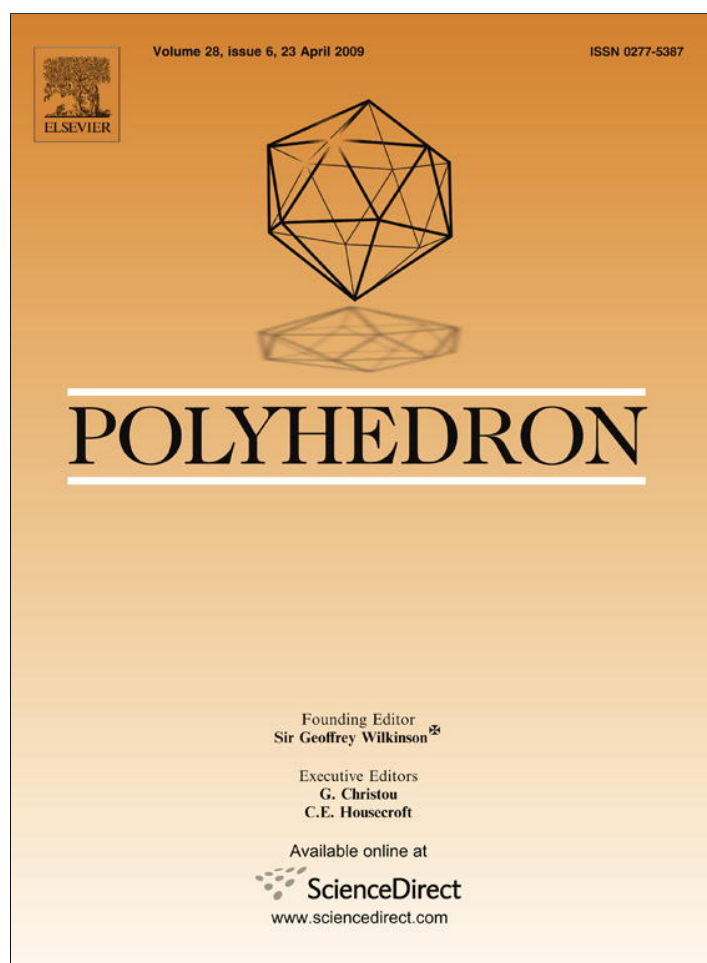


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Complexes based on asymmetrically substituted pyridine–dithiolene ligands [M(4-pedt)₂] (M = Au, Cu, Ni; 4-pedt = 1-(pyridin-4-yl)-ethylene-1,2-dithiolate): Synthesis, structure and physical properties

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ABSTRACT

The monoanionic Ni, Au and Cu bisdithiolene complexes based on the 1-(pyridin-4-yl)-ethylene-1,2-dithiolate were prepared and isolated as [PPh₄]⁺, [n-Bu₄N]⁺ and [Na(18C6)]⁺ salts which were characterised by single-crystal X-ray diffraction, cyclic voltammetry, EPR and magnetic susceptibility measurements. All the complexes adopt a square planar coordination geometry with a trans arrangement of the substituent pyridine rings whose planes are rotated from 13° to 33° relatively to the central MS₄ core. The C–C and C–S bond lengths are consistent with ene-1,2-dithiolate form of the ligand and M^{III} oxidation state. The Ni complexes are paramagnetic with an effective magnetic moment of ~1.7 BM.

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1. Introduction

Transition metal bis(dithiolene) complexes have attracted research attention for more than 30 years and, due to their rich redox behaviour and favourable solid state interactions in their square-planar geometry, they have been widely used in the preparation of conducting and magnetic materials [1]. These complexes can be seen as inorganic analogues of the corresponding TTF type donors where the transition metal replaces the central C=C bond. The TTF type donors have been at the basis of the large majority of all known molecular conductors and superconductors, and these inorganic analogues offer the additional advantage that depending on the oxidation state and on the transition metal they can be either diamagnetic or paramagnetic with different magnetic moments.

Recently there has been an increasing focus of attention on the preparation of donors which, in addition to their electroactive role, can bind directly to transition metals and some TTF derivatives substituted with groups containing N coordinating atoms [2] and their complexes have been recently described [3]. The corresponding inorganic analogues, bis(dithiolene) complexes with ligands bearing nitrogen coordinating groups have been however a lot less explored. Having in mind such type of complexes, we recently fo-

cused our interest on bis(dithiolene) complexes based on thio-azo ligands bearing heterocyclic groups and recently described the first neutral Ni bis(dithiolene) complex (formally Ni^{IV}) with alkylpyridyl substituted ligands, Ni(dpesdt)₂ (dpesdt = bis(2-pyridylethylsulfanyl)-2-dithiolate) [4].

Asymmetrically substituted dithiolenes have been significantly less studied in spite of providing also interesting properties [5] namely for magnetic materials [6] and optoelectronics [7]. One example of bis(dithiolene) complexes bearing heterocyclic groups are the M(*n*-pedt)₂ complexes (*n* = 2, 3 or 4), based on the asymmetrically substituted ligand *n*-pedt = S–C(H)=C(R)–S; R = 4-pyridyl. Ligand 4-pedt was previously presented in a preliminary short report [8]. More recently monoanionic gold bisdithiolene complexes with R = *n*-pyridyl ligands were also described [9].

In this paper, we describe the preparation and characterisation of monoanionic [M(4-pedt)₂][–] complexes of nickel, copper and gold obtained as tetrabutylammonium, tetraphenylphosphonium or sodium 18-crown-6 ether salts.

2. Experimental

2.1. Materials and methods

All manipulations were carried out under anaerobic conditions, unless stated otherwise. Whenever required, the solvents were

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dried according to the standard literature procedures [10], freshly distilled, and saturated with nitrogen prior to use. All starting reagents were purchased from commercial sources and used without further purification or synthesised from published methods. The 4-(4-pyridyl)-1,3-dithiol-2-one was synthesised according to literature reports [8,11].

Elemental analyses of the compounds isolated in these studies were performed at ITN analytical services using an EA 110 CE Instruments automatic analyser. Melting points were performed on a Stuart Scientific SMP2.

2.2. Synthesis

2.2.1. Tetraphenylphosphonium salt of bis[1-(4-pyridin-4-yl)-1,2-ethylenedithiolato]nickel, $\text{PPh}_4[\text{Ni}(4\text{-pedt})_2]$ (**1**)

The 4-(4-pyridyl)-1,3-dithiol-2-one (0.50 g; 2.56 mmol) was added to a sodium methoxide solution (0.147 g; 6.40 mmol; 13 mL). After 45 min of stirring, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.37 g, 1.28 mmol) was added. One hour later the red solution was filtered to an aqueous PPh_4Cl solution (0.96 g, 2.56 mmol, 100 mL). A black precipitate appeared immediately from the brown solution. The solid was recovered by filtration, washed with water and recrystallised from acetonitrile to afford black crystals of the nickel salt suitable for X-ray diffraction. 50% yield (0.47 g, 0.64 mmol); m.p. 217–218 °C. $\text{C}_{38}\text{H}_{30}\text{NiN}_2\text{PS}_4$ (Mol. Wt.: 732.59). Elemental Anal. Calc.: C, 62.30; H, 4.13; N, 3.82; S, 17.51. Found: C, 62.09; H, 4.06; N, 3.77; S, 17.31%.

2.2.2. Tetraphenylphosphonium salt of bis[1-(4-pyridin-4-yl)-1,2-ethylenedithiolato]copper $\text{PPh}_4[\text{Cu}(4\text{-pedt})_2]$ (**2**)

The oxo compound (0.10 g; 0.51 mmol) was added to a freshly made sodium methoxide solution (0.023 g; 1.02 mmol, 3 mL) and stirred at room temperature, until total dissolution, followed by drop wise addition of a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.043 g; 0.25 mmol) in methanol (2 mL). The solution was stirred for 1 h and filtered to a PPh_4Br methanol solution (0.214 g, 0.51 mmol, 3 mL). No precipitate formation was observed. The reaction vial was opened to the air, a few H_2O drops were slowly added until start of incipient precipitation and the mixture was left overnight at 4 °C. The oil that formed was separated from the mixture by centrifugation, dried under vacuum (P_2O_5) and recrystallised from dichloromethane/hexane to be recovered as a microcrystalline precipitate. 48% yield (0.089 g, 0.12 mmol); m.p. 162–163 °C. $\text{C}_{38}\text{H}_{30}\text{N}_2\text{CuS}_4$ (Mol. Wt.: 737.44). Elemental Anal. Calc.: C, 61.89; H, 4.10; N, 3.80; S, 17.39. Found: C, 61.72; H, 4.92; N, 3.84; S, 18.03%.

