, 1.34 Å, and 1.761 Å, respectively (Figure 9). The packing diagram of ClPhTTF (**6**), shown in the Figure 10, shows that the molecules are arranged in a slanting manner leading to the layered like arrangement. As expected, we found short S···S contacts in which the interplanar distances between stacks is 3.439 Å. These are the S···S separations that are even less than the sum of their van der Waals radii (3.70 Å). This S···S interaction is shown in Figure 11, which is another view of the packing of the molecules in compound **6**.

Crystal Structure Description of Compound [Ni($ClPhdt)_2$] (8): Comparison with Compounds [Bu_4N][Ni($FPhdt)_2$] (3) and [Bu_4N][Ni($ClPhdt)_2$] (4). Dark greenish block crystals of neutral nickel(IV) compound [Ni($ClPhdt)_2$] (**8**), suitable for X-ray structure determination, could be grown from a CH_3CN solvent by diffusion of ether. Single crystal X-ray structure analysis shows that the crystals belong to the monoclinic system with a space group *P*2(1)/*c* and half of the molecule in the asymmetric unit. Figure 12 shows molecular structure of compound **8** with the atom labeling scheme.

The basic crystallographic data are presented in Table 5, and the selected interatomic distances and bond angles are presented in Table 7. The four sulfur atoms surrounding the nickel ion provide a perfect square planar coordination (deviation of the nickel ion from the {S_4} square plane = 0.000 Å) with average S−Ni−S angle of 90°. In the five membered chelate ring containing the nickel atom, the average Ni−S, C−S, and C═C bond distances are 2.126 Å, 1.696 Å, and 1.373 Å, respectively (Table 7). The corresponding average C−S values in the crystal structures of compounds [Bu_4N][Ni($FPhdt)_2$] (**3**) and [Bu_4N][Ni($ClPhdt)_2$] (**4**) are considerably larger (1.726 Å for compound **3** and 1.724 Å for compound **4**, Tables 3 and 4, respectively). On the other hand, the C═C bond in neutral compound **8** is larger (1.373 Å) than average C═C bonds in compounds **3** and **4** (1.349 Å for compound **3** and 1.337 Å for compound **4**). In this context, it is worth mentioning that monoanionic compounds [Bu_4N][Ni($FPhdt)_2$] (**3**) and [Bu_4N][Ni($ClPhdt)_2$] (**4**) have nickel ions in formally +3 oxidation states, and neutral compound **8** is formally a Ni(IV) complex that was isolated by iodine oxidation of compound **4** (vide supra). Thus, it is possible that electron delocalization due to the higher oxidation state of nickel in compound **8** results in a shorter C−S bond and a relatively longer C═C bond. The average Ni−S bond length, found in the crystal structure of compound **8**, is typical of a neutral Ni(IV)-dithiolene complex.[40]

The packing diagram of the neutral compound [Ni($ClPhdt)_2$] (**8**) viewed down to the crystallographic *b* axis is depicted in Figure 13a, which shows that molecules pack in a layered structure on the crystallographic *ac* plane. We found that the closest Ni···Ni distance is 6.362(1) Å and the shortest interstack S···S contact is 3.616(2). This distance (between S(1) and S(2) in the crystal structure) is comparable to the sum of their van der Waals radii (3.70 Å). Similar neutral systems with such S···S contacts have been reported earlier.[41]

The short S···S contacts (in compound **8**) are shown in Figures 13b and 14. Further, the $\pi-\pi$ stacking interactions among the external aromatic rings on the dithiolene part of compound [Ni($ClPhdt)_2$] (**8**) lead to a chain type arrangement as shown in Figure 15. The relevant centroid−centroid (Cg−Cg) distance is 4.3032(17) Å, and the mean plane separation is 3.450 Å between aromatic rings.

Supramolecular Cl···Cl Interactions in Compounds (ClPhTTF) (6) and [Ni($ClPhdt)_2$] (8). The chlorine substitution on the outer phenyl ring on the dithiolene moiety (in compounds **6** and **8**) suggests the possibility of the existence of Cl···Cl interactions in the relevant crystals. The weak intermolecular interactions between chlorine atoms have been a subject of interest and debate for many decades.[42] Two hypotheses have been proposed that account for the short Cl···Cl contacts in the crystal structure of chlorinated molecules. It was originally suggested that the atomic charge density of chlorine has a nonspherical shape, producing a decreased repulsion and thus closer Cl···Cl contacts in certain directions.[43] Afterward, an alternative hypothesis was given according to which the Cl···Cl associates are the results of a specific attractive force (for example, “donor−acceptor”, “secondary”, or “charge-transfer” interaction, or “incipient electrophilic and nucleophilic attack”, involving a weak form of covalent bonding) that produces short Cl···Cl contacts in certain directions.[44] Desiraju and Parthasarathy reported Cl···Cl close contacts in the crystal structures of chlorinated hydrocarbons.[45] Afterward, several reports on Cl···Cl interactions appeared.[46] In many cases, intermolecular interactions associated with these Cl···Cl contacts are shorter than the sum of the van

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der Waals radii of the contacting chlorine atoms. In the present work, strong Cl···Cl interactions are evidenced by the Cl···Cl separations of 3.279 Å and 3.275 Å in the crystal structures of compounds ClPhTTF (**6**) and [Ni(ClPhdt)$_2$] (**8**), respectively. These interactions in compound **8** are shown in Figure 16. Each of these Cl···Cl contacts is considerably shorter than the sum of the van der Waals radii of the concerned chlorine atoms (van der Waals radius of chlorine is 1.76 Å). Compound **6** is a tetrathiafulvalene derivative. Among the numerous halogenated tetrathiafulvalenes the synthesis of which has been described so far, only a few have been crystallographically characterized.[47] Thus, compound **6** is one of rare structurally characterized tetrathiafulvalene that shows short Cl···Cl contacts. To the best of our knowledge, compound [Ni(ClPhdt)$_2$] (**8**) exhibits the first structure of a transition metal dithiolene complex in which short Cl···Cl contacts have been observed.

