Unusual desulfurization of a nickel dithiolene by bis(2-diphenylphosphinophenyl)phenylphosphine (tp) to produce Ni(tp)(R_4btimdt) [R_4btimdt = 5,5′-bis(1,3-dialkyl-4-imidazolidine-2-thione-4-thiolate], the first complex of this class of ligands

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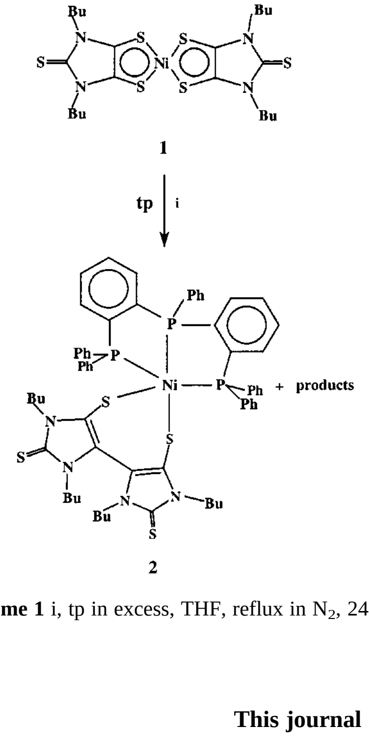
A novel desulfurization reaction induced on the title nickel dithiolenes by a tripodal phosphine producing the first complex of the S,S-dianionic title ligand, which belongs to a novel family of redox active heterocycles, and the fully oxidised trimeric form of this ligand are described.

The interest in the [Ni(R_2timdt)$_2$] complexes **1** (R_2timdt is the −1 charged 1,3-dialkyl-imidazolidine-2,4,5-trithione)[1, 2] and related derivatives,[3] is related both to their possible application as near-IR dyes,[4] and for their chemistry. In fact they are promising candidates in neodymium lasers (which operate at 1064 nm) technology, since they show low-energy electronic absorption,[4] typical of this class of complexes, at *ca.* 1000 nm with remarkably high absorption coefficients coupled with a high thermal and photochemical stability. Moreover these complexes show a rich and peculiar chemistry, being the source of a variety of unusual products including mixed-valence complexes[2] and new sulfur-rich donors which have not been obtained, as yet, by other routes.[3]

As a further example of a peculiar behaviour of this class of nickel dithiolenes, we report here, the results obtained by reacting **1** with mono- and poly-functional phosphines. While with mono- (PPh_3) or bi-functional [dppe = 1,2-bis(diphenylphosphino)ethane] phosphines the reagents are recovered unchanged, the reaction of **1** with a tri-functional phosphine [tp = bis(2-diphenylphosphinophenyl)phenylphosphine] unexpectedly produces [Ni(tp)(R_4btimdt)] (R = Bu, **2**) [R_4btimdt = 5,5′-bis(1,3-dialkyl-4-imidazolidine-2-thione-4-thiolate] according to Scheme 1.[5]

The molecular structure of [Ni(tp)(Bu_4btimdt)] **2**,[6] is shown in Fig. 1 with the corresponding atom-labelling scheme. The nickel ion is coordinated in a trigonal bipyramidal geometry with the three P atoms of the tp ligand lying on a face of the bipyramid. The chelation of tp produces the formation of two pentaatomic rings showing an 'envelope' conformation. The newly formed ligand Bu_4btimdt acts as a bidentate ligand being coordinated to the metal through the two thiolato sulfur atoms, in such a way that a heptaatomic ring including the metal is formed.

Complex **2** contains the first example of the S,S dinegative chelating ligand Bu_4btimdt, generated *in situ* by elimination of one of the two vicinal sulfur atoms on each ligand coordinated



Scheme 1 i, tp in excess, THF, reflux in N_2, 24 h.

