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Sequential Generation of One-Dimensional Networks Based on a Differentiated Bischelate-Type Ligand Bearing Both 4,5-Diazafluorene and Dithiolene Units

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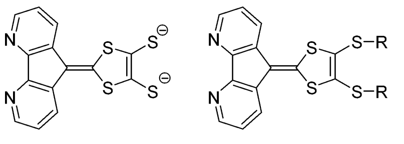
A novel dithiolene ligand appended with a 4,5-diazafluorene moiety has been synthesized and used for the preparation of discrete nickel and mercury complexes and a one-dimensional polymer in the presence of sodium cations.

Metal dithiolene complexes have been the matter of active research owing to their relevance to biology, catalysis, and material science.[1] In particular, these complexes have been used for the preparation of superconductors, single-component metals, and ferromagnets.[2] This versatility makes them interesting building blocks for the construction of extended molecular architectures.[3] Although metal dithiolene complexes have been reported with ligands such as maleonitriledithiolate and derivatives[4] 2,3-dichalcogenopyrazine,[5] dithiooxalate,[6] or pyridine-functionalized dithiolene,[7] only a few coordination networks and assemblies have been described with these ligands.[4−7] S-protected dithiolenes ligands such as **1** and **2** (Chart 1) bearing the 4,5-diazafluorene unit as the coordinating site have been reported.[8] For these ligands, because the sulfur atoms are protected as thioethers, they only bind metal centers through the diazafluorene moiety.[9] However, surprisingly, the deprotected ligand **L** (Chart 1), which offers several interesting coordinating features, has not been exploited for the preparation of either discrete complexes or infinite coordination frameworks. Ligand **L**, dianionic in nature, provides two differentiated coordinating chelates, one based on the dithiolate moiety and the other on the 4,5-diazafluorene unit. This peculiarity may be used for the sequential generation of heterometallic architectures. Indeed, owing to the stronger binding propensity of the dithiolate unit with respect to the diazafluorene unit, the initial binding of metal centers should occur through the anionic chelate, leading thus to complexes offering further peripheral chelate-type coordinating sites. We report herein on the preparation and crystal structures of Ni(II) and Hg(II) complexes **6** and **7** formed with ligand **L** as well as the solid-state structure of the first infinite one-dimensional network generated upon treatment of **7** with sodium thiocyanate.

Chart 1



L **1**, R = CH$_3$; **2**, R = CH$_2$-CH$_3$

Ligand **L** was prepared as its sulfur-protected precursor **5**[10] by trimethyl phosphite coupling of 4,5-diazafluoren-9-one **3**[11a] with **4**[11b] (Scheme 1). The desired ligand **L** was generated in situ upon treatment of **5** at low temperature with (n-Bu$_4$N)OH in MeOH and was directly used for the preparation of its metal complexes **6** and **7**.[11]

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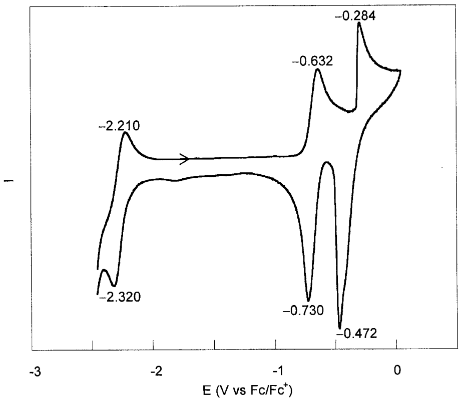


Figure 1. Cyclic voltammogram of **6** in DMF [0.1 M (n-Bu_4N)PF_6; scan rate 100 mV s^{-1}].

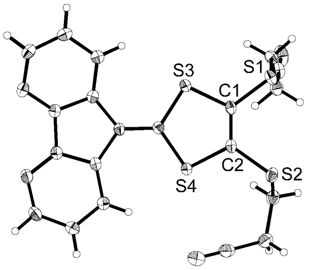


Figure 2. ORTEP view of **5**. Selected bond lengths (Å): S1−C1, 1.7570(12); S2−C2, 1.7579(12); C1−C2, 1.3508(18).

