New Neutral Nickel Dithiolene Complexes derived from 1,3-Dialkylimidazolidine-2,4,5-trithione, showing Remarkable Near-IR Absorption

Francesco Bigoli,[a] Paola Deplano,*[b] Francesco A. Devillanova,[b] Vito Lippolis,[b] Peter J. Lukes,[b] Maria Laura Mercuri,[b] Maria Angela Pellinghelli[a] and Emanuele F. Trogu[b]

[a] *Dipartimento di Chimica Generale ed Inorganica, Analitica, Chimica Fisica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze 78, I-43100 Parma, Italy*

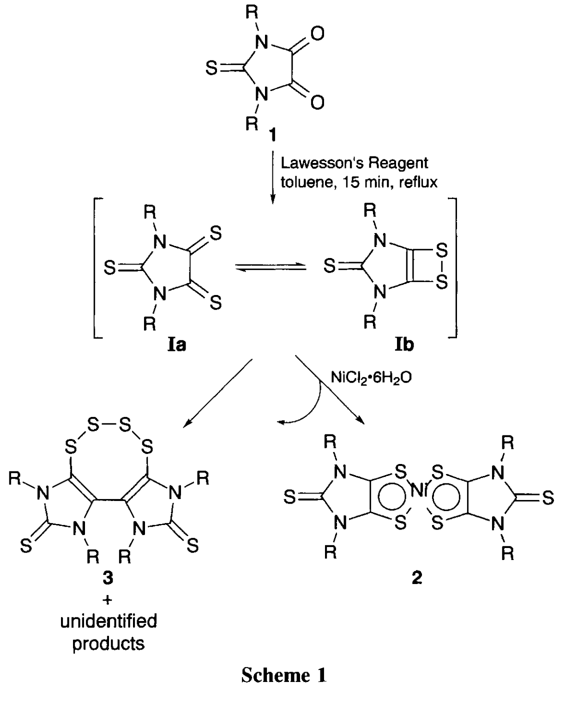
[b] *Dipartimento di Chimica e Tecnologie Inorganiche e Metallorganiche, Via Ospedale 72, I-09124 Cagliari, Italy*

The synthesis, solution redox properties and electronic spectra of a new series of stable, neutral nickel–dithiolene complexes $[Ni(R_2timdt)_2]$ (where R_2timdt is the monoreduced anion of the first example of 1,3-dialkylimidazolidine-2,4,5-trithione and alkyl = Et, Pr^i, Bu), showing an intense electronic absorption at $\lambda \approx 1000$ nm, as well as the crystal structure of the Pr^i derivative are reported.

The chemistry of dithiolene complexes has been known for a long time,[1] and is currently receiving considerable attention within the area of new materials science since these systems can exhibit electrical conductivity[2] and strong near-IR absorption.[3] A high degree of electron delocalization, which is not limited to the ligands, but includes the metal atom is responsible for the latter; while the overlap of partially filled delocalized π-orbitals between adjacent molecules is responsible for the former. The coplanarity of the ligand π-system and the dithiolene as well as the electron-withdrawing nature of the substituents on the carbon atoms of the unsubstituted parent dithiolene play an important role in determining both properties. In particular, electron-donating substituents, such as NR_2, are capable of shifting to lower energies the absorption maximum at the near-IR edge of the visible of the unsubstituted parent nickel–dithiolene.[3] This is important in creating materials with intense absorptions in the 1.0–1.6 μm region to be employed in the application of NIR dyes in Q-switching infrared lasers.[3]

Among the known nickel dithiolene systems, some $C_3S_5^{2-}$ (dmit) derivatives[4] exhibiting coplanarity and peripheral thionic sulfurs (which are important in promoting interactions among the molecules) are now extensively investigated for their conductive and superconductive properties.[5]

In this communication we report on the synthesis and characterization of a new class of dithiolenes, *i.e.* $[Ni(R_2timdt)_2]$ (**2**, Scheme 1), that are analogues of $[Ni(dmit)_2]$[6] where the substitution of endocyclic sulfur atoms with the better donor NR groups does not modify the planarity of the ligand.



