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A new approach to divalent thio-azo ligands; $Ni(dpesdt)_2$

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Abstract

The preparation of a new bis(2-pyridylethylsulfanyl)-1,3-dithiole-2-one (**1**) and the first example of a tetra-azo substituted bisdithiolene transition metal complex, $Ni(dpesdt)_2$ (**2**) are reported. This complex crystallizes in two polymorphs, one is triclinic, and the other is monoclinic, $P2_1/n$ space group.

Keywords: Thioazo ligands; Bisdithiolene; Nickel complexes

1. Introduction

Ligands offering the possibility of coordinating two different metals in specific and controlled ways by two ligand sites are expected to be quite versatile building blocks in the preparation of molecular materials. This possibility is quite interesting namely in the field of molecular magnetic materials since such ligands can be used as key elements to build heterobimetallic networks.

We have recently focused our attention to dithio-diazo ligands, capable of coordinating both by *S* and *N* sites, which have different metal coordination abilities. These ligands are therefore expected to act as bridging units between different metals in magnetic networks.

One approach to this type of divalent ligands is provided by dialkylpyridyldithiolene ligands. Divalent transition metal complexes of alkylpyridyl derivatized dmit ligands have been already reported in the past [1,2], but to the best of our knowledge, no previous attempt succeeded in obtaining a bisdithiolene complex with pyridyl substituted ligands.

2. Experimental

Where required, the solvents were dried according to the standard literature procedures [3]. $(n\text{-}Et_4N)_2[Zn(dmio)_2]$ were prepared by the literature methods [4].

2.1. Synthesis of 4,5-bis(2-pyridylethylsulfanyl)-1,3-dithiole-2-ona (*1*)

A solution of $TEA_2[Zn(dmio)_2]$ (5 g, 7.28 mmol) and 2-vinylpiridine (6.3 eq, 5.06 ml, 48 mmol) in $CHCl_3$/AcOH (3:1, 100 ml) was prepared. The mixture was heated under reflux overnight. The resulting solution was filtered; the filtrate was washed with water, sat. aq. solution of $NaHCO_3$, sat. aq. solution of NaCl and water, dried with $MgSO_4$ and concentrated under vacuum. The residue was chromatographed on a silica-gel column using EtOAc/Hexane (2:1) as the eluent. The product was recovered as a TLC and NMR pure oil (Rf = 0.27). Yield: 1.86 g (4.74 mmol), 65.17% based on $TEA_2[Zn(dmio)_2]$.

Anal. Calc. for $C_{17}H_{16}N_2OS_4$: C, 52.01; H, 4.11; N, 7.14; S, 32.67. Found: C, 51.15; H, 4.37; N, 7.53; S, 31.66%. ^1H

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NMR (300 MHz, $CDCl_3$): δ 3.12 (t, 4H, SCH_2), 3.28 (t, 4H, CH_2Py), 7.13–7.19 (m, 4H, Py–H), 7.61 (dt, 2H, Py–H), 8.54 (d, 2H, Py–H). ^{13}C NMR, $CDCl_3$: δ 35.78 (CH_2), 38.06 (CH_2Py), 121.78 (Py–C), 123.21 (Py–C), 127.38 (Py–C), 136.49 (C=C), 149.38 (Py–C), 158.48 (C–N), 189.75 (C=O). IR (KBr): 1439, 1478, 1571, 1596, 1651 cm^{-1}.

The same product could be obtained with a different synthetic route, by oxymercuration using the corresponding thione as the starting material. This thione was synthesized according to the method reported in the literature by Becher et al. [1]. The yield was 76% based on 4,5-bis(2-pyridylethylsulfanyl)-1,3-dithiole-2-thione.

