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Article

Influence of the Thiazole Backbone on the Structural, Redox, and Optical Properties of Dithiolene and Diselenolene Complexes

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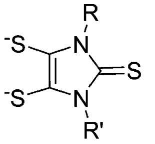
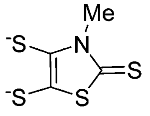
Metalation of *N*-methyl-1,3-thiazoline-2-thione followed by reaction with elemental S or Se affords a simple and efficient approach to *N*-methyl-1,3-thiazoline-2-thione-4,5-dithiolate (Me-thiazdt) and the diselenolate (Me-thiazds) analogue. In the presence of metal II centers such as Zn, Ni, and Pd these ligands afford the corresponding dianionic dithiolene and diselenolene complexes. The Ni and Pd dianionic complexes are easily oxidized into the monoanionic species. Complexes were isolated and characterized by single-crystal X-ray crystallography. Most often a substitutional S/N–Me disorder is observed, attributable to the square-planar trans complexes disordered on two positions or coexistence of both cis and trans isomers on inversion centers. Monoanionic complexes exhibit a strong NIR absorption band with ϵ values up to 33 750 M^{-1} cm^{-1}.

Introduction

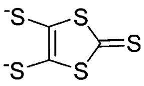
An enormous amount of research has been devoted to the synthesis and electrical and optical properties of various 1,2-dithiolene and diselenolene ligand-based metal complexes.[1,2] Among them, the $[M(dmit)_2]^n$ ($M = Ni, Pd$, $n = -2, -1, -0.5, 0$) complexes (dmit = 4,5-dimercapto-1,3-dithiole-2-thione) have been extensively investigated as precursors of various conducting and superconducting radical ion salts.[1,3] Specifically, the sulfur-rich framework and fully conjugated structure of the dmit ligand play a crucial role in favoring specific supramolecular organizations in the solid state but also affording interesting optoelectronic properties such as a strong NIR absorption. It is also possible to modulate the redox as well as optical properties of these complexes by modifying the substituents on the dithiolate ligand.[4,5] For instance, replacement of the outer 1,3-dithiole-2-thione ring of the dmit ligand by an imidazole one in the timdt ligand induces a large cathodic shift of the redox potentials associated with the −2/−1 and −1/0 redox processes.[6,7]



R,R'-timdt



Me-thiazdt



dmit

Similarly, an important bathochromic shift of the NIR absorption band characteristic in the monoanionic and neutral dithiolene complexes is observed when the imidazole core in the timdt dithiolate ligand replaces the dithiole one in the dmit ligand.

A promising class of dithiolene complexes whose electronic features are intermediate between the dmit and timdt types has been recently reported by Arca et al. based on the *N*-ethyl-1,3-thiazoline-2-thione-4,5-dithiolate (Et-thiazdt).[8] The reported synthesis involved sulfuration of the *N*-ethyl-

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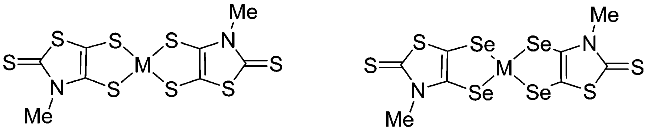
2-thioxothiazolidine-4,5-dione with Lawesson's reagent in the presence of the metal or its salt in order to form the corresponding M(Et-thiazdt)$_2$ (M = Ni, Pt, Pd) as the neutral species. However, using this strategy the dithiolene complexes M(Et-thiazdt)$_2$ (Ni, Pt) were obtained in rather low yields (15% for Ni and 18% for Pt), and these complexes were not structurally characterized neither in their neutral form nor in their mono- or dianionic forms.

In the course of our earlier work on the preparation of dithiadiazafulvalene derivatives as TTF analogues,[9,10] we recently presented easy access to 1,3-thiazoline-2-thione-4,5-dithiolate (Me-thiazdt) through the bimetallation of the *N*-methyl-1,3-thiazoline-2-thione followed by in situ sulfur insertion into the carbon−lithium bonds. The dithiolate was isolated as the dianionic zinc dithiolene complex, $[NEt_4]_2$-[Zn(Me-thiazdt)$_2$], in 64% yield, which was further engaged in an alkylation reaction with 1,2-dibromethane.[11] We therefore decided to investigate this route for the synthesis of the corresponding Ni and Pd dithiolene complexes.

Herein, we present an easy route to reach the [M(Me-thiazdt)$_2$]$^{2-,1-}$ complexes (M = Ni, Pd) isolated as dianionic species which can then be easily oxidized to the monoanionic ones. We also describe their structural and redox properties. Moreover, we show that the synthetic strategy used for the preparation of these novel dithiolene complexes can be extended to the preparation of their selenium analogues, that is the *N*-methyl-1,3-thiazoline-2-thione-4,5-diselenolate (Me-thiazds), demonstrating the generality of our synthetic procedure. Furthermore, comparisons of their structural, redox, and spectral properties with the well-known dmit and dsit (1,3-dithiole-2-thione-4,5-diselenolate) ligands will be performed in order to evaluate the consequences brought by replacement of one sulfur atom in the outer dithiole ring of dmit by a N−Me group in the Me-thiazdt ligand.



[M(Me-thiazdt)$_2$]^n **[M(Me-thiazds)$_2$]^n**

n = 0, -1, -2

Experimental Section

All reagents were commercially available and used without further purification. Tetrahydrofuran was distilled from sodium benzophenone. CH_2Cl_2 was distilled from P_2O_5. Melting points were measured using a Kofler hot-stage apparatus. ^1H and ^{13}C NMR spectra were recorded on Bruker AC 300P spectrometer. Chemical shifts are reported in ppm referenced to TMS for ^1H NMR and ^{13}C NMR. UV−vis−NIR spectra were recorded on a Cary 5 spectrophotometer in CH_2Cl_2. Mass spectra were recorded with Varian MAT 311 instrument and a ZABSpec TOF instrument by the Centre Régional de Mesures Physiques de l'Ouest, Rennes. Elemental analyses were performed at the Centre Régional de Mesures Physiques de l'Ouest, Rennes). Cyclic voltammetry was carried out on a 10^{-3} M solution of metal complex derivative in CH_3CN containing 0.1 M *n*-Bu_4NPF_6 as supporting electrolyte. Voltammograms were recorded at 0.1 V s^{-1} on a platinum disk electrode (1 mm^2). Potentials were measured versus Saturated Calomel Electrode (SCE).

