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# Synthesis, structure and properties of new unsymmetrical nickel dithiolene complexes useful as near-infrared dyes

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The new unsymmetrical [Bu$_4$N][Ni(Pr$^i_2$timdt)(dmit)] **4** and [Bu$_4$N][Ni(Pr$^i_2$timdt)(mnt)] **5** dithiolene complexes (Pr$^i_2$timdt is the mono-anion of 1,3-diisopropylimidazolidine-2,4,5-trithione; dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate; mnt = maleonitriledithiolate) have been prepared from the reaction of the neutral complex [Ni(Pr$^i_2$timdt)$_2$] **1** with the bi-anionic nickel dithiolene complexes [Bu$_4$N]$_2$[Ni(dmit)$_2$] **2** or [Bu$_4$N]$_2$[Ni(mnt)$_2$] **3**, respectively. A strong near-IR electronic absorption is observed in the spectra of **4** and **5** in CH$_3$CN at $\lambda_{max}$ = 1194 and 1070 nm, respectively. Diiodine oxidation of **4** and **5** affords the [Ni(Pr$^i_2$timdt)(dmit)] **6** and [Ni(Pr$^i_2$timdt)(mnt)] **7** neutral compounds ($\lambda_{max}$ at 883 nm in CH$_3$CN). Features in the electronic spectra suggest that the properties of unsymmetrical nickel dithiolene complexes as near-infrared dyes can be tuned by a combination of the ligands and by the charge on the complexes. A crystal of **6** has been analysed by X-ray diffraction methods. Structural data show that the nickel ion exhibits square-planar co-ordination. Chains along *b* are formed through contacts between the terminal sulfur atoms of the Pr$^i_2$timdt and dmit ligands [S $\cdots$ S 3.243(2) Å]. The formal charge of the ligands in **4** and **6** is estimated from the frequency of the Raman C=C stretching vibration.

## Introduction

For the [Ni(R$_2$timdt)$_2$] nickel dithiolene complexes **1** (R$_2$timdt is the mono-anion of the 1,3-dialkylimidazolidine-2,4,5-trithione)[1,2] a low-energy electronic absorption is observed at approximately 1000 nm with a remarkably high absorption coefficient ($\varepsilon \approx 80{,}000$ dm$^3$ mol$^{-1}$ cm$^{-1}$ in CHCl$_3$). This is believed to be due to the high degree of electron delocalisation in the dithiolene metallocycle and has been assigned to a $\pi \longrightarrow \pi^*$ ($b_{1u} \longrightarrow b_{2g}$) transition between the HOMO and the LUMO.[3] These properties, coupled with the photostability of the complex towards long wavelength radiation, together with its stability in solution, are of notable interest in the field of the near-infrared (NIR) dyes, in particular for applications in IR-laser technology. Mueller-Westerhoff *et al.*[3] have shown that the properties of these complexes as NIR dyes can be tuned by appropriate choice of the ligands. In fact donor substituents in the parent dithiolene raise the energy of the HOMO more than that of the LUMO. This results in a consequent shift of the low-energy band to lower frequencies. However, very strong donors that should give rise to a strong shift to lower frequencies may also force the HOMO to become antibonding. Consequently, an induced undesirable increased reactivity leading to the loss of one or two electrons may be observed.

Interest in the unsymmetrical dithiolene complexes is also related to the solid-state properties of possible derived systems with the aim of using these complexes for the preparation of molecular conductors. Molecular superconductors derived from [M(dmit)$_2$] systems (M = Ni or Pd; dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate) have been reported.[4] Although a number of unsymmetrical TTF-based conductors and superconductors are known,[5] only a few examples of unsymmetrical metal complexes as components of molecular conductors have been described. Yet, some salts of TTF (tetrathiafulvalene) and BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] with unsymmetrical complex anions and showing metallic behaviour have been obtained.[6]

We report here the synthesis, structure and optical properties of new "unsymmetrical" nickel dithiolene complexes involving both the Pr$^i_2$timdt and dmit or mnt (mnt = maleonitriledithiolate) ligands. These complexes are obtained either as mono-anionic salts or as neutral compounds. Electrochemical studies suggest that the physical-chemical properties of these systems are intermediate between those of the corresponding symmetrical systems. The possibility of tuning the NIR absorption by the combination of different ligands in these unsymmetrical (mixed-ligand) complexes is also investigated.

## Results and discussion

When treating the neutral complex [Ni(Pr$^i_2$timdt)$_2$] **1**[1] with [Bu$_4$N]$_2$[Ni(dmit)$_2$] **2** or [Bu$_4$N]$_2$[Ni(mnt)$_2$] **3** the new mono-anionic unsymmetrical dithiolene complexes [Bu$_4$N][Ni(Pr$^i_2$timdt)(dmit)] **4** and [Bu$_4$N][Ni(Pr$^i_2$timdt)(mnt)] **5** have been obtained according to Scheme 1.

