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Neutral gold and nickel bis[1-(pyridin-4-yl)-ethylene-1,2-dithiolene] complexes: Synthesis, structure and physical properties

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ABSTRACT

The Ni and Au bis(dithiolene) complexes based on the 1-(pyridine-4-yl)-ethylene-1,2-dithiolate ligand were prepared in their neutral state and characterized namely by single-crystal X-ray diffraction, electronic UV–Vis–NIR spectroscopy, EPR and magnetic susceptibility measurements. The crystal structure of the neutral complex [Ni(4-pedt)$_2$]^0 lacks a regular and multidimensional extended network of short contacts and as a consequence electrical conductivity measurements in single crystals show a semi-conducting behavior with room temperature values of the order of 10^{-6} S/cm, while the magnetic measurements of the gold compounds indicate a reduced effective magnetic moment due to strong anti-ferromagnetic interactions between radical neutral complex units. The nitrogen coordination ability of theses complexes was demonstrated by the coordination of pyridine to a sodium ion observed in the [Au(4-pedt)$_2$]$_2$NaPF$_6$ complex which was also characterized by single-crystal X-ray diffraction and magnetization. In this compound the Na ions in half occupied positions are coordinated by anion fluorine atoms and nitrogen and carbon atoms from the neutral [Au(4-pedt)$_2$] complexes.

1. Introduction

Square-planar bis(dithiolene) complexes have been intensively studied for more than 40 years and among several other applications, they have been seen as key building blocks for preparing conducting and magnetic materials [1–6]. The large potential of these complexes in this context stems essentially from their ability to adopt several oxidation states, a behavior strongly dependent on the type of ligands which in general have what is called a non-innocent role [7]. In general, the monoanionic state is the most stable in the bisdithiolene complexes, but in some cases they can be easily obtained as neutral complexes or even in higher oxidation states. These metal complexes have been used to prepare charge-transfer salts with different donors, either acting as more or less inactive counterions, being dia- or paramagnetic, depending on the metal and oxidation state but they can be also directly responsible for metallic [8–14] or even superconducting [15] properties, when partially oxidized. More recently, high electrical conductivity and true metallic properties have been found in some of these complexes in their neutral state [16–20].

The square-planar metal bis(dithiolene) complexes can be viewed as the inorganic analogues of TTF donors and, there has been an increasing focus of attention on the preparation of derivatives of such electroactive molecules with the ability of binding directly to transition metals. TTF derivatives substituted with coordinating groups and their complexes have already been described [21–24]. However, bis(dithiolene) complexes with ligands bearing coordinating atoms have been a lot less explored [25,26]. Having in mind such type of complexes, and their possible use as building blocks of more complex coordination structures we have focused our interest on bis(dithiolene) complexes based on thio-azo ligands bearing heterocyclic groups. After having reported the first neutral Ni bis(dithiolene) complex with alkylpyridyl substi-tuted ligands [27], Ni(dpesdt)$_2$ (dpesdt = bis(2-pyridylethylsulfa-nyl)-,2-dithiolate), we later described the preparation and characterization of the monoanionic Ni, Cu and Au [M(4-pedt)$_2$] complexes [28], based on the asymmetrically substituted ligand 4-pedt = 1-(pyridin-4-yl)-ethylene-1,2-dithiolate (Scheme 1).

In this paper, we describe the preparation and characterization of neutral [Ni(4-pedt)$_2$] and [Au(4-pedt)$_2$] complexes and the salt [Au(4-pedt)$_2$]$_2$NaPF$_6$, demonstrating the capability of these complexes to coordinate alkaline ions.
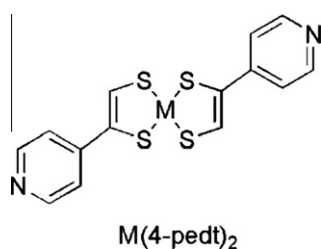
2. Experimental

2.1. Materials and physical methods

Whenever required, the solvents were dried and purified by standard procedures [29], freshly distilled, and saturated with

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Scheme 1. Metal bis[1-(pyridin-4-yl)-ethylene-1 1,2-dithiolene] complexes.

nitrogen prior to use. All starting reagents were purchased from commercial sources and used without further purification or synthesized from published methods. The monoanionic [Ni(4-pedt)$_2$]$^-$ and [Au(4-pedt)$_2$]$^-$ salts were prepared as previously described [28]. Elemental analysis 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. Visible-near-IR(VIS–NIR) absorbance spectra were recorded using a Varian Gary 5G spectrometer. A 1 cm quartz cell was used.