2.2. Synthesis of nickel(IV) bis(2-pyridylethylsulfanyl)-1,2-ditihiolene complex (**2**)

The nickel (IV) complex was obtained, using freshly distilled solvents and under an inert atmosphere. In a schlenk tube ligand **1** (0.2 g; 0.5 mmol) was dissolved in methanol (3 mL) and a sodium methoxide solution (Na 0.0234 g; 1 mmol; methanol 8 mL) was added dropwise to the solution. A solution of nBu$_4$NBr (0.164 g, 0.5 mmol) in methanol (5 mL) was added, followed by a solution of $NiCl_2 \cdot 6H_2O$ (0.0604 g, 0.25 mmol) in the same solvent. The mixture was cooled and no visible precipitate was observed. The mixture was concentrated under nitrogen flux, and an oil was obtained. This crude material was recrystallized by a slow diffusion of hexane in a dichloromethane saturate solution at a low temperature (−20 °C). After 2 days, dark green crystals suitable for X-ray diffraction were collected. The yield (0.011 g, 5.11%) was based on the [Ni-(dpesdt)$_2$]. *Anal.* Calc. for $C_{32}H_{32}N_4N_iS_8$: C, 48.78; H, 4.09; N, 7.11; S, 32.56. Found: C, 49.54; H, 3.65; N, 7.07; S, 31.46%.

2.3. X-ray structural determination of **2**

X-ray diffraction experiments for monocrystal were performed with a Bruker AXS APEX CCD detector diffractometer using graphite monochromated Mo Kα radiation (λ = 0:71073 Å), at 150 K in the φ and ω scans mode. A semiempirical absorption correction was carried out using SADABS [5]. Data collection, cell refinement and data reduction were done with the SMART and SAINT programs [6]. The structures were solved by the direct methods using SIR97 [7] and refined by full-matrix least-squares methods using the program SHELXL97 [8] using the winGX software package [9]. Non-hydrogen atoms were refined with anisotropic thermal parameters, whereas H-atoms were placed in idealized positions and allowed to refine riding on the parent C atom. Molecular graphics were prepared using ORTEP 3 [10]. A summary of the crystal data, structure solution and refinement are given in Table 1. The selected bond distances and angles of the nickel (IV) complex are listed in Table 2.

Table 1
Crystal data and structure refinement for **2**

Empirical formula	$C_{32}H_{32}N_4NiS_8$
Formula weight	787.81
Temperature (K)	150(2)
Wavelength (A)	0.71069
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	
a (Å)	5.4194(3)
b (Å)	13.2804(7)
c (Å)	13.3549(7)
α (°)	63.564(3)
β (°)	80.134(3)
γ (°)	80.615(3)
Volume (Å^3)	843.83(8)
Z	1
D_{calc} (g/cm^{-3})	1.550
Absorption coefficient (mm^{-1})	1.101
F(000)	408
Crystal size (mm)	0.26 × 0.06 × 0.01
θ Range (°)	2.90–26.34
Index range	$-2 \leqslant h \leqslant 6$, $-16 \leqslant k \leqslant 14$, $-16 \leqslant l \leqslant 16$
Reflections collected	12334
Independent reflections [R_{int}]	3399 [0.0716]
Completeness to θ (%)	26.34 98.8
Maximum and minimum transmission	0.9891 and 0.7628
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	3399/0/205
Goodness-of-fit on F^2	0.906
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0428$, $wR_2 = 0.0674$
R indices (all data)	$R_1 = 0.1031$, $wR_2 = 0.0766$
Largest difference in peak and hole (e Å^{-3})	0.463 and −0.376

Table 2
Selected bond and lengths (Å) and angles (°) for (**2**)

Bond lengths (Å)	
Ni(1)–S(1)	2.1260(8)
Ni(1)–S(2)	2.1293(9)
S(1)–C(1)	1.693(3)
S(2)–C(9)	1.710(3)
S(3)–C(1)	1.763(3)
S(3)–C(2)	1.803(3)
S(4)–C(9)	1.743(3)
S(4)–C(10)	1.821(3)
C(1)–C(9)	1.400(4)
Bond angles (°)	
S(1)–Ni(1)–S(2)	92.18(3)
C(1)–S(1)–Ni(1)	104.53(11)
C(9)–S(2)–Ni(1)	104.66(11)
C(1)–S(3)–C(2)	102.02(15)
C(9)–C(1)–S(1)	120.1(2)
C(1)–C(9)–S(2)	118.5(3)
C(9)–C(1)–S(3)	118.6(3)
S(1)–C(1)–S(3)	121.29(17)
C(1)–C(9)–S(4)	119.4(2)
S(2)–C(9)–S(4)	122.08(18)

3. Results and discussion

4,5-Bis(2-pyridylethylsulfanyl)-1,3-dithiole-2-ona (**1**) (Fig. 1) was used as the key precursor of the divalent ligand diethylpyridyldithiolene (dpesdt).

