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A Straightforward Synthesis of Diverse Nickel Dithiolene Complexes Appended with Hydrogen-Bond Donor/Acceptor Groups

Stéphane A. Baudron, Narcis Avarvari,* and Patrick Batail*

Chimie, Ingénierie Moléculaire et Matériaux d'Angers (CIMMA), UMR 6200 CNRS–Université d'Angers, Bâtiment K, 2 boulevard Lavoisier, 49045 Angers, France

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Nickel dithiolene complexes symmetrically appended with hydrogen-bond donor/acceptor functionalities such as imide, amide, or cyano/amide groups have been synthesized by a straightforward method of wide applicability starting from one single precursor. Single-crystal X-ray structures reveal the occurrence of one type of ribbon common to all compounds that is based on a recurrent self-complementary intermolecular hydrogen-bonded ring motif linking the symmetrically substituted complexes.

An enormous amount of work has been devoted to metallic and superconducting salts based on nickel dithiolene complexes[1,2] and, recently, to the advent of single-component molecular metals.[3] Nevertheless, hydrogen-bonding interactions—and their redox-activated intermolecular patterns—which are the focus of much current attention in the field of molecular materials,[4] have not been used per se to direct the solid-state structures of metal dithiolene complexes and manipulate the electronic structure of a class of conducting and magnetic materials where the double-band concept[2,3,5] has yet to reach its full potential. This is because metal dithiolene complexes appended with hydrogen-bond donor/acceptor functionalities are not available. Typically then, crystal engineering issues[6] featuring an important class of functional redox complexes have thus far focused solely on interactions between ammonium or pyridinum cations and paramagnetic nickel dithiolene anionic complexes such as $[Ni(mnt)_2]^-$[7] or on the organization of the countercations by themselves.[8] Herein, we report on the straightforward synthesis—starting from one single precursor—of a series of nickel dithiolene complexes symmetrically functionalized by hydrogen-bond donor/acceptor groups, including imides, orthodiamides, and dual complexes, ortho-functionalized by a cyano group and a primary amide group. This reaction is important, as it also provides the network designer with a set of unprecedented models whose patterns of self-assembly in the solid state is analyzed.

Neiland's 4,5-diamido-2-oxo-1,3-dithiole,[9] **1**, was selected as the starting material for the preparation of amide-functionalized nickel dithiolene complexes. Paralleling the work of the Riga group for the preparation of the complex bearing a uracil-type dithiolate ligand, this dithiocarbonate is reacted with 4 equiv of sodium methanolate in methanol. Subsequent metathesis with nickel nitrate and an ammonium or phosphonium halide salt unexpectedly affords $[Ni(midt)_2]^{2-}$ (**2**$^{2-}$), a complex of the ligand maleimide dithiolate (midt). It is of interest to note the dual effect of sodium methanolate, which acts both as a nucleophile for opening the dithiocarbonate ring and as a base, abstracting protons and inducing a synchronous, intramolecular reaction between the two ortho-amide functionalities to produce an imide upon ring closure and subsequent elimination of ammonia (Scheme 1).

Note also that the reaction occurs when only 2 equiv of sodium methanolate are used. This complex can be further oxidized with iodine to produce $[Ni(midt)_2]^-$ (**2**$^-$). Analysis of the crystal structure of these complexes reveals one-dimensional chains generated out of self-complementary intermolecular hydrogen-bond motifs (Figure 1 and Table 1), a feature common to both dianionic $(Bu_4N)_2Ni(midt)_2$ and $(Ph_4P)_2Ni(midt)_2$ salts, as well as to the monoanionic, paramagnetic complex $(Ph_4P)Ni(midt)_2$. In the case of both dianionic complexes, the cations form isolated chains (Supporting Information), whereas in $(PPh_4)Ni(midt)_2$, two chains run parallel to each other, albeit with a slight offset (Figure

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* To whom correspondence should be addressed. E-mail: patrick.batail@univ-angers.fr (P.B.), narcis.avarvari@univ-angers.fr (N.A.).

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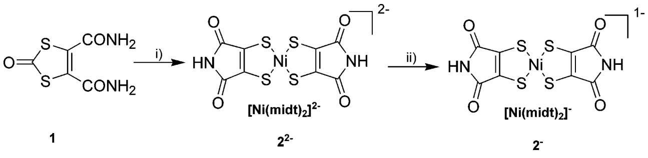
Scheme 1. Synthesis of $[Ni(midt)_2]^{2-/1-}$ [a]



[a] (i) NaOMe, $Ni(NO_3)_2\cdot6H_2O$; (ii) $^1/_2I_2$

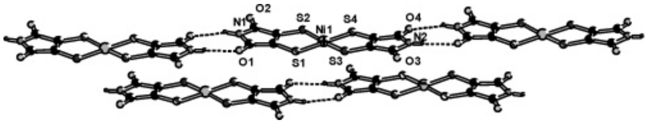


Figure 1. Discrete set of two parallel chains as observed in $(PPh_4)Ni(midt)_2$. Selected bond lengths (Å) and angles (deg): Ni1−S1 2.174(1), Ni1−S2 2.172(1), Ni1−S3 2.170(1), Ni1−S4 2.176(1); S1−Ni1−S2 93.62(4), S3−Ni1−S4 93.66(4), S1−Ni1−S3 86.15(4), S2−Ni1−S4 86.62(4).