The course of the reactions to produce the $-1$ charged unsymmetrical dithiolene complexes has been followed spectrophotometrically. In Fig. 1 the spectra of the reagents **1** and **2**, together with those recorded after partial and complete formation of **4**, are reported. In particular, the spectrum **a** (taken 20 minutes after mixing) shows the formation of the corresponding symmetrical mono-anionic dithiolene complexes as reaction

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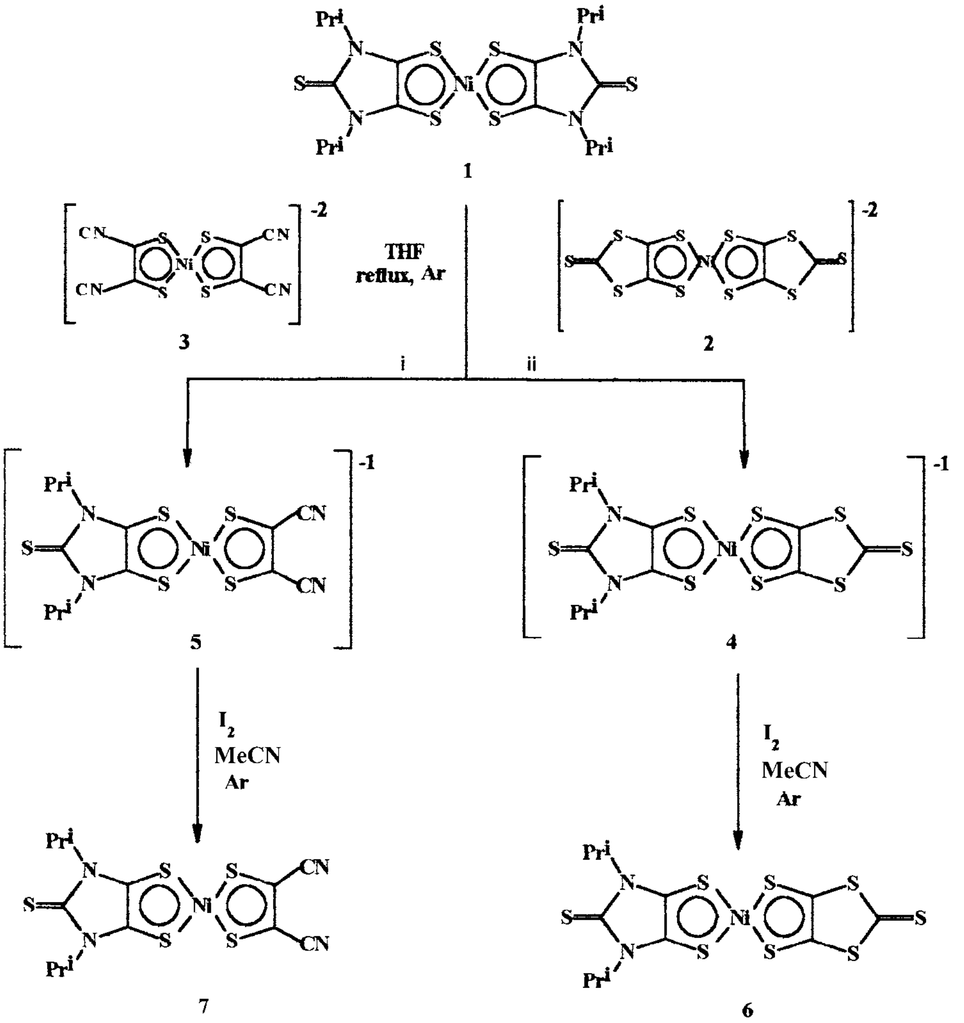

**Scheme 1** *Reagents and conditions*: i, 3 days for 80% conversion of **1** ($c = 1.81 \times 10^{-3}$ mol dm$^{-3}$); ii, 5 h for disappearance of **1** ($c = 6.17 \times 10^{-4}$ mol dm$^{-3}$).

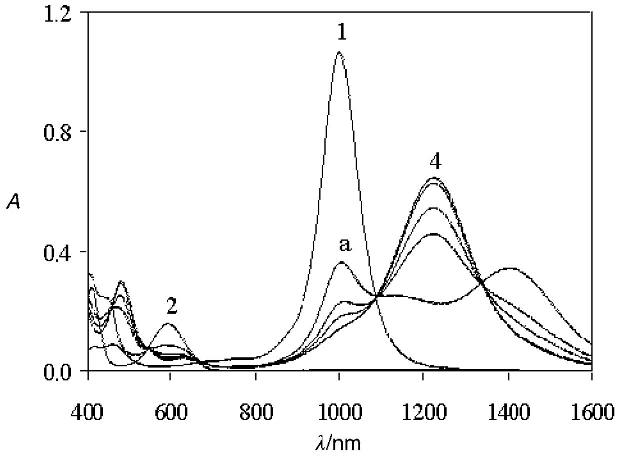

**Fig. 1** Spectra of a THF solution in a 0.1 cm silica cell at 35 °C of: the complex [Ni(Pr$^i_2$timdt)$_2$] **1** ($c = 1.50 \times 10^{-4}$ mol dm$^{-3}$), [Bu$_4$N]$_2$-[Ni(dmit)$_2$] **2** ($c = 1.50 \times 10^{-4}$ mol dm$^{-3}$), **a** a mixture of **1** and **2** obtained by withdrawal of suitable amounts from the 1 : 1 reaction mixture and dilution ($t = 0$, $c = 1.50 \times 10^{-4}$ mol dm$^{-3}$) 20 min after mixing and **4** five hours after mixing. The intermediate curves are taken after 1 h 20 min, 2 h and 3 h 50 min.

