Syntheses, X-ray Crystal Structures, and Spectroscopic Properties of New Nickel Dithiolenes and Related Compounds

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The direct addition of nickel powder to the reaction mixtures of 1,3-dialkyl-4,5-dioxoimidazolidine-2-thione (**1**) with the thionation Lawesson reagent produces [$Ni^{II}(R_2timdt^-)_2$] (R_2timdt = 1,3-dialkylimidazolidine-2,4,5-trithione). These complexes belong to a new class of nickel−dithiolenes, showing remarkably high absorption ($\epsilon \approx 80\,000$ $dm^3\ mol^{-1}\ cm^{-1}$, $\lambda \approx 1000$ nm) in the near-infrared region (near-IR), accompanied by high photochemical stability that makes these complexes promising near-IR dyes. In the absence of nickel the reaction yields generally the compounds 4,5,6,7-tetrathiocino[1,2-*b*:3,4-*b*′]diimidazolyl-1,3,8,10-tetraalkane-2,9-dithione (**2**) instead of the expected 1,3-dialkylimidazolidine-2,4,5-trithione. However, with bulky substituents on the nitrogen atoms, well-characterized reaction products have not been obtained until now. Only in the R = Pr^i case, the new tetrathiocino isomer (4,5,9,10-tetrathiocino[1,2-*b*:5,6-*b*′]diimidazolyl-1,3,6,8-tetraisopropane-2,7-dithione (**3**) in trace amounts and the bis(1,3-diisopropyl-2-thioxoimidazolin-4-yl) disulfide (**4**) were isolated from the reaction with the Lawesson reagent and P_4S_{10}, respectively. Reaction of **5** with different amounts of I_2 leads to a variety of products, and among them the following derivatives have been characterized: [$Ni^{II}(Pr^i_2timdt^-)_2$]·$2I_2$ (**6**) a neutral adduct in which each I_2 molecule interacts with each peripheral thione sulfur atom of **5**; [$Ni^{II}(Pr^i_2timdt^-)_2$]·$2I_2$·$^1/_2I_2$ (**7**), which differs from **6** with the presence of half diiodine as a guest; with a larger diiodine excess (starting from a 1:10 molar ratio) a partial oxidation of **5** is achieved and [$Ni^{II}(Pr^i_2timdt^-)_2$] [$Ni^{II}(I)_2(Pr^i_2timdt)_2$]·$5I_2$ (**8**) is formed, a ligand mixed-valence compound in which the square-planar complex **5** and the octahedral complex [$Ni^{II}(I)_2(Pr^i_2timdt)_2$] (the ligand in neutral form) are bound by diiodine molecules in such a way that a sequence of 12 iodine atoms ($S·I_2···I_2···I^-···I_2···I^-···I_2···I_2·S$) is formed. Spectroscopic and X-ray diffractometric studies of **3** (monoclinic, space group $P2_1/n$, $a = 13.104(6)$ Å, $b = 15.091(6)$ Å, $c = 6.067(7)$ Å, $\beta = 103.00(2)°$, $Z = 2$), **4** (monoclinic, space group $C2/c$, $a = 18.717(5)$ Å, $b = 8.846(5)$ Å, $c = 14.475(5)$ Å, $\beta = 97.78(2)°$, $Z = 4$), **5** (orthorhombic, space group $Pna2_1$, $a = 18.806(5)$ Å, $b = 5.628(7)$ Å, $c = 23.665(5)$ Å, $Z = 4$), **7** (triclinic, space group $P\bar{1}$, $a = 9.126(7)$ Å, $b = 9.153(7)$ Å, $c = 12.924(6)$ Å, $\alpha = 82.11(2)$, $\beta = 70.14(2)$, $\gamma = 72.51(2)°$, $Z = 1$), and **8** (monoclinic, space group $C2/c$, $a = 21.971(6)$ Å, $b = 28.081(5)$ Å, $c = 12.207(8)$ Å, $\beta = 93.57(2)°$, $Z = 4$) are given.

Introduction

Nickel−dithiolenes represent a class of compounds which show important and peculiar properties such as the very intense electronic transition in the near-IR,[1] the capability to exist in different well-defined oxidation states connected through reversible processes,[2] and in some instances electrical conductivity.[3] These square-planar complexes exhibit a high degree of electron delocalization in the ring, including the metal ("aromaticity"), which is responsible for the low-energy electronic absorption assigned to a $\pi \rightarrow \pi^*$ transition between the HOMO and the LUMO, which occurs at unusually low energy. The proper substitution of R = H in the parent neutral nickel−dithiolene [$Ni^{II}(C_2H_2S_2^-)_2$], which has an electronic absorption maximum

at 720 nm ($\epsilon = 14\,000$ $dm^3\ mol^{-1}\ cm^{-1}$), produces a shift to lower frequency. These studies extensively performed by the Mueller−Westerhoff group,[1] with a view to prepare near-IR dyes, have shown that donor substituents raise the energy of the HOMO more than the LUMO and consequent shifts of the low-energy absorption to lower frequencies occur. Donor substituents fixed in coplanarity with the dithiolene ring gave the best results in achieving low-frequency shifts and an increase in the extinction coefficients.

We have recently published the synthesis and characterization of a new class of dithiolenes, [$Ni^{II}(R_2timdt^-)_2$] (R_2timdt = 1,3-dialkylimidazolidine-2,4,5-trithione).[4] In these complexes, obtaining the coplanarity of the ring structure containing the electron-donor substituents with the dithiolene moiety allowed us to obtain materials showing the near-IR absorption at approximately 1000 nm (near the emission frequency of neodymium lasers) with a remarkably high extinction coefficient ($\epsilon \approx 80\,000$ $dm^3\ mol^{-1}\ cm^{-1}$, to our knowledge the highest

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value ever achieved in similar near-IR dithiolene dyes). These interesting properties prompted us to improve the method of their synthesis and to investigate their chemical behavior.

In this paper we describe the results obtained starting from the 1,3-diisopropyl-4,5-dioxoimidazolidine-2-thione (**1**), and in particular the improved synthesis of [Ni^{II}(Pr^i_2timdt$^-$)$_2$] (**5**), the characterization of the products obtained by reaction of **5** with I$_2$: the neutral addition complexes [Ni^{II}(Pr^i_2timdt$^-$)$_2$]·2I$_2$ (**6**), [Ni^{II}(Pr^i_2timdt$^-$)$_2$]·2I$_2$·^{1}/$_2$I$_2$ (**7**), and the ligand mixed-valence compound [Ni^{II}(Pr^i_2timdt$^-$)$_2$]·[Ni^{II}(I)$_2$(Pr^i_2timdt)$_2$]·5I$_2$ (**8**). Moreover the isolation and characterization of the sulfurization products of **1** 4,5,9,10-tetrathiocino[1,2-*b*:5,6-*b′*]diimidazolyl-1,3,6,8-tetraisopropane-2,7-dithione (**3**) and bis(1,3-diisopropyl-2-thioxoimidazolin-4-yl) disulfide (**4**), obtained by the Lawesson reagent and P$_4$S$_{10}$, respectively, are reported.