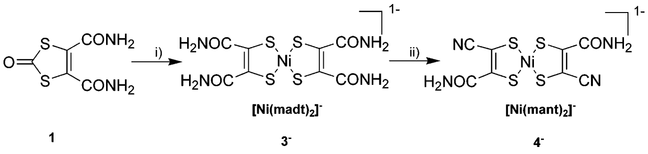
Table 1. Hydrogen-Bond Distances and Angles Averaged over the Two, Essentially Symmetrical Dimer Motifs

compound	N···O (Å)	H···O (Å)	$\alpha_{N-H\cdots O}$ (deg)
$(Bu_4N)_2Ni(midt)_2$	2.914	2.055	174.5
$(PPh_4)_2Ni(midt)_2.CH_3CN$	2.863	2.03	163.5
$(PPh_4)Ni(midt)_2$	2.925	2.08	168
$(PPh_4)Ni(madt)_2$	2.938	2.08	170.5
$(PPh_4)Ni(mant)_2$	2.878	2.02	175
$(Bu_4N)_2Ni(mant)_2$	2.925	2.07	173

1),[10] giving rise to two intermolecular interactions amounting to $\beta_I = 0.17$ and $\beta_{II} = 0.19$ eV, as determined by extended Hückel calculations. This suggests an alternated spin chain magnetic behavior in agreement with the observed temperature evolution of the magnetic susceptibility (Supporting Information).

It is of interest to note that only the dimer motif is present here, in contrast to the preference for a catemer chain established by a recent CSD analysis of hydrogen-bond networks involving imide functionalities.[11] Cyclic voltammetry experiments for $(PPh_4)Ni(midt)_2$ in MeCN reveal a reversible wave at −0.14 V/SCE, corresponding to the couple $[Ni(midt)_2]^{2-/1-}$, and an ill-defined oxidation at +0.72 V/SCE, corresponding to the formation of $[Ni(midt)_2]^0$. The latter electrochemical event observed at such "normal" concentrations (>1 mM) indicates a rather modest stability of the neutral complex, as typically observed in nickel dithiolene complexes bearing attracting groups, such as CN in $[Ni(mnt)_2]^{n-}$.[12] Note that $[Ni(midt)_2]^-$ is a paramagnetic analogue of pyrometillimide (bis-imide of benzene-1,2,4,5-tetracarboxylic acid) and that its deprotonated form is a potential ligand for bimetallic complexes.[13]

Scheme 2. Synthesis of $(PPh_4)[Ni(madt)_2]$ and $(PPh_4)[Ni(mant)_2]$[a]



[a] (i) NaSMe, $Ni(NO_3)_2\cdot6H_2O$; (ii) MeOH reflux.

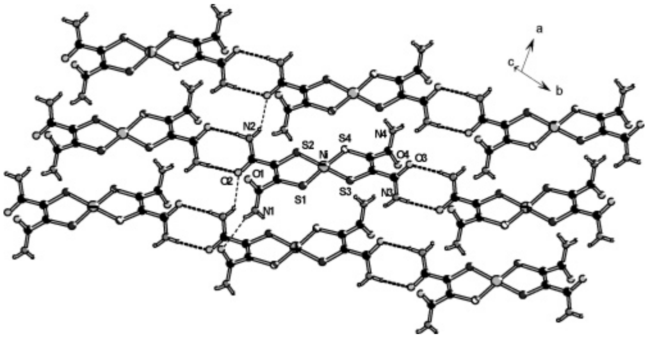


Figure 2. Slab of complexes in $(PPh_4)Ni(madt)_2$, with an emphasis on the formation of ribbons through the $R_2^2(8)$ motif (thick dotted bonds). The thin dotted lines represent N−H···O bonds within stacks. Selected bond lengths (Å) and angles (deg): Ni−S1 2.150(1), Ni−S2 2.149(1), Ni−S3 2.145(1), Ni−S4 2.150(1); S1−Ni−S2 91.60(5), S3−Ni−S4 91.49(5), S1−Ni−S3 88.15(5), S2−Ni−S4 88.83(5).