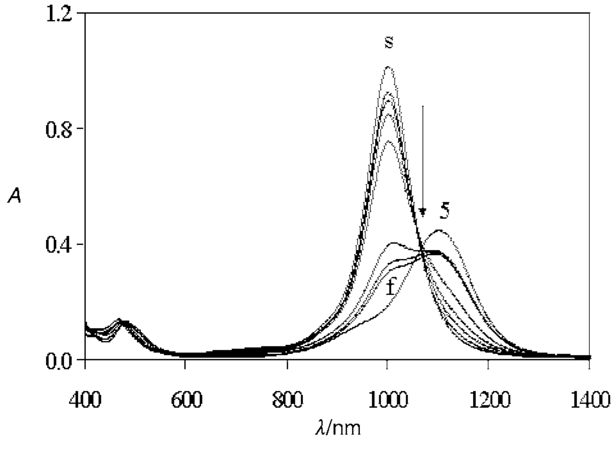

**Fig. 2** Spectra of a THF solution in a 0.1 cm silica cell at 35 °C of **s** a mixture of complexes **1** and **3** obtained by withdrawal of suitable amounts from the 1 : 1 reaction mixture and dilution ($t = 0$, $c = 1.45 \times 10^{-4}$ mol dm$^{-3}$) 40 minutes after mixing, **f** three days after mixing. The intermediate curves are taken after 1 h 30 min, 3 h 10 min, 5 h, 7 h 50 min and 20 h 40 min. **5** is the spectrum of a THF solution of the isolated [Bu$_4$N][Ni(Pr$^i_2$timdt)(mnt)] ($c = 2.90 \times 10^{-4}$ mol dm$^{-3}$).

intermediates (peaks at 1400 and 1130 nm for [Ni(Pr$^i_2$timdt)$_2$]$^-$ and [Ni(dmit)$_2$]$^-$, respectively[7]). After a time the symmetrical mono-anionic dithiolene complex gradually disappears to produce **4** and the reaction is complete in five hours. The corresponding reaction of reagents **1** and **3** produces **5**, but no symmetrical mono-anionic intermediates are observed (Fig. 2).

The high yields different from that expected for a random reorganisation (30%) suggest that the formation of the products is thermodynamically favoured. Indeed, no backward reaction is observed upon dilution and upon lowering the temperature.

The new mixed-ligand nickel dithiolene complexes **4** and **5** show in CH$_3$CN strong absorption bands at $\lambda = 1194$

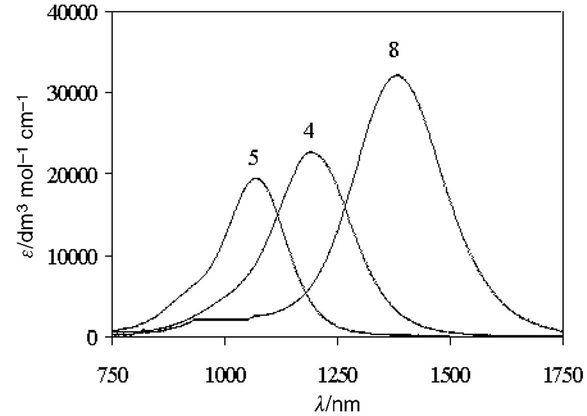

**Fig. 3** Comparison of the spectra in $CH_3CN$ of $[Bu_4N][Ni(Pr^i_2timdt)(mnt)]$ **5**, $[Bu_4N][Ni(Pr^i_2timdt)(dmit)]$ **4** and $[Bu_4N][Ni(Pr^i_2timdt)_2]$ **8** in the NIR region.

**Table 1** Electrochemical data for the unsymmetrical and related symmetrical complexes; $E_a$ = anodic potential, $E_{1/2}$ = half wave potential

| Complex | $E_a$/V ($ML_2^- \longrightarrow ML_2^0 + e^-$) | $E_{1/2}$[a]/V[b] ($ML_2^- + e^- \rightleftharpoons ML_2^{2-}$) |
|---|---|---|
| 4 | +0.234[b] | −0.402 |
| 5 | +0.386[c] | −0.307 |
| $[Ni(Pr^i_2timdt)_2]$ | −0.100[c] | −0.598 |
| $[Ni(dmit)_2]^{2-}$ | +0.316[b] | −0.109 |
| $[Ni(mnt)_2]^{2-}$ | +1.110[b] | +0.270 |

[a] Measured using a platinum wire working electrode, platinum wire as counter electrode, Ag–AgCl (KCl saturated) as reference electrode at a 100 mV $s^{-1}$ scan rate, $CH_3CN$ as solvent containing 0.1 mol $dm^{-3}$ $Bu_4NPF_6$ electrolyte. Half-wave potential for ferrocene–ferrocenium couple (internal standard) is 0.43 V under the above conditions. Temperature 25 °C. [b] Irreversible. [c] Reversible one-electron oxidation: $E_{1/2}(\mathbf{5}) = +0.354$; $E_{1/2}$ ($[Ni(Pr^i_2timdt)_2]$) = −0.134 V.

($\varepsilon$ = 22,800) and 1070 nm ($\varepsilon$ = 19,400 $dm^3$ $mol^{-1}$ $cm^{-1}$), respectively. The spectra of **4**, **5** and $[Bu_4N][Ni(Pr^i_2timdt)_2]$ **8** (in $CH_3CN$, $\lambda$ = 1384 nm, $\varepsilon$ = 32,100 $dm^3$ $mol^{-1}$ $cm^{-1}$) are shown in Fig. 3. Both **4** and **5** contain the same $Pr^i_2$timdt ligand, which bears strong electron-donor nitrogen atoms fixed into coplanarity within a ligand where extensive π delocalisation takes place. The dmit and the mnt ligands exhibit increasing electron-withdrawing power. Thus, the observed trend of the NIR absorption bands is in accordance with expectations.

Electrochemical data of complexes **4** and **5**, together with those of related samples, are shown in Table 1. One reversible mono-electronic reduction wave for both complexes and one oxidation wave, irreversible for **4** and reversible for **5**, are observed in the corresponding cyclic voltammograms. The half-wave potential values, $E_{1/2}$, are intermediate between those of the corresponding parent symmetrical complexes, thus suggesting that also the electrochemical properties of these unsymmetrical dithiolene complexes can be tuned by a combination of ligands.