Results and Discussion

With the aim of synthesizing [Ni^{II}(R$_2$timdt$^-$)$_2$], we attempted to apply the well-established method to prepare the ligand by reduction of the proper vicinal dithione.[1] However, the sulfurization of **1** did not produce the expected 1,3-dialkylimidazolidine-2,4,5-trithione following a procedure used to prepare dithiooxamides. The isolated products were, generally, the structurally characterized tetrathiocino derivatives **2**.[5] With bulky substituents on the nitrogen atoms (R = Pr^i, and similars), compound **2** was not obtained. After many attempts and in trace amounts for R = Pr^i an orange-red solid **3** having elemental analysis in accordance with **2**, but showing different spectral and solubility features, was isolated from the reaction mixture using the Lawesson reagent as sulfurization reagent.[6] Structural characterization (*vide infra*) demonstrated that **3** is 4,5,9,10-tetrathiocino[1,2-*b*:5,6-*b′*]diimidazolyl-1,3,6,8-tetraisopropane-2,7-dithione, an isomer of **2**. By sulfurization of **1** with P$_4$S$_{10}$, a different pale-orange solid **4**, characterized as bis-(1,3-diisopropyl-2-thioxoimidazolin-4-yl) disulfide, was isolated. The reason why five-membered cyclic dithiooxamides cannot be obtained, while six-membered cyclic dithiooxamides are prepared by this way,[7] is not well-understood. The only well-characterized five-membered rings containing a dithiooxamide group are 1,1-dimethyl-2,5-bis(chlorodimethylsilyl)-1-sila-2,5-diazacyclopentane-3,4-dithione and similar compounds.[8] Since vicinal dithiones can exist in an equilibrium mixture of the dithiacyclobutene isomers with the vicinal dithione form, the different behavior of the six- and five-membered rings could be due to an increased reactivity of the dithiacyclobutene isomer in the five-membered case (see intermediates **I** in Scheme 1).

To avoid the isolation of dithione intermediate (**I**), NiCl$_2$·6H$_2$O was added to the reaction mixture and [Ni^{II}(Pr^i_2timdt$^-$)$_2$] (**5**) was obtained in low yields as recently reported by us.[4] Since these products are presumably formed through the reduction of intermediate **I**, we have added to the reaction mixture Ni powder, and the yields substantially improved from approximately 10 to 40%.

Compound **5** is an analog of [Ni^{II}(dmit$^-$)$_2$] (dmit = C$_3$S$_5$).[9] While **5** is an electrical insulator, the dmit complexes and their Se-counterparts in which endo- and/or exocyclic sulfur have

been substituted by selenium atoms[10] are now extensively investigated for their conductive and superconductive properties,[11] for which overlap of partially filled delocalized π-orbitals between adjacent molecules is required. The planarity of the dmit ligand has not been modified in Pr$^i_2$timdt (see Structural Characterization), but the presence of bulky Pr^i groups, which are important for increasing the solubility of the complexes, prevent the formation of stacks with short S···S intermolecular contacts. Therefore these complexes with bulky substituents are promising as near-IR dyes but not suitable for producing molecular electrical conductors.[3] Compound **5** was reacted with diiodine in different molar ratios, producing [Ni^{II}(Pr^i_2timdt$^-$)$_2$]·2I$_2$ (**6**) and [Ni^{II}(Pr^i_2timdt$^-$)$_2$]·2I$_2$·^{1}/$_2$I$_2$ (**7**) (in both two I$_2$ molecules interact with each of the peripheral sulfur atoms of the ligands; in **7** the remaining diiodine is present as a guest) and [Ni^{II}(Pr^i_2timdt$^-$)$_2$][Ni^{II}(I)$_2$(Pr^i_2timdt)$_2$]·5I$_2$ (**8**), consisting of a ligand mixed-valence compound formed by **5** and by the complex [Ni^{II}(I)$_2$(Pr^i_2timdt)$_2$], where the Ni(II) is octahedrally coordinated with two iodides at the apices, and with the two chelating ligands in the neutral form as shown by its structural features, connected with **5** through diiodine molecules. The ligand in the neutral form represents a well-documented example of cyclic pentaatomic dithiooxamide. Compound **8** is an insulator (2.30 × 10^{-8} Ω^{-1} cm^{-1} at liquid N$_2$ with some slight conductivity at room temperature).

The synthetic procedures used to prepare the products discussed here are summarized in Scheme 1.

Structural Characterization

Structural data for compounds **3**–**5**, **7**, and **8** are reported in Table 1. Selected bond lengths, intermolecular contacts, and angles are reported in Table 2.

Compound 3: C$_{18}$H$_{28}$N$_4$S$_6$. The molecular structure together with the atomic labeling scheme is shown in Figure 1. The imidazoline ring of this centrosymmetric molecule is planar, and its substituents lie out of the corresponding plane with a maximum deviation of −0.068(3) Å for S(3). The Pr^i groups, one of which results disordered (see Experimental Section), are perpendicular to the imidazoline ring, as indicated by the values of the dihedral angle between the corresponding weighted least-squares planes [88(3) and 92(1)°, respectively for the two images of the disordered group, and 93.3(7)° for the other]. The oxidation of the ligand molecule, which gives the dimer, causes a remarkable lengthening of two C−S bonds, while the intermolecular contact S(1)···S(2) (^{1}/$_2$ + x, ^{1}/$_2$ − y, ^{1}/$_2$ + z) 3.589(6) Å, which is the most important for the packing, causes only a little lengthening of the peripheral C−S bond. The structural data of the imidazoline rings indicate the formation of a six-π-electron aromatic system. The value of 2.097(5) Å for the S−S bond distance falls within the range observed in similar compounds.[12] Compound **3** is the structural analog of C$_6$S$_{10}$,[12] where instead of the two planar imidazoline rings are present two planar C$_3$S$_3$ groups similarly interconnected by two persulfide bonds. The eight-membered ring shows a chair conformation (see Figure 1) as indicated by the torsion angles [S−S−C−C, −82(1) and 79(1)°; C−S−S−C, 101.8(6)°]. The

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Scheme 1

R = Pr^i

P$_4$S$_{10}$, R = Pr^i
Tol., 30 min reflux

Lawesson's Reagent

Tol., 15 min reflux

2 **3** **4** **1**

I

Ni

(1:2)

R = Pr^i (1:5)

(1:20)