To form the nickel dithiolene tetraamide complex, one therefore has to avoid proton abstraction from the amide, the primary event toward ring closure and formation of the imide. Thus, a nonbasic nucleophile has to be used to generate the dithiolate. Hence, and as expected, sodium methanethiolate, NaSMe, successfully promotes the quantitative formation of diamido-dithiolate, as demonstrated by reacting the dithiocarbonate **1** with 2 equiv of NaSMe and subsequent cation exchange, which affords the complex $[Ni(madt)_2]^-$ ($\mathbf{3}^-$, madt = maleamide dithiolate) (Scheme 2).

The crystal structure of $\mathbf{3}^-$ (Figure 2) shows,[10] somewhat surprisingly, an "open" type of conformation of the maleodiamide framework; that is, there is no intramolecular hydrogen bond, in contrast of the structure of EDT-TTF-$(CONH_2)_2$ (EDT = ethylenedithio).[14] To our knowledge, only one such open form of primary 1,2-diamides has been observed so far in the case of a dihydro barrelene tetra-

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(10) Crystal data for $(PPh_4)Ni(midt)_2$ ($\mathbf{2}^-$) ($C_{32}H_{22}N_2O_4PS_4Ni$): triclinic, space group $P\bar{1}$, $a = 10.9413(17)$ Å, $b = 11.9501(17)$ Å, $c = 13.0235(16)$ Å, $\alpha = 77.422(16)°$, $\beta = 76.190(17)°$, $\gamma = 74.858(17)°$, $V = 1574.1(4)$ Å^3, $T = 293(2)$ K, $Z = 2$, 15845 reflns measured, 5657 unique reflns ($R_{int} = 0.061$) were used in the refinement by full-matrix least-squares methods on F^2, $R = 0.0396$, $R_w = 0.0783$ (all data). Crystal data for $(PPh_4)Ni(madt)_2$ ($\mathbf{3}^-$) ($C_{32}H_{24}N_4O_5PS_4Ni$): triclinic, space group $P\bar{1}$, $a = 10.3180(14)$ Å, $b = 13.0706(19)$ Å, $c = 15.399(2)$ Å, $\alpha = 114.341(15)°$, $\beta = 94.651(16)°$, $\gamma = 101.106(17)°$, $V = 1826.5(4)$ Å^3, $T = 293(2)$ K, $Z = 2$, 18612 reflns measured, 6595 unique reflns ($R_{int} = 0.0635$) were used in the refinement by full-matrix least-squares methods on F^2, $R = 0.0549$, $R_w = 0.1938$ (all data). Note the presence of a highly disordered solvent molecule, isotropically refined as O5. Crystal data for $(PPh_4)Ni(mant)_2$ ($\mathbf{4}^-$) ($C_{32}H_{24}N_4O_2PS_4Ni$): triclinic, space group $P\bar{1}$, $a = 10.1114(16)$, $b = 13.1679(17)$, $c = 14.002(2)$ Å, $\alpha = 72.019(16)$, $\beta = 70.639(17)$, $\gamma = 77.020(17)°$, $V = 1657.3(4)$ Å^3, $T = 293(2)$ K, $Z = 2$, 16291 reflns measured, 5918 unique reflns ($R_{int} = 0.1411$) were used in the refinement by full-matrix least-squares methods on F^2, $R = 0.0515$, $R_w = 0.1162$ (all data). Crystallographic data for the structure reported in this paper and in the Supporting Information have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 257976−257981. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge, CB21EZ, U.K. (Fax: (+44) 1223-336-033. E-mail: deposit@ccdc.cam.ac.uk.)

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amide.[15] In $\mathbf{3}^-$, ribbons of complexes symmetrically linked by self-complementary intermolecular ring motifs (Figure 2 and Table 1), also encountered in the crystalline structure of **2**, run along *b* and stack upon each other along *a*, connected by self-complementary, transverse, and larger ring motifs based on longer N−H···O distances.

Although, upon dithiolate generation, the same workup conditions as for the preparation of $\mathbf{2}^{2-}$ were used, the monoanionic complex is obtained directly this time. Very likely, this behavior finds its origin in the lower 2−/1− oxidation potential for the $[\mathrm{Ni(madt)_2}]^{2-}$ complex. Indeed, cyclic voltammetry experiments for $\mathrm{(PPh_4)Ni(madt)_2}$ in MeCN show a reversible wave at −0.28 V/SCE, corresponding to the couple $[\mathrm{Ni(madt)_2}]^{2-/1-}$, and an irreversible oxidation wave at +0.5 V/SCE, corresponding to the formation of $[\mathrm{Ni(madt)_2}]^0$. The lower stability of $\mathbf{3}^{2-}$ species, when compared with $\mathbf{2}^{2-}$, could be the consequence of the nonplanarity of the diamide groups, as observed in the X-ray structure of $\mathrm{(PPh_4)Ni(madt)_2}$ (vide supra), strongly hampering conjugation with the dithiole ring and hence diminishing their electron-withdrawing effects. Thus, the synthesis of such highly functionalized nickel dithiolene complexes demonstrates that the use of alkylthiolates as nonbasic nucleophiles in the ring opening of dithiolones constitutes a straightforward method for the generation of dithiolates in smooth conditions, one that could be generalized to other such functional dithiolones, sensitive to "classical" basic reagents generally used in this kind of chemistry.