Scheme 1

Scheme 1 summarizes the synthetic procedure. A convenient route for the synthesis of dithiolenes *via* α-dithiones by sulfurization of α-diones, has been previously reported.[3] However, most vicinal dithiones undergo decomposition and can exist in an equilibrium mixture with their dithiacyclobutene isomers.[7] We tried to synthesize 1,3-dialkylimidazolidine-2,4,5-trithione by sulfurization of 1,3-dialkylimidazolidine-2-thione-4,5-dione **1** using Lawesson's reagent[8] in refluxing toluene. The isolated products were the structurally characterized tetrathiacino derivatives[9] **3**, whose formation might be explained by the C–S bond rupture of the dithiacyclobutene isomer **Ib** in equilibrium with the vicinal dithione intermediate **Ia**. All our attempts to isolate **Ia** as well as **Ib** have been unsuccessful, and, to the best of our knowledge, no reports on these derivatives are known.† However, when $NiCl_2{\cdot}6H_2O$ is added to the reaction mixture (Scheme 1) an olive-green colour gradually appears. After a further period of reflux, dark green solids of **2** (alkyl = Et, Pr^i, Bu) are isolated in low yields

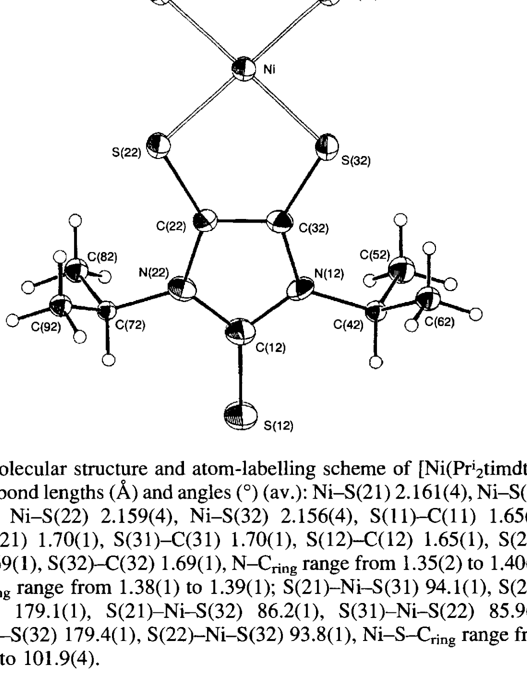


Fig. 1 Molecular structure and atom-labelling scheme of $[Ni(Pr^i_2timdt)_2]$. Selected bond lengths (Å) and angles (°) (av.): Ni–S(21) 2.161(4), Ni–S(31) 2.158(4), Ni–S(22) 2.159(4), Ni–S(32) 2.156(4), S(11)–C(11) 1.65(1); S(21)–C(21) 1.70(1), S(31)–C(31) 1.70(1), S(12)–C(12) 1.65(1), S(22)–C(22) 1.69(1), S(32)–C(32) 1.69(1), $N–C_{ring}$ range from 1.35(2) to 1.40(2), $C_{ring}–C_{ring}$ range from 1.38(1) to 1.39(1); S(21)–Ni–S(31) 94.1(1), S(21)–Ni–S(22) 179.1(1), S(21)–Ni–S(32) 86.2(1), S(31)–Ni–S(22) 85.9(1), S(31)–Ni–S(32) 179.4(1), S(22)–Ni–S(32) 93.8(1), $Ni–S–C_{ring}$ range from 101.2(4) to 101.9(4).