General Procedure for the Synthesis of $[NEt_4]_2$[M(Me-thiazdt)$_2$] 2−4 and $[PPh_4]_2$[Ni(Me-thiazdt)$_2$] 3b. LDA solution was prepared in a dried argon-filled flask fitted with a rubber septum at −10 °C by addition of *n*-BuLi (5.7 mmol, 3.6 mL, 1.6 M in hexane) to a stirred solution of diisopropylamine (5.7 mmol, 0.58 g in 15 mL of dry THF). After 15 min, a solution of 1,3-thiazoline-2-thione **1** (3.8 mmol, 0.5 g) in dry THF (40 mL) was added in one portion with continuing stirring at −10 °C for 30 min. To the mixture, 0.18 g of sulfur S_8 (5.7 mmol) was added. After 30 min, a solution of LDA (7.6 mmol, 4.76 mL of *n*-BuLi in hexane added to 7.6 mmol, 0.77 g of diisopropylamine in 20 mL of dry THF) was added. The reaction mixture was stirred at −10 °C for 3 h; then sulfur S_8 (0.24 g, 7.6 mmol) was added. After 30 min, $ZnCl_2$ (1.9 mmol, 0.26 g for **2**), $NiCl_2$ (1.9 mmol, 0.24 g for **3**), or $PdCl_2$ (1.9 mmol, 0.33 g for **4**) was added followed by 1 equiv of tetraethylammonium bromide NEt_4Br (3.8 mmol, 0.8 g) or PPh_4Cl (3.8 mmol, 1.43 g). The mixture was left to reach room temperature, and stirring was continued for 15 h. The precipitate thus obtained was filtered, washed with ethanol, and dried in a desiccator. Recrystallization in acetonitrile afforded the following.

$[NEt_4]_2$[Zn(Me-thiazdt)$_2$] 2. Light brown crystals; 64% yield, mp 232 °C; ^1H NMR (300 MHz; CD_3CN) δ 1.19 (t, 24H, CH_3), 3.14 (q, 16H, CH_2), 3.70 (s, 6H, NCH_3); ^{13}C NMR (75 MHz; CD_3CN) δ 6.8, 37.9, 52.2, 116.3, 141.1, 179.7. Anal. Calcd for $C_{24}H_{46}N_4S_8Zn$: C, 40.45; H, 6.51; N, 7.86; S, 36.00. Found: C, 40.42; H, 6.53; N, 7.91; S, 36.32. UV−vis−NIR (CH_2Cl_2): λ_{max} = 393 nm (ϵ = 28 380 M^{-1} cm^{-1}).

$[NEt_4]_2$[Ni(Me-thiazdt)$_2$] 3a. Deep red precipitate, 40% yield, mp = 248 °C; ^1H NMR (CD_3CN, 500 MHz) δ 1.25 (t, 24H, CH_3), 3.24 (q, 16H, CH_2), 3.44 (s, 6H, CH_3). Anal. Calcd for $C_{24}H_{46}N_4S_8Ni$: C, 40.84; H, 6.57; N, 7.94; S, 36.34. Found: C, 40.43; H, 6.52; N, 8.07; S, 36.11.

$[PPh_4]_2$[Ni(Me-thiazdt)$_2$] 3b. Deep red precipitate, 39% yield, mp = 234 °C; ^1H NMR (CD_3CN, 200 MHz) δ 3.43 (s, 6H, CH_3); 7.68−7.96 (m, 40H, Ph). UV−vis−NIR (CH_2Cl_2): λ_1 = 329 nm (ϵ = 44 847 M^{-1} cm^{-1}), λ_2 =433 nm (ϵ =18 134 M^{-1} cm^{-1}).

$[NEt_4]_2$[Pd(Me-thiazdt)$_2$] 4. Brown precipitate, 40% yield, mp = 254 °C; ^1H NMR (CD_3CN, 200 MHz) δ = 1.24 (t, 24H, CH_3), 3.21 (q, 16H, CH_2), 3.58 (s, 6H, CH_3).

General Procedure for the Synthesis of $[NEt_4]_2$[M(Me-thiazds)$_2$] 5−7. Same procedure as for **2**−**4** using selenium powder instead of sulfur. Recrystallization in acetonitrile afforded the following.

$[NEt_4]_2$[Zn(Me-thiazds)$_2$] 5. Light yellow green crystals; 61% yield, mp 249 °C; ^1H NMR (300 MHz; CD_3CN) δ 1.11 (t, 24H, CH_3), 3.06 (q, 16H, CH_2), 3.69 (s, 6H, NCH_3); ^{13}C NMR (75 MHz; CD_3CN) δ 6.4, 40.2, 51.8, 108.1, 137.5, 183.7. UV−vis−NIR (CH_2Cl_2): λ_{max} = 386 nm (ϵ = 30 060 M^{-1} cm^{-1}). Anal. Calcd for $C_{24}H_{46}N_4S_4Se_4Zn$: C, 32.02; H, 5.15; N, 6.22; S, 14.25. Found: C, 31.99; H, 5.27; N, 6.20; S, 14.08.

$[NEt_4]_2$[Ni(Me-thiazds)$_2$] 6. Deep red precipitate, 31% yield, mp = 230 °C; ^1H NMR (CD_3CN, 500 MHz) δ 1.24 (t, 24H, CH_3), 3.22 (q, 16H, CH_2), 3.74 (s, 6H, CH_3).

$[NEt_4]_2$[Pd(Me-thiazds)$_2$] 7. Deep orange precipitate, 30% yield, mp = 253 °C; ^1H NMR (CD_3CN, 200 MHz) δ 1.24 (t, 24H, CH_3), 3.22 (q, 16H, CH_2), 3.63 (s, 6H, CH_3).

4,5-Bis(2′-cyanoethylthio)-1,3-thiazol-2-thione 8. To a solution of Zn complex **2** (0.5 g, 0.7 mmol) dissolved in 20 mL of dry CH_3-

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Table 1. Crystallographic Data[a]