2.2.3. Tetrabutylammonium salt of bis[1-(4-pyridyl)-1,2-ethylenedithiolato]nickel $n\text{-Bu}_4\text{N}[\text{Ni}(4\text{-pedt})_2]$ (**3**)

The procedure was similar to the described above. The oxo compound was added (0.10 g; 0.51 mmol) to a freshly made sodium methoxide solution (0.023 g; 1.02 mmol, 3 mL) and stirred at room temperature, until total dissolution, followed by dropwise addition of a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.061 g; 0.25 mmol) in methanol (2 mL). The red solution was stirred for 1 h and then filtered into $n\text{-Bu}_4\text{NBr}$ methanol solution (0.165 g, 0.51 mmol, 3 mL). No precipitate formation was observed. The reaction vial was opened to the air, a few H_2O drops were slowly added until start of incipient precipitation and the mixture was left overnight at 4 °C. The reddish oil formed was separated from the mixture by centrifugation, dried under vacuum (P_2O_5) and recrystallised from acetone to be recovered as a microcrystalline precipitate. 65% yield (0.105 g, 0.16 mmol); m.p. 133–134 °C. $\text{C}_{30}\text{H}_{46}\text{N}_3\text{NiS}_4$ (Mol. Wt.: 635.66) Elemental Anal. Calc.: C, 56.68; H, 7.29; N, 6.61; S, 20.18. Found: C, 56.01; H, 7.89; N, 6.12; S, 19.75%.

2.2.4. Tetrabutylammonium salt of bis[1-(4-pyridyl)-1,2-ethylenedithiolato]copper, $n\text{-Bu}_4\text{N}[\text{Cu}(4\text{-pedt})_2]$ (**4**)

Following the same general procedure used for $n\text{-Bu}_4\text{N}[\text{Ni}(4\text{-pedt})_2]$, the oxo compound was added (0.10 g; 0.51 mmol) to a freshly made sodium methoxide (0.023 g; 1.02 mmol, 3 mL) stirred until total dissolution, followed by drop wise addition of a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.043 g; 0.25 mmol) in methanol (2 mL). The solution was stirred for 1 h and afterwards filtered onto an $n\text{-Bu}_4\text{NBr}$ methanol solution (0.165 g, 0.51 mmol, 3 mL). No precipitate formation was observed. A few H_2O drops were slowly added until start of incipient precipitation and the mixture was left overnight at 4 °C. The oil formed was separated from the mixture by centrifugation, dried under vacuum (P_2O_5) and recrystallised from dichloromethane/hexane to be recovered as a microcrystalline precipitate. 41% yield (0.065 g, 0.10 mmol); m.p. 160–162 °C. $\text{C}_{30}\text{H}_{46}\text{N}_3\text{CuS}_4$ (Mol. Wt.: 640.51) Elemental Anal. Calc.: C, 56.26; H, 7.24; N, 6.56; S, 20.02. Found: C, 55.83; H, 7.01; N, 6.12; S, 19.84%.

2.2.5. Tetrabutylammonium salt of bis[1-(4-pyridyl)-1,2-ethylenedithiolato]gold $n\text{-Bu}_4\text{N}[\text{Au}(4\text{-pedt})_2]$ (**5**)

Following the same general procedure used for $n\text{-Bu}_4\text{N}[\text{Ni}(4\text{-pedt})_2]$, the oxo compound (0.10 g; 0.51 mmol) was dissolved in a freshly prepared methoxide solution (0.024 mg; 1.02 mmol, 3 mL). The total dissolution of the oxo compound was followed by drop wise addition of a $\text{KAuCl}_4 \cdot 4\text{H}_2\text{O}$ methanol solution (0.097 g; 0.25 mmol, 2 mL). The brown solution was filtered into an $n\text{-Bu}_4\text{NBr}$ methanol solution (0.165 g, 0.51 mmol, 3 mL). After the addition of a few milliliters of water, the reaction vial was kept for several hours at 4 °C. The brown oil formed was recovered by centrifugation, dried under vacuum (P_2O_5) and recrystallised from dichloromethane/hexane to be recovered as a microcrystalline precipitate. 60% yield (0.115 g, 0.15 mmol); m.p. 127–129 °C. $\text{C}_{30}\text{H}_{46}\text{N}_3\text{AuS}_4$ (Mol. Wt.: 773.93). Elemental Anal. Calc.: C, 46.56; H, 5.99; N, 5.43; S, 16.57. Found: C, 46.21; H, 5.52; N, 5.25; S, 16.39%.

2.2.6. Crown ether $[\text{Na}(18\text{C}6)]$ salt of bis[1-(4-pyridyl)-1,2-ethylenedithiolato]nickel $[\text{Na}(18\text{C}6)][\text{Ni}(4\text{-pedt})_2]$ (**6**)

The oxo compound (0.20 g; 1.03 mmol) was added to a freshly prepared methoxide solution (0.047 g, 2.05 mmol, 5 mL). After stirring until total dissolution, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ methanol solution (0.122 g; 0.51 mmol, 5 mL) was added. The red solution was stirred for 1 h and then filtered into an 18-crown-6 methanol solution (0.271 g, 1.03 mmol, 1 mL). The mixture was left at 4 °C for two weeks. A mixture of amorphous brown and darker polycrystalline precipitate was recovered by vacuum filtration. The mixture was dissolved in dichloromethane and an insoluble precipitate was removed. By slow diffusion of hexane into the dichloromethane solution, it was possible to recover compound **6** as a dark brown polycrystalline material. 58% yield (0.197 g; 0.29 mol) m.p. 260–261 °C. $\text{C}_{26}\text{H}_{34}\text{N}_2\text{NaNiO}_6\text{S}_4$ (Mol. Wt.: 680.5). Elemental Anal. Calc.: C, 45.89; H, 5.04; N, 4.12; S, 18.85. Found: C, 45.43; H, 5.35; N, 4.12; S, 18.30%.

2.2.7. Crown ether $[\text{Na}(18\text{C}6)]$ salt of bis[1-(4-pyridyl)-1,2-ethylenedithiolato] gold $[\text{Na}(18\text{C}6)][\text{Au}(4\text{-pedt})_2]$ (**7**)

The oxo compound (0.10 g, 0.51 mmol) was added to a freshly prepared sodium methoxide solution (0.0235 g, 1.02 mmol, 5 mL) and stirred for 45 min. The dark red solution was removed from the inert atmosphere and solid $\text{KAuCl}_4 \cdot 4\text{H}_2\text{O}$ (0.097 g, 0.25 mmol) was added. The mixture was stirred for 2 h, filtered over Celite to a solution of 18C6 (0.0677 g, 0.25 mmol) in methanol (1 mL), layered with pentane and left at 4 °C. A few days later, an amorphous brown precipitate was recovered by vacuum filtration. From an attempt to recrystallise from dichloromethane/hexane, an oil was

obtained which was dried and characterised. Yield 0.088 g, 0.11 mmol (44%); m.p. 145–146 °C. C₂₆H₃₄O₆N₂S₄AuNa (Mol. Wt.: 818.08). Elemental Anal. Calc.: C, 38.14; H, 4.19; N, 3.42; S, 15.63. Found: C, 38.38; H, 4.91; N, 3.50; S, 15.28%.

2.3. Physical characterisation

Cyclic voltammetry data were obtained using a BAS C3 Cell Stand. The measurements were performed at room temperature in CH₂Cl₂ solutions, containing [*n*-Bu₄]PF₆ (0.1 M) as supporting electrolyte, with a scan rate of 100 mV/s using platinum wire working and counter electrodes and a Ag/AgCl reference electrode. The [(Me₅C₅)₂Fe]⁺/[(Me₅C₅)₂Fe] ([Fc⁺]/[Fc]) couple was used as the internal reference and the potentials of the redox couples observed were referenced to that.