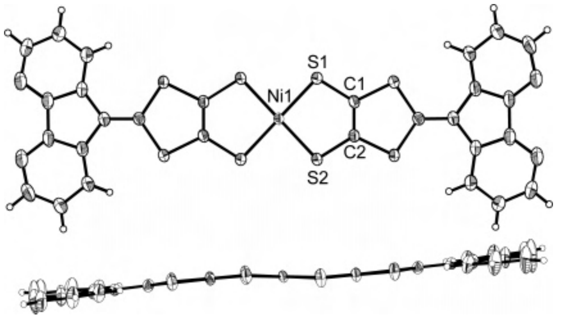


Figure 3. Top and side views of complex $[NiL_2]^{2-}$ in **6**. Selected bond lengths (Å) and angles (deg): Ni1−S1, 2.2037(10); Ni1−S2, 2.2050(9); S1−C1, 1.736(4); S2−C2, 1.738(3); C1−C2, 1.351(5); S1−Ni1−S2, 93.17(3); Ni1−S1−C1, 101.06(13); Ni1−S2−C2, 100.86(12).

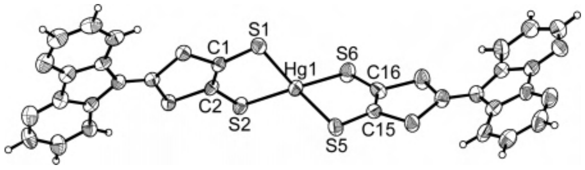
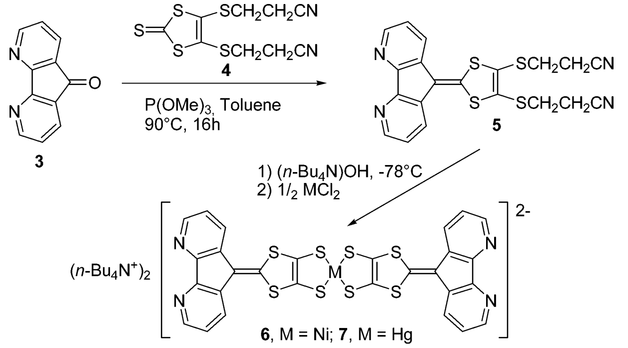


Figure 4. ORTEP view of complex $[HgL_2]^{2-}$ in **7**. Selected bond lengths (Å) and angles (deg): Hg1−S1, 2.5797(18); Hg1−S2, 2.5225(17); Hg1−S5, 2.5471(17); Hg1−S6, 2.5213(19); S1−C1, 1.737(6); S2−C2, 1.749(6); S5−C15, 1.737(7); S6−C16, 1.725(7); C1−C2, 1.363(8); C15−C16, 1.343(10); S1−Hg1−S2, 87.92(5); S1−Hg1−S5, 112.97(6); S1−Hg1−S6, 127.30(6); S2−Hg1−S5, 127.19(6); S2−Hg1−S6, 117.30(6); S5−Hg1−S6, 88.55(6).

The electrochemical behavior of the precursor **5** and the two complexes **6** and **7** was investigated in solution. Owing to the rather low solubility of **5**−**7** in both MeCN and CH_2Cl_2, cyclic voltammetry was performed in DMF. The cyclic voltammogram of **6** (Figure 1) shows one reduction and two oxidation waves. Starting with the dianionic complex, the first oxidation step ($E_{ox}^1 = -0.681$ V vs Fc^0/Fc^+) corresponding to the formation of the monoanionic species is quasi-reversible, whereas the second oxidation leading to the neutral complex ($E_{ox}^2 = -0.378$ V vs Fc^0/Fc^+) appears to be not fully reversible because of the formation of a solid material on the electrode. The reduction process ($E_{red} = -2.255$ V vs Fc^0/Fc^+) seems to be ligand-centered given that, under the same conditions, the precursor **5** shows an irreversible reduction at −2.10 V vs Fc^0/Fc^+. The rather low oxidation potential of the nickel(II) complex **6** suggests that the latter may be of interest for the formation of neutral conducting material.[2c] Under the same conditions, the mercury(II) complex **7** displays two close and irreversible oxidation waves at −0.05 and 0.02 V as well as one irreversible reduction wave at −1.52 vs Fc^0/Fc^+.