	3b	**5**	**10**	**11**
formula	$C_{56}H_{46}N_2NiP_2S_8$	$C_{24}H_{46}N_4S_4Se_4Zn$	$C_{16}H_{26}N_3NiS_8$	$C_{16}H_{26}N_3PdS_8$
fw (g·mol^{-1})	1124.08	900.10	575.59	623.28
cryst syst	triclinic	monoclinic	monoclinic	triclinic
space group	*P*-1	Pc	*C*2/*c*	*P*-1
a (Å)	6.8346(12)	9.0355(5)	21.7845(19)	11.0748(4)
b (Å)	12.817(2)	9.4837(5)	6.3878(6)	14.1195(5)
c (Å)	15.437(3)	20.1155(11)	18.8278(16)	16.2086(6)
α (deg)	97.647(9)	90	90	77.589(2)
β (deg)	102.055(8)	90.886(3)	110.857(3)	86.946(2)
γ (deg)	103.035(9)	90	90	75.875(2)
V (Å^3)	1265.1(4)	1723.49(16)	2448.3(4)	2400.48(15)
T (K)	100(2)	100(2)	100(2)	100(2)
Z	1	2	4	4
D_{calcd} (g·cm^{-3})	1.475	1.734	1.562	1.725
μ (mm^{-1})	0.819	5.200	1.484	1.479
total reflns	25 813	24 131	12 093	34 743
abs corr	multiscan	multiscan	multiscan	multiscan
Uniq. refls. (R_{int})	5696 (0.0339)	7536 (0.0539)	2800(0.0315)	10823(0.0431)
unique reflns	4844 ($I > 2\sigma(I)$)	4931 ($I > 2\sigma(I)$)	2406 ($I > 2\sigma(I)$)	8080 ($I > 2\sigma(I)$)
R_1, wR_2	0.0299, 0.0696	0.0511, 0.1224	0.034, 0.0791	0.0568, 0.1169
R_1, wR_2 (all data)	0.0392, 0.0744	0.0941, 0.1435	0.0422, 0.0829	0.0844, 0.1279
GoF	1.031	1.026	1.098	1.11

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

CN 3-bromopropionitrile (0.47 g, 3.5 mmol) was added. The reaction mixture was heated at reflux for 12 h and then allowed to reach room temperature. The medium was filtered and concentrated under vacuum. Dichloromethane (25 mL) was added to the residue, the organic phase was washed with water (3 × 25 mL) and dried over Na_2SO_4, and the solvent was evaporated. The thiazoline thione **8** was recrystallized from EtOH and gave **8** as a yellow precipitate 85% yield; mp 122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.72 (t, 2H, CH_2CN, $^3J = 7.2$ Hz), 2.75 (t, 2H, CH_2CN, $^3J = 7.2$ Hz), 3.10 (t, 2H, SCH_2, $^3J = 7.2$ Hz), 3.11 (t, 2H, SCH_2, $^3J = 7.2$ Hz), 3.82 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 18.67$ (CH_2CN), 18.73 (CH_2CN), 31.73 (SCH_2), 31.86 (SCH_2), 36.88 (NCH_3), 117.29 (2CN), 125.68 (=C), 136.07 (=C), 187.91 (C=S). Anal. Calcd for $C_{10}H_{11}N_3S_4$: C, 39.84; H, 3.68; N, 13.94; S, 42.54. Found: C, 39.82; H, 3.78; N, 14.09; S, 42.48.

4,5-Bis(2′-cyanoethylseleno)-1,3-thiazol-2-thione 9. Same procedure as above for **8**. The thiazoline thione **9** was recrystallized from EtOH and gave **9** as a beige precipitate in 65% yield; mp 112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.84 (t, 2H, CH_2CN, $^3J = 6.9$ Hz), 2.87 (t, 2H, CH_2CN, $^3J = 6.9$ Hz), 3.09 (t, 2H, SCH_2, $^3J = 6.9$ Hz), 3.11 (t, 2H, SCH_2, $^3J = 6.9$ Hz), 3.89 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 19.4$ (CH_2CN), 23.7 (CH_2CN), 24.6 ($SeCH_2$), 38.7 ($SeCH_2$), 117.8 (2CN), 117.9 (=C), 131.8 (=C), 189.3 (C=S). Anal. Calcd for $C_{10}H_{11}N_3S_2Se_2$: C, 30.38; H, 2.80; N, 10.63; S, 16.22. Found: C, 30.12; H, 2.80; N, 10.56; S, 16.51.

$[NEt_4]_2[M(Me\text{-}thiazdt)_2]$ 3a (M = Ni), 4 (M = Pd), and $[NEt_4]_2[M(Me\text{-}thiazds)_2]$ 6 (M = Ni) and 7 (M = Pd). To a dry two-neck flask containing 1.65 mmol of **8** (0.5 g for **3a** and **4**) or **9** (0.65 g for **6** and **7**), 14 mL of 1 M NaOEt in EtOH was added under nitrogen at room temperature with stirring. The mixture was stirred for 20 min. Then, a solution containing 1 mmol of $NiCl_2$ (0.13 g) for **3a** and **6** or $PdCl_2$ (0.18 g) for **4** and **7** in 50 mL of EtOH and 1.65 mmol of NaI (0.25 g) for **4** and **7** were added to the reaction mixture. In the course of the addition of 20 mL of an EtOH solution containing 2.47 mmol of NEt_4Br (0.52 g) the complex precipitated out and was isolated by filtration to afford **3** in 95% yield, **4** in 50% yield, **6** in 90% yield, and **7** in 48% yield.

General Procedure for Generation of the Radical Anion 10−13. To a solution of ferricinium hexafluorophosphate (0.6 mmol) in 15 mL of CH_2Cl_2 under inert atmosphere the dianionic species **3**−**4** or **6**−**7** (0.6 mmol) was added. After stirring for 1 h, addition of pentane (80 mL) afforded a precipitate, which was filtered out. Recrystallization of the precipitate in acetonitrile gave crystals of the monoanionic species in quantitative yield.

$[NEt_4][Ni(Me\text{-}thiazdt)_2]$ 10. Mp 239 °C; ^{1}H NMR (300 MHz; CD_3CN) δ 1.24 (t, 12H, CH_3), 3.20 (q, 8H, CH_2); UV−vis-NIR (CH_2Cl_2): λ_{max}= 1284 nm (ϵ = 29 080 M^{-1} cm^{-1}). HRMS Calcd for $C_8H_6N_2S_8{}^{58}Ni$ [$C_{16}H_{26}N_3S_8Ni-NEt_4$]: 443.7650. Found: 443.7636. Anal. Calcd for $C_{16}H_{26}N_3S_8Ni$: C, 33.39; H, 4.55; N, 7.30; S, 44.56. Found: C, 33.83; H, 4.66; N, 7.52; S, 44.88.

$[NEt_4][Pd(Me\text{-}thiazdt)_2]$ 11. Mp 207 °C; ^{1}H NMR (CD_3CN, 200 MHz) δ 1.24 (t, 12H, CH_3), 3.21 (q, 8H, CH_2). UV−vis−NIR (CH_2Cl_2): λ_{max}= 1556 nm (ϵ = 33 750 M^{-1} cm^{-1}). HRMS Calcd for $C_8H_6N_2S_8{}^{108}Pd$ [$C_{16}H_{26}N_3S_8Pd-NEt_4$]: 493.7335. Found: 493.7334.