Single crystals suitable for X-ray crystallographic analyses were obtained by recrystallisation in acetonitrile, for compound **1**, and by slow diffusion of hexane into a saturated solution of dichloromethane, for compounds **2**, **3**, **5** and **6**. In compound **6** two water molecules were incorporated in the crystal structure to yield compound **6 · 2H₂O**, due to the presence of air humidity.

The data for compounds **1**, **2**, **3**, **5** and **6 · 2H₂O** were collected on a Bruker AXS APEX CCD area detector X-ray diffractometer equipped with an Oxford Cryosystems low-temperature device at 150 K in the ω and φ scans mode. A semi empirical absorption correction was carried out using SADABS [12]. Data collection, cell refinement and data reduction were done with the SMART and SAINT programs [13]. The structures were solved by direct methods using SIR97 [14] and refined by fullmatrix least-squares methods with the

SHELXL97 [15] program using the WINGX software package [16]. Non-hydrogen atoms were refined with anisotropic thermal parameters whereas H-atoms were placed in idealised positions and allowed to refine riding on the parent C atom. In **3** and **5** one of the butyl groups on the cation show disorder that was modelled over two positions with the following occupation factors: 52%:48% and 55%:45%, respectively. The final difference Fourier map revealed the existence of residual electron densities of: 2.4/−0.89 e Å^{−3} for compound **5**, which are located near the Au atom. Molecular graphics were prepared using ORTEP3 [17] and MERCURY 1.4.2 [18]. A summary of the crystal data, structure solution and refinement is listed in Table 1.

EPR spectra were obtained at room temperature on powders using a conventional X-band spectrometer (Bruker ESP 300E) equipped with a microwave bridge ER041XX, a rectangular cavity operating in T102 mode and a field controller ER 032M system. The modulation amplitude was kept well below the linewidth and the microwave power well below saturation.

Static magnetic susceptibility measurements in the range 2–300 K were performed using a superconducting longitudinal Faraday system (Oxford Instruments) under a magnetic field of 5 T and field gradient of 1 T/m. A polycrystalline sample (~20 mg) was placed inside a previous calibrated thin-wall Teflon bucket. The force was measured with a microbalance (Sartorius S3D-V), applying forward and reverse field gradients. Magnetisation data were corrected for contributions due to the core diamagnetism, estimated from tabulated Pascal constants as -385×10^{-6} , -379×10^{-6} and -348×10^{-6} emu/mol for **1**, **3** and **6**, respectively.

Table 1

Crystallographic data and refinement parameters for complexes Ph₄P[Ni(4-pedt)₂] (**1**), Ph₄P[Cu(4-pedt)₂] (**2**), *n*-Bu₄N[Ni(4-pedt)₂] (**3**), *n*-Bu₄N[Au(4-pedt)₂] (**5**) and [Na(18C6)][Ni(4-pedt)₂] · 2H₂O (**6 · 2H₂O**).

Compound	1	2	3	5	6 · 2H₂O
Formula	C ₃₈ H ₃₀ N ₂ NiPS ₄	C ₃₈ H ₃₀ CuN ₂ PS ₄	C ₃₀ H ₄₆ N ₃ NiS ₄	C ₃₀ H ₄₆ AuN ₃ S ₄	C ₂₆ H ₃₈ N ₂ NaNiO ₈ S ₄
Formula weight (g mol ^{−1})	732.58	737.39	635.65	773.90	712.49
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	monoclinic, C2/c	monoclinic, C2/c	triclinic, P1	triclinic, P1	monoclinic, P2 ₁ /n
<i>a</i> (Å)	26.8750(5)	26.9179(8)	9.0033(2)	8.6211(1)	11.7067(14)
<i>b</i> (Å)	17.3528(3)	17.3541(6)	11.2258(2)	11.1196(2)	9.7243(12)
<i>c</i> (Å)	18.1609(3)	18.1969(5)	16.9070(3)	17.6962(3)	14.3179(18)
α (°)	90	90	107.7870(10)	74.646(1)	90
β (°)	127.5650(10)	127.3820(10)	90.3960(10)	88.829(1)	96.103(2)
γ (°)	90	90	98.3450(10)	80.336(1)	90
<i>V</i> (Å ³), <i>Z</i>	6713.4(2), 8	6754.5(4), 8	1607.48(5), 2	1612.14(4), 2	1620.7(3), 2
ρ_{calc} (Mg/m ³), μ (mm ^{−1})	1.450, 0.906	1.450, 0.973	1.313, 0.887	1.594, 4.846	1.468, 0.918
<i>F</i> (000)	3032	3040	678	780	750
Crystal size (mm)	0.4 × 0.3 × 0.08	0.30 × 0.20 × 0.16	0.28 × 0.24 × 0.20	0.38 × 0.30 × 0.28	0.20 × 0.12 × 0.10
θ range (°)	2.83–25.03	2.74–25.68	3.21–25.35	2.64–25.68	2.73–25.68
Collected <i>hkl</i>	−31 ≤ <i>h</i> ≤ 31 −20 ≤ <i>k</i> ≤ 20 −21 ≤ <i>l</i> ≤ 21	−32 ≤ <i>h</i> ≤ 32 −21 ≤ <i>k</i> ≤ 21 −20 ≤ <i>l</i> ≤ 22	−10 ≤ <i>h</i> ≤ 10 −13 ≤ <i>k</i> ≤ 13 −20 ≤ <i>l</i> ≤ 20	−10 ≤ <i>h</i> ≤ 10 −13 ≤ <i>k</i> ≤ 13 −21 ≤ <i>l</i> ≤ 21	−14 ≤ <i>h</i> ≤ 12 −11 ≤ <i>k</i> ≤ 11 −17 ≤ <i>l</i> ≤ 17
Reflections collected	41 666	23 618	13 680	17 908	7273
Independent reflections [<i>R</i> _{int}]	5910 [0.0424]	6409 [0.0656]	5821 [0.0422]	6122 [0.0306]	3051 [0.0414]
Completeness to θ (%)	25.03 (99.7)	25.68 (99.7)	25.35 (98.9)	25.68 (99.7)	25.68 (99.3)
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents
Max. and min. transmission	0.8052 and 0.7133	0.8599 and 0.7590	0.8425 and 0.7893	0.3440 and 0.2603	0.9139 and 0.8378
Refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	5910/0/418	6409/0/418	5821/6/370	6122/2/370	3051/2/201
Goodness-of-fit on <i>F</i> ²	1.069	1.049	1.079	1.071	1.035
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0276, <i>wR</i> ₂ = 0.0711	<i>R</i> ₁ = 0.0396, <i>wR</i> ₂ = 0.0868	<i>R</i> ₁ = 0.0366, <i>wR</i> ₂ = 0.0899	<i>R</i> ₁ = 0.0254, <i>wR</i> ₂ = 0.0590	<i>R</i> ₁ = 0.0376, <i>wR</i> ₂ = 0.0791
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0341, <i>wR</i> ₂ = 0.0740	<i>R</i> ₁ = 0.0644, <i>wR</i> ₂ = 0.0945	<i>R</i> ₁ = 0.0482, <i>wR</i> ₂ = 0.0947	<i>R</i> ₁ = 0.0401, <i>wR</i> ₂ = 0.0630	<i>R</i> ₁ = 0.0659, <i>wR</i> ₂ = 0.0853
Largest difference in peak and hole (e Å ^{−3})	0.416 and −0.355	0.422 and −0.473	0.556 and −0.280	2.348 and −0.895	0.392 and −0.502

3. Results and discussion

3.1. Synthesis

The synthesis of the nickel, copper and gold complexes **1–7** were performed following standard procedures for complexes with this type of dithiolene ligands (Scheme 1). The dithiolate ligand (**L**) was obtained from the corresponding oxo compound by hydrolytic cleavage with sodium methoxide and without intermediate isolation it was reacted with the selected metal salt to give an anionic complex which is precipitated as a salt in the presence of the selected cation. The presence of water was necessary to precipitate the bisdithiolene complex from the solution. In case of **1**, a water solution of the cation was added and the bisdithiolene complex precipitated immediately as a black precipitate. In the case of compounds **2**, **3**, **4** and **5** a few drops of water were added at the end of the reaction until the start of incipient precipitation and after keeping the reaction mixture at 4 °C it was possible to collect the product as fine precipitate which tends to form an oil. Compounds **6** and **7** were obtained without adding water after keeping the solution a few days at 4 °C until complexes precipitated. These complexes were obtained after recrystallisation from acetonitrile, acetone or dichloromethane/hexane in overall yields between 41% and 65%.