6

5 + I$_2$ → **6 · 1/2 I$_2$** **7**

8
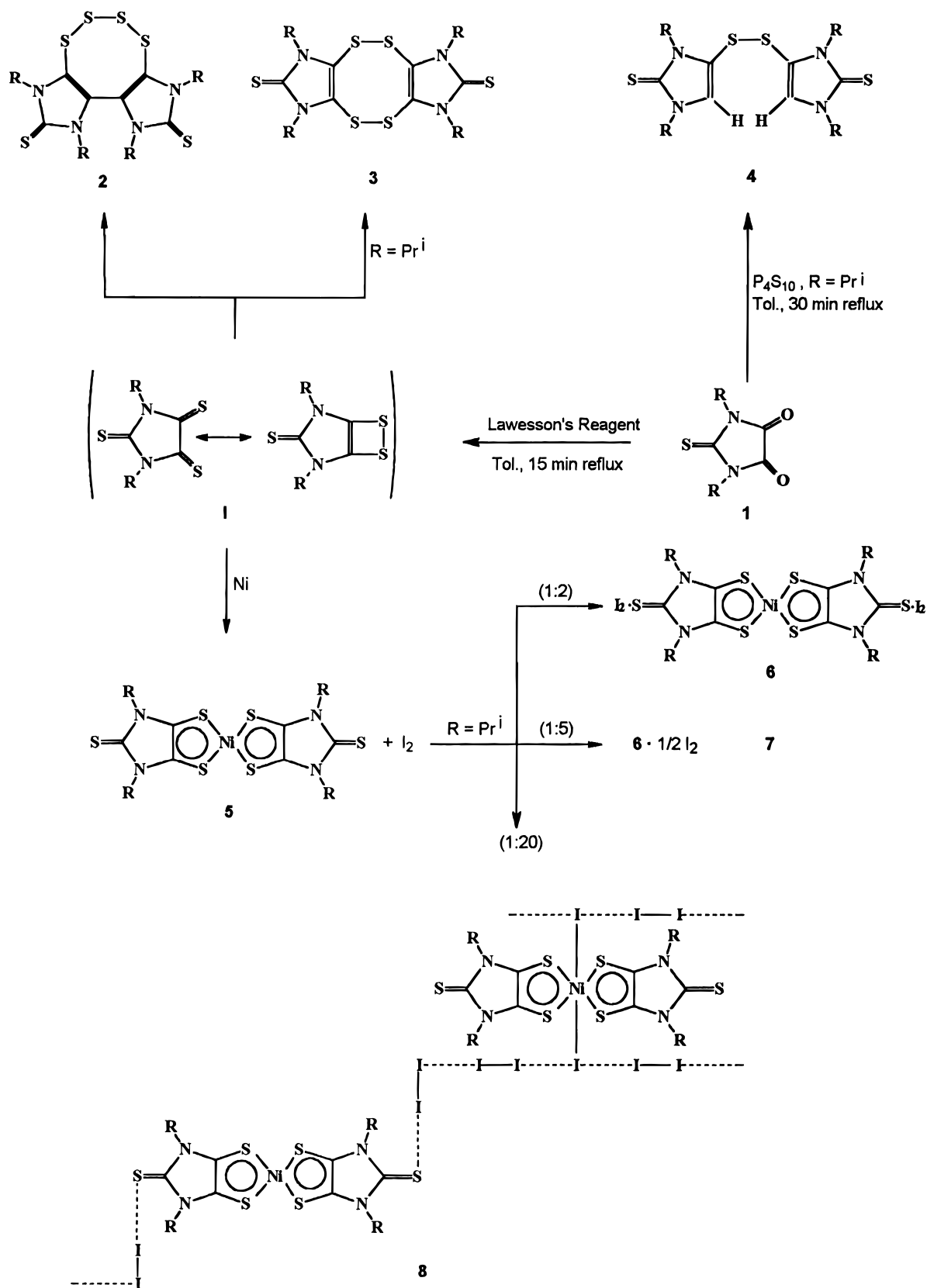
dihedral angle between the mean least-squares planes containing S(3), S(3^i), C(3), C(3^i) and C(2), S(2), S(3^i), respectively, is 89.5(4)°. The correlation between the S−S bond distance and the values of the S−S−C−C torsion angles, and the value of 101.9(4)° for the C−S−S angle are similar to those observed in the 4,5,6,7-tetrathiocino[1,2-*b*;3,4-*b'*]diimidazolyl-1,3,8,10-tetrasubstituted-2,9-dithiones, synthesized by some of us,[5] in

its adduct with diiodine,[13] and in its complexes with Cd(II), Cu(II), and Cu(I).[14] The other contacts determining the packing are of the type S···^{i}C, ^{i}C···^{i}C.

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Table 1. Crystallographic Data of Compounds **3−5**, **7**,and **8**

	3	**4**	**5**	**7**	**8**
formula	$C_{18}H_{28}N_4S_6$	$C_{18}H_{30}N_4S_4$	$C_{18}H_{28}N_4NiS_6$	$C_{18}H_{28}I_{4.5}N_4NiS_6$	$C_{36}H_{56}I_{12}N_8Ni_2S_{12}$
fw	492.81	430.70	551.52	1122.59	2625.89
cryst syst	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic
space group	$P2_1/n$	$C2/c$	$Pna2_1$	$P\bar{1}$	$C2/c$
a/Å	13.104(6)	18.717(5)	18.806(5)	9.126(7)	21.971(6)
b/Å	15.091(6)	8.846(6)	5.628(7)	9.153(7)	28.081(5)
c/Å	6.067(7)	14.475(5)	23.665(5)	12.924(6)	12.207(8)
α/deg				82.11(2)	
β/deg	103.00(2)	97.78(2)		70.14(2)	93.57(2)
γ/deg				72.51(2)	
V/Å³	1169(2)	2375(2)	2505(3)	967.7(1.2)	7517(6)
Z	2	4	4	1	4
D_c/Mg m⁻³	1.400	1.205	1.463	1.926	2.320
wavelength	Cu Kα (λ = 1.541 838 Å)	Cu Kα (λ = 1.541 838 Å)	Cu Kα (λ = 1.541 838 Å)	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
temp/K	295	295	295	295	295
μ/cm⁻¹	55.00	37.41	58.94	44.28	57.95
θ-range for intens collcn/deg	3−70	3−70	3−70	3−27	3−24
no. of measd reflcns	2529	2348	2429	3749	6188
no. of reflcns with $I > 2\sigma(I)$	709	1578	1448	1591	2798
no. of refined params	107	119	202	162	208
min/max height in final $\Delta\rho$ map/(c Å⁻³)	−0.33/0.37	−0.24/0.19	−0.40/0.51	−1.25/1.54	−0.92/1.21
largest shift/esd	0.53	0.48	0.26	0.36	0.45
$R = \sum|\Delta F|/\sum|F_o|$	0.0660	0.0472	0.0463	0.0732	0.0356
$R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$	0.0639	0.0646	0.0621	0.0748	0.0450

Compound 4: $C_{18}H_{30}N_4S_4$. In the molecule (Figure 2) the two moieties are related by a crystallographic 2-fold axis. The imidazoline ring is not exactly planar (maximum deviation, −0.009(3) Å for C(1)). The two isopropyl substituents lie quite perpendicular to the ring: the dihedral angles between the corresponding weighted least-squares planes are 95.5(2) and 91.1(1)°, respectively. The C(2) atom is synclinal with respect to C(2ⁱⁱⁱ) [C(2)−S(2)−S(2ⁱⁱⁱ)−C(2ⁱⁱⁱ) 76.2(1)°]. The value of the S−S bond distance is similar to that found in **3**. The hydrogen bond S(1)···H(1)−C(2) (x, 1 − y, $^1/_2$ + z) [S···C, 3.653(3) Å; S···H, 2.77 Å; S···H−C, 153°] is important in forming polymeric chains in the c direction. The chains are bound together by interactions of the type S···C and C···C.

Compound 5: $C_{18}H_{28}N_4NiS_6$. The packing, which is determined by weak contacts of the type S···ⁱC and ⁱC···ⁱC, shows the presence of a pseudo-glide plane in the c direction, and this is shown with the atomic labeling scheme in Figure 3. The square-planar coordination around the metal atom involves two vicinal sulfur atoms from each of the two independent chelating molecules. The complex molecule shows a pseudo-symmetry center and results in a roughly planar configuration if the S(12) atom and the Prⁱ groups are excluded. The dihedral angle between the least-squares planes of the two planar moieties
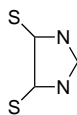
is 1.3(1)°.