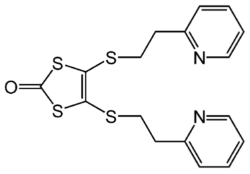

Fig. 1. 4,5-Bis(2-pyridylethylsulfanyl)-1,3-dithiole-2-ona (**1**).

By the hydrolytic cleavage of **1** with a sodium methoxide solution in the presence of n-Bu_4NBr and nickel dichloride, nickel(IV) bis(2-pyridylethylsulfanyl)-1,2-ditihiolene complex (**2**) was obtained.

Due to the lower solubility presented by complex **2** in solvents such as DCM and CH_3CN cyclic voltammetry was performed in THF. In spite of the anaerobic preparative conditions employed and the starting Ni(II) oxidation state the complex obtained was neutral corresponding to a formal Ni(IV) oxidation state. This agrees with the rather low oxidation potentials revealed in the cyclic voltammetry

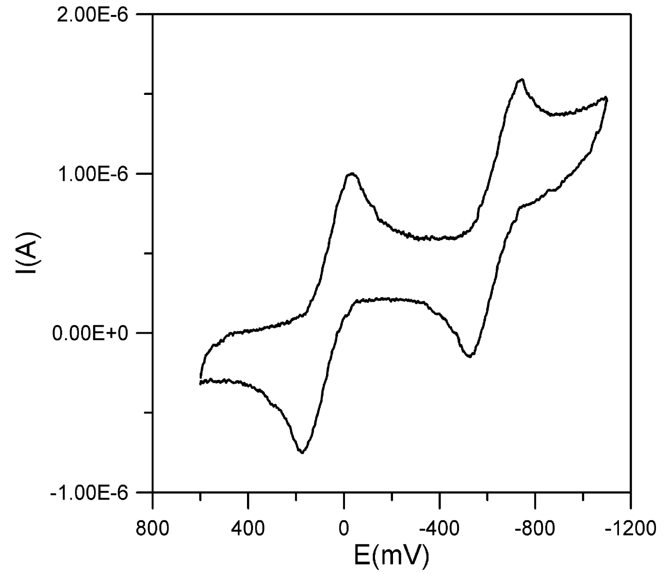

Fig. 2. Cyclic voltammetry of 2, in THF vs. Ag/AgCl, 0.1 M TBAPF6.