Complexes **1–7** were characterised by elemental analyses and cyclic voltammetry studies. The elemental analyses after the recrystallisations are consistent with a 1:1 cation:anion stoichiometry, in agreement with the X-ray crystal structure determination of the diffracting single crystals. While this is expected for $M = Au$, for Cu and Ni even though starting from a $Ni^{II}Cl_2$ or $Cu^{II}Cl_2$ salt, the dianionic bisdithiolene complexes could not be obtained, even under nitrogen atmosphere and the monoanionic dithiolene complexes were obtained as evidenced by the X-ray structure determination or by the electronic paramagnetic resonance (EPR) spectroscopy. Whereas complexes **1**, **2**, **3**, **5** and **6**· $2H_2O$ were unambiguously characterised by single X-ray structure determination, compounds **4**, **6** and **7** could not be studied by single X-ray diffraction due to their poor crystal quality.

3.2. Crystal structure

Compounds **1**, **2**, **3**, **5** and **6**· $2H_2O$ have been characterised by single crystal X-ray diffraction technique. The ORTEP views of these compounds are shown in Figs. 1–5. Selected bond angles and distances are given in Table 2.

The monoanionic Ph_4P salts **1** and **2** are isostructural and crystallise in the monoclinic system, space group $C2/c$, $Z = 8$, the asymmetric unit comprising one cation $[PPh_4]^+$ located in a general position and two independent half-anions $[M(4-pedt)_2]^-$ ($M = Ni$ and Cu for compounds **1** and **2**, respectively) both with the metals located at an inversion centre. The angle between the two $[M(4-pedt)_2]^-$ units mean planes is about 49.47° and 49.52° for compounds **1** and **2**, respectively.

The monoanionic $n-Bu_4N$ salts **3** and **5** are isostructural and crystallise in the triclinic system, $P\bar{1}$ space group, $Z = 2$. The asym-

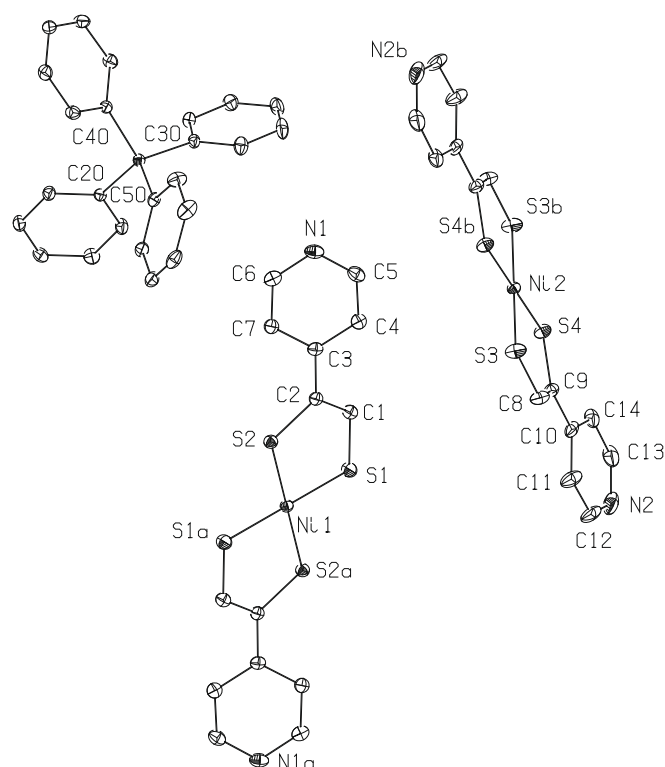


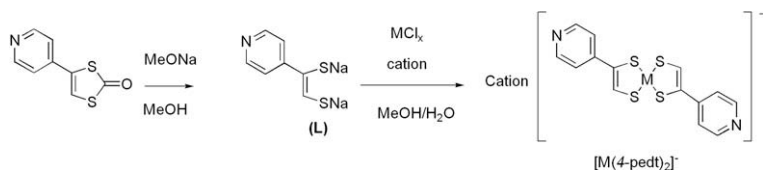
Fig. 1. ORTEP views of the cation and the two independent anion units of $Ph_4P[Ni(4-pedt)_2]$ (**1**), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (a) $2 - x, 1 - y, 1 - z$; (b) $1.5 - x, 1.5 - y, 1 - z$].

metric unit comprises two independent half-anion units. Both the metal atoms located at inversion centres and with one cation unit located at a general position. The angle between the anionic units mean planes is between 88.98° and 89.81° for **3** and **5**, respectively.

The compound **6**· $2H_2O$ crystallises in the monoclinic system, space group $P2_1/n$, $Z = 2$. The asymmetric unit comprises one independent half-anion unit and one independent half-cation unit located at inversion centres.

In all complexes, the centrosymmetric anion $[M(4-pedt)_2]^-$ ($M = Ni, Cu$ or Au) adopts a square-planar coordination geometry and a *trans* conformation. The central core of the anions, constituted by the metal atom, the four sulfur atoms and the four carbon atoms, is essentially planar (rms deviations of fitted atoms are 0.0091 and 0.0057 Å for compound **1**; 0.0182 and 0.0237 Å for compound **2**; 0.0152 and 0.0268 Å for compound **3**; 0.0537 and 0.0250 Å for compound **5**; 0.0125 Å for compound **6**· $2H_2O$).

Important bond lengths within the MS_2C_2 metallocycle are collected in Table 2. The average M–S bond lengths are in good agreement with values found in other Ni, Cu and Au monoanionic bisdithiolene complexes, respectively [1c,19–21]. While the central core of the complexes is planar, the two pyridine rings are rotated out of the central core plane with dihedral angles between



(Ph_4P)[$Ni(4-pedt)_2$] (**1**) 50% yield; (Ph_4P)[$Cu(4-pedt)_2$] (**2**) 48% yield; ($n-Bu_4N$)[$Ni(4-pedt)_2$] (**3**) 65% yield; ($n-Bu_4N$)[$Cu(4-pedt)_2$] (**4**) 41% yield; ($n-Bu_4N$)[$Au(4-pedt)_2$] (**5**) 60% yield; [$Na(18c6)$][$Ni(4-pedt)_2$] (**6**) 58% yield; [$Na(18c6)$][$Au(4-pedt)_2$] (**7**) 44% yield

Scheme 1.

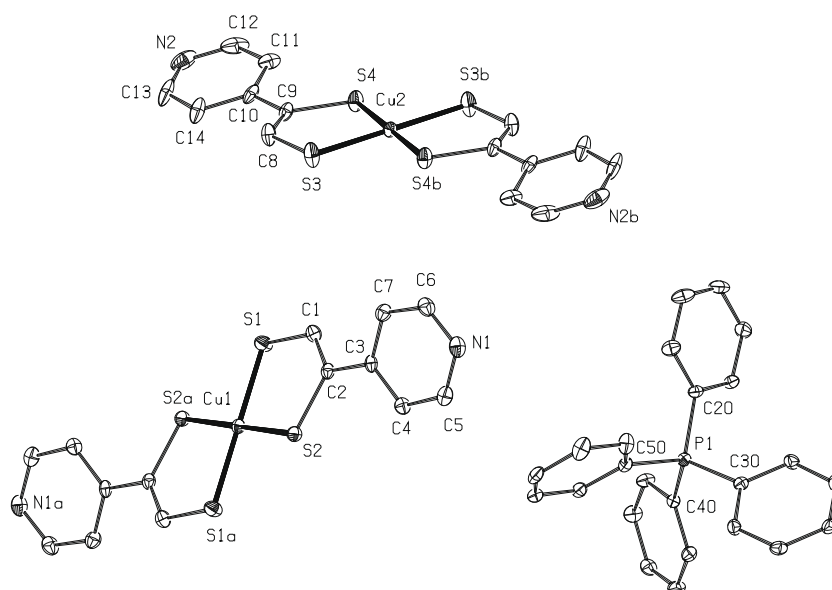


Fig. 2. ORTEP views of the cation and the two independent anion units of $\text{Ph}_4\text{P}[\text{Cu}(4\text{-pedt})_2]$, (**2**), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (a) $1-x, 1-y, z$; (b) $0.5-x, 1.5-y, -z$].