The Prⁱ groups are perpendicular to the imidazoline rings, the dihedral angle between the corresponding mean-weighted least-squares planes ranging from 87.1(7) to 92.3(5)°. The maximum deviation from the mean weighted least-squares plane containing all of the atoms involved in the coordination is 0.010(4) Å for S(21) and S(22). The Ni−S bond lengths are exactly similar, and the structural data of the two

ligand molecules are similar to those observed in compound **3**, if the smaller lengthening of the C−S bond is excluded. The Ni−S−C angles range from 99.7(7) to 101.9(4)°.

Compound 7: $C_{18}H_{28}I_5N_4NiS_6$. The crystal used gave analytical results in accordance with this formulation; however, during the data collection the sample showed a systematic decay and lost diiodine, and thus, the structure has been poorly resolved in accordance with $C_{18}H_{28}I_{4.5}N_4NiS_6$. In the molecule of the adduct (Figure 4) the metal lies on a symmetry center and is coordinated by the two vicinal sulfur atoms of the chelating ligand in a square-planar geometry as observed in **5**, with the isopropyl groups almost perpendicular to the plane of the complex. The two diiodine molecules are perpendicular to the imidazoline ring. The S−I and I−I bond distances are correlated as generally found (S−I *versus* I−I distances fitting a hyperbole).[15] The packing is determined by the interaction I(1)···I(1) (2 − x, −y, −z) 4.090(3) Å, forming chains, which are held together by interactions of the type S···S, S···C, C···C. The interactions of the guest diiodine molecules are of the type I···I, I···S, I···C.

Compound 8: $C_{18}H_{28}I_6N_4NiS_6$. Compound **8** consists of two types of complexes: [Niⁱⁱ(Prⁱ₂timdt⁻)₂] interacting through the exocyclic sulfur atoms with two I₂ and showing structural features approximately the same as those in **7**, and [Niⁱⁱ(I)₂(Prⁱ₂-timdt)₂] interacting through the iodides with the remaining I₂. In both complexes the metal atom lies on a 2-fold axis. The [Niⁱⁱ(I)₂(Prⁱ₂timdt)₂] moiety is shown in Figure 5. In this last complex the metal atom coordination is octahedral and involves two chelating molecules of the ligand Prⁱ₂timdt and two iodide ions at the apices. The π-electron distribution in the ligand Prⁱ₂timdt is different from that in the monoanion Prⁱ₂timdt⁻ since the C−C bond in the ring shows a greater single-bond character and the C−S bond lengths indicate a greater double-bond character. Moreover, the Ni−S distances are about 0.20 Å longer than those in the first complex. These features indicate that the ligand is in the neutral form. The remarkable interactions of the coordinated iodides with the two adjacent diiodine molecules (Figure 6) [I(2)···I(1), 3.389(2) Å; I(2)···I(3), 3.217-(2) Å] could be also envisaged as producing roughly planar I₈²⁻

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Table 2. Selected Bond Lengths, Intermolecular Contacts (Å), and Angles (deg) with Esd's in Parentheses for Compounds **3−5**, **7**, and **8**[a]

(a) In Compound 3

S(2)−S(3^i)	2.097(5)	N(1)−C(3)	1.38(2)
S(1)−C(1)	1.67(1)	N(2)−C(1)	1.32(2)
S(2)−C(2)	1.74(1)	N(2)−C(2)	1.40(2)
S(3)−C(3)	1.76(1)	C(2)−C(3)	1.36(2)
N(1)−C(1)	1.37(1)		

C(2)−S(2)−S(3^i)	101.9(4)	S(2)−C(2)−N(2)	126.0(1.0)
C(3)−S(3)−S(2^i)	101.9(4)	N(2)−C(2)−C(3)	105.1(1.0)
C(1)−N(1)−C(3)	110.5(1.0)	S(2)−C(2)−C(3)	128.9(1.1)
C(1)−N(2)−C(2)	111.7(1.2)	N(1)−C(3)−C(2)	108.3(1.2)
N(1)−C(1)−N(2)	104.4(1.0)	S(3)−C(3)−N(1)	127.3(9)
S(1)−C(1)−N(2)	127.7(1.2)	S(3)−C(3)−C(2)	124.4(9)
S(1)−C(1)−N(1)	127.9(9)		

(b) In Compound 4

S(1)−C(1)	1.677(3)	N(1)−C(3)	1.372(3)
S(2)−C(2)	1.727(3)	N(2)−C(1)	1.364(4)
S(2)−S(2^{iii})	2.096(1)	N(2)−C(2)	1.408(3)
N(1)−C(1)	1.375(3)	C(2)−C(3)	1.348(4)

C(2)−S(2)−S(2^{iii})	104.8(1)	S(1)−C(1)−N(1)	125.1(2)
C(1)−N(1)−C(3)	109.8(2)	S(2)−C(2)−N(2)	126.9(2)
C(1)−N(2)−C(2)	109.1(2)	N(2)−C(2)−C(3)	106.9(2)
N(1)−C(1)−N(2)	106.0(2)	S(2)−C(2)−C(3)	125.9(2)
S(1)−C(1)−N(2)	129.0(2)	N(1)−C(3)−C(2)	108.2(2)

(c) In the Ligand or in The Corresponding Adduct

	compound 5		compound 7	compound 8	
	molecule 1	molecule 2		molecule 1	molecule 2
I−I			2.815(3)	2.790(2)	
I−S			2.825(6)	2.850(3)	
S(1)−C(1)	1.65(1)	1.65(1)	1.68(2)	1.68(1)	1.63(1)
S(2)−C(2)	1.70(1)	1.69(1)	1.71(2)	1.68(1)	1.65(1)
S(3)−C(3)	1.70(1)	1.69(1)	1.69(2)	1.68(1)	1.65(1)
N(1)−C(1)	1.38(1)	1.40(2)	1.34(3)	1.37(1)	1.39(1)
N(1)−C(3)	1.38(1)	1.37(2)	1.44(2)	1.38(1)	1.35(1)
N(2)−C(1)	1.40(1)	1.37(2)	1.42(3)	1.37(1)	1.38(1)
N(2)−C(2)	1.35(2)	1.40(2)	1.36(2)	1.40(1)	1.36(1)
C(2)−C(3)	1.38(1)	1.39(1)	1.33(4)	1.38(1)	1.49(1)
C(1)−S−I			97.4(8)	90.2(4)	
S−I−I			177.5(2)	178.75(8)	

(d) For Coordination in Compound 5

Ni−S(21)	2.161(4)	S(21)−Ni−S(31)	94.1(1)
Ni−S(31)	2.158(4)	S(22)−Ni−S(32)	93.8(1)
Ni−S(22)	2.159(4)	S(21)−Ni−S(32)	86.2(1)
Ni−S(32)	2.156(4)	S(31)−Ni−S(22)	85.9(1)

(e) For Coordination in Compound 7

Ni−S(2)	2.166(7)	S(2)−Ni−S(3)	94.5(2)
Ni−S(3)	2.159(7)	S(3)−Ni−S(2^i)	85.5(2)