The neutral $[Ni(Pr^i_2timdt)(dmit)]$ **6** and $[Ni(Pr^i_2timdt)(mnt)]$ **7** complexes have been prepared by chemical oxidation of **4** and **5** with $I_2$. A significant shift of the NIR absorptions to higher frequencies is observed upon oxidation of **5** to **7** (see Fig. 4; comparison of the spectra of **4** and **6** in the same solvent could not be made due to solubility reasons). Thus, as previously found in the symmetrical parent complexes,[8] these compounds show electrochromism. In conclusion, regarding optical properties, unsymmetrical nickel dithiolene complexes are NIR dyes where the NIR absorption can be tuned by a combination of the ligands and/or the charge of the complexes.

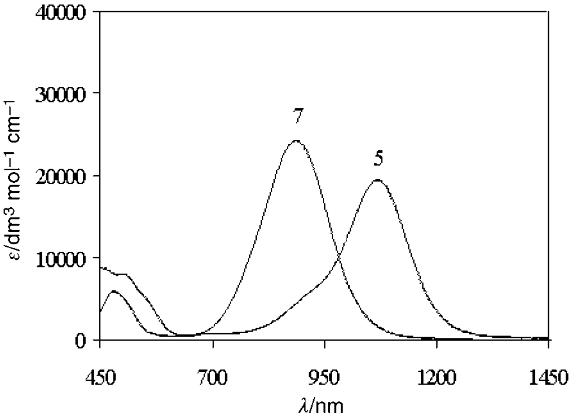

**Fig. 4** Comparison of the spectra in $CH_3CN$ of $[Bu_4N][Ni(Pr^i_2timdt)(mnt)]$ **5** and $[Ni(Pr^i_2timdt)(mnt)]$ **7** in the NIR region.

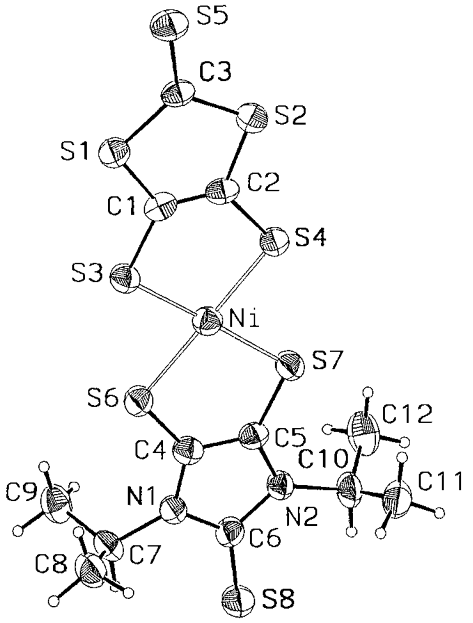

**Fig. 5** Molecular structure of complex **6** and the corresponding atom-labelling scheme.

**Table 2** Bond lengths (Å) and angles (°) for $[Ni(Pr^i_2timdt)(dmit)]$ **6**

| | | | |
|---|---|---|---|
| Ni–S(4) | 2.1457(16) | S(5)–C(3) | 1.607(5) |
| Ni–S(3) | 2.1476(16) | S(6)–C(4) | 1.693(6) |
| Ni–S(6) | 2.1734(17) | S(7)–C(5) | 1.695(5) |
| Ni–S(7) | 2.1741(17) | S(8)–C(6) | 1.651(6) |
| S(1)–C(1) | 1.744(5) | N(1)–C(4) | 1.367(6) |
| S(1)–C(3) | 1.766(5) | N(1)–C(6) | 1.387(6) |
| S(2)–C(2) | 1.739(5) | N(2)–C(5) | 1.375(6) |
| S(2)–C(3) | 1.745(5) | N(2)–C(6) | 1.393(6) |
| S(3)–C(1) | 1.737(6) | C(1)–C(2) | 1.289(8) |
| S(4)–C(2) | 1.751(5) | C(4)–C(5) | 1.377(7) |
| C(1)–S(1)–C(3) | 96.9(3) | S(2)–C(2)–S(4) | 121.0(3) |
| C(2)–S(2)–C(3) | 97.7(3) | S(5)–C(3)–S(2) | 125.0(3) |
| C(4)–N(1)–C(6) | 108.0(4) | S(5)–C(3)–S(1) | 124.3(3) |
| C(4)–N(1)–C(7) | 128.0(5) | S(2)–C(3)–S(1) | 110.7(3) |
| C(6)–N(1)–C(7) | 124.0(4) | N(1)–C(4)–C(5) | 108.4(5) |
| C(5)–N(2)–C(6) | 107.5(4) | N(1)–C(4)–S(6) | 129.5(4) |
| C(5)–N(2)–C(10) | 127.9(5) | C(5)–C(4)–S(6) | 122.1(4) |
| C(6)–N(2)–C(10) | 124.6(4) | N(2)–C(5)–C(4) | 108.4(4) |
| C(2)–C(1)–S(3) | 121.8(4) | N(2)–C(5)–S(7) | 129.8(4) |
| C(2)–C(1)–S(1) | 117.5(4) | C(4)–C(5)–S(7) | 121.8(4) |
| S(3)–C(1)–S(1) | 120.7(4) | N(1)–C(6)–N(2) | 107.6(4) |
| C(1)–C(2)–S(2) | 117.2(4) | N(1)–C(6)–S(8) | 126.7(4) |
| C(1)–C(2)–S(4) | 121.7(4) | N(2)–C(6)–S(8) | 125.7(4) |

Crystals of complex **6** suitable for an X-ray diffraction study have been obtained. Bond distances and angles are reported in Table 2. The structure of **6** and the corresponding atom-labelling scheme are shown in Fig. 5. The square-planar co-ordination around the metal atom involves two vicinal sulfur atoms from each of the two independent chelating ligands.