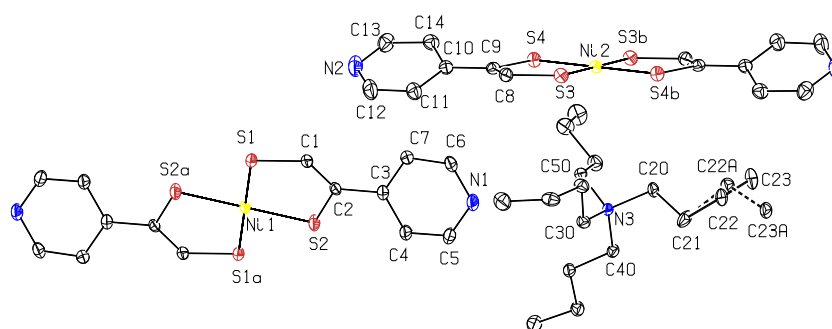


Fig. 3. ORTEP views of the cation and the two independent anion units of $n\text{-Bu}_4\text{N}[\text{Ni}(4\text{-pedt})_2]$, (**3**), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (a) $-x, -y, -z$; (b) $1-x, 1-y, 1-z$].

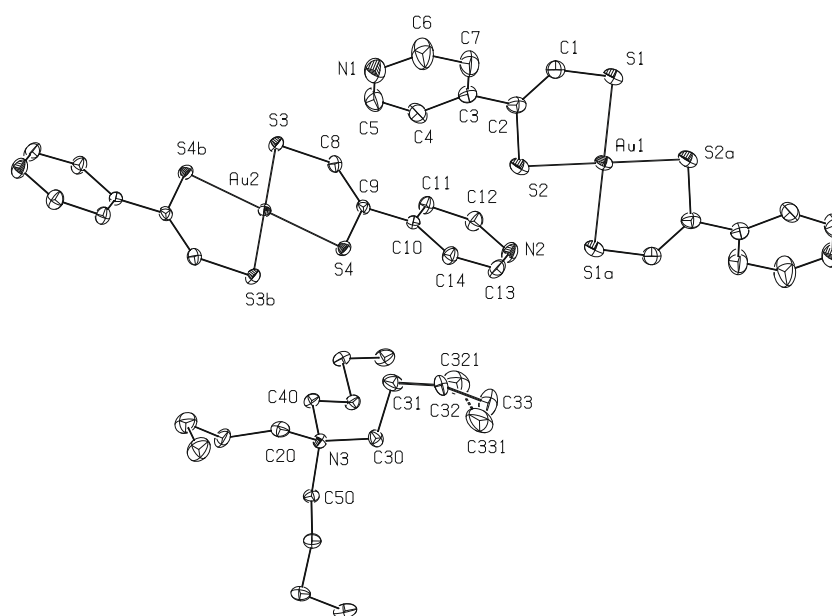


Fig. 4. ORTEP views of the cation and the two independent anion units of $n\text{-Bu}_4\text{N}[\text{Au}(4\text{-pedt})_2]$, (**5**), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (a) $-x, -y, -z$; (b) $1-x, 1-y, 1-z$].

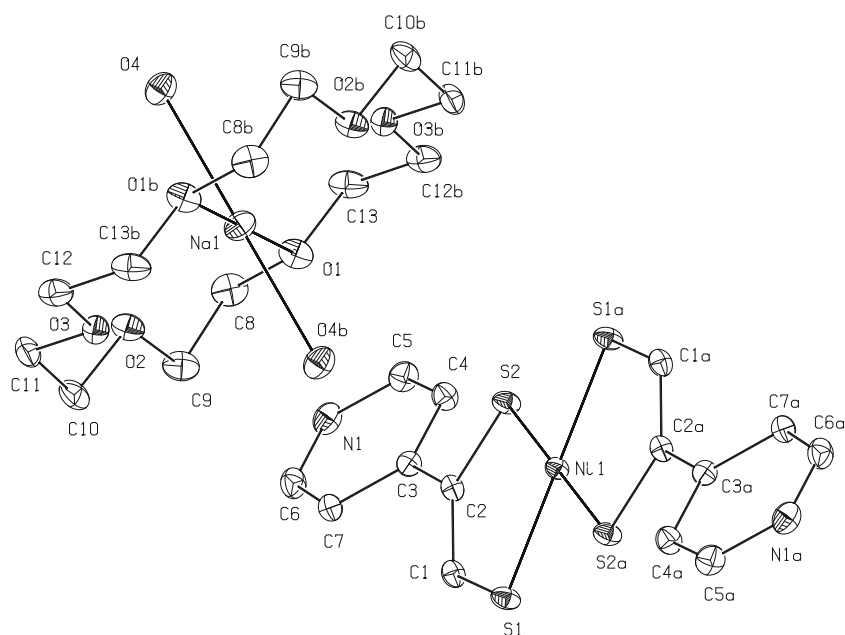
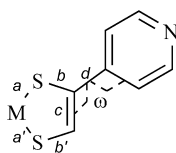


Fig. 5. ORTEP views of the cation and anion units of $[\text{Na}(18\text{C}6)][\text{Ni}(4\text{-pedt})_2] \cdot 2\text{H}_2\text{O}$, (**6** · **2H₂O**), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (a) $-x, -y, -z$; (b) $2-x, 1-y, 1-z$].

Table 2
Important bond lengths (in Å) within the metalocycle, the torsion angle ω (in °) between the pyridine group plane and the metalocycle plane and δ -parameter (defined below) for compounds **1**, **2**, **3**, **5** and **6** · **2H₂O**.



Compound	1	3	6 · 2H₂O	2	5				
M = Ni2	M = Ni1	M = Ni1	M = Ni2	M = Ni	M = Cu1	M = Cu2	M = Au2	M = Au1	
M–S (<i>a</i>)	2.1293(5)	2.1507(5)	2.1383(5)	2.1549(6)	2.1375(7)	2.1871(7)	2.1626(7)	2.3078(10)	2.3183(13)
M–S (<i>a'</i>)	2.1474(5)	2.1416(5)	2.1463(6)	2.1478(7)	2.1531(7)	2.1797(8)	2.1812(8)	2.3053(11)	2.3082(11)
S–C (<i>b</i>)	1.737(2)	1.742(2)	1.739(2)	1.740(3)	1.738(3)	1.771(3)	1.765(3)	1.768(4)	1.771(4)
S–C (<i>b'</i>)	1.715(2)	1.715(2)	1.713(2)	1.715(2)	1.714(3)	1.735(3)	1.740(3)	1.742(4)	1.735(5)
C=C (<i>c</i>)	1.353(3)	1.351(3)	1.364(3)	1.351(3)	1.354(4)	1.335(4)	1.328(4)	1.345(6)	1.336(6)
C–C (<i>d</i>)	1.478(3)	1.476(3)	1.474(3)	1.476(3)	1.469(4)	1.481(4)	1.483(4)	1.477(5)	1.476(7)
ω	13.14(6)	28.50(8)	29.51(8)	28.64(7)	33.56(7)	28.92(12)	13.90(8)	21.83(13)	33.44(17)
δ	1.26	1.55	1.49	1.44	1.38	2.03	1.42	1.47	2.03

$$\delta = 100(b - b')/b.$$

13° and 33°; depending on the complex, with the majority of them between 21° and 33°, only one of the anionic units in the Ph₄P salts **1** and **2** presents a smaller angle of about 13°. The rotation of the pyridine rings is induced by steric hindrance between hydrogen atoms at the 2-position of the pyridine ring and in the metalocycle carbon but this rotation is also assisted by the interaction with neighbouring molecular units in the solid. The salts **5** and **6** · **2H₂O** present the higher pyridine rotation values (~33°) and this large value can be ascribed to cation interactions (and also anion interactions in the case of complex **5**) as denoted by several short contacts (see Tables S1 and S2 and Figs. S1 and S2).