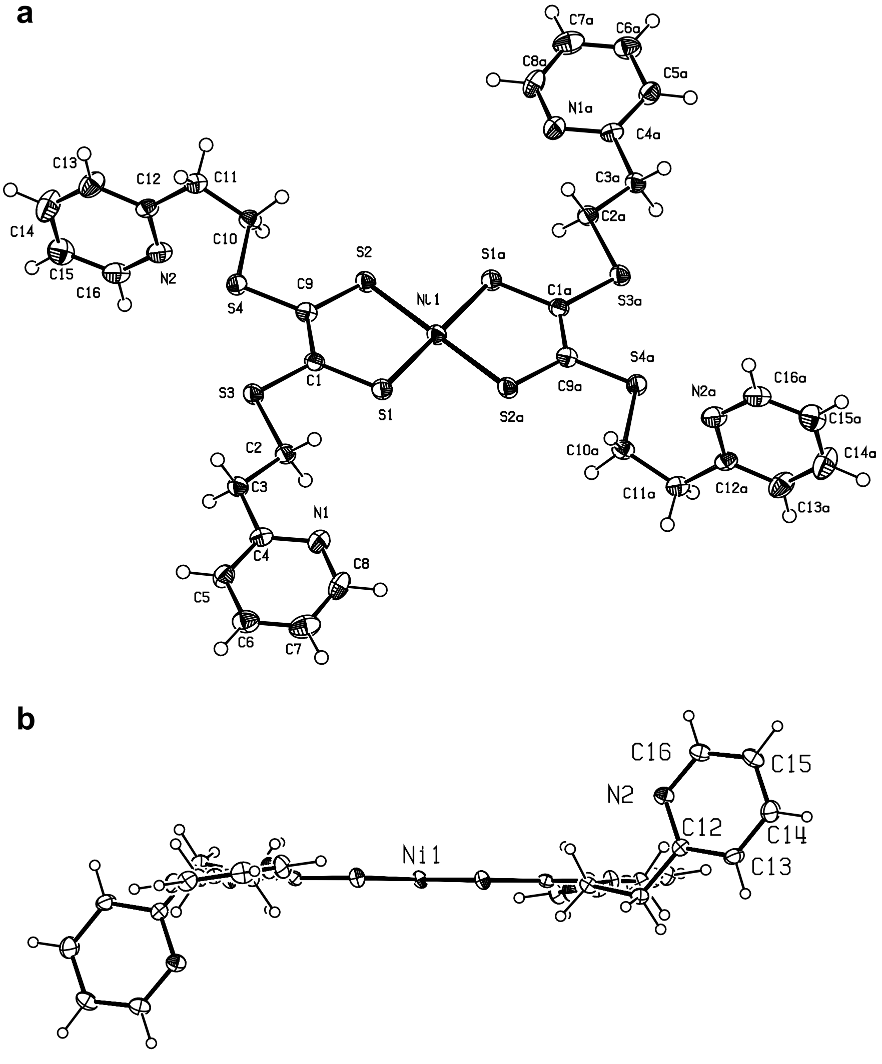

Fig. 3. ORTEP views and atomic numbering scheme of **2**, with thermal ellipsoid at 40% probability.

study of this complex in THF showing two quasi reversible pairs of waves centered at −636 mV and 69 mV versus Ag/AgCl (Fig. 2) which are described to the redox couples $Ni(dpesdt)_2^{2-}/Ni(dpesdt)_2^{-}$ and $Ni(dpesdt)_2^{-}/Ni(dpesdt)_2$, respectively.

These potentials are significantly less positive than those of the simple alkyl-thio substituted bisdithiolene complexes previously reported in which the preparation of the neutral complex required oxidation by iodine [12b]. Although not directly conjugated to the central Ni–S core the pyridine rings clearly stabilize the higher oxidation states. However, this effect is not strong enough to achieve the stabilization cationic states of the complex, since in cyclic voltammetry there are no signs of any additional oxidative wave up to 0.8 V. This contrasts with similar Nickel bis-alkylthio-ethylene-1,2-dithiolene [12b] and $Ni(dddt)_2$ [11] complexes in which the formation of cationic species are shown at circa 1.1 and 0.8 V, respectively.

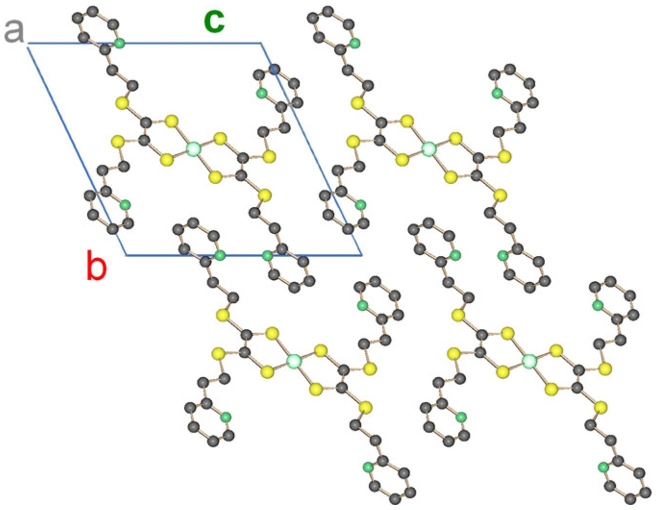

Fig. 4. View of the crystal structure of **2** along *a*.

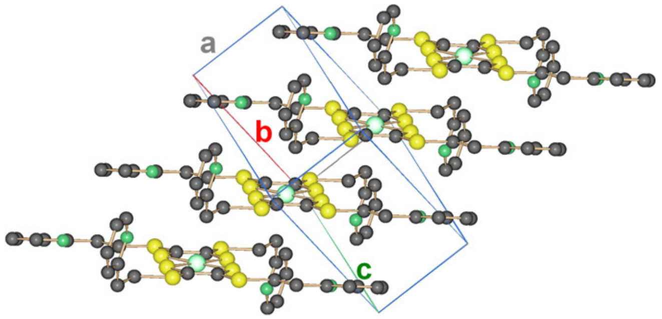

Fig. 5. Partial view of column of $[Ni(dpesdt)_2]$ units.