$[NEt_4][Ni(Me\text{-}thiazds)_2]$ 12. Mp 212 °C. UV−vis−NIR (CH_2Cl_2): λ_{max}=1187 nm (ϵ = 22 300 M^{-1} cm^{-1}). ^{1}H NMR (300 MHz; CD_3CN) δ 1.24 (t, 12H, CH_3), 3.22 (q, 8H, CH_2), Anal. Calcd for $C_{16}H_{26}N_3S_4Se_4Ni$: C, 25.18; H, 3.43; N, 5.50; S, 16.80. Found: C, 25.04; H, 3.46; N, 5.62; S, 16.95.

$[NEt_4][Pd(Me\text{-}thiazds)_2]$ 13. ^{1}H NMR (CD_3CN, 200 MHz) δ 1.24 (t, 12H, CH_3), 3.22 (q, 8H, CH_2). HRMS Calcd for $C_8H_6N_2S_4Se_4{}^{104}Pd$ [$C_{16}H_{26}N_3S_8Pd-NEt_4$]: 681.5136. Found: 681.5114. UV−vis−NIR (CH_2Cl_2): λ_{max}= 1512 nm (ϵ = 29 135 M^{-1} cm^{-1}).

Crystallography. Crystals were picked up with a cryoloop and then frozen at $T = 100$ K under a stream of dry N_2 on a APEX II Brucker AXS diffractometer for X-ray data collection (Mo Kα radiation, $\lambda = 0.71073$ Å). Structures were solved by direct methods (SIR97)[12] and refined (SHELXL-97)[13] by full-matrix least-squares methods as implemented in the WinGX software package.[14] Absorption corrections were applied. Hydrogen atoms were introduced at calculated positions (riding model) included in structure factor calculations but not refined. Details of the final refinements are given in Table 1 for all compounds.

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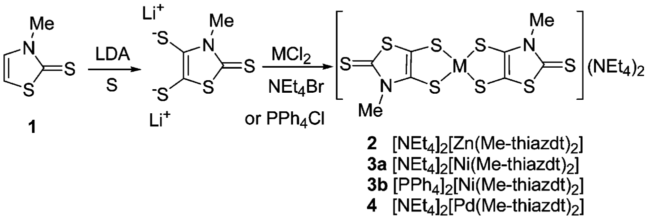
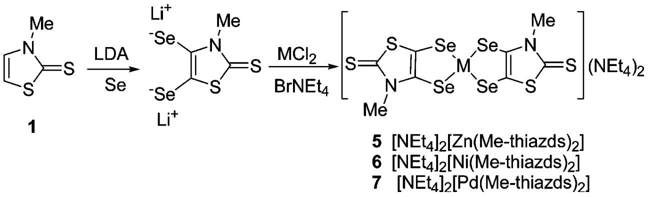
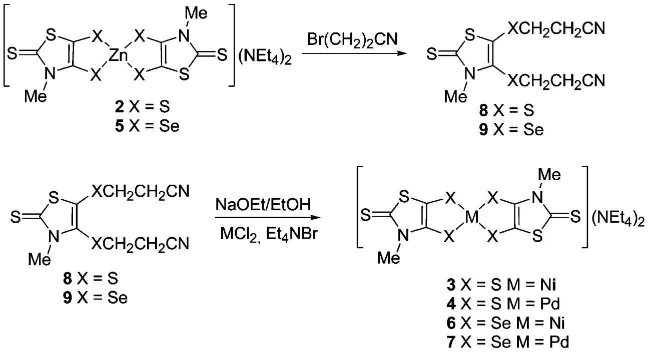
Scheme 1



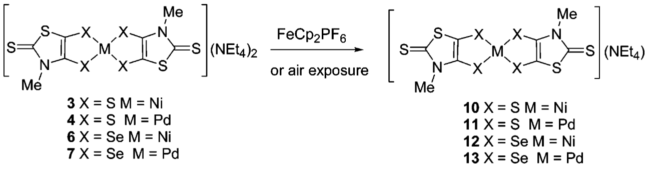
Scheme 2



Scheme 3



Scheme 4



Results and Discussion

Synthesis. The Ni and Pd dithiolene complexes were prepared directly from the *N*-methyl-1,3-thiazoline-2-thione **1** as outlined in Scheme 1. The dithiolate was formed by treating *N*-methyl-1,3-thiazoline-2-thione[15] **1** at −10 °C in THF in a two-step procedure by adding successively 1.5 equiv of lithium diisopropylamide (LDA) and sulfur twice (Scheme 1). Then MCl$_2$ was added to the solution, followed by addition of Et$_4$NBr or PPh$_4$Cl to the reaction mixture. The corresponding dithiolene complexes, [NEt$_4$]$_2$[Ni(Me-thiazdt)$_2$], **3a**, and [PPh$_4$]$_2$[Ni(Me-thiazdt)$_2$], **3b**, for Ni and [NEt$_4$]$_2$[Pd(Me-thiazdt)$_2$][NEt$_4$]$_2$, **4**, were obtained and isolated in 40% yield as dark red powders.

Similarly, we investigated this strategy in order to prepare the diselenolene analogues [M(Me-thiazds)$_2$]. Indeed, once the bimetalation is performed with LDA, use of selenium powder[16] instead of sulfur allowed us to form *N*-methyl-1,3-thiazoline-2-thione-4,5-diselenolate which is trapped with MCl$_2$ as described in Scheme 2. The Zn **5**, Ni **6**, and Pd **7** dianionic complexes were obtained in 61%, 31%, and 30% yield, respectively.

Another route toward the Ni (**3** and **6**) and Pd (**4** and **7**) complexes was also investigated starting from the dithiolene and diselenolene Zn complexes **2** and **5**. Indeed, due to their stability, zinc complexes **2** and **5** are easier to purify from the various salts formed in the reaction medium than the Ni (**3** and **6**) and Pd (**4** and **7**) complexes. Therefore, **2** and **5** were converted into a purely organic dithiolate or diselenolate hidden form (Scheme 3) by simply refluxing **2** and **5** with 3-bromopropionitrile in acetonitrile.[17] The *N*-methyl-bis-(cyanoethylthio)-1,3-thiazoline-2-thione **8** and *N*-methyl-bis-(cyanoethylseleno)-1,3-thiazoline-2-thione **9** where the two thiolate and selenolate functions are protected by cyanoethyl groups are obtained in 85% and 65% yield, respectively. Deprotection of the thiolate and selenolate functions was realized in basic medium using sodium ethanolate. Addition of NiCl$_2$ or PdCl$_2$ followed by NEt$_4$Br allowed us to isolate the dithiolene complexes **3a** and **4** [NEt$_4$]$_2$[M(Me-thiazdt)$_2$] and the diselenolene complexes **6** and **7** [NEt$_4$]$_2$[M(Me-thiazds)$_2$] (M = Ni, Pd). Even if this route is longer than the previous one described in Schemes 1 and 2, its main advantage is the easy isolation and purification of the complexes.