(approximately 10%) by cooling the reaction mixture. Crystals of **2** may be grown by slow evaporation of CH_2Cl_2 solutions.[‡]

The crystal structure[§] of the isopropyl derivative (Fig. 1) shows that the metal is coordinated by the two vicinal exocyclic sulfur atoms of the two chelating ligands in a square-planar geometry. The complex has a pseudo-symmetry centre and is roughly planar (excluding the isopropyl groups) with a maximum deviation from the mean-weighted least-squares planes of 0.11(1) Å for C(12). The isopropyl groups are perpendicular to the imidazoline rings [the dihedral angles between the mean-weighted least-squares planes of the isopropyl groups and of the corresponding imidazoline ring vary from 87.1(7) to 92.3(5)°] and therefore prevent the formation of stacks with short intermolecular contacts. This is consistent with the insulating behaviour of the compound (see footnote ‡), while $[Ni(dmit)_2]$, with short interstack S···S distances, is a semiconductor.[6] The packing, which is determined by weak contacts of the type: S···C(Pr^i) and C···C, shows the presence of a pseudo-glide plane. Bond distances and angles in the NiS_4C_4 framework (see caption of Fig. 1) are similar to those reported for other nickel dithiolenes.[6,10]

The electrochemical properties of **2** have been studied using cyclic voltammetry and the half-wave potentials are reported in Table 1. The two reversible one-electron reductions E_2 and E_3 are shifted to significantly more negative values with respect to those usually found in nickel–dithiolene complexes.[11] The substitution of the endocyclic sulfurs with NR groups in the dmit ring therefore produces a stabilization of the neutral state of the complexes. This is reflected in the direct isolation of neutral complexes with R_2timdt and in the greater stability of the anionic complexes with dmit. Oxidation of the complexes past the neutral state can also be observed in voltammograms performed in CH_2Cl_2, though the oxidation process is irreversible.

The characteristic long-wavelength transitions are found in the three complexes at ≈ 1000 nm and have intensities ($\varepsilon \approx$ 80 000 $dm^3\ mol^{-1}\ cm^{-1}$) much higher than those reported for previous nickel–dithiolene complexes (ε in the range 15 000–40 000 $dm^3\ mol^{-1}\ cm^{-1}$).[3] As an example the UV–VIS–NIR spectrum for R = Pr^i is shown in Fig. 2. Thanks to this greatly enhanced absorption intensity, these materials are excellent candidates for use as near-IR dyes in Q-switching neodymium lasers, which operate at 1060 nm.[3]

Table 1 Half-wave redox potentials for the $[Ni(R_2timdt)_2]$ complexes (1×10^{-3} mol dm^{-3}). All potentials *vs.* SCE were recorded in CH_2Cl_2, in the presence of NBu_4BF_4 (≈ 0.1 mol dm^{-3}); scan rate = 100 mV s^{-1}

$[Ni(R_2timdt)_2]$	R = Et	Pr^i	Bu
E_1/V	+0.83	+0.78	+0.82
E_2/V	−0.06	−0.12	−0.07
E_3/V	−0.51	−0.60	−0.54

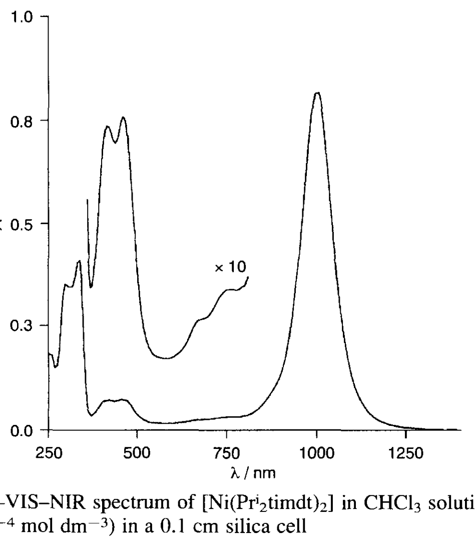


Fig. 2 UV-VIS-NIR spectrum of $[Ni(Pr^i_2timdt)_2]$ in $CHCl_3$ solution (c = 1.05×10^{-4} mol dm^{-3}) in a 0.1 cm silica cell

Overall features of these neutral $[Ni(R_2timdt)_2]$ complexes suggest that R_2timdt can be considered the monoreduced anion of 1,3-dialkylimidazolidine-2,4,5-trithione. The chemistry of these complexes is under investigation.