Scheme 1. Synthetic Pathway for the Preparation of **5**−**7**



The solid-state structures of compounds **5**−**7** were determined by single-crystal X-ray diffraction methods. Precursor **5** (crystallizes triclinic, $P\bar{1}$) with one molecule in the asymmetric unit (Figure 2).[12a] The core of the molecule is

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(10) (a) **5**: A mixture of **3** (1 g, 5.48 mmol) and **4** (2.67 g, 8.76 mmol) in dry toluene (300 mL) and freshly distilled $P(OMe)_3$ (70 mL) was heated at 90 °C overnight. The precipitate was recovered by filtration and recrystallized from hot $CHCl_3$, affording yellow prisms (0.520 g, 22%). Mp: 199−201 °C (dec). IR (KBr/cm^{-1}): ν_{CN} 2249. ^1H NMR (300 MHz, $CDCl_3$): δ 8.68 (dd, $J = 1.3$ and 4.8 Hz, 2H), 7.98 (dd, $J = 1.3$ and 8.0 Hz, 2H), 7.35 (dd, $J = 4.8$ and 8.0 Hz, 2H), 3.26 (t, $J = 6.9$ Hz, 4H), 2.85 (t, $J = 6.9$ Hz, 4H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 154.1, 147.4, 143.8, 133.0, 131.0, 129.9, 129.4, 123.4, 119.5, 113.7, 31.5, 18.8. Anal. Calcd for $C_{20}H_{14}N_4S_4$: C, 54.77; H, 3.22; N, 12.77. Found: C, 54.54; H, 3.32; N, 12.67. UV−vis (DMF): λ_{max}/nm (log ϵ) 283 (4.28), 306 (4.20), 317 (4.24), 402 (4.51), 416 (4.54). The symmetrical tetrathiafulvalene was also isolated but not the bis(diazafluorene) derivative. (b) **6**: To a solution of **5** (150 mg, 0.34 mmol) in tetrahydrofuran (7 mL) was added (n-Bu_4N)OH (2 mL, 1 M in MeOH) at −78 °C under argon. The mixture was gently warmed to room temperature, at which it became dark blue. It was then cooled to −78 °C, and a solution of $NiCl_2 \cdot 6H_2O$ (41 mg, 0.17 mmol) in degassed MeOH (3 mL) was added. The solution was gently warmed to room temperature overnight, and the resulting black solid was recovered by filtration (116 mg, 55%). X-ray-quality single-crystalline black rods were obtained by recrystallization from MeCN. Anal. Calcd for $C_{60}H_{84}N_6NiS_8$: C, 59.83; H, 7.03; N, 6.98. Found: C, 59.63; H, 6.84; N, 6.56. UV−vis (DMF): λ_{max}/nm (log ϵ) 274 (4.66), 305 (4.80), 317 (4.80), 368 (4.35), 458 (4.65), 631 (4.33). (c) **7**: Under the same conditions using $HgCl_2$, **7** was obtained as a shiny purple solid (65.2%). Recrystallization from MeCN afforded X-ray-quality purple platelets. Anal. Calcd for $C_{60}H_{84}HgN_6S_8$: C, 53.52; H, 6.29; N, 6.24. Found: C, 52.72; H, 6.35; N, 6.22. ^1H NMR (300 MHz, DMSO-d_6): δ 8.55 (dd, $J = 1.5$ and 4.8 Hz, 4H), 8.15 (dd, $J = 1.5$ and 8.1 Hz, 4H), 7.50 (dd, $J = 4.8$ and 8.1 Hz, 4H), 3.14 (m, 16H), 1.55 (m, 16H), 1.29 (m, 16H), 0.91 (t, $J = 7.2$ Hz, 24H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 152.6, 147.7, 145.3, 131.1, 128.9, 124.9, 122.9, 108.3, 58.0, 23.5, 19.7, 13.9. UV−vis (DMF): λ_{max}/nm (log ϵ) 271 (4.67), 308 (4.77), 318 (4.75), 361 (4.71), 406 (4.21), 537 (4.64).