**Table 3** Most significant bond lengths (Å) in complex **6** compared to those of related complexes

| Compound | $d$(N–C)$_{\text{ring}}$ | $d$(C=C) | $d$(C=S) | $d$(C–S) | $d$(Ni–S) | Charge |
|---|---|---|---|---|---|---|
| $[Bu_4N]_2[Ni(dmit)_2]$[6] | — | 1.39 | 1.68 | 1.75 | 2.216 | −2 |
| $[Bu_4N][Ni(dmit)_2]$[6] | — | 1.35 | 1.63 | 1.73 | 2.156 | −1 |
| $[TTF][Ni(dmit)_2]_2$[6] | — | 1.42 | 1.66 | 1.70 | 2.17 | −0.5 |
| $[Bu_4N]_{0.29}[Ni(dmit)_2]$[6] | — | 1.39 | 1.64 | 1.70 | 2.153 | −0.29 |
| $[Ni(dmit)_2]$[6] | — | 1.391 | 1.625 | 1.699 | 2.147 | 0 |
| $[Bu_4N][Ni(Pr^i{}_2timdt)_2]$[7] | 1.37–1.39 | 1.35 | 1.66 | 1.70 | 2.161–2.166 | −1 |
| $[Ni(Pr^i{}_2timdt)_2]$[1] | 1.37–1.39 | 1.38 | 1.65 | 1.69 | 2.158–2.160 | 0 |
| $[[Ni(Pr^i{}_2timdt)_2]\cdot 2I_2$ in $[Ni(Pr^i{}_2timdt)_2]\cdot 2I_2[NiI_2(Pr^i{}_2timdt)_2]\cdot 3I_2$[1] | 1.37–1.40 | 1.38 | 1.68 | 1.68 | 2.165, 2.169 | 0 |
| $[NiI_2(Pr^i{}_2timdt)_2]\cdot 3I_2$ in $[Ni(Pr^i{}_2timdt)_2]\cdot 2I_2[NiI_2(Pr^i{}_2timdt)_2]\cdot 3I_2$[1] | 1.35–1.39 | 1.49 | 1.63 | 1.65 | 2.365, 2.377 | |
| **6** ($Pr^i{}_2$timdt ligand) | 1.37–1.39 | 1.38 | 1.65 | 1.69 | 2.173–2.174 | |
| **6** (dmit ligand) | — | 1.29 | 1.61 | 1.74 | 2.146–2.148 | |

Both S–Ni–S angles are near to 93°. The molecule is planar and the $Pr^i$ groups are perpendicular to the imidazoline rings. Chains along $b$ are formed through S(5)···S(8) ($x$, $1 + y$, $z$) interatomic distances shorter than the sum of the van der Waals radii (3.243(2) Å). Other short contacts between planar molecules parallel to each other and belonging to chains lying above or below the basic one are in the 3.613(4)–3.817(4) Å range for S···S and 3.599(7)–3.746(4) Å for S···C. A comparison of the most significant bond lengths in **6** with those of related complexes is reported in Table 3.

The C=C distances, which should be most significant for determining the charge of the ligand,[9] are shorter in the dmit fragment than those in $[Bu_4N][Ni(dmit)_2]$ and similar in $Pr^i{}_2$timdt to those found in $[Ni(Pr^i{}_2timdt)_2]$. The latter complex being neutral, structural data could suggest that the negative charge is more localised on dmit than on $Pr^i{}_2$timdt. However, it has previously been observed that bond length comparisons in the $M(dmit)_2$-based compounds in different oxidation states do not show any clear trend.[10] Vibrational data may be more useful in assigning the charge in these derivatives. Several attempts have been made to correlate selected characteristic vibrations to the charge distribution in charge-transfer (CT) salts or in neutral complexes of interest in the field of molecular conductors. A linear correlation between the charge and the frequencies of the IR active CN stretching vibration was obtained in the CT adducts of TCNQ (tetracyanoquinodimethane) with a variety of donors.[11] Raman scattering seemed to be even more suitable than IR to correlate the C=C frequency and the charge for $[BEDT\text{-}TTF]^m$ and $[M(dddt)_2]^n$ ($m = +1, \ldots, 0$;[12] $n = +1, 0, -1$).[13] Indeed, this symmetrical stretching mode is Raman active and not coupled with conduction electrons.[13,14] Recently, Raman spectra have also been used to relate the charge of the complexes in the $[M(dmit)_2]^{n-}$ ($n = 0, 0.29, 0.5, 1$ or 2; M = Ni or Pd) series to the C=C stretching mode $A_g(1)$ and a linear correlation of this vibration *versus* the charge has been found.[14] The corresponding Raman peaks which can be assigned to the C=C stretching vibration for the $[Ni(Pr^i{}_2timdt)(dmit)]^{n-}$ compounds ($n = 0$, 1388 cm$^{-1}$; $n = 1$, 1396 cm$^{-1}$) have been observed and reported in this correlation (Fig. 6). The position of these bands is very near to the frequency of the C=C peak of the monoanionic $[Ni(dmit)_2]^-$ complex (Fig. 7). Thus, the charge on $[Ni(Pr^i{}_2timdt)(dmit)]$ and $[Ni(Pr^i{}_2timdt)(dmit)]^-$ is similar to those found or predicted for the $[Ni(dmit)_2]^-$ and $[Ni(dmit)_2]^{1.2-}$ complexes, respectively. Moreover, an asymmetric distribution of the charge in the mixed-ligand complexes may be assumed when considering that the composition of the HOMO and the LUMO, described as π orbitals delocalised over both ligands in the neutral symmetrical complexes,[2,9,15] should be modified in the asymmetrical mixed-ligand complexes. Orbitals residing at lower energy (dmit and mnt) should contribute more to the HOMO, while orbitals at higher energy ($Pr^i{}_2$timdt is a more electro-donating ligand) should contribute more to the LUMO. Since the C=C bond components in this orbital (the LUMO) are bonding,[16] the population of this orbital should cause an increase of negative charge on the electro-donating ligand.