(f) For Coordination in Compound 8

Ni(1)−S(21)	2.169(3)	I(2)−Ni(2)−S(22)	90.09(9)
Ni(1)−S(31)	2.165(3)	I(2)−Ni(2)−S(32)	91.15(8)
Ni(2)−S(22)	2.365(3)	I(2)−Ni(2)−S(32^{iv})	87.78(8)
Ni(2)−S(32)	2.377(3)	I(2)−Ni(2)−S(22^{iv})	91.00(9)
Ni(2)−I(2)	2.840(1)	I(2)−Ni(2)−I(2^{iv})	178.46(3)
S(21)−Ni(1)−S(31)	94.6(1)	S(22)−Ni(2)−S(32)	89.3(1)
S(21)−Ni(1)−S(21^{iii})	85.7(1)	S(22)−Ni(2)−S(22^{iv})	89.3(1)
S(31)−Ni(1)−S(31^{iii})	85.2(1)	S(32)−Ni(2)−S(32$^{(iv)}$)	92.1(1)

(g) Involving the Other Halogen Atoms in Compound 8

I(1)−I(1^{ii})	2.783(2)	I(2)−I(1)−I(1^{ii})	174.40(5)
I(3)−I(4)	2.786(2)	I(1)−I(2)−I(3)	153.03(4)
I(1)−I(2)	3.389(2)	I(2)−I(3)−I(4)	175.75(5)
I(2)−I(3)	3.217(2)	I(3)−I(4)−I(6^v)	176.24(4)
I(4)−I(6^v)	3.671(2)	I(4)−I(6^v)−I(5^v)	86.56(4)

[a] Symmetry code: (i) $-x$, $1 - y$, $1 - z$; (ii) $1 - x$, y, $-z - \frac{1}{2}$; (iii) $-x$, y, $\frac{1}{2} - z$; (iv) $1 - x$, y, $\frac{1}{2} - z$; (v) x, y, $1 + z$.

units with the sequence I(4)−I(3)···I(2)···I(1)−I(1^{ii})···I(2^{ii})··· I(3^{ii})−I(4^{ii}) (ii indicates position $1 - x$, y, $-z - \frac{1}{2}$) and, as a consequence, polymeric chains of octahedral complexes running parallel to [001]. These I$_8^{2-}$ units connect the adducts (**5·2I₂**),

which show a Z-shape in the projection along [010], when the Pr^i groups are excluded, through the interaction I(4)···I(6^v) 3.671(2) Å (v indicates position x, y, $1 + z$), thus determining a sequence of twelve iodine atoms: S·I$_2$···I$_2$···I$^-$···I$_2$···I$^-$···
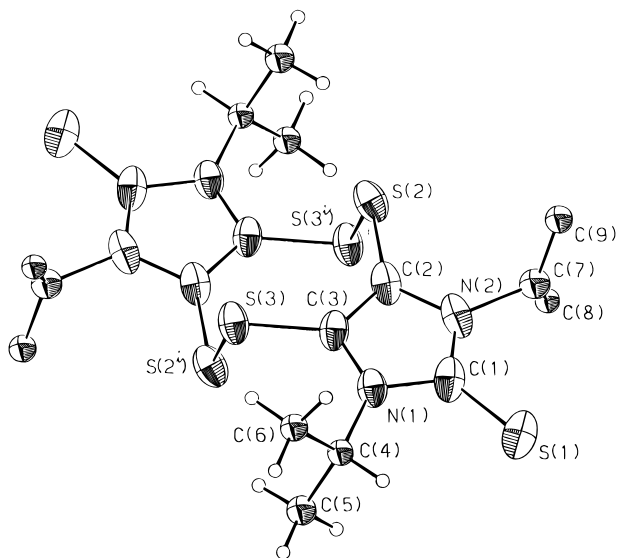
Figure 1. Perspective view of the molecule of **3**. Thermal ellipsoids are drawn at the 30% probability level.

Figure 3. Projection of the structure of [Ni^{II}(Pr$^i_2$timdt$^-$)$_2$] (**5**) along [010].

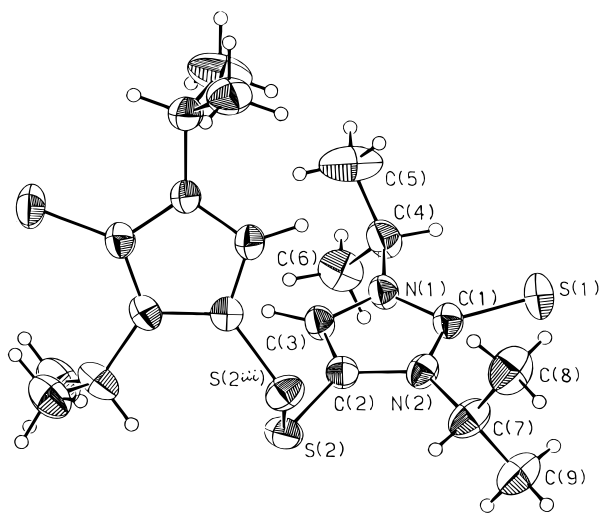**Figure 2.** Perspective view of the molecule of **4**. Thermal ellipsoids are drawn at the 30% probability level.

I$_2$···I$_2$·S. It is noteworthy that the bond lengths in all the diodine molecules are very similar and fall in the 2.783-2.790(2) Å range.

The other long contacts determining the packing are of the type I···S, I···C$_{ring}$ [minimum value, 3.60(1) Å], I···^{i}C, S···S, S···^{i}C, and ^{i}C···^{i}C.

Electrochemistry

The cyclic voltammogram of **5** in CH$_2$Cl$_2$ is reported in Figure 7. Compound **5** is reduced in two reversible one electron reduction steps to the mono- (**5**$^-$) and dinegative (**5**$^{2-}$) species, respectively (half-wave redox potentials are $E_{1/2}^1 = -0.12$ V and $E_{1/2}^2 = -0.60$ V, some irreversibility is noted as the scan rate is increased above 100 mV s^{-1}). The cyclic voltammogram shows also one irreversible oxidation at potential $E_{pc}^3 = +0.78$ V. Taking into account the structure of **8**, it is reasonable to assign this process to the oxidation of the ligand. Recently a similar irreversible wave at more positive potential than +0.80 V has been observed for the [Ni(dddt)$_2$] species (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate),[16] and unusual cationic nickel
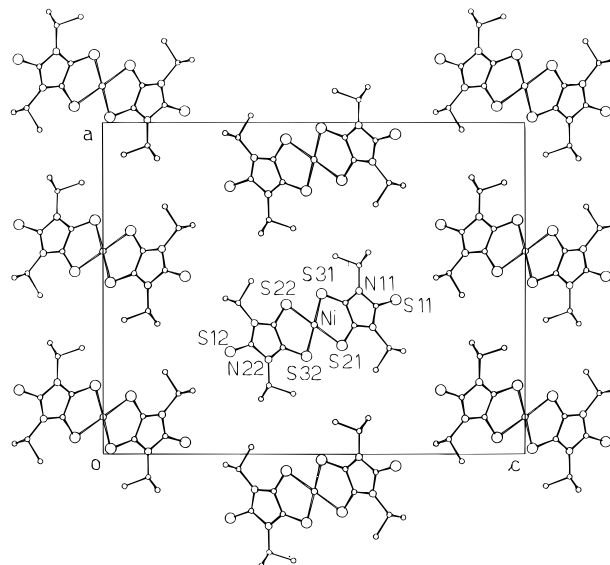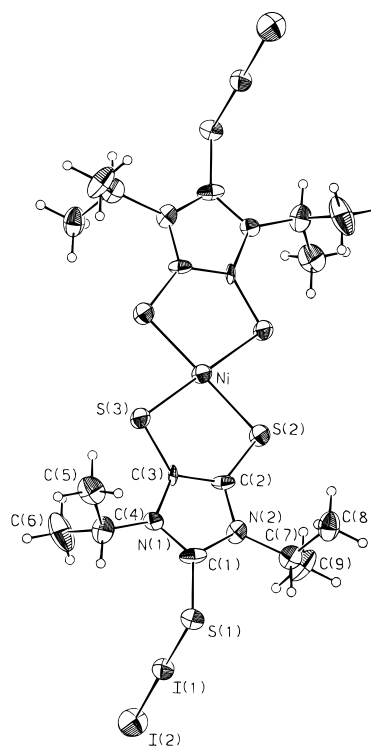