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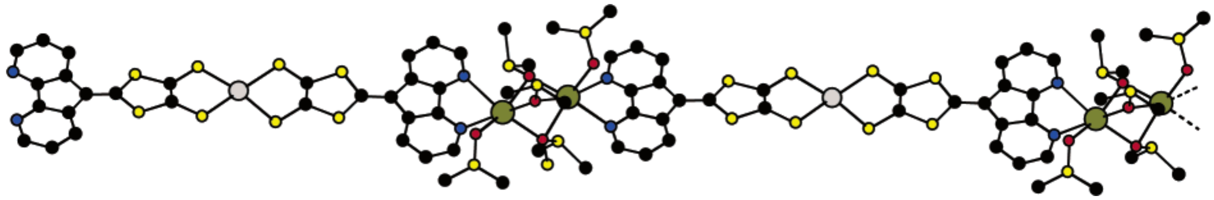

Figure 5. Fraction of the one-dimensional polymer **8**. Mercury, sodium, sulfur, oxygen, carbon, and nitrogen atoms in gray, green, red, yellow, black, and blue, respectively. Hydrogen atoms have been omitted for clarity.

rather flat, with the two propionitrile chains located on the same side of the main plane. Stacks of molecules along the *a* axis with interplanar distances of 3.483(2) and 3.527(2) Å resulting from $\pi-\pi$ and S···S interactions [$d_{S\cdots S} = 3.762$ (2) and 3.774(2) Å] are observed. Similar stacking has been described for the manganese complexes of **1**.[9]

Compound **6** crystallizes (monoclinic, $P2_1/c$) with one nickel complex located on an inversion center and one cation in the general position.[12b] Ni(II) adopts the square-planar coordination geometry as is usually observed with Ni-bis-(1,2-dithiolene) complexes (Figure 3).[1a] As is expected and observed for **5**, the organic part **L** is again flat. However, the entire complex is not fully planar because an angle of 7.27° around the S- - -S hinge is observed between the ligand **L** and the plane defined by the NiS_4 unit (Figure 3, bottom). The intramolecular bond distances are as expected for such complexes.[1a] Despite the presence of the $(n\text{-}Bu_4N)^+$ cations, an overlap of the diazafluorene moieties is observed with an interplanar distance of 3.535(4) Å.

Compound **7** crystallizes (monoclinic, $C2/c$) with one $[Hg\mathbf{L}_2]^{2-}$ complex and two $(n\text{-}Bu_4N)^+$ cations in general positions.[12c] The Hg center is in a distorted tetrahedral environment (Figure 4) with bond distances in agreement with reported Hg-bis(dithiolene) complexes.[13] Angles of 16.23° and 20.01° are observed around the S- - -S hinges. Owing to the distorted nature of the tetrahedral coordination geometry, the angle between the two 4,5-diazafluorene moieties is not 90° but 69.87°. In contrast with the Ni complex in **6**, the presence of the cations prevents $\pi-\pi$ interaction, and thus no stacking of the metal complexes is observed.

On the basis of the design of ligand **L**, one would expect the formation of an infinite network in the presence of an additional metal center through its binding by the 4,5-diazafluorene units. This was indeed demonstrated in the case of complex **7** using Na^+ as connectors. A solution of **7** in DMSO was layered with a MeCN solution of NaSCN. Red crystals were obtained after about 1 week and structurally characterized. $[Hg\mathbf{L}_2(Na_2(DMSO)_5)]$ polymer **8** crystallizes (monoclinic, Cc) with one $[Hg\mathbf{L}_2]^{2-}$ complex, two Na^+, cations, and five DMSO molecules in general positions.[12d] The polymer is generated upon bridging, via nitrogen atoms of the 4,5-diazafluorene groups, of consecutive $[Hg\mathbf{L}_2]^{2-}$ complexes by $[(DMSO)Na(\mu\text{-}DMSO)_3Na(DMSO)]^{2+}$ units (Figure 5). The overall geometry of the $[Hg\mathbf{L}_2]^{2-}$ complex is similar to the discrete complex **7**. Within a bridging unit, the two Na^+, in a distorted octahedral environment, are separated by 3.11 Å. The average Na−N and Na−O_{DMSO} distances are 2.495 and 2.400 Å, respectively, in agreeement with distances reported for Na^+ salts of Cu and Ni complexes of 2,3-dichalcogenodithiolates.[5]