The smaller pyridine rotations of only ~13°, in **1** and **2**, are associated with anionic and cationic interactions, including π – π interactions between the pyridine groups of the $[\text{M}(4\text{-pedt})_2]^-$ units: (see Tables S3 and S4 and Fig. S3). The two pyridine rings involved

are coplanar with distances close to the sum of the van der Waals radii, clearly denoting significant π – π interactions (Fig. S3c).

A feature related to the unsymmetrical nature of the 4-pedt ligand, is the S–C bond length difference within the metalocycle (Table 2). The shortening of the **b'** bond when compared with the **b** bond can be evaluated in terms of a parameter $\delta = 100(b - b')/b$, as previously done on other unsymmetrical bisdithiolenes complexes such as the $[\text{Ni}(\text{adt})_2]^-$ (adt = acrylonitrile-1,2-dithiolate) or $[\text{Ni}(\text{tfadt})_2]^-$ (tfadt = 2-(trifluoromethyl)acrylonitrile-1,2-dithiolate) [6,22]. In our case δ values are between 1.26% and 2.03% in the four structures analysed and it can be attributed to the mesomeric effect of the pyridine group.

A long debated aspect of the dithiolenes complexes is the so called “non-innocence” of the ligands, which may lead to formal ambiguities in the description of the different oxidation states of

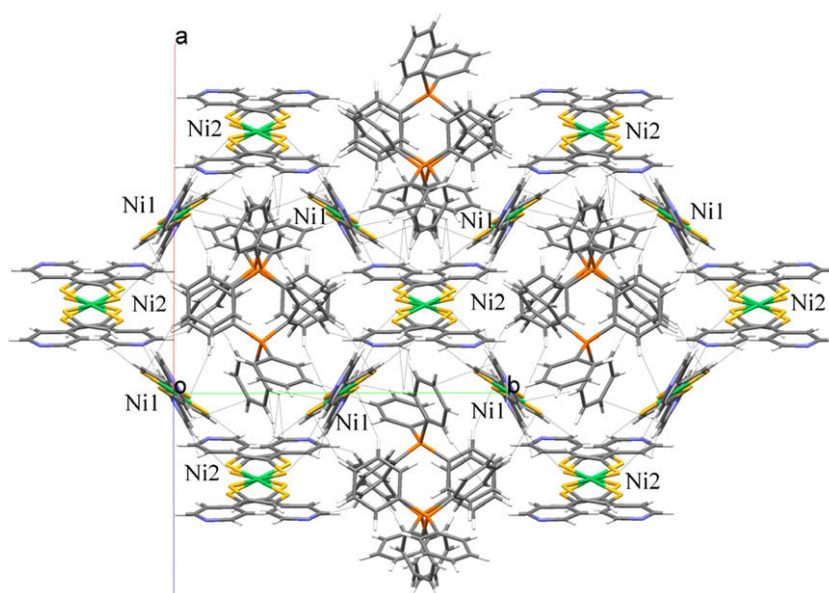


Fig. 6. Crystal structure of **1**, viewed along the cation stacking axis.

these complexes [19]. In these monoanionic complexes the ligand may have a significant contribution to the frontier orbitals and can be viewed as being present in one of two extreme forms: the dianionic ene-1,2-dithiolate or the neutral dithioiketone [1a,19]. In this particular case of the $[M(4\text{-pedt})_2]^-$ dithiolenes where the dithiole ring is not fused to any aromatic ring the lengths of the C–C and C–

S bonds provide a direct indication on the nature of a dithiolene ligand. In all complexes studied the C=C (1.32–1.36 Å) and C–S (1.71–1.77 Å) bond lengths were found in the range typical of sp^2 C hybridisation [23] indicative of the ene-1,2-dithiolate form of the dithiolene and M(III) oxidation state. In the solid state, the monoanionic $[M(4\text{-pedt})_2]^-$ species with M = Ni, Cu and Au,

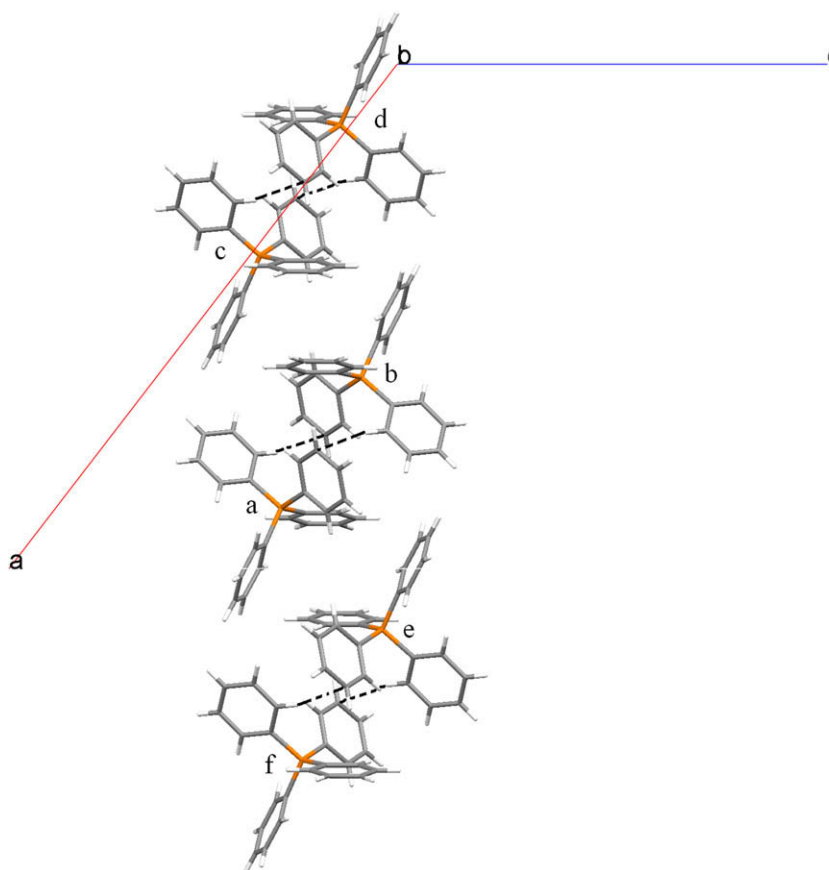


Fig. 7. Chain of $[PPh_4]^+$ cations in compound **1** viewed along *b*. [Symmetry codes: (a) x, y, z ; (b) $1.5 - x, \frac{1}{2} - y, 1 - z$; (c) $-1/2 + x, 1/2 - y, -1/2 + z$; (d) $1 - x, y, 1/2 - z$; (e) $2 - x, y, 1.5 - z$; (f) $1/2 + x, 1/2 - y, 1/2 + z$].

present different packing patterns and interactions depending on the cation type complexes. The compounds **1** and **2** are isostructural with the previously reported $(\text{PPh}_4)[\text{Au}(4\text{-pedt})_2]$ [9]. A characteristic of their crystal structure is the occurrence of cation columns along $b+c$, isolated by an alveolar anion arrangement (Fig. 6). As **1** and **2** are isostructural, we will only focus our structural analysis on the compound **1**. In the cation column, it is possible to observe cation pairs and the only intra column short contact is $\text{H}25\cdots\text{C}54$ (2.785(3) Å) (Fig. 7). Such inversion-centred arrangements of PPh_4^+ cations are a recurrent feature among molecules bearing at least three phenyl rings on the same atoms [24]. In the alveolar anionic arrangement there are no S–S short contacts, but there are several other N \cdots H, S \cdots H, H \cdots H short contacts and π – π interactions (Table S3). Of particular note are the $\text{C}52\cdots\text{H}52\cdots\text{N}2$ (3.514(4) Å) and $\text{C}6\cdots\text{H}6\cdots\text{N}2$ (3.537(3) Å) weak hydrogen bonding interactions.