This research was carried out as part of the 'Progetto Finalizzato Materiali Speciali per Tecnologie Avanzate' of the 'Consiglio Nazionale delle Ricerche'.

Received, 25th October 1994; Com. 4/06544A

Footnotes

[†] While six-membered cyclic dithiooxamides are prepared by sulfurization of corresponding oxamides, the five-membered derivatives are not obtained in this way [R. Isaksson, T. Liljefors and J. Sandstrom, *J. Chem. Res.*, 1981, (*S*) 43]. 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 (H. W. Roesky, H. Hofman, W. Clegg, M. Noltemeyer and G. M. Sheldrick, *Inorg. Chem.*, 1982, **21**, 3798).

[‡] The compounds, diamagnetic and insulating, gave satisfactory elemental analyses and mass spectra.

[§] *Crystal data* for $[Ni(Pr^i_2timdt)_2]$: $C_{18}H_{28}N_4NiS_6$, orthorhombic, space group $Pna2_1$, a = 18.806(5), b = 5.628(7), c = 23.665(5) Å, V = 2505(3) $Å^3$, Z = 4, D_c = 1.463 g cm^{-3}, T = 295 K. A Siemens AED diffractometer employing nickel-filtered Cu-Kα radiation (λ = 1.541 838 Å) was used for all measurements. A total of 2429 reflections ($3 \leqslant \theta \leqslant 70°$) which yielded 1448 [$I \geqslant 2\sigma(I)$] observed reflections were collected. The structure was solved by the Patterson method and subsequent Fourier maps, and submitted to full-matrix least-squares refinement with the non-hydrogen atoms, with the exception of those of the isopropyl groups, treated anisotropically, and the hydrogen atoms placed at their geometrically calculated positions (C–H = 0.96 Å) and refined by 'riding' on the corresponding carbon atoms. The final agreement factors were R = 0.0463 and R_w = 0.0621 for 202 variables. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49; R. P. Burns and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 303.
2 J. R. Ferraro and J. M. Williams, *Introduction to Synthetic Electrical Conductors*, Academic, New York, 1987.
3 U. T. Mueller-Westerhoff, B. Vance and D. I. Yoon, *Tetrahedron*, 1991, **47**, 909.
4 G. Steimecke, H. J. Sieler, R. H. Kirmse and E. Hoyer, *Phosphorus Sulfur*, 1979, **7**, 49.
5 R. M. Olk, B. Olk, W. Dietzsch, R. Kirmse and E. Hoyer, *Coord. Chem. Rev.*, 1992, **117**, 99; P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark and A. E. Underhill, *Coord. Chem. Rev.*, 1991, **110**, 115.
6 L. Valade, J.-P. Legros, M. Bousseau, P. Cassoux, M. Garbauskas and L. V. Interrante, *J. Chem. Soc., Dalton Trans.*, 1985, 783.
7 N. Jacobsen, P. de Mayo and A. C. Weedon, *Nouv. J. Chem.*, 1978, **2**, 331.
8 S. Scheibye, B. S. Pedersen and S. O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 229.
9 D. Atzei, F. Bigoli, P. Deplano, M. A. Pellinghelli and E. F. Trogu, *Phosphorus Sulfur*, 1988, **37**, 189.
10 M. Bousseau, L. Valade, J. P. Lagros, P. Cassoux, M. Garbauskas and L. V. Interrante, *J. Am. Chem. Soc.*, 1986, **108**, 1908; J. P. Cornelissen, B. Pomarède, A. L. Spek, D. Reefman, J. G. Haasnoot and J. Reedijk, *Inorg. Chem.*, 1993, **32**, 3720; X. Yang, D. D. Doxsee, T. B. Rauchfuss and S. R. Wilson, *J. Chem. Soc., Chem. Commun.*, 1994, 821.
11 R. Kato, H. Kobayashi, A. Kobayashi and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 627; D. Y. Noh, M. Mizuno and J. H. Choy, *Inorg. Chim. Acta*, 1994, **216**, 147.