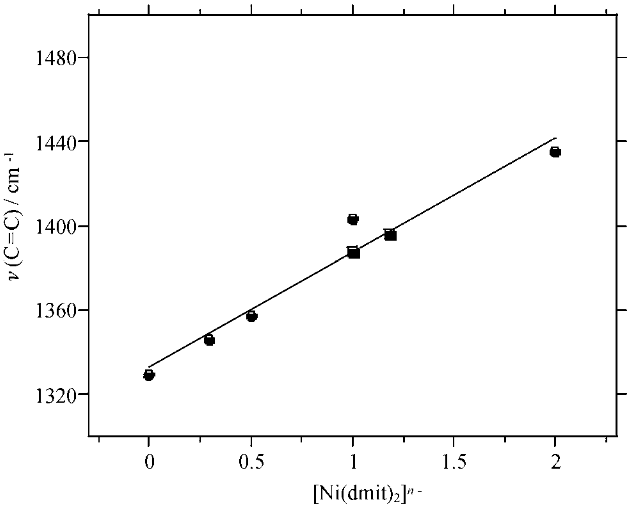

**Fig. 6** The C=C vibration *versus* the charge ($n^-$) of dmit-based nickel complexes (●), showing a linear correlation.[14] Raman shifts of complexes **4** and **6** are included (■).

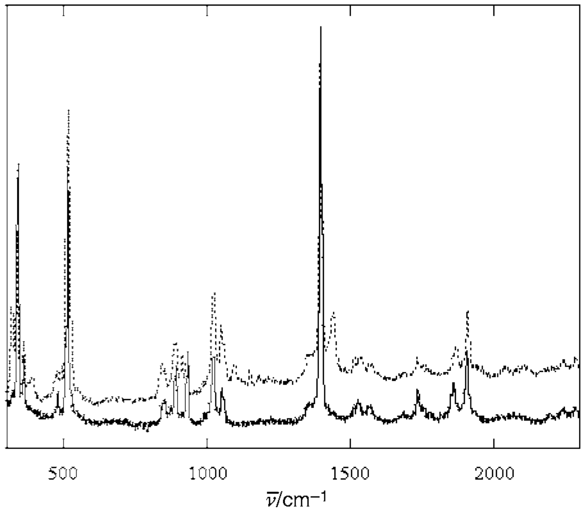

**Fig. 7** Comparison of Raman spectra (intensity in arbitrary units) of $[Bu_4N][Ni(Pr^i{}_2timdt)(dmit)]$ (···) and $[Bu_4N][Ni(dmit)_2]$ (—) recorded with He–Ne (λ = 632, 817 nm) laser excitation.

Consequently, this suggests that the dmit ligand in the neutral mixed-ligand complex **6** might bear a more negative charge than $Pr^i{}_2$timdt. Similarly, $[Ni(Pr^i{}_2timdt)(mnt)]$ shows a strong peak at 1425 cm$^{-1}$ very near to the frequency of the C=C peak for $[Ni(mnt)_2]^-$ in accordance with a higher content of the negative charge on the mnt ligand.[17,18] The difference in the charge distribution should be higher in the neutral than in the mono-anionic mixed-ligand complexes.

It is clear that calculations (that are in progress[16]) on the electronic structure and harmonic vibrational frequencies, together with Mulliken, Natural Bond Orbital, or Electron Localisation Function analysis, will help in estimating the extent of polarisation induced by two different ligands in the studied mixed-ligand complexes and should be very useful to confirm the charge distribution proposed above. Nevertheless, the whole experimental results seem to be in agreement with the above interpretation and suggest that the mixed-ligand complexes are still describable as (delocalised) dithiolene rather than dithiolate–dithione derivatives.

## Experimental

All manipulations were performed under an argon atmosphere.

### Preparations

**[Bu$_4$N][Ni(Pr$^i_2$timdt)(dmit)] 4.** A mixture of complexes **1**[1] (102 mg) and **2**[19] (178 mg, 1 : 1 molecular ratio) was refluxed in 300 mL THF. The solution turned from green to red, and after five hours the reaction was complete. The course of the reaction to produce the mono-anionic unsymmetrical dithiolene complex was followed spectrophotometrically in a 0.1 cm silica cell at 35 °C. Periodically, a fixed volume (6 mL) of the mixture was withdrawn and diluted to 25 mL to gain suitable absorbances (see Fig. 1). When the typical absorption of **1** disappeared (five hours), the solution was rotary-evaporated and the crude product dissolved in warm $CH_3CN$. Well formed red-brown crystals of **4** were obtained from the solution on addition of $Et_2O$ (yield = 70%). When the reaction is performed in an open vessel and after long standing, the formation of small amounts of the bimetallic dmit-based complex (μ-tetrathiooxalato-bis[2-thioxo-1,3-dithiolo-4,5-dithiolate)nickelate(II)] salt) and of **1** is observed.[20] Calc. for $C_{28}H_{50}N_3NiS_8$: C 45.21, H 6.77, N 5.65, S 34.48. Found: C 44.57, H 6.78, N 5.33, S 35.94%. IR [KBr pellets, cm$^{-1}$]: 2965m; 2940m; 2880m; 1480m; 1465m; 1445m; 1375vs; 1315vs; 1283vs; 1175w; 1155w; 1090w; 1060vs; 1035s; 885m; 740w; 515m; 473w; 422s and 371w. UV-vis (in $CH_3CN$), $\lambda$/nm ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 275 (24300); 313 (25700); 367 (25300); 477 (11800) and 1194 (22800).