The crystal structure of the two tetrabutylammonium salts (**3** and **5**) can be seen as made from parallel mixed chains constituted by pairs of cations alternating with an anion. The parallel chains alternate with sheets of anions (Fig. 8). These two compounds have several short intermolecular contacts but none of them corresponds to S–S interactions (for compound **5** Table S1).

The crystal structure of compound **6** · 2H₂O can be described in terms of parallel alternated layers of $[\text{Ni}(4\text{-pedt})_2]^-$ anions and $\text{Na}(\text{18C}6)^+$ cations. The coordination sphere of the sodium cation is completed by two water molecules, one on each side (Fig. 9). The angle between the anionic units mean plan is about 44.53. Only between anions and cations, there are relevant interactions. Besides several N \cdots O, N \cdots H, C \cdots H, O \cdots S, S \cdots H short contacts a hydrogen bond $\text{N}1\cdots\text{H}4\text{A}\cdots\text{O}4$ (2.916(4) Å) is present, which is the most important, governing the chain-like arrangement anion–cation–anion(…) as depicted in Fig. 10.

3.3. Redox behaviour

The redox behaviour of the different complexes was studied by cyclic voltammetry in CH_2Cl_2 solution containing $[\text{n-Bu}_4\text{N}]\text{PF}_6$ (0.1 M) as electrolyte. Each of the compounds **1**, **3** and **6** containing the Ni complex (cyclic voltammogram of compound **6**, Supplementary data, Fig. 4S) exhibit two quasi reversible redox waves, at circa -0.52 V and 0.30 V versus $[\text{Fc}]^+ / [\text{Fc}]$ which are ascribed to the couples $[\text{Ni}(4\text{-pedt})_2]^{2-} / [\text{Ni}(4\text{-pedt})_2]^-$ and $[\text{Ni}(4\text{-pedt})_2]^- / [\text{Ni}(4\text{-pedt})_2]^0$ (Table 3). The $E^{1/2}$ potentials for the Ni complexes in these three compounds are identical. The variation in the scan rate (from 10 to 200 mV s^{-1}) monitoring the wave profile, the separation of the peak potentials ($\Delta E > 59$ mV), and the ratio of the cathodic and anodic currents ($-I_p^c / I_p^a \approx 1$) indicate that the processes are quasi reversible. The low values of the first process explain the difficulty in preparing the dianionic complex, which can be spontaneously oxidised by minor amounts of oxygen or other oxidising agents. On the other hand the low value of the second process predicts that the neutral complex can be prepared. However attempts to isolate it were so far not successful.

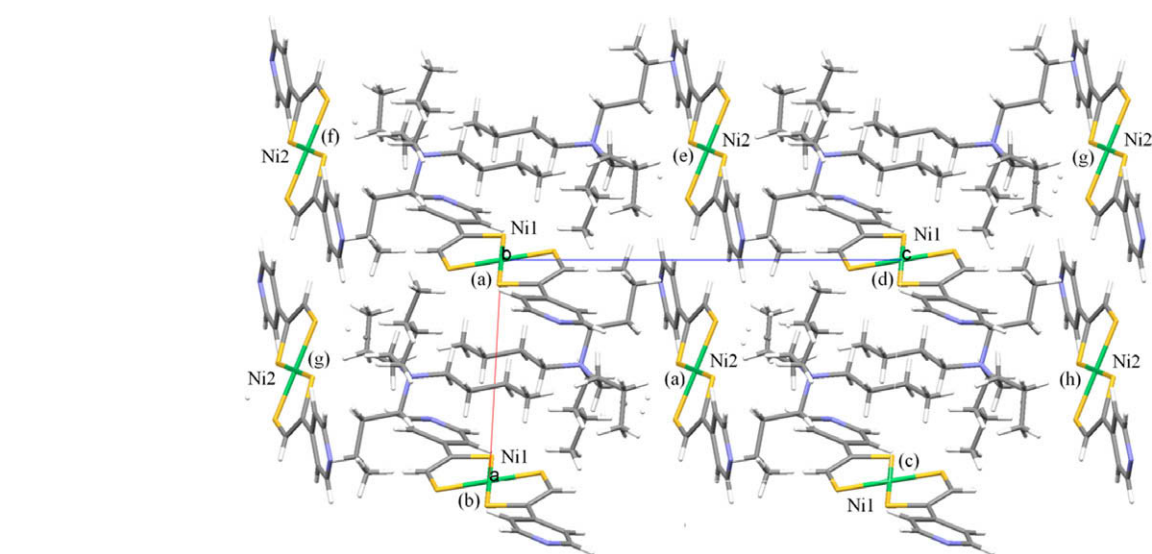


Fig. 8. Crystal structure of **3**, viewed along the b -axis. [Symmetry codes: (a) x, y, z ; (b) $1+x, y, z$; (c) $1+x, 1+y, 1+z$; (d) $x, 1+y, 1+z$; (e) $-1+x, y, z$; (f) $-1+x, -1+y, -1+z$; (g) $x, -1+y, -1+z$; (h) $x, 1+y, 1+z$; (i) $-1+x, 1+y, 1+z$].

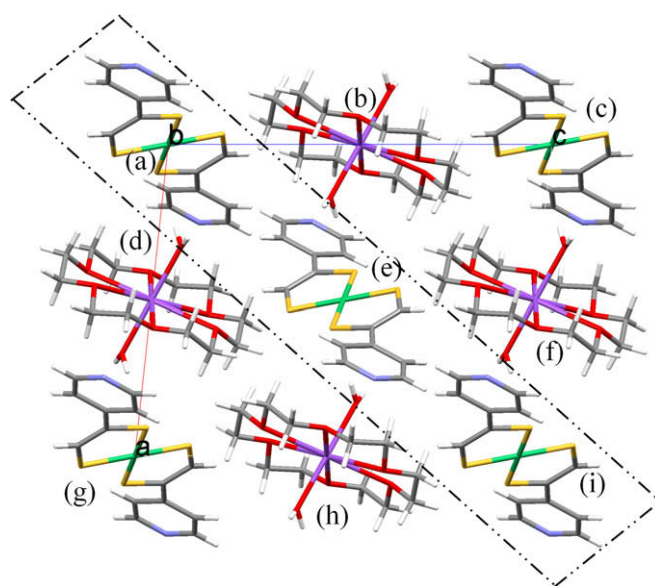


Fig. 9. Crystal structure of **6** · 2H₂O, viewed along the b -axis. The dashed box marks a layer of $[\text{Ni}(4\text{-pedt})_2]^-$ anions. [Symmetry codes: (a) x, y, z ; (b) $-1+x, y, z$; (c) $x, y, 1+z$; (d) $1.5-x, -1/2+y, 1/2-z$; (e) $1/2-x, 1/2+y, 1/2-z$; (f) $1.5-x, -1/2+y, 1.5-z$; (g) $1+x, y, z$; (h) $x, -1+y, z$; (i) $1+x, y, 1+z$].

$\text{pedt})_2]^0$ (Table 3). The $E^{1/2}$ potentials for the Ni complexes in these three compounds are identical. The variation in the scan rate (from 10 to 200 mV s^{-1}) monitoring the wave profile, the separation of the peak potentials ($\Delta E > 59$ mV), and the ratio of the cathodic and anodic currents ($-I_p^c / I_p^a \approx 1$) indicate that the processes are quasi reversible. The low values of the first process explain the difficulty in preparing the dianionic complex, which can be spontaneously oxidised by minor amounts of oxygen or other oxidising agents. On the other hand the low value of the second process predicts that the neutral complex can be prepared. However attempts to isolate it were so far not successful.