Both approaches allowed us to isolate the dianionic dithiolene complexes **3** and **4** and diselenolene complexes **6** and **7**. Interestingly, while performing ^{1}H NMR experiments in CD$_3$CN of complexes **3** and **4** we noticed an evolution of the spectra. For instance, for **3a** three signals were observed, two for the Et$_4$N$^+$ counterions and one singlet due to the methyl group on the nitrogen of the thiazole core. Actually, the same NMR solution investigated 1 h later exhibited only two signals due to the Et$_4$N$^+$ cations and no longer the one characteristic for the methyl substituents. The dianionic complexes **6** and **7** exhibit the same behavior, which finds its origin in the fact that the dianionic complexes **3**, **4**, **6**, and **7**, which are diamagnetic complexes, are easily oxidized in solution upon air exposure into the anion radical species which are paramagnetic. This was confirmed by the following quantitative experiments. Indeed, treating the dianionic complexes [NEt$_4$]$_2$[M(Me-thiazdt)$_2$](M = Ni(**3**) or Pd (**4**)) with 1 equiv of [Cp$_2$Fe][PF$_6$] afforded the corresponding monoanionic paramagnetic species [NEt$_4$][M(Me-thiazdt)$_2$] (Scheme 4) with M = Ni (**10**) and Pd (**11**). The same reaction performed on the diselenolene complexes **6** and **7** afforded the radical anion complexes [NEt$_4$][M(Me-thiazds)$_2$] with M = Ni (**12**) and Pd (**13**). All ^{1}H NMR spectra of these monoanionic paramagnetic species (**10**−**13**) exhibit only the signals attributed to the NEt$_4$ counterions. These monoanionic species are isolated in good yield as air-stable crystalline solids.

Crystal Structure Determinations. Good-quality single crystals for X-ray diffraction have been obtained for two dianionic salts after recrystallization of **3b**, [PPh$_4$]$_2$[Ni(Me-

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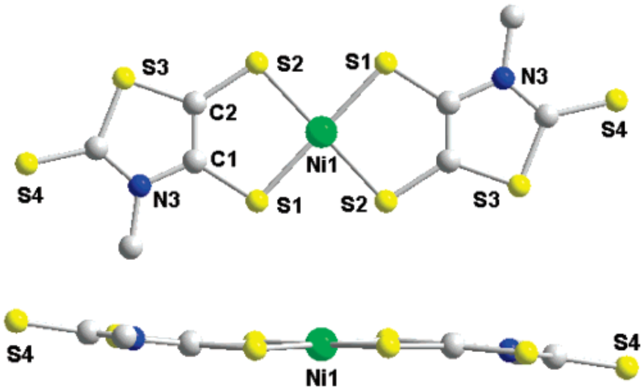

Figure 1. Molecular view of the [Ni(thiazdt)$_2$]$^{2-}$ complex in **3b**: [PPh$_4$]$_2$-[Ni(thiazdt)$_2$] perpendicular (top) and parallel (bottom) to the molecular plane.

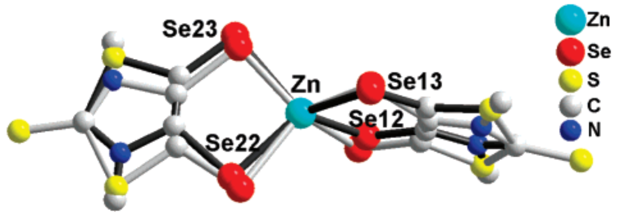

Figure 2. View of the [Zn(Me-thiazds)$_2$]$^{2-}$ complex in **5** showing the orientational disorder of the two Me-thiazds ligands in the coordination sphere of the Zn metal cation. Hydrogen atoms are omitted for clarity. The two disordered moieties are highlighted with light and dark gray bonds, respectively.

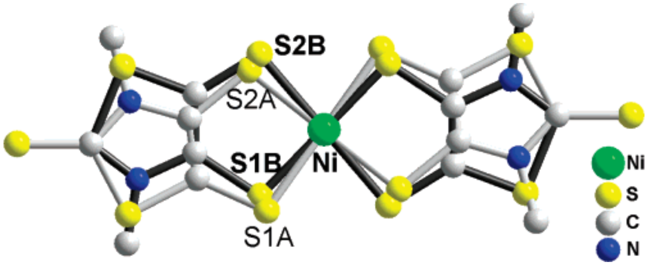

Figure 3. Molecular view of the anion radical species: [Ni(Me-thiazdt)$_2$]$^-$ in [NEt$_4$][Ni(Me-thiazdt)$_2$] **10**. Hydrogen atoms are omitted for clarity. The two disordered moieties are highlighted with light and dark gray bonds, respectively.

thiazdt)$_2$], and **5**, [NEt$_4$]$_2$[Zn(Me-thiazds)$_2$], in acetonitrile. Single crystals of the radical anion species have been obtained by slow diffusion of pentane into a dichloromethane solution of **11**, [NEt$_4$][Pd(Me-thiazdt)$_2$], and slow diffusion of toluene into an acetonitrile solution of **10**, [NEt$_4$][Ni(Me-thiazdt)$_2$].

[PPh$_4$]$_2$[Ni(Me-thiazdt)$_2$] **3b** crystallizes in the triclinic system, space group *P*-1, with the PPh$_4^+$ cation in general position and [Ni(Me-thiazdt)$_2$]$^{2-}$ species on an inversion center. As shown in Figure 1, the nickel atom is coordinated in a square-planar environment with Ni−S1 and Ni−S2 bond distances of 2.1944(6) and 2.1988(6), respectively, and a ligand bite angle of 94.22(2)°. These values are comparable to those observed in various dianionic salts of [Ni(dmit)$_2$].[4] Another interesting feature with this compound is that only the trans conformation of the complex is observed in the solid state. Indeed, in a square-planar conformation these complexes are susceptible to exist in both their trans and cis forms due to the dissymmetrical character of the S$_2$C$_2$RR′ dithiolene ligand where R ≠ R′. An equilibrium between those two forms has already been observed by variable-temperature NMR experiments, for example, in the dianionic nickel complex derived from the tfadt dithiolate ligand[18] [tfadt = S$_2$C$_2$(CN)(CF$_3$)] or in the neutral nickel complex derived from the S$_2$C$_2$HPh dithiolate ligand.[19] In these compounds, signals due to the presence of both the cis and the trans isomers were obtained at low temperatures which coalesce upon warming. Accordingly, we also investigated the VT-NMR behavior of the diamagnetic **3b** complex dissolved in CD$_3$CN/(CD$_3$)$_2$CO (1/2). One single signal is observed at room temperature, indicating a fast exchange. Cooling to 183 K did not allow us to observe any splitting of the signal, which would indicate that we reached the slow exchange temperature domain.