Table 3
Short contacts (Å) in the crystal structure of **2**

H(8)–H(13)	2.373
H(11B)–C(5)	2.851
H(5)–S(3)	2.922
S(3)–H(10B)	2.977
H(16)–H(10A)	2.358

The crystal quality made possible to solve the crystal structure of **2**. The complex **2** crystallizes in the triclinic system, $P\bar{1}$ space group, $Z = 1$. Complex presents the nickel atom on an inversion center with the usual square planar coordination (Fig. 3) and Ni–S bond lengths typical of Ni(IV) [12] (Table 2). The central core of the complex (Ni1, S1, S2, C1, C9, S3, S4) is essentially planar, there is no significant deviation of the atoms relatively to the average plane. Two of the complex's pyridine rings (C12, C13, C14, C15, C16, N2) are out of the central core plane with 80.43° and the others pyridine rings (C4, C5, C6, C7, C8, N1) are almost in the central core plane (8.82°). The dihedral angle between the pyridine rings is 76.54°.

The supramolecular arrangement of complex **2** consists on parallel columns of $[Ni(dpesdt)_2]$ units, stacked along *a* (Fig. 4). The shortest S···S distances within the chain

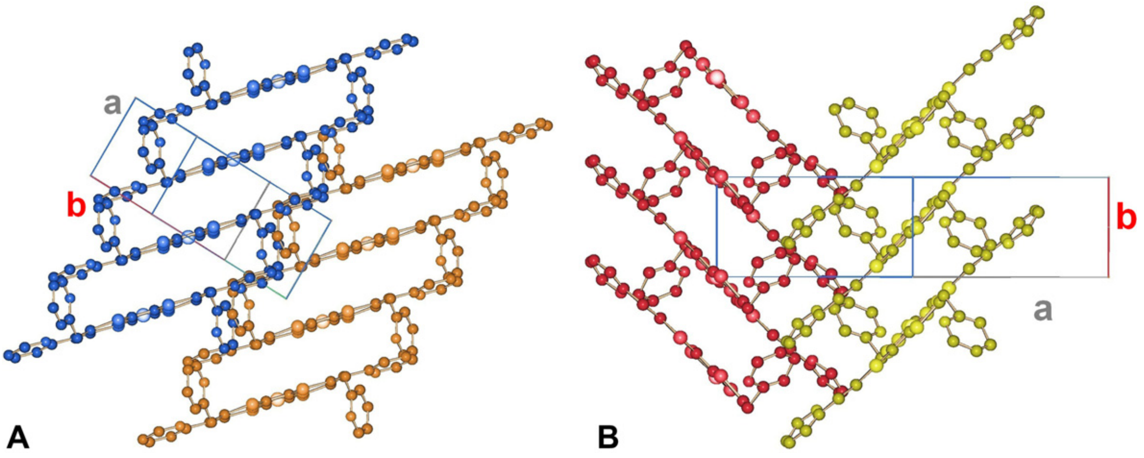

Fig. 6. Partial view of two adjacent columns of $[Ni(dpesdt)_2]$ in case the triclinic structure (A) and in case the monoclinic structure (B).

are 3.879 and 3.917 Å (Fig. 5). The interactions between the [Ni(dpesdt)$_2$] units are established through several short contacts involving hydrogen atoms (Table 3).

Other similar preparations afforded crystals of a poorer diffraction quality, insufficient for crystal structure refinement which however indicated a different space group and distinct crystal packing. This denotes the occurrence of polymorphism in this compound. This new phase crystallizes in the monoclinic system, space group $P2_1/n$ ($a = 18.725(6)$, $b = 5.277(4)$ Å, $c = 19.628(10)$ Å; $\alpha = 90.00(4)°$, $\beta = 114.50(4)°$, $\gamma = 90.00(4)°$; $V = 1764.9(16)$ Å^3, $Z = 2$). Although the data are not good enough for structural refinement, they show a different supramolecular arrangement consisting on the parallel columns of [Ni(dpesdt)$_2$] units related by screw axes and the molecules are tilted in an alternated orientation towards the stacking axe b (Fig. 6).

In conclusion the first example of a tetra-azo bisdithiolene complex was prepared and characterized. This nickel complex is the first member of a large family of compounds based on divalent ligands and it is expected to open new possibilities in the preparation of heterobimetallic networks.

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Appendix A. Supplementary material

CCDC 626084 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.12.027.

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