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

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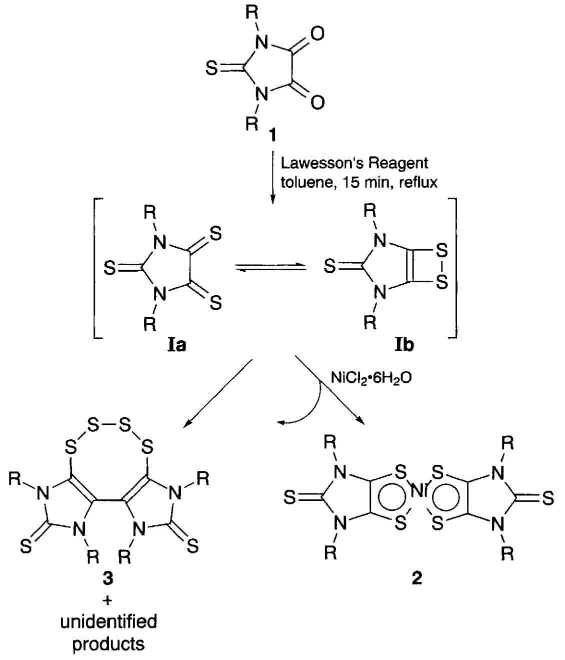
The synthesis, solution redox properties and electronic spectra of a new series of stable, neutral nickel–dithiolene complexes [Ni(R_2timdt)$_2$] (where R_2timdt is the monoreduced anion of the first example of 1,3-dialkylimidazolidine-2,4,5-trithione and alkyl = Et, Pr^i, Bu), showing an intense electronic 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

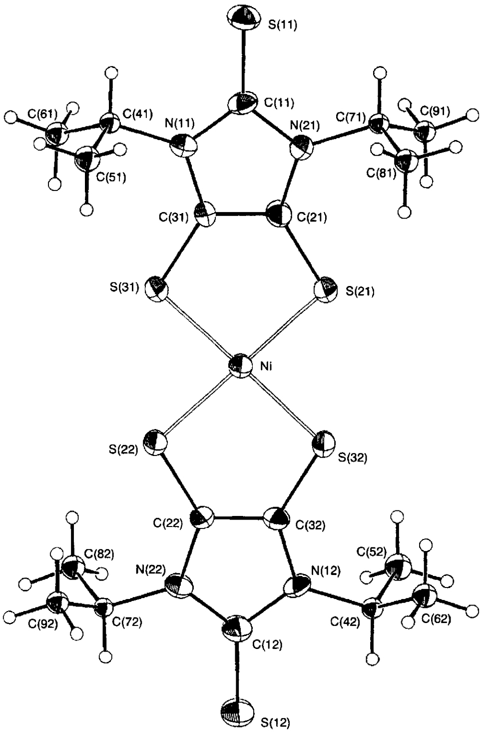


Fig. 1 Molecular structure and atom-labelling scheme of [Ni(Pr$^i_2$timdt)$_2$]. Selected bond lengths (Å) and angles (°) (av.): Ni–S(21) 2.161(4), Ni–S(31) 2.158(4), Ni–S(22) 2.159(4), Ni–S(32) 2.156(4), S(11)–C(11) 1.65(1); S(21)–C(21) 1.70(1), S(31)–C(31) 1.70(1), S(12)–C(12) 1.65(1), S(22)–C(22) 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$_2$timdt 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 (ε ≈ 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$_2$timdt)$_2$] 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$_2$timdt)$_2$]	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

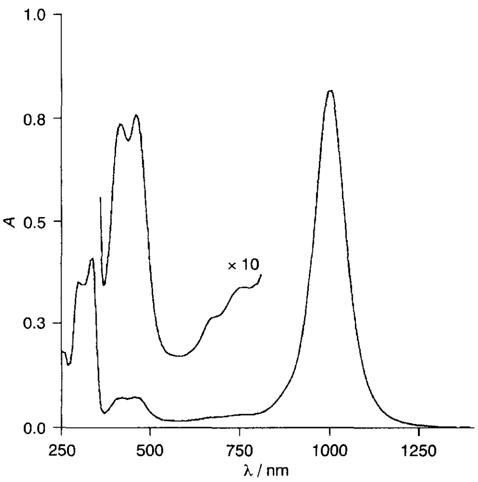


Fig. 2 UV–VIS–NIR spectrum of [Ni(Pr$^i_2$timdt)$_2$] in $CHCl_3$ solution ($c = 1.05 \times 10^{-4}$ mol dm^{-3}) in a 0.1 cm silica cell

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

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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$^i_2$timdt)$_2$]: $C_{18}H_{28}N_4NiS_6$, 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.

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