The Zn diselenolene complex **5** crystallizes in the monoclinic system, space group *Pc*. It is isostructural to the Zn dithiolene complex **2** described earlier.[11] Both Et$_4$N$^+$ cation and [Zn(Me-thiazds)$_2$]$^{2-}$ complexes are located in general positions in the unit cell. One of the Et$_4$N$^+$ cations is disordered on two positions with a 50:50 occupation. As shown in Figure 2, the Zn atom is coordinated in a distorted tetrahedral environment. Also, one observes a strong disorder in the diselenolene moieties, which corresponds to a superposition of the two possible orientations of the unsymmetrical diselenolene ligand. The refined occupation parameters for those diselenolene orientations shown with dark bonds in Figure 2 are 0.46 and 0.54 for the Se12/Se13 and Se22/Se23 pairs, respectively, which is close to a 50:50 distribution.

We also succeeded in obtaining crystals of the anion radical species which are air-stable species. The nickel complex [Et$_4$N][Ni(Me-thiazdt)$_2$] **10** crystallizes in the monoclinic system, space group *C*2/*c*. The Et$_4$N$^+$ cation is located on a 2-fold axis, while the dithiolene complex is located on an inversion center. As shown in Figure 3, the unsymmetrical dithiolene is disordered on two positions, as already observed above in the zinc complex. Refinement of the occupation parameter converged to a 70:30 distribution in this dithiolene complex **10**. Because of their localization on inversion centers it is not possible here to determine if the disorder is only attributable to the trans form of the complexes or if we are in the presence of a cis−trans mixture. Also, as a consequence of this structural disorder, it is difficult to analyze the evolution of the geometrical characteristics of the complexes when going from the dianionic to the oxidized monoanionic complexes. In the solid state (Figure 4), the radical anion species are separated from each other by the Et$_4$N$^+$ cations in the (*a*,*c*) plane while they form chains running along *b* with weak lateral interactions.

The Pd salt **11** with the Me-thiazdt ligand, [Et$_4$N][Pd(Me-thiazdt)$_2$], is not isostructural with its nickel analogue; it crystallizes indeed in the triclinic system, space group *P*-1, with two Et$_4$N$^+$ cations and two Pd complexes located in a

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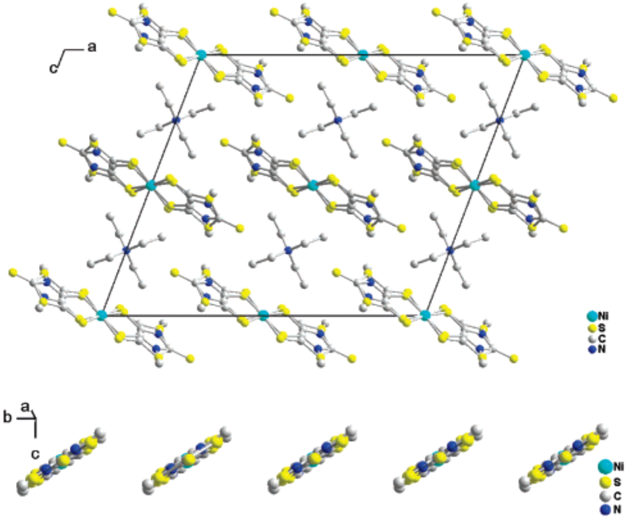

Figure 4. (Top) Projection view along *b* of the unit cell of **10** $[Et_4N][Ni(Me\text{-}thiazdt)_2]$. (Bottom) View of the chains of **10** $[Ni(Me\text{-}thiazdt)_2]^-$ species running along *b*.

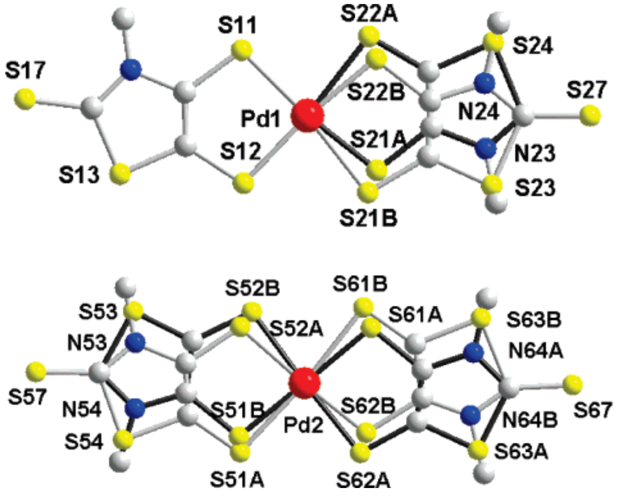

Figure 5. Molecular structure view of the two crystallographically independent anion radical species $[Pd(Me\text{-}thiazdt)_2]^-$ in **11** $[NEt_4][Pd(Me\text{-}thiazdt)_2]$. Hydrogen atoms are omitted for clarity. The two disordered moieties are highlighted with light and dark gray bonds, respectively.

general position in the unit cell. As shown in Figure 5, the two complexes are affected by disorder in a different way since the one based on Pd1 exhibits disorder on one side only, indicating unambiguously the presence of a cis−trans mixture on this site, with 46% trans isomer (based on S21A, S22A) and 54% cis isomer (based on S21B, S22B). Concerning the complex built on Pd2, refinement of the occupation parameters afforded 35% on S51A,S52A and 65% on S51B,S52B on one side, 80% on S61A,S62A, 20% on S61B, S62B on the other side, indicating a predominant trans form, associated with the S51B,S52B/S61A,S62A coordination around the Pd2 atom. In the solid state, packing of the Pd salt in **11** is also relatively complicated. As shown in Figure 6, the anions associate four by four into tetrameric motifs with overlap interactions limited to the outer ends on the complexes.