Figure 4. Perspective view of the molecule [Ni^{II}(Pr$^i_2$timdt$^-$)$_2$]·2I$_2$ in **7** (the guest I$_2$ appears in the projection of the structure). Thermal ellipsoids are drawn at the 30% probability level.

dithiolene complexes have been synthesized.[17] No oxidation over the neutral state has been observed for the structurally analogous [Ni(dmit)$_2$]$^-$ complex, which shows an irreversible oxidation to the neutral species at potential +0.22 V.[18]

Vibrational Spectroscopy

FT-IR and Raman spectra of compounds **5**−**8** are reported in the Experimental Section. The main feature of Raman spectra

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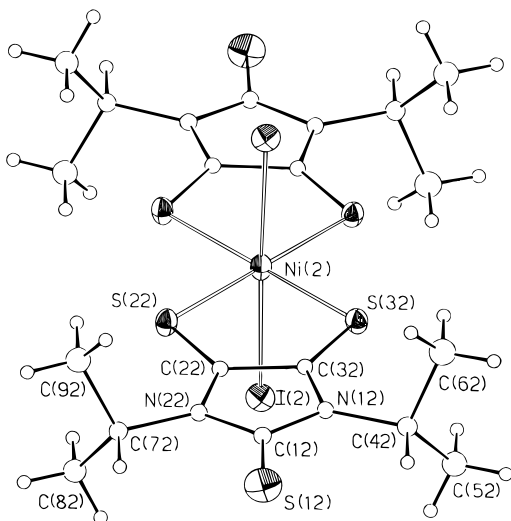(18) Kato, R.; Kobayashi, H.; Kobayashi, A.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 627.

Figure 5. Perspective view of the molecule of the octahedral complex [Ni(I)$_2$(Pr$^i_2$timdt)$_2$] of **8**. Thermal ellipsoids are drawn at the 30% probability level.

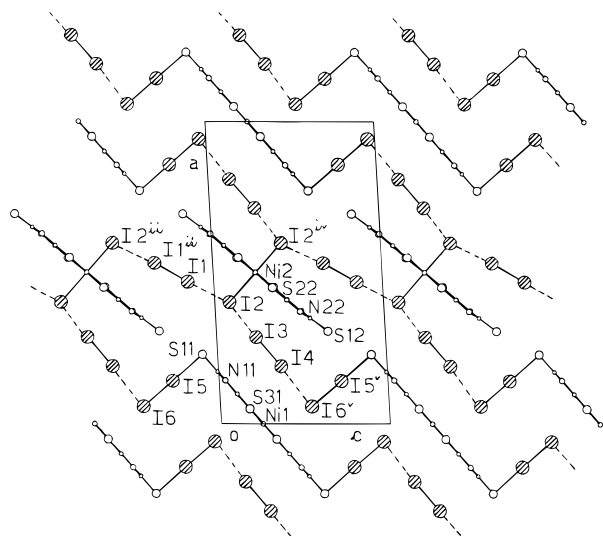**Figure 6.** Projection of the structure of [Ni^{II}(Pr$^i_2$timdt$^-$)$_2$][Ni(I)$_2$-(Pr$^i_2$timdt)$_2$]·5I$_2$ (**8**) along [010]. The Pr^i groups have been omitted for clarity.
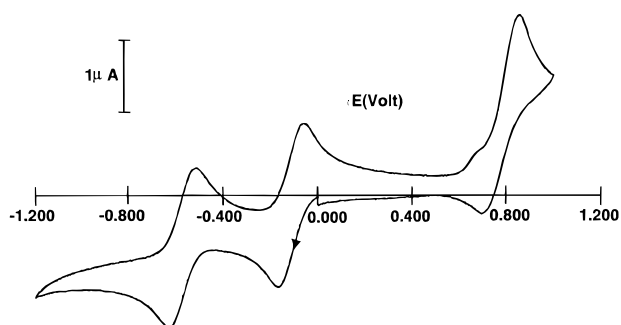
Figure 7. Cyclic voltammetric response recorded at a platinum electrode on a CH$_2$Cl$_2$ solution of **5** (1 × 10^{-3} mol dm^{-3}): TBAFA supporting electrolyte (1 × 10^{-1} mol dm^{-3}); scan rate, 100 mV s^{-1}.

is the presence of a very strong peak at 346−348 cm^{-1} which dominates the other peaks so strongly that even the peaks related to the interiodine vibrations (otherwise strong) in **6**−**8** appear as weak or medium intensity peaks. Since the samples strongly absorb at the wavelength of the excitation source (Nd:YAG laser), the very strong peak observed is probably enhanced by resonance effects. Resonance Raman spectra of square-planar

bis(tetraalkylammonium) bis(maleonitriledithiolato)nickelate(II) have been previously reported,[19] and a strong peak at 335 cm^{-1} has been assigned to a NiS vibration, which in the D_{2h} symmetry gives rise to an a$_g$ Raman active mode. The peak at 346−348 cm^{-1} in compounds **5**−**8** is analogously assigned. The interiodine vibrations of complexes **6**−**8** appear as weak to medium peaks at approximately 153 cm^{-1} for **6** and **7** and 159 cm^{-1} for **8**. The fact that the neutral adducts **6** and **7** and the ligand mixed valence compound **8** show similar spectra in this region is in agreement with the structural features of these derivatives. In fact, in **8** all of the diiodine molecules show bond lengthenings comparable to that produced in I$_2$ by the interaction with the thionic-sulfur atom in **7** (see Structural Characterization), and all data for the present compounds agree well with the correlation previously found between the Raman frequencies and the I−I bond distances.[20] However, due to the presence of the very strong peak at 346−348 cm^{-1}, an unambiguous identification of the interiodine vibrations in **6**−**8** would not have been possible in the absence of X-ray structural support.

Visible Spectroscopy

The long-wavelength electronic band characteristic of the class of nickel−dithiolenes appears in **5** at 1002 nm with an unusually high intensity ($\epsilon \approx 80\,000$ dm^3 mol^{-1} cm^{-1}), even compared to those reported in ref 1. Exposure of a CH$_2$Cl$_2$ solution of **5** to the radiation of the laser source (at full power) of the FTR spectrometer (Nd:YAG laser) for 1 day caused no measurable decrease in the absorbance. This is an important property since it is necessary that the dye solution is photochemically stable to be applied as a near-IR dye. The same spectral features are mantained in the solid state (Figure 8a,b). On addition of diiodine a band at a longer wavelength region appears in the reflectance spectra, as shown in Figure 8b.