In conclusion, we have reported the in situ preparation of the ligand **L** and its Ni(II) and Hg(II) complexes. These complexes exhibit interesting redox properties, suggesting their possible use for the formation of single-component metals.[2c] Owing to the strong electronic differentiation between the two chelating units of **L**, the latter was used for the stepwise formation of an infinite one-dimensional network in the presence of a sodium cation. This type of ligand offers many other design possibilities such as control of the geometry and redox characteristics of the central metal cation bound to the dithiolate group and extension into larger discrete polynuclear homo- and/or heterometallic complexes as well as infinite networks. Investigations are currently underway to explore all of these features.

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Supporting Information Available: X-ray crystallographic data for compounds **5**−**8** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) (a) Crystal data for **5** ($C_{20}H_{14}N_4S_4$): $M_w = 438.59$, triclinic, $P\bar{1}$, $a = 9.0091(2)$ Å, $b = 10.1626(3)$ Å, $c = 11.4232(3)$ Å, $\alpha = 88.7850(10)°$, $\beta = 82.8110(10)°$, $\gamma = 65.0610(10)°$, $V = 940.31(4)$ Å^3, $Z = 2$, $D_{calc} = 1.549$, $T = 173(2)$ K, $\mu = 0.520$ mm^{-1}, 14 427 reflns measured, 5508 unique reflns ($R_{int} = 0.0273$), $R = 0.0312$ [$I > 2\sigma(I)$], $R_w = 0.0864$ (for all data). (b) Crystal data for **6** ($C_{60}H_{84}N_6NiS_8$): $M_w = 1204.52$, monoclinic, $P2_1/c$, $a = 11.9414(3)$ Å, $b = 16.2499(5)$ Å, $c = 16.2344(5)$ Å, $\beta = 104.168(2)°$, $V = 3054.41(15)$ Å^3, $Z = 2$, $D_{calc} = 1.303$, $T = 173(2)$ K, $\mu = 0.634$ mm^{-1}, 41 497 reflns measured, 8886 unique reflns ($R_{int} = 0.0544$), $R = 0.0749$ [$I > 2\sigma(I)$], $R_w = 0.2141$ (for all data). (c) Crystal data for **7** ($C_{60}H_{84}HgN_6S_8$): $M_w = 1346.80$, monoclinic, $C2/c$, $a = 40.8172(17)$ Å, $b = 9.5600(5)$ Å, $c = 33.7035(16)$ Å, $\beta = 106.945(2)°$, $V = 12580.5(10)$ Å^3, $Z = 8$, $D_{calc} = 1.422$, $T = 173(2)$ K, $\mu = 2.754$ mm^{-1}, 70 136 reflns measured, 14 453 unique reflns ($R_{int} = 0.1138$), $R = 0.0526$ [$I > 2\sigma(I)$], $R_w = 0.1557$ (for all data). (d) Crystal data for **8** ($C_{38}H_{42}HgN_4Na_2O_5S_{13}$): $M_w = 1298.11$, monoclinic, Cc, $a = 25.4856(8)$ Å, $b = 14.2965(4)$ Å, $c = 17.7647(10)$ Å, $\beta = 129.5640(10)°$, $V = 4989.9(4)$ Å^3, $Z = 4$, $D_{calc} = 1.728$, $T = 173(2)$ K, $\mu = 3.692$ mm^{-1}, 27 477 reflns measured, 11 132 unique reflns ($R_{int} = 0.0425$), $R = 0.0321$ [$I > 2\sigma(I)$], $R_w = 0.0987$ (for all data). (e) Data collections were carried out at 173 K on a Bruker SMART CCD diffractometer with Mo Kα radiation. The structures were solved using *SHELXS-97* and refined by full-matrix least-squares on F^2 using *SHELXL-97* with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were introduced at calculated positions and not refined (riding model). In **6**, the butyl chains of the cation show high positional disorder, refined accordingly. In **8**, the DMSO molecules show severe positional disorder.

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