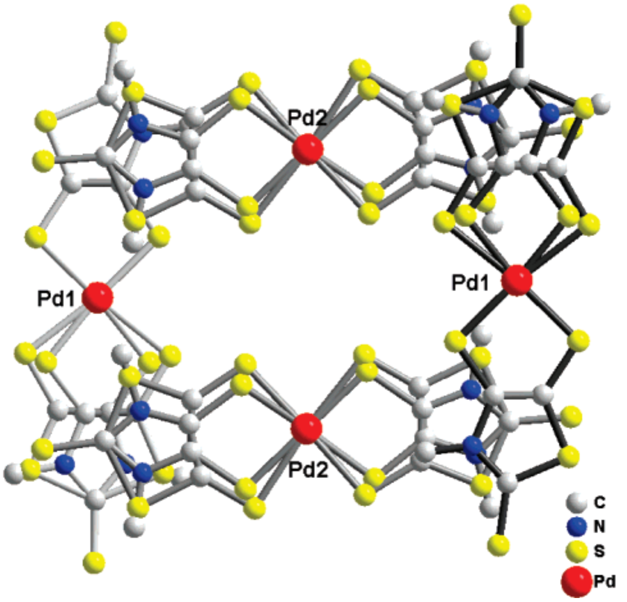

Figure 6. Detail of the tetrameric motif found in the solid-state organization of the $[Pd(Me\text{-}thiazdt)_2]^-$ moieties in **11**.

Electrochemical Properties. The redox behavior of the various $[NEt_4]_2[M(Me\text{-}thiazdt)_2]$ and $[NEt_4]_2[M(Me\text{-}thiazds)_2]$ complexes described above was investigated by cyclic voltammetry in CH_3CN with 0.1 M nBu_4NPF_6 as supporting electrolyte. The zincate complexes **2** and **5** exhibit an irreversible oxidation wave, while the five other complexes, namely, **3a**, **3b**, **4**, **6**, and **7**, exhibit two oxidation waves. Cyclic voltammograms for all compounds are essentially the same. As shown in Figure 7, the first process is fully reversible and corresponds to oxidation of the dianion into the radical anion while the second one, which is not fully reversible due to adsorption phenomena on the electrode, corresponds to oxidation of the radical anion into the neutral species. The redox potentials of the dithiolene complexes are collected in Table 2 together with their dmit and timdt analogues for comparison, while the redox potentials of the diselenolene complexes are collected in Table 3 together with their sulfur analogues.

Concerning the dithiolene complexes, it is worth noting that a similar adsorption phenomenon was observed with the dmit analogues.[4] Actually, this adsorption phenomenon was not observed by Arca et al.,[8] probably due to the fact that the ethyl group they used on the thiazole ring instead of a methyl one brings more solubility to the oxidized species. As expected, the nature of the counterion does not modify the redox potentials (e.g., **3a** vs **3b**). The first oxidation potential of complexes **3** and **4** is intermediate between the timdt and dmit analogues with the most electron-rich dithiolene in the series timdt > thiazdt > dmit. This is consistent with the observations made by Arca et al., who also noticed this influence while analyzing the redox potentials from the neutral $M(Et\text{-}thiazdt)_2$ (Ni, Pt) complexes when compared with the $M(dmit)_2$ analogues.[8] Comparison of the redox potentials of the Pd complexes with the Ni complexes shows a shift toward higher potentials, also observed in the dmit or timdt series. The observation (vide supra) that the dithiolene complexes **3** and **4** were easily oxidized in solution into the radical anion species is in accordance with the values of their redox potentials. Simi-

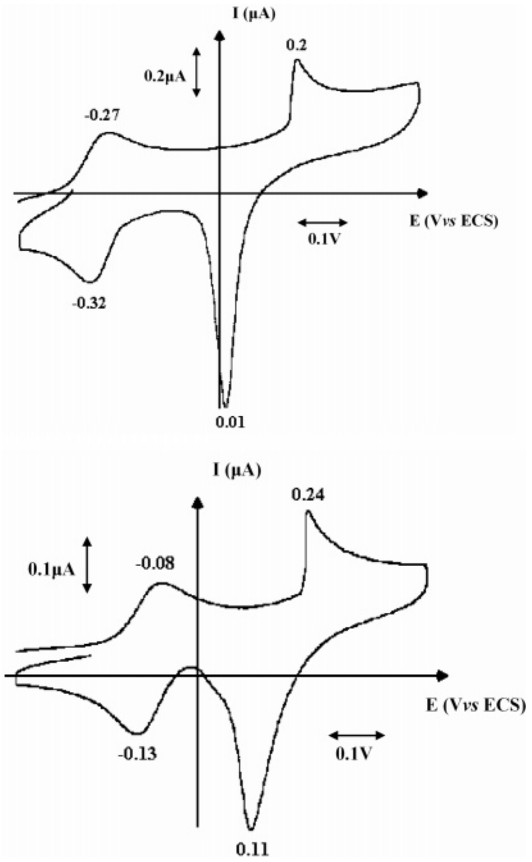

Figure 7. Cyclic voltammetry of **3a** (up) and **4** (down) in CH_3CN with 0.1 M $NnBu_4PF_6$ as supporting electrolyte at a scan rate of 100 $mV{\cdot}s^{-1}$. Pt working electrode.

Table 2. Redox Potentials for the Various Metal Dithiolene Complexes E in V vs SCE in CH_3CN

compound	$E_1^{2-/\bullet-}$	$E_{pa2}/E_{pc2}^{\bullet-/0}$	ref
$[NBu_4]_2[Ni(dmit)_2]$	−0.175	+0.34/0.228	20
3a $[NEt_4]_2[Ni(Me\text{-}thiazdt)_2]$	−0.29	+0.20/0.01	this work
	−0.34[a]	+0.22/0.00[a]	this work
3b $[PPh_4]_2[Ni(Me\text{-}thiazdt)_2]$	−0.29	+0.21/0.03	this work
$[Ni(Me_2\text{-}timdt)_2]$[a]	−0.58	−0.13	21
$[NBu_4]_2[Pd(dmit)_2]$	+0.05	+0.16	22
4 $[NEt_4]_2[Pd(Me\text{-}thiazdt)_2]$	−0.11	+0.24/0.11	this work
$[Pd(Et_2\text{-}timdt)_2]$[a]	−0.49	−0.12	20

[a] In CH_2Cl_2 solution.

Table 3. Redox Potentials for the Various Metal Diselenolene Complexes E in V vs SCE in CH_3CN

	$E_1^{2-/\bullet-}$	$E_{pa2}/E_{pc2}^{\bullet-/0}$	ref
5 $[NEt_4]_2[Zn(Me\text{-}thiazds)_2]$	0.13^ir		this work
6 $[NEt_4]_2[Ni(Me\text{-}thiazds)_2]$	−0.24	0.21/0.03	this work
$[NBu_4]_2[Ni(dsit)_2]$	−0.138	0.25/0.07	20
7 $[NEt_4]_2[Pd(Me\text{-}thiazds)_2]$	−0.03	0.08/−0.04	this work
	−0.12[a]	0.17/0.04[a]	
$[NBu_4]_2[Pd(dsit)_2]$	0.00/−0.06		23

[a] In CH_2Cl_2 solution.

larly, the timdt series were found to be easier to isolate under their neutral form.