2.2. Synthesis of the [Ni(4-pedt)$_2$] (1)

The neutral complex **1**, obtained as a dark green powder was prepared by I$_2$ oxidation of the corresponding monoanionic complex. To a filtered solution of [n-Bu$_4$N] [Ni(4-pedt)$_2$)] (0.121 g, 0.2 mmol) in 50 mL of dry CH$_3$CN, a solution of I$_2$ (0.05 g, 0.19 mmol) in 10 mL of the same solvent was added dropwise, and allowed to stir for 1 h. The resulting green precipitate was filtered and washed with cold methanol. Single crystals suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into a THF solution of the solid. 51% yield (0.04 g, 0.102 mmol); m.p. 263–268 °C. C$_{14}$H$_{10}$N$_2$NiS$_4$ (Mol. Wt.: 393,196). Elemental *Anal.* Calc.: C, 42.76; H, 2.56; N, 7.12; S, 32.62. Found: C, 42.41; H, 2.66; N, 7.28; S, 32.41%. IR(KBr pellet): (υ/cm^{-1}) = 1624, 1492 (C=C), 1195 (C=S), 785 (C–S), 419 (Ni–S). UV–Vis–NIR (DMF): λ_{max} (ε, M^{-1} cm^{-1}) = 800 nm.

2.3. Synthesis of [Au(4-pedt)$_2$] (2)

The neutral complex **2** was obtained as a dark brown powder, by I$_2$ oxidation of the corresponding [Ph$_4$P][Au(4-pedt)$_2$] complex. To a filtered solution of [Ph$_4$P][Au(4-pedt)$_2$] (0.174 g, 0.2 mmol) in 50 mL of dry CH$_3$CN, a solution of I$_2$ (0.05 g, 0.19 mmol) in 10 mL of the same solvent was added dropwise, and allowed to stir for 1 h. The resulting dark brown precipitate was filtered and washed with cold methanol. 49% yield (0.05 g, 0.098 mmol); m.p. 295–298 °C. C$_{14}$H$_{10}$N$_2$AuS$_4$ (Mol. Wt.: 531.469). Elemental *Anal.* Calc.: C, 31.64; H, 1.90; N, 5.27; S, 24.13. Found: C, 31.56; H, 2.44; N, 4.99; S, 23.87%. IR(KBr pellet): (υ/cm^{-1}) = 1622, 1490 (C=C),1242, 1198 (C–S), 926, 782 and 622. UV–Vis–NIR (DMF): λ_{max} (ε, M^{-1} cm^{-1}) = 1446 nm.

2.4. Synthesis of [Au(4-pedt)$_2$]$_2$NaPF$_6$ (3)

A solution of NaPF$_6$ (0.0145 g, 0.086 mmol) in 10 ml of methanol was added to a solution of [Ph$_4$P] [Au(4-pedt)$_2$] (0.05 g, 0.056 mmol) in 5 ml of CH$_2$Cl$_2$. The solution was allowed to stir overnight and a reddish-brown precipitate was collected and washed with CH$_2$Cl$_2$. 8.6% yield (0.006 g, 4.97 µmol); m.p. >350 °C. C$_{28}$H$_{20}$Au$_2$F$_6$N$_4$PS$_8$ (Mol. Wt.: 1207.91): Elemental *Anal.* Calc.: C, 27.32; H, 1.64; N, 4.55; S, 20.84. Found: C, 26.97; H, 2.08; N, 4.02; S, 20.52%. Crystals of this neutral complex **3** were obtained by an alternative procedure using slow diffusion of reagents

in solution. A solution of [Ph$_4$P][Au(4-pedt)$_2$] (0.02 g, 0.026 mmol) in 4 mL of dry CH$_3$CN was placed into a test tube and layered with a solution of NaPF$_6$ (2.18 mg, 0.013 mmol) in a methanol:ethanol (3:1) solution. The tube was tightly closed and the layered solutions were kept undisturbed for several days. The dark precipitate formed was filtered and washed with dichloromethane and single crystals suitable for X-ray diffraction could be isolated.