We further report here our discovery that reflux of complex $\mathbf{3}^-$ in methanol affords the bis-dehydrated complex $\mathrm{(PPh_4)}$-[Ni(mant)] $\mathbf{4}^-$, where mant = maleamido-nitrilo-dithiolate (Scheme 2). This reaction was all the more unexpected in that water elimination from 1,2-diamides typically requires such drastic conditions as reflux in acetic anhydride for the preparation of *ortho*-cyanobenzamide from phthalamide.[16] Here, the reaction occurs smoothly, probably because the electron-rich character of the present diamide favors a protonation of a carbonyl oxygen followed by water elimination. Note that, in addition to its inherent hydrogen-bond donor/acceptor character, complex $\mathbf{4}^-$ also contains two trans cyano groups, capable of engaging in coordination with other metallic centers. $\mathrm{(PPh_4)[Ni(mant)_2]}$ crystallized in the triclinic system, space group $P\bar{1}$, with two independent half-complexes located on inversion centers and one independent cation in a general position.[10] Here, again, the recurrent, robust self-complementary ring motif (Table 1) links the symmetrically functionalized complexes into ribbons running along *b* and connected along *a* by self-complementary, larger ring motifs based on very short (2.235 Å for H···O) N−H···O bonds (Figure 3). The cyano groups protrude out of the dithiolene slab and are engaged in weaker hydrogen bonds with phenyl protons of the cations.

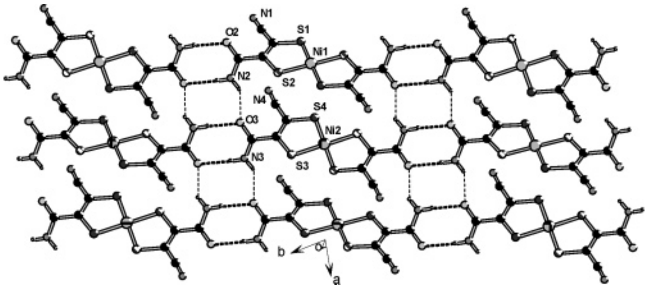

Figure 3. Fragment of the slab of complexes in $\mathrm{(PPh_4)Ni(mant)_2}$, emphasizing the two self-complementary ring motifs. Selected bond lengths (Å) and angles (deg): Ni1−S1 2.139(2), Ni1−S2 2.146(2), Ni2−S3 2.140(2), Ni2−S4 2.147(2); S1−Ni1−S2 92.08(7), S3−Ni2−S4 92.01(7).

Cyclic voltammetry experiments for $\mathrm{(PPh_4)[Ni(mant)_2]}$ in MeCN reveal a reversible wave at −0.1 V/SCE corresponding to the couple $[\mathrm{Ni(mant)_2}]^{2-/1-}$, and an irreversible oxidation wave at +0.67 V/SCE, corresponding to the formation of $[\mathrm{Ni(mant)_2}]^0$. Thus, electrocrystallization of $(n\text{-}\mathrm{Bu_4N})_2[\mathrm{Ni(mant)_2}]$ ($\mathbf{4}^{2-}$) is performed through the reduction of $(n\text{-}\mathrm{Bu_4N})[\mathrm{Ni(mant)_2}]$ ($\mathbf{4}^-$) (Supporting Information). Note that the same self-complementary ring motifs link the dianionic forms $\mathbf{4}^{2-}$ into discrete 1D ribbons isolated from each other by the cations.

In summary, we have reported the synthesis of a series of three nickel dithiolene complexes appended with hydrogen-bond donor/acceptor functionalities. One very attractive feature of complexes $[\mathrm{Ni(midt)_2}]^{2-/1-}$ and $[\mathrm{Ni(mant)_2}]^{2-/1-}$, distinctive from any other metal dithiolene complexes, is that they contain outer NH and CN groups, respectively, for coordination reactions to additional metal complexes to prepare extended networks by a building block approach. All of the complexes described herein show extended networks based on self-complementary, hydrogen-bonded ring motifs that direct their supramolecular organization in the solid state. Of particular note is the introduction, disclosed here, of NaSMe as a new nonbasic dithiocarbonate ring-opening reagent. Use of this reagent in other areas such as highly functionalized tetrathiafulvalenes can be envisioned with great prospect. The extension of the chemistry of these three new dithiolene ligands to other metal centers is also under way.

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Supporting Information Available: Experimental details for syntheses and X-ray structures in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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