Concerning the diselenolene complexes **5**−**7**, all oxidation potentials are shifted toward lower values when compared with the dsit series, indicating the similar electron-releasing influence of the thiazole rings on the electron density of the dithiolene and diselenolene[20,23] complexes. In the case of **7** investigated in acetonitrile, both reduction waves merge, while in dichloromethane the classical two redox stages are observed. There are some differences between the voltammograms of **7** and $[Pd(dsit)_2]$ as for the latter only one oxidation wave is observed.[23] It is interesting to note that all the diselenolene complexes exhibit higher oxidation potentials than the dithiolene complexes. For instance, a 110 mV positive shift is observed for the zincate complex **5** when compared to the corresponding dithiolene **2**.

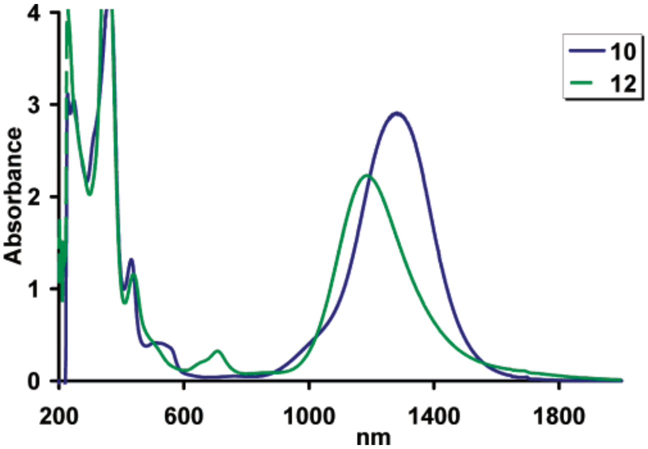

Figure 8. UV−vis−NIR absorption spectra of **10** and **12** in dichloromethane (10^{-4} M).

UV−vis−NIR Spectra. Absorption spectra of the dianionic and monoanionic species are measured in dichloromethane. Freshly prepared solutions of the oxidation-sensitive dianions exhibit absorption bands in the UV−vis region only. On the contrary, the monoanionic species exhibit a strong electronic absorption in the near-IR region, as shown in Figure 8 for the monoanionic complexes **10** and **12**. This band is a common feature of all monoanionic and neutral square-planar species and attributed to a $\pi-\pi$ transition of HOMO−LUMO character for the neutral species.[5]

The absorption maxima and extinction coefficients of this intense absorption band in the NIR are collected in Table 4 for complexes **10**−**13** together with the characteristics of their parent complexes in the dithiolene series. The Pd complexes exhibit a strong bathochromic shift of the NIR band compared to the Ni complexes. This shift amounts to 272 nm in the case of the dithiolenes from **10** to **11** and 325 nm for the diselenolenes from **12** to **13**. Also, the sulfur/selenium substitution, with the same thiazole backbone, brings only a limited change in the NIR absorption band for the **10**/**12** or **11**/**13** couples, observed at slightly higher energy in the diselenolenes. It is difficult to compare the NIR absorption band of the diselenolene complexes **12** and **13** with their

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Table 4. NIR Absorption Band and Extinction Coefficient of the Monoanionic Species in CH_2Cl_2

compound	λ (nm)	ϵ ($M^{-1}\cdot cm^{-1}$)	ref
$[NBu_4][Ni(dmit)_2]$	1153	19 900	24
$[NEt_4][Ni(Me\text{-}thiazdt)_2]$ **10**	1284	29 080	this work
$[Ni(Et\text{-}thiazdt)_2]^-$	1219		8
$[Ni(R,R\text{-}timdt)_2]^{-\,a}$	1370−1440		25
$[NBu_4][Pd(dmit)_2]^{-\,a}$	1431	26 000	24
$[NEt_4][Pd(Me\text{-}thiazdt)_2]$ **11**	1556	33 750	this work
$[Pd(R,R\text{-}timdt)_2]^{-\,a}$	1670−1745		25
$[NEt_4][Ni(Me\text{-}thiazds)_2]$ **12**	1187	22 300	this work
$[NEt_4][Pd(Me\text{-}thiazds)_2]$ **13**	1512	29 135	this work

[a] The λ values of the monoanionic species were determined during spectroelectrochemical investigations carried out on the neutral species.

parent analogues as, to the best of our knowledge, the NIR absorption bands of the $[M(dsit)_2]^{-\bullet}$, M = Ni, Pd, have not been reported yet while the corresponding R,R′-imidazolediselenolene (R,R′-timds) ligand has never been prepared so far. Finally, concerning the influence of the thiazole core on the dithiolene derivatives, both **10** and **11** exhibit a NIR band located midway between those of the dmit and timdt complexes, as already noticed in one Ni derivative by Arca et al.[8] Interestingly also, their extinction coefficients are higher than the ones observed for the corresponding dmit complexes.

Conclusion

Simple and efficient approaches to the *N*-methyl-1,3-thiazoline-2-thione-4,5-dithiolate ligand (Me-thiadt) have been described and successfully extended to the diselenolene analogues. It provides ready access to the reduced forms of these dithiolene (and diselenolene) complexes, which are particularly attractive, by comparison with their neutral analogues as they simultaneously exhibit a higher solubility and strong NIR absorption at even lower energies, two conditions required for use in optical devices such as Q switches[26] or NIR photodetectors.[27] Moreover, our synthetic pathway allowed us not only to isolate the mono- and dianionic species but also to structurally characterize these derivatives for the first time. This procedure also opens wide perspectives for (i) the elaboration of magnetic salts based on the $S = 1/2$ monoanionic species with various counterions,[3e] eventually blessed with attractive bistable properties,[28] and (ii) functionalization of the dithiolene (or diselenolene) ligand through the nitrogen substituent as the Me group used here in Me-thiazdt (or Me-thiazds) can be easily replaced by many different aliphatic and aromatic amines. Let us mention as an example chiral amines as well as di- and triamines for elaboration of cage-like structures such as those described, for example, from 3-amido-1,2-benzenedithiolate derivatives.[29,30]

Supporting Information Available: X-ray crystallographic files in CIF format for complexes **3b**, **5**, **10**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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