2.5. Physical characterization

Electronic spectra of complexes in DMF solutions were recorded at room temperature with a Varian Cary 5G spectrophotometer in the UV–Vis–NIR range.

The X-ray diffraction data for compounds **1** and **3** 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 [30]. Data collection, cell refinement and data reduction were done with the SMART and SAINT programs [31]. The structures were solved by direct methods using SIR97 [32] and refined by full-matrix least-squares methods with the SHELXL97 [33] program using the WINGX software package [34]. 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 ORTEP3 [35] and MERCURY 1.4.2 [36]. 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 ER041XK, a rectangular cavity operating in T102 mode and a field controller ER 032M system. The modulation amplitude was kept well below the line width and the microwave power well below saturation.

Magnetic measurements of polycrystalline samples (10–15 mg) in previously measured gelatine capsules were performed in a 7 Tesla S700X SQUID magnetometer (Cryogenic Ltd.) in the temperature range 1.6–300 K. The paramagnetic contribution was obtained from experimental data after correction for the core diamagnetism, estimated from tabulated Pascal constants as 334×10^{-6} emu/mol and 706×10^{-6} emu/mol for [Au(4-pedt)](**2**) and [Au(4-pedt)$_2$]$_2$ NaPF$_6$ (**3**) respectively.

3. Results and discussion

3.1. Synthesis

The monoanionic bis(dithiolene) complexes, [M(4-pedt)$_2$]$^-$ M = Ni and Au, were synthesized under anaerobic conditions following previously described procedures [28]. As previously reported these monoanionic complexes [M(4-pedt)$_2$] M = Ni and Au are easily oxidized just by air exposure upon recrystallisation. The neutral complexes [Ni(4-pedt)$_2$] (**1**) and [Au(4-pedt)$_2$] (**2**) could be more easily obtained in circa 50% yields by the oxidation of the nickel and gold monoanionic complexes with iodine in acetonitrile. The air oxidation of gold monoanionic complex in the NaPF$_6$ presence gives [Au(4-pedt)$_2$]$_2$ NaPF$_6$ (**3**), a compound of the neutral gold complex, in which the N pyridine atoms are coordinating Na ions.

3.2. Molecular and crystal structures

Single crystals of nickel complex **1** crystallises in the orthorhombic system, space group *Pbca* (see Table 1), with the asymmetric unit comprising one [Ni(4-pedt)$_2$] unit located in a general position. The Ni complex in **1** presents an almost perfect square-planar geometry of the central dithiolene core with the pyridine

Table 1
Crystal data and structure refinement for [Ni(4-pedt)$_2$] (**1**) and [Au(4-pedt)$_2$]$_2$NaPF$_6$ (**3**).

Compound	1	3
Formula	C$_{14}$H$_{10}$N$_2$NiS$_4$	C$_{56}$Au$_4$F$_{12}$N$_8$P$_2$S$_{16}$Na$_2$H$_{40}$
Formula weight (g mol^{-1})	393.19	2461.719
Wavelength (Å)	0.71073	0.71073
Crystal system	orthorhombic	triclinic
Space group	*Pbca*	*P$\bar{1}$*
a (Å)	7.3935(3)	11.4105(6)
b (Å)	11.9027(4)	13.3870(6)
c (Å)	33.3079(13)	13.8133(6)
α (°)	90	97.49(2)
β (°)	90	108.34(2)
γ (°)	90	103.07(2)
V (Å^3), *Z*	2931.18(19), 8	1904.05(16), 1
ρ_{calc} (Mg/m^3), μ (mm^{-1})	1.782, 1.884	2.1469, 82.460
F(000)	1600	1164.0
Crystal size (mm)	0.16 × 0.10 × 0.05	0.17 × 0.08 × 0.06
θ Range (°)	3.30–25.02	2.93–25.03
Collected *hkl*	$-8 \leqslant h \leqslant 7$	$-13 \leqslant h \leqslant 11$
	$-14 \leqslant k \leqslant 13$	$-15 \leqslant k \leqslant 15$
	$-39 \leqslant l \leqslant 39$	$-16 \leqslant l \leqslant 15$
Reflections collected	25 673	9150
Independent reflections	2585 [*R*(int) = 0.1008]	5501 [*R*(int) = 0.0316]
Completeness to θ	25.02 99.8 %	25.03 81.6 %
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents
Maximum and minimum transmission	0.9117 and 0.7525	0.6375 and 0.3346
Refinement method	full-matrix least-squares on *F*^{2}	full-matrix least-squares on *F*^{2}
Data/restraints/parameters	2585/0/190	5501/48/491
Goodness-of-fit on *F*^{2}	1.130	1.084
Final *R* indices [*I* > 2σ*I*)]	*R*$_1$ = 0.0695, *wR*$_2$ = 0.1399	*R*$_1$ = 0.0581, *wR*$_2$ = 0.1593
R indices (all data)	*R*$_1$ = 0.0970, *wR*$_2$ = 0.1461	*R*$_1$ = 0.1129, *wR*$_2$ = 0.1733
Largest difference peak and hole (e Å^{-3})	0.895 and −1.434	2.183 and −1.181