**[Bu$_4$N][Ni(Pr$_2^i$timdt)(mnt)] 5.** This compound was prepared as above starting from **1** (200 mg) and **3**[21] (299 mg) dissolved in 200 mL THF and the reaction followed spectrophotometrically in a similar way. Periodically, a fixed volume (2 mL) of the mixture was withdrawn and diluted to 25 mL to gain suitable absorbances (see Fig. 2). After three days under reflux, a conversion of approximately 80% of the starting products was obtained, and the solution was rotary-evaporated. The crude product was recrystallised, first from $CH_3CN$–$Et_2O$ (unchanged **1** was removed by filtration from the $CH_3CN$ solution, where it has poor solubility), then by fractional precipitation from THF–light petroleum (bp 60–80 °C). The first fraction, formed by unchanged [Bu$_4$N]$_2$[Ni(mnt)$_2$], was filtered off, and on further addition of light petroleum the mixed-ligand dithiolene complex was obtained as red-brown crystals with a 50% yield. Spectrophotometric experiments performed under argon do not evidence a backward reaction upon dilution and lowering of the temperature. However, during the experiments to isolate the products partial formation of the starting reagents was observed. Calc. for $C_{29}H_{50}N_5NiS_5$: C 50.65, H 7.33, N 10.18, S 23.31. Found: C 49.88, H 7.49, N 9.99, S 22.69%. IR [KBr pellets, cm$^{-1}$]: 2962m; 2932w; 2874w; 2223w; 2205m; 1479m; 1382vs; 1318vs; 1303s; 1292s; 1255vw; 1154m; 1122s; 1084vw; 1028w; 880w; 761w; 738w; 549vw; 508w and 426m. UV-vis (in $CH_3CN$), $\lambda$/nm ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 273 (33500); 308 (31400); 367 (27200); 480 (5900) and 1070 (19400).

**[Ni(Pr$_2^i$timdt)(dmit)] 6.** A $CH_3CN$ solution of complex **4** (109 mg) and $I_2$ (38 mg) was allowed to react at 0 °C. The solution turned from red-brown to dark green and a precipitate appeared. After a few hours crystals (80% yield) were collected by decantation and washed with $Et_2O$. Crystals suitable for X-ray analysis have been obtained from $CS_2$–$Et_2O$. Calc. for $C_{12}H_{14}N_2NiS_8$: C 28.74, H 2.81, N 5.58, S 51.15. Found: C 28.53, H 2.80, N 5.37, S 50.53%. IR [KBr pellets, cm$^{-1}$]: 2969w; 2925w; 2860w; 1462m; 1418s; 1383m; 1341s; 1338s; 1311s; 1257vs; 1179w; 1113s; 1081s; 1057s; 1034w; 933m; 874w; 780w; 430m and 338m. UV-vis (in $CS_2$), $\lambda$/nm ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 455 (8900); 710 (5700) and 1056 (38700).

**Table 4** Crystallographic data for compound [Ni(Pr$^i_2$timdt)(dmit)] **6**

| | |
|---|---|
| Chemical formula | $C_{12}H_{14}N_2NiS_8$ |
| Formula weight | 501.44 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ (no. 14) |
| $a$/Å | 16.723(5) |
| $b$/Å | 17.039(5) |
| $c$/Å | 7.124(7) |
| $\beta$/° | 102.36(2) |
| $V$/Å$^3$ | 1983(2) |
| $Z$ | 4 |
| Wavelength, $\lambda$/Å | Cu-Kα (1.541838) |
| $T$/K | 293 |
| $\mu$/cm$^{-1}$ | 92.70 |
| Reflections collected | 4046 |
| Independent reflections | 3743 [$R$(int) = 0.0487] |
| $R[I > 2\sigma(I)]$ | 0.0635 |
| $wR2$(all data) | 0.1979 |

**[Ni(Pr$_2^i$timdt)(mnt)] 7.** This compound was prepared as above with a 70% yield, starting from **5** (172 mg) and $I_2$ (95 mg). Calc. for $C_{13}H_{14}N_4NiS_5$: C 35.07, H 3.17, N 12.58, S 36.00. Found: C 35.20, H 3.35, N 12.59, S 35.57. IR [KBr pellets, cm$^{-1}$]: 2995w, 2218m, 1463m, 1428s, 1385vs, 1345s, 1305s, 1273vs, 1250w, 1115s, 1085s, 1062m, 1050m, 1035w, 1025vw, 880m, 785w, 750vw, 435m and 400w. UV-vis (in $CH_3CN$), $\lambda$/nm ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 517 (7400) and 883 (24100).

### Measurements

Elemental analyses were performed by means of a Carlo Erba CHNS elemental analyser model EA1108. IR spectra (4000–300 cm$^{-1}$) were recorded on a Perkin-Elmer model 983 Spectrophotometer as KBr pellets. Raman spectra were measured at room temperature on a single crystal by use of a Raman microscope (BX 40, Olimpus) spectrometer (ISA xy 800) equipped with a He–Ne ($\lambda$ = 632, 817 nm, Melles-Criot) laser, available in the Physics Department of Cagliari University. A 180° reflective geometry was adopted. The samples were mounted on a glass microscope slide and the scattering peaks calibrated against a silicon standard ($\nu$ 520 cm$^{-1}$). A typical spectrum was collected with a 500 s time constant at 1 cm$^{-1}$ resolution and averaged over 5 scans. No sample decomposition was observed during the experiments. Electronic spectra were recorded with a Cary 5 spectrophotometer.