The compounds **2** and **4** containing the Cu complex (cyclic voltammogram of compound **2**, Supplementary data, Fig. 5S) show also identical cyclic voltammograms with one quasi reversible redox process at ca -0.38 V, ascribed to the couples $[\text{Cu}(4\text{-pedt})_2]^{2-} / [\text{Cu}(4\text{-pedt})_2]^-$ (Table 3). Scans to higher positive potentials

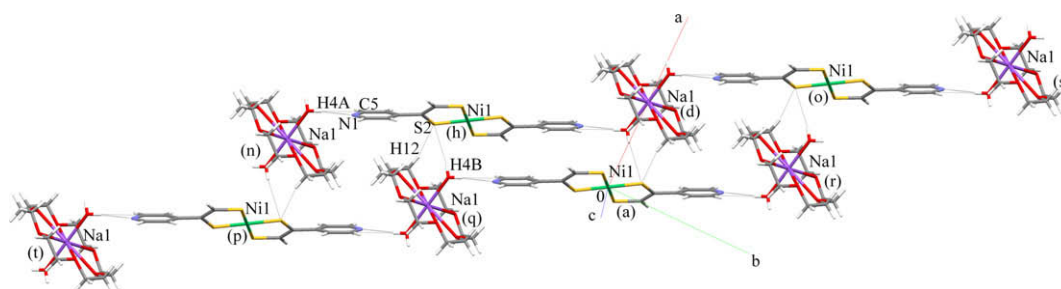


Fig. 10. Detail of the mixed layer in **6** · 2H₂O, two adjacent mixed chains. [Symmetry codes: (a) x, y, z ; (d) $1.5 - x, -1/2 + y, 1/2 - z$; (n) $1/2 - x, -2.5 + y, 1/2 - z$; (o) $1 + x, 1 + y, z$; (p) $-1 + x, -2 + y, z$; (q) $1/2 - x, -1.5 + y, 1/2 - z$; (r) $1.5 - x, 1/2 + y, 1/2 - z$; (s) $2.5 - x, 1.5 + y, 1/2 - z$; (t) $-1/2 - x, -3.5 + y, 1/2 - z$].

Table 3

Redox potentials (mV, vs. [Fc]⁺/[Fc]) of **1–6** at room temperature in CH₂Cl₂ containing [*n*-Bu₄N]PF₆ (0.1 M) with a 100 mV s⁻¹ scan rate.

Compound	[ML ₂] ²⁻ /[ML ₂] ⁻	[ML ₂] ⁻ /[ML ₂] ⁰
[<i>n</i> -Ph ₄ P][Ni(4-pedt) ₂] (1)	-519	297
[<i>n</i> -Ph ₄ P][Cu(4-pedt) ₂] (2)	-374	676
[<i>n</i> -Bu ₄ N][Ni(4-pedt) ₂] (3)	-523	303
[<i>n</i> -Bu ₄ N][Cu(4-pedt) ₂] (4)	-379	771
[<i>n</i> -Bu ₄ N][Au(4-pedt) ₂] (5)		585
[Na(18C6)][Ni(4-pedt) ₂] (6)	-518	298
[Na(18C6)][Au(4-pedt) ₂] (7)		588

(~0.6 V versus [Fc]⁺/[Fc]) reveal the existence of an irreversible process which should correspond to the couple [Cu(4-pedt)₂]⁻/[Cu(4-pedt)₂]⁰.

Compounds **5** and **7** containing the [Au(4-pedt)₂]⁻ complex (cyclic voltammogram of compound **7**, Supplementary data, Fig. 6S) both exhibit one oxidation and a reduction process, assigned to the couples [Au(4-pedt)₂]⁻/[Au(4-pedt)₂]⁰ (Table 3). For both gold compounds, the *E*^{1/2} potentials are very similar. A variation in the scan rate (from 10 to 200 mV s⁻¹) monitoring the wave profile, the separation of the peak potentials ($\delta E > 59$ mV), and the ratio of the cathodic and anodic currents ($-I_p^c/I_p^a = 1$) indicate that the oxidation is not electrochemically reversible.

It is known that the nature of the R substituent in the complexes Ni(S₂C₂R₂)₂ affects the redox potentials and even a small variation in the electron withdrawing substituent can tune the redox potential [1a,25]. In this case we observe that the pyridine groups, which are only partially rotated relatively to the central bisdithiolene plane, thus retaining the possibility of interacting via their π systems, make the 4-pedt complexes easier to oxidise than phenyl substituted or even unsubstituted edt ligands [5].

3.4. EPR measurements

While the monoanionic Cu and Au complexes are diamagnetic the monoanionic Ni complexes, as d⁷ system in a square planar coordination are expected to be paramagnetic *S* = 1/2 systems. Indeed the EPR spectra of **1**, **3** and **6** as powders, show a signal typical of monoanionic Ni dithiolene complexes [1,26,27,28] with rhombic symmetry, with *g*₁ = 2.1035, *g*₂ = 2.0518, *g*₃ = 2.0128 compound **1** and *g*₁ = 2.1153, *g*₂ = 2.0480, *g*₃ = 2.0087 for the compound **6**. In the case of compound **3** the EPR spectrum denotes the existence of two Ni sites with different *g*₁ (2.0849 and 2.0834) and *g*₃ (2.0183 and 2.0113) values but with the same (or very close) *g*₂ value (2.0701). This should be related with the different crystallographic environments of the two anionic Ni units in the asymmetric unit of the compound **3**. In fact Ni1 unit besides quite asymmetric Ni–S bonds lengths has several short S...H–C contacts

with cations which are absent in unit Ni2. In spite of the existence of two different anionic Ni^{III} units in the asymmetric unit of **1**, the two sets of *g* principal values for this compound are not distinguishable within experimental error in agreement with the fact that the two Ni units present comparable short contacts between the S atoms.

3.5. Magnetic susceptibility

The magnetic susceptibility measurements of the compounds **1** and **3** in the range 2–300 K indicate a paramagnetic behaviour with effective magnetic moments essentially temperature independent down to ~15 K with values at room temperature of 1.72 and 1.79 BM, respectively. For compound **6**, the room temperature magnetic moment is 1.67 BM, but it slightly increases upon cooling down to 11 K (1.85 BM), denoting weak ferromagnetic interactions that are not effective at lower temperature (confirmed by magnetisation versus magnetic field at 3.1 K – see Supplementary data). These values are consistent with a *S* = 1/2 state, due to an unpaired electron of a d⁷ system in a quadrangular coordinating geometry. The calculated magnetic moment for the three compounds assuming a Curie law for *S* = 1/2 and *g* values *g*_{av} from EPR is 1.78 BM.

4. Conclusion

The new paramagnetic complex, [Ni(4-pedt)₂]⁻, with the dithio-azo 4-pedt ligand has been synthesised, and isolated as the [PPh₄]⁺, [*n*-Bu₄N]⁺ and Na⁺(18C6) salts, which were characterised by single crystal X-ray diffraction, cyclic voltammetry EPR and magnetic susceptibility. These three compounds present three distinct crystal structures and similar magnetic and redox behaviour, characteristic of monoanionic Ni complexes with quadrangular coordinating geometry and exhibit two quasi reversible redox waves, attributed to the [Ni(4-pedt)₂]²⁻/[Ni(4-pedt)₂]⁻ and [Ni(4-pedt)₂]⁻/[Ni(4-pedt)₂]⁰ redox processes.

Two other complexes with the same dithio-azo ligand have been synthesised, [Au(4-pedt)₂]⁻ and [Cu(4-pedt)₂]⁻, isolated as the [*n*-Bu₄N]⁺ and Na⁺(18C6) salts in case Au and as the [PPh₄]⁺ and [*n*-Bu₄N]⁺ salts in case Cu, all of them exhibiting diamagnetic behaviour.

The [*n*-Bu₄N]⁺ and [PPh₄]⁺ salts of Au and Cu complexes are isostructural with the correspondent Ni ones. Both Ni and Cu complexes present a similar quasi reversible redox process corresponding to the couple [ML₂]²⁻/[ML₂]⁻ but they differ in the couple [ML₂]⁻/[ML₂]⁰ which is a quasi reversible process for Ni and an irreversible one for Cu. For the Au complexes only the couple [ML₂]⁻/[ML₂]⁰ is observed.

The ability of the pyridine groups of these complexes to coordinate other metals is presently under study and will be reported subsequently.

Acknowledgements

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Appendix A. Supplementary data

CCDC 698755, 698756, 698757, 698758 and 698759 contain the supplementary crystallographic data for **1**, **2**, **3**, **5** and **6** · 2H₂O. 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.poly.2009.01.015.

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