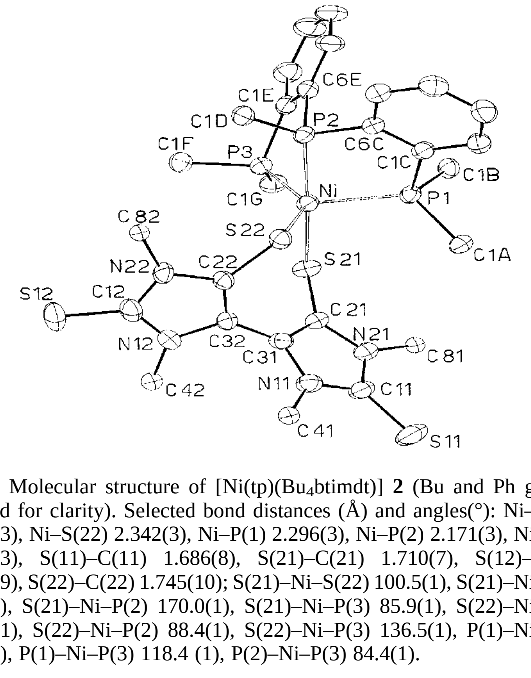


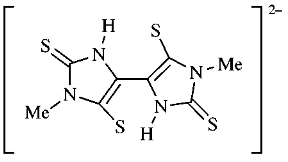
Fig. 1 Molecular structure of [Ni(tp)(Bu_4btimdt)] **2** (Bu and Ph groups omitted for clarity). Selected bond distances (Å) and angles(°): Ni–S(21) 2.270(3), Ni–S(22) 2.342(3), Ni–P(1) 2.296(3), Ni–P(2) 2.171(3), Ni–P(3) 2.203(3), S(11)–C(11) 1.686(8), S(21)–C(21) 1.710(7), S(12)–C(12) 1.698(9), S(22)–C(22) 1.745(10); S(21)–Ni–S(22) 100.5(1), S(21)–Ni–P(1) 97.6(1), S(21)–Ni–P(2) 170.0(1), S(21)–Ni–P(3) 85.9(1), S(22)–Ni–P(1) 103.5(1), S(22)–Ni–P(2) 88.4(1), S(22)–Ni–P(3) 136.5(1), P(1)–Ni–P(2) 84.7(1), P(1)–Ni–P(3) 118.4 (1), P(2)–Ni–P(3) 84.4(1).

to the metal in the nickel dithiolene with concomitant C–C coupling between the two imidazole rings.

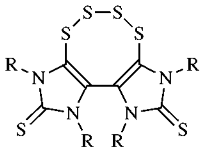
A dianion, H_2X^{2-}, belonging to the same class of Bu_4btimdt^{2-} has been obtained *via* an unusual method by reacting elemental sulfur with 1-methylimidazole.[7] This anion was isolated in the solid state as the salt $(PPh_4)_2H_2X$ structurally characterized, and proposed as a new ligand of special interest owing to its multi-electron redox properties. However, to the best of our knowledge, its coordination chemistry is still unexplored. Also a neutral compound obtained from oxidation of this ligand has been isolated but not characterized.

These ligands are related to the class of 4,5,6,7-tetrathiocino[1,2-*b*:3,4-*b*′]diimidazolyl-1,3,8,10-tetraalkane-2,9-dithiones **3**[8] which exhibit promising anticancer properties now under testing *in vivo* by National Cancer Institute of Bethesda (USA).

By reacting **3** with an alcoholate, the R_4btimdt anion is formed in solution and can be isolated in the complex [Ni(dppe)(R_4btimdt)], when [Ni(dppe)Cl_2] is added to the reaction mixture, buffered with ammonium acetate. When non-coordinated, the anion is oxygen sensitive and attempts to isolate it as a salt gave a mixture from which the new macrocycle **4** was isolated in low yield. Macrocycle **4** is prepared more conveniently (40% yield) by buffering with ammonium acetate and oxidizing the reaction mixture with O_2 or H_2O_2.[9] **4** can be considered as a trimer of R_4btimdt where the monomeric units are linked together through disulfide bridges.



H_2X^{2-}



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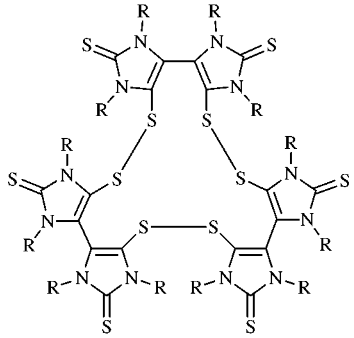

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Crystals suitable for structural characterization were obtained for **4**·2EtOH (R = Et). Its molecular structure,[6] is shown in Fig. 2 with the corresponding atom-labelling scheme. The molecule has a twofold axis. The structural data are similar to those previously observed by us in thione derivatives with similar moieties.[2,8] Interactions of the type S···C and C···C[3.46(1)–3.79(3) Å] determine the packing so that the eighteen-membered rings of the molecules give rise to channels, parallel to *c*, which contain the guest solvent molecules.