Cyclic voltammograms were obtained using a conventional three-electrode cell consisting of a platinum wire working electrode, a platinum wire as counter electrode, and Ag–AgCl (KCl saturated) as reference electrode. The experiments were performed at room temperature (25 °C) at a 50–200 mV s$^{-1}$ scan rate, in anhydrous $CH_3CN$ as solvent containing 0.1 mol dm$^{-3}$ $Bu_4NPF_6$ electrolyte. A stream of argon was passed through the solution prior to the scan. The half-wave potential for the ferrocene–ferrocenium couple (internal standard) is 0.43 V under the above conditions. Data were recorded on a computer-controlled EG & G (Princeton Applied Research) potentiostat-galvanostat model 273, using electrochemical analysis software model 270.

### Crystal structure determination of complex 6

A Siemens AED diffractometer was used. Table 4 contains a summary of crystal data, data collection conditions and refinement parameters.

CCDC reference number 186/2246.

See http://www.rsc.org/suppdata/dt/b0/b006206p/ for crystallographic files in .cif format.

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7 The values at 1400 and 1130 nm have been read directly from the experimental spectra and compared with experimental values obtained for $[\mathrm{Ni(Pr^i{}_2timdt)_2}]^-$ and $[\mathrm{Ni(dmit)_2}]^-$. Although a peak deconvolution could have helped in establishing the actual number of peaks and their positions, the results summarised in Fig. 1 strongly indicate that a fast redox equilibrium reaction, shifted to the right, occurs before the transformation of the symmetrical derivatives to the unsymmetrical one: $[\mathrm{Ni(Pr^i{}_2timdt)_2}] + [\mathrm{Ni(dmit)_2}]^{2-} \rightleftharpoons [\mathrm{Ni(Pr^i{}_2timdt)_2}]^- + [\mathrm{Ni(dmit)_2}]^- \longrightarrow 2\ [\mathrm{Ni(Pr^i{}_2timdt)(dmit)}]^-$. This is reflected in the apparent isosbestic points where $\varepsilon([\mathrm{Ni(Pr^i{}_2timdt)_2}]^-) + \varepsilon([\mathrm{Ni(dmit)_2}]^-) \approx 2\varepsilon([\mathrm{Ni(Pr^i{}_2timdt)(dmit)}]^-)$. The symmetrical species, which are equimolar, appear and disappear simultaneously as they are a single species having an apparent $\varepsilon = \varepsilon([\mathrm{Ni(Pr^i{}_2timdt)_2}]^-) + \varepsilon([\mathrm{Ni(dmit)_2}]^-)$. No influence of the increasingly small amount of the reagents was observed.

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9 A possible correlation between the C=C bond order with the charge on the ligand would imply neglecting the charge on the metal. In the most widely accepted model for metal bis(dithiolene) complexes (Z. S. Herman, R. F. Kirchner, G. H. Loew, U. T. Mueller-Westerhoff, A. Nazzal and M. C. Zerner, *Inorg. Chem.*, 1982, **21**, 46) the metal atom is believed to remain in a formal oxidation state +2 with a $d^8$ configuration, these complexes being thus depicted as a 14 π-electron system with 5 π electrons at each ligand and 4 at the nickel. In the most recent theoretical study using density functional calculations (see ref. 15 below) it is stated that "the natural population analysis confirms that the metal $M^{2+}$ does accept electrons from the ligands but to a lesser extent than expected". Therefore, the $M^{2+}$-based simple and chemically intuitive model seems still appropriate in the present case for a qualitative discussion.

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18 The assignment of the C=C vibration in $\mathrm{Pr^i{}_2timdt}$ complexes is less unequivocal than in dmit and mnt complexes. Indeed, it does not appear as a strong band in the Raman spectrum and should likely fall in the IR region (1400–1260 $cm^{-1}$) where other bands may appear and other vibrations are expected (mainly the vibrations related to CN modes and also the CH bending of the side groups). The observed trend of a group of three strong bands in this range for $[\mathrm{Ni(Pr^i{}_2timdt)_2)}]$ (1362, 1332–1306, 1272 $cm^{-1}$), $[\mathrm{Ni(Pr^i{}_2timdt)(dmit)}]$ (1383, 1341–1338, 1257 $cm^{-1}$), $[\mathrm{Ni(Pr^i{}_2timdt)(mnt)}]$ (1385, 1345–1305, 1273 $cm^{-1}$), $[\mathrm{Ni(Pr^i{}_2timdt)_2)}]^-$ (1371, 1309, 1260 $cm^{-1}$), $[\mathrm{Ni(Pr^i{}_2timdt)(dmit)}]^-$ (1375, 1315, 1283 $cm^{-1}$) and $[\mathrm{Ni(Pr^i{}_2timdt)(mnt)}]^-$ (1382, 1318–1303, 1292 $cm^{-1}$) cannot straightforwardly be accounted for. It should be noted that the lowest unfilled molecular orbital (LUMO) in the symmetrical neutral derivative is a π orbital whereas the C=C bond regions are bonding. Thus, if the $\nu$(C=C) vibration could unambiguously be identified, a shift to higher frequencies may be expected since the population of the orbitals where the C=C bond regions are bonding increases. Moreover, a coupling of the cited vibrations cannot be excluded and this might explain the difficulty found in the assignment of the corresponding bands.

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