Structural Relationships between Neutral [Ni(ClPhdt)$_2$] (8) and ClPhTTF (6): Emergence of an Inorganic Counterpart of Tetrathiafulvalene. We have synthesized two TTF derivatives, ClPhTTF(**6**) and BrPhTTF (**7**); one of these (compound **6**) has been characterized unambiguously by crystal structure analysis. In this section, we have described a very interesting structural relationship between the neutral compound [Ni^{IV}(ClPhdt)$_2$] (**8**) and tetrathiafulvalene **6** based on their structural similarities in terms of their S···S contacts and packing diagrams. Moreover, as discussed in the preceding section, compounds **6** and **8** show Cl···Cl contacts of almost the same distances (3.279 Å for compound **6** and 3.275 Å in compound **8**). Figures 17a and 17b depict molecular structures of compounds ClPhTTF (**6**) and [Ni(ClPhdt)$_2$] (**8**), respectively. At the first glance, it appears that both structures become identical if the metal center (Ni^{4+} ion) in compound **8** is replaced by a C=C double bond or the central C=C double bond in compound **6** is substituted by a Ni^{4+} ion. Both operations would give identical molecular structures.

In the case of compound [Ni(ClPhdt)$_2$] (**8**), the C−S (the average bond lengths of C(1)−S(1) and C(2)−S(2)) and C=C (C(1)−C(2)) bond lengths of nickel chelate five membered rings are 1.696 Å and 1.373 Å, respectively (Figure 12). Similarly, the five membered ring of the tetrathiafulvalenes has average C−S and C=C bond lengths of 1.752 Å and 1.34 Å, respectively (Figure 9). Thus, for compound [Ni(ClPhdt)$_2$] (**8**), the average C−S bond distance is 0.056 Å less than that of compound **6**. This clearly indicates that the degree of delocalization is more in compound **8** than that in compound **6**.

Both compounds exhibit the intermolecular S···S contacts in their solid states, and interestingly, all four sulfur atoms of each compound interact with sulfur atoms of adjacent molecules along the stacking direction (Figures 11, 14, and 17). In the compound [Ni(ClPhdt)$_2$] (**8**), the average S···S contact distance is 0.177 Å larger than that in compound ClPhTTF (**6**). In both cases, the external phenyl rings are twisted considerably from their respective least-squares planes of the rest of the molecules, e.g., nickel bis-dithiolene chelate in compound [Ni(ClPhdt)$_2$] (**8**). The concerned dihedral angle, in compound **8**, is 4.53° larger that in compound **6**. This might be the reason for the slightly larger S···S contact for compound **8** than that in compound **6**. Thus, on the basis of the remarkable similarity between compounds **6** and **8** (see Figure 17) in terms of molecular structures, bond distances, and angles, S···S contacts, and overall molecular packing diagrams along with strong Cl···Cl interactions, we have classed compound [Ni(ClPhdt)$_2$] (**8**) as the "inorganic counterpart to the organosulfur donor tetrathiafulvalene". We believe that Cl···Cl interactions play an important role in this common structuring. Similar analogy was offered previously for F···F interactions.[48]

Conclusion

We have presented a rational synthetic strategy for the preparation of a new series of asymmetrically substituted bis(dithiolene) monoanionic Ni(III) complexes [Bu$_4$N]-[Ni(XPhdt)$_2$] (where X = H, F, Cl, Br, and NO$_2$) and a neutral Ni(IV) complex [Ni(ClPhdt)$_2$]. We have demonstrated that, by varying the substituents of the dithiolene moiety of the complexes, one can tune their NIR absorption maxima. Moreover, small changes of substitution (for example, from fluorine to chlorine) on the dithiolene results in a diversity of structural arrangements. We have observed that the nature of the substituents on the dithiolene moiety plays an important role in tuning the redox potentials. The nickel complexes **1**−**5** in this present study are in a Ni^{3+} oxidation state as confirmed by the ESR studies. We have presented the synthesis and characterization of two new asymmetrically substituted halogen derivatives of tetrathiafulvalene. Such tetrathiafulvalene derivatives as precursors to new substituted tetrathiafulvalene derivatives with C−C bond formation can be synthesized, which are otherwise difficult to prepare using normal synthetic routes. Finally, we have discussed the structural analogy between a neutral unsymmetrical Ni(IV) dithiolene complex and a TTF derivative and argued that, the neutral compound [Ni(ClPhdt)$_2$] can be classed as the "inorganic counterpart to tetrathiafulvalene". We have reported a C−H···F hydrogen bonding interaction in the solid-state structure of compound **3**, which is rarely known in metal dithiolene chemistry. Furthermore, we have described noncovalent strong Cl···Cl interactions (compound **8**), which is a new addition to metal dithiolene chemistry.

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Supporting Information Available: Synthetic procedures (along with synthesis schemes) for thione derivatives which have been used as starting precursors for the preparation of compounds **1** through **5** (PDF) and complete X-ray crystallographic files in CIF format for four compounds **3**, **4**, **6**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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