In conclusion a novel desulfurization reaction with concomitant C–C coupling between two imidazoline rings, not reported previously, has been described. This reaction represents a promising template synthesis to prepare, starting from nickel dithiolenes, new chelating S,S-dianionic ligands, which are not easily attained by other routes.

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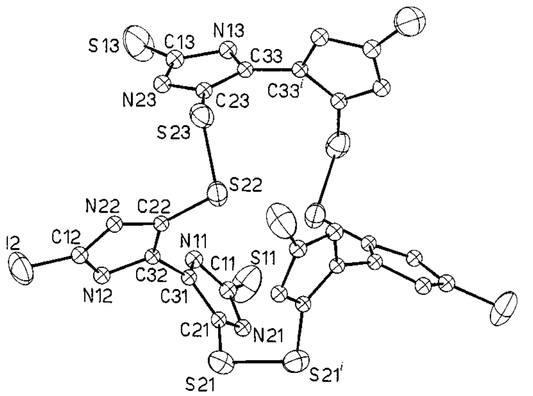

Fig. 2 Molecular structure of **4** (Et groups and sovent molecules omitted for clarity). Selected bond distances (Å) and angles(°): S(21)–S(21ⁱ) 2.087(4), S(22)–S(23) 2.074(3), S(11)–C(11) 1.657(7), S(12)–C(12) 1.666(7), S(13)–C(13) 1.676(8), S(21)–C(21) 1.740(7), S(22)–C(22) 1.725(7), S(23)–C(23) 1.750(8); C(21)-S(21)– S(21ⁱ) 106.8(3), C(22)–S(22)–S(23) 107.1(2), C(23)–S(22)–S(23) 107.9(3). [ⁱ: $-y$, $-x$, $3/2 - z$].

Notes and references

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5 *Preparation of* **2**: [Ni(Bu_2timdt)$_2$] (50 mg) and an excess of tp bis (2-diphenylphosphinophenyl)phenylphosphine[10] (200 mg) (1:4 molar ratio) were mixed and refluxed in THF (50 mL), under N_2 for 24 h. The solution turned from olive-green to purple. The solvent was removed *in vacuo* and by repeated fractional crystallization from MeCN–Et_2O of the crude product, a complete separation of **2** from the excess of the less solubie tp was achieved. Well shaped pure red–brown crystals (70 mg, 72% yield), were obtained.

6 *Crystal data for compound* **2**: $C_{64}H_{69}N_4NiP_3S_4$, M = 1174.09, triclinic, $P\bar{1}$, a = 11.057(4), b = 12.973(6), c = 23.023(9) Å, α = 78.69(2), β = 75.88(2), γ = 69.89(2)°, V = 2984(2) Å^3, Z = 2, μ = 28.66 cm^{-1}, T = 293(2) K, 11299 reflections measured, 11299 unique data. For 4879 observed reflections with [$I > 2\sigma(I)$] and 606 parameters the final R_1 = 0.0882 [wR_2 = 0.3283(all data)]. For compound **4**: $C_{46}H_{72}N_{12}O_2S_{12}$, M = 1209.88, tetragonal, $P4_32_12$, a = 12.915(6), c = 36.122(5) Å, V = 6025(4) Å^3, Z = 4, μ = 44.15 cm^{-1}, T = 293(2) K, 6328 reflections measured, 5724 unique data (R_{int} = 0.0495), Flack abs. structure parameter = 0.04(5). For 4184 observed data with [$I > 2\sigma(I)$] and 260 parameters the final R_1 = 0.0817 [wR_2 = 0.2932(all data)]. Data were collected from an Enraf-Nonius CAD4 diffractometer (Cu-Kα radiation, λ = 1.54184 Å). In the final refinement rigid-body constraints for all butyl groups in **2** and for solvent molecules in **4**, occupancy factor of 0.55 and 0.45 for the atoms of the two images of the disordered ethyl group in **4**. CCDC 182/1406.

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9 *Preparation of* **4**: Compound **3** (R = Et) (0.50 g) and Na (1.0 g) in dry methanol were stirred overnight under nitrogen. The obtained clear yellow solution was buffered with an excess of ammonium acetate. Air was bubbled over a period of 1 h and an orange–yellow solid precipitated. The crude product contained white–yellowish crystals of sulfur which were removed by washing with CS_2, in which the desired product is less soluble. The product was recrystallized from CH_2Cl_2–EtOH to give pure orange–red crystals (0.17 g, 40% yield).

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