Conclusions

[Ni^{II}(Pr$^i_2$timdt$^-$)$_2$] belongs to a new class of nickel−dithiolenes, showing the near-IR absorption at approximately 1000 nm with a remarkably high extinction coefficient (to our knowledge the highest value even achieved for this class of compounds). These properties, coupled with their high thermal and photochemical stabilities, make these materials promising candidates as near-IR dyes in Q-switching neodymium lasers, which operate at 1064 nm.

Moreover, by virtue of the presence of the better donor NR groups compared to the sulfur atoms of the structural analog dmit complex, the oxidation over the neutral state of the complex is achieved. The chemical oxidation of **5** produces **8**, which consists of a ligand mixed-valence compound where two of the four chelating ligands are in the neutral form as shown by their structural features. Thus, the coordination to the metal produces the stabilization of the 1,3-dialkylimidazolidine-2,4,5-trithione compound, which has not been previously isolated.

Experimental Section

Preparations. All solvents and reagents were of the best Aldrich quality and used as purchased.

Compound 3. The procedure followed has been described to prepare derivatives of **2**.[5] The crude product was extracted with CH$_2$Cl$_2$, treated with activated carbon, and filtered and the solution evaporated to dryness. The solid was dissolved in Et$_2$O, treated again

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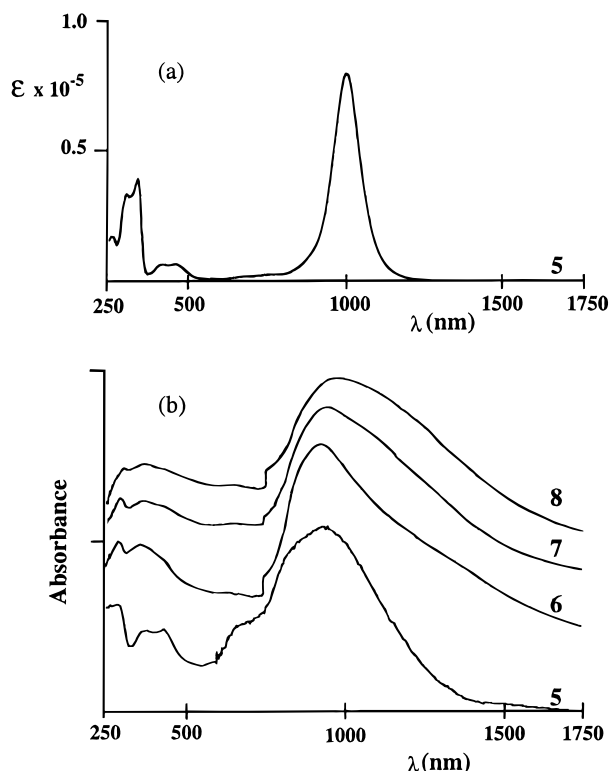
Figure 8. (a) CHCl₃ solution spectrum of **5** (molar extinction coefficients *versus* wavelengths) and (b) diffuse reflectance spectra of **5**−**8** (absorbance in arbitrary units *versus* wavelengths) in the UV−visible−near-IR range.

with activated carbon, and filtered, and the solution was allowed to stand for 1 day. Few orange-red crystals precipitate. Anal. Calcd for C₁₈H₂₈N₄S₆: C, 43.87; H, 5.73; N, 11.37; S, 39.04. Found: C, 43.9; H, 6.0; N, 11.3; S, 39.3. IR [cm⁻¹, KBr and polyethylene (below 400 cm⁻¹) pellets] 1426−1414s, 1383m, 1368m, 1327vs, 1310s, 1277s, 1207m, 1180m, 1132m, 1082w, 1061m, 1046w , 899mw, 742m, 728w, 670vw, 660vw, 445w, 427vw, 404ms, 374vw. Raman (cm⁻¹): 1506−1496s, 1426−1412m, 1336w, 1277w, 1209m, 1128w, 476vs [ν(S−S)] 423m, 335m, 231w, 184w, 134m. (v, very; w, weak; s, strong; m, medium; sh, shoulder; br, broad).

Compound 4. A mixture of 1,3-diisopropyl-4,5-dioxoimidazolidine-2-thione (**1**,⁵ 1.0 g), P₄S₁₀ (1.2 g), and toluene (100 mL) was refluxed for 30 min. The reaction mixture was filtered and the filtrate concentrated under reduced pressure. The residue was washed with MeOH and crystallized from CH₂Cl₂/MeOH, giving pale-orange crystals of **4** (mp 168−169 °C). Anal. Calcd for C₁₈H₃₀N₄S₄: C, 50.19; H, 7.02; N, 13.01; S, 29.78. Found: C, 49.7; H, 7.3; N, 12.8; S, 29.4. IR [cm⁻¹, KBr and polyethylene (below 400 cm⁻¹) pellets] 1555ms, 1430−1415s, 1397−1387m, 1358s, 1335ms, 1310vs, 1288ms, 1188−1173s, 1145−1135m, 1098s, 1067m, 1023mw, 893m, 820ms, 750ms, 517mw, 480m, 465mw, 434w−415ms, 398−388w, 350w, 315mw, 269w, 226mbr, 186w, 167w, 87mw. Raman (cm⁻¹): 1548vs, 1433m, 1396w, 1360m, 1328vw, 1298m, 1230m, 1180−1170w, 1142w, 1062mw, 1024vw, 885mw, 747mw, 643−632mw, 556mw, 517w, 479−462w, 435s [v(S−S)], 396w, 346vw, 277w, 218−206w−br, 151w, 115w, 93w.

Compound 5. A 2.2 g amount of 1,3-diisopropyl-4,5-dioxoimidazolidine-2-thione (**1**) was placed in a round bottomed flask and heated with stirring in 50 mL of toluene, and 5.0 g of Lawesson reagent was then added to the hot solution. The solution was then refluxed with stirring for 5 min, becoming brown. Then an excess of Ni powder was added to the hot solution which was refluxed for a further 1 h and slowly became dark-green. After that the solution was evaporated by rotary evaporation. The green precipitate formed was washed with ethanol and recrystalized from CH₂Cl₂/EtOH, yielding 1.08 g (38%) mp >300 °C. Anal. Calcd for C₁₈H₂₈N₄NiS₆: C, 39.20; H, 5.12; N, 10.16; S, 34.88; Ni, 10.64. Found: C, 39.4; H, 5.1; N, 10.2; S, 34.3; Ni, 10.0. IR [cm⁻¹, KBr and polyethylene (below 400 cm⁻¹) pellets]:

1413m, 1361s, 1322s, 1305s, 1273s−br, 1174−1154w, 1121s, 1082s, 1030m, 899w, 879mw, 765sh−751w, 667w, 548w, 436s, 425sh, 388s, 329w, 272ms, 222m, 200vw, 160−151w, 140w, 129sh, 125w, 100m−br. Raman (cm⁻¹, KBr pellets): 1429s,1292s, 864wbr, 770m, 691w, 625w, 552mw, 432m, 385w, 346vs, 199m, 152w, 120w.

Compound 6 was formed by addition in the 2:1 molar ratio of a CH₂Cl₂ solution of diiodine (0.024 g) to a CHCl₃ solution of the nickel complex **5** (0.026 g). After standing for a few days dark shining crystals of **6** precipitated; they were washed with petroleum ether and air-dried. Anal. Calcd for C₁₈H₂₈I₄N₄NiS₆: C, 20.41; H, 2.66; N, 5.29; S, 18.16. Found: C, 20.3; H, 2.6; N, 5.4; S, 18.0. IR [cm⁻¹, KBr and polyethylene (below 400 cm⁻¹) pellets]: 1385w, 1361m, 1350sh, 1305m, 1250vs−br, 1125m, 1082mw, 1045w, 899vw, 879w, 440sh, 425s, 384s, 325−313w, 272w, 220−211w, 171m, 133s−br, 120sh, 100sh. Raman (cm⁻¹, KBr pellets): 1429mw, 1395w, 1295m, 1265mw, 1125m, 748w−br, 696mw, 546w, 421m−br, 348vs, 198mw, 153mw, 122m.

Compound 7 was formed similarly by addition of a CHCl₃ solution of diiodine (0.0575 g) to a CHCl₃ solution of the nickel complex **5** (0.025 g) in the 5:1 molar ratio. The same product is obtained with use of 4:1 or 3:1 ratios. However, on standing or during collection of structural data the product lost diiodine. Anal. Calcd for C₁₈H₂₈I₅N₄NiS₆: C, 18.23; H, 2.38; N, 4.72; S, 16.22. Found: C, 18.3; H, 2.4; N, 4.6; S, 16.0. IR and Raman spectra of **7** are almost superimposable on those of **6**.

Compound 8 also was prepared by the same synthetic procedure, but working with the molecular ratios 20:1 [I₂ (0.23 g), **5** (0.025 g)] in CHCl₃. Anal. Calcd for C₁₈H₂₈I₆N₄NiS₆: C, 16.47; H, 2.15; N, 4.27; S, 14.65. Found: C, 16.7; H, 2.2; N, 4.4; S, 14.9. IR [cm⁻¹, KBr and polyethylene (below 400 cm⁻¹) pellets]: 1430m, 1416m, 1390mw, 1370m, 1345m, 1300m, 1250vs−br, 1125ms, 1078w, 1068w, 1035w, 745w, 705mw, 675mw, 565vw, 427s, 384s, 325−313w, 269m, 225−210w, 176m, 150sh, 139s, 121sh, 93w. Raman (cm⁻¹, KBr pellets): 1428m, 1395w, 1293m, 1266w, 1125m, 767w−br, 696mw, 549w, 425mbr, 348vs, 197mw, 177sh, 159m, 130sh, 120m.

Cyclic Voltammetry. Cyclic voltammetry of **5** (1 × 10⁻³ mol dm⁻³) was performed at room temperature on an EG&G Model 273 using a conventional three electrode cell with a standard SCE reference electrode. The reference electrode was separated from the sample compartment by a Luggin capillary. The solvent CH₂Cl₂ (anhydrous grade) and the electrolyte tetrabutylammonium tetrafluoroborate (TBAFA) (~1 × 10⁻¹ mol dm⁻³) were used without further purification. The micro-working electrode was constructed from a platinum wire sealed into a glass tube and then ground and polished to obtain a platinum disk with a diameter of 0.5 mm. Cyclic voltammograms were recorded at different scan rate values ranging from 30 to 300 mV s⁻¹.

Spectroscopic Measurements. IR Spectra. IR spectra (300−4000 cm⁻¹) were recorded on a Perkin-Elmer Model 983 spectrophotometer as KBr pellets; the far-FTIR spectra have been recorded on a Bruker IFS55 spectrometer working at room pressure and using a flow of dried air.

FT-Raman Spectra. FT-Raman spectra (resolution ± 4 cm⁻¹) were recorded on a Bruker RFS100 FTR spectrometer, fitted with an indium−gallium−arsenide detector (room temperature) and operating with an excitation frequency of 1064 nm (Nd:YAG laser). The power level of the laser source was 40 mW for the solid samples **3** and **4**. Microcrystals were packed into a suitable cell and then fitted into the compartment designed for use with 180° scattering geometry. No sample decomposition was observed during the experiments. Many problems were found in obtaining satisfactory spectra of **5**−**8** due to the fact that the samples strongly absorb at the excitation frequency of the Nd laser. For the solid samples, only in the case of **5** a Raman spectrum of poor quality was obtained. Raman spectra of the other nickel complexes were obtained in CHCl₃ solutions or KBr pellets.

UV−Visible Measurements. Electronic spectra were recorded in CHCl₃ solutions and on KBr pellets with a Cary 5 spectrophotometer, equipped with a diffuse reflectance accessory.

Electrical Properties. The electrical properties of **5** and **8** were detected by use rf penetration depth measurements (cryostat cooled by pumped liquid ⁴He) or with a Lake Shore cryotonics 7221 ac susceptometer operating with a 1 G modulation field at a frequency of 125 Hz. No superconductivity was observed.

Data Collection and Structure Determination. Table 1 summarizes the crystallographic data. All data were collected at room temperature on a Siemens AED for **3**–**5** and **7** and Philips PW 1100 for **8**. A decay correction was applied for **7** as a consequence of the systematic variation in intensity of a standard reflection which was measured every 50 reflections (maximum ratio, 1.44). The space groups were chosen on the basis of the systematic extinctions and intensity statistics. The intensities recorded by the $\theta/2\theta$ scan technique were corrected for Lorentz and polarization factors. An absorption correction was also applied after the last isotropic refinement cycle for **4** and **7** following the empirical method of Walker and Stuart[21] (transmission coefficients 0.724–1.000 and 0.469–1.000 for **4** and **7**, respectively). An empirical absorption correction for **8** was made by measuring four reflections with a χ value near 90° at different φ values (0–180°, in steps of 10°). The structures were solved by use of Patterson methods with the use of SHELXS-86[22] and refined by the full-matrix least-squares method, using SHELX-76,[23] first with isotropic thermal parameters and then with anisotropic thermal parameters for all non-hydrogen atoms of **4** excluding those of the Pr^i groups of **3** and **5** and those of two guest diiodine molecules in compound **7**, and for Ni, I, and S atoms only of **8**. The crystal of **7** resulted from the loss of diiodine molecules, so the refinement of the site occupancy factors results in values of 0.1080 for I(3) and of 0.1400 for I(4). The hydrogen atoms of all compounds (excluding those of the disordered Pr^i groups of **3**, which were not considered) were placed at their geometrically calculated positions (C–H = 0.96 Å) and refined by use of a "riding" model correction on the corresponding carbon atoms. Atomic scattering factors and the anomalous scattering coefficients were taken from International Tables for X-ray Crystallography.[24] All calculations were carried out on the GOULD-POWER NODE 6040 and ENCORE 91 computers of the "Centro di Studio per la Strutturistica Diffrattometrica del CNR.", Parma.

Supporting Information Available: Projections of the structures of **4** and **7** along [010] (2 pages). X-ray crystallographic files in CIF format for compounds **3**–**5**, **7**, and **8** are available on the Internet only. Access and ordering information is given on any current masthead page.

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