groups in a *trans* configuration, which has been commonly observed in solid-state studies of asymmetrically substituted dithiolene complexes [37]. The pyridine groups are rotated 43.11(0.20)° and 6.44(0.18)° out of this plane. Fig. 1 shows the ORTEP diagram of **1**. The central nickel–dithiolene core, constituted by the metal atom, the four sulfur atoms and the four carbon atoms presents only small deviations from planarity (rms 0.0302 Å). The bond lengths within the NiS$_4$C$_4$ metallocycle are comparable with those reported for other neutral nickel dithiolene complexes [38], and when compared to the corresponding values in the monoanionic complex, it can be seen that upon oxidation the Ni–S bond distance remains essentially constant while the C–S bond shortens and the C=C double bond length increases (Table 2).

The rotation of the pyridine rings out of the nickel–dithiolene central core seems to be largely determined by intermolecular hydrogen bonds and π–π interactions as discussed in detail below. In the structure of the monoanionic Ni dithiolene complex, previously reported, both pyridine rings are clearly rotated out of the nickel–dithiolene core [28], while in this compound one of the rings is almost coplanar with dihedral angles 6.44(0.18)° because it is sandwiched in between neighboring complexes and the other ring presents a more typical rotation of 43.11(0.20)°.
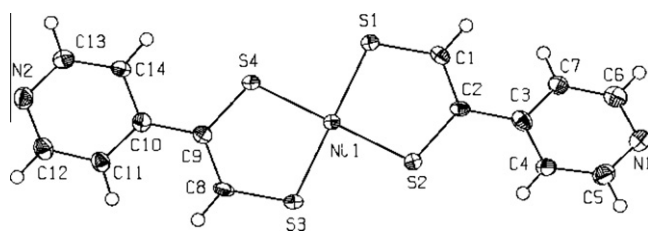

Fig. 1. ORTEP diagram of complex **1** with atomic displacement parameters drawn at the 40% probability level and the atomic numbering scheme.

As shown in Fig. 2a, the crystal structure of **1** contains [Ni(4-pedt)$_2$] units stacked in a regular head to tail fashion along *a*. The more rotated pyridine groups are out of the stacks and the almost coplanar pyridine groups are sandwiched between neighboring molecules in the stacks with distances close to the sum of Van der Waals radii. The overlap mode between [Ni(4-pedt)$_2$] units presents a large slide of the molecules along their long axis in a way that the Ni atoms sits far from each other (5.53 Å) close to the bond between the pyridine and the dithiolene core (Fig. 2(b)). The interplanar distance between two adjacent units is about 3.5 Å, and all intrastack distances are above the sum of the Van der Waals radii, being the shorter ones between S(4)···S(4) (a#) 3.710(3) Å (a# = *x* − 1/2, +*y*, −*z* + 1/2) (Length/VdW = 0.110), and C(2)···C(13) (a#) 3.447(3) Å (a# = *x* − 1/2, +*y*, −*z* + 1/2) (Length/VdW = 0.047) (Fig. 3b). As shown in Fig. 3(a) the stacks are arranged in layers, parallel to the *a*, *b* plane, of [Ni(4-pedt)$_2$] units. Between stacks in the layers there are S···S short contacts, S(3)···S(1) (#b) 3.552(3) Å (#b = −*x* + 1/2, +*y* + 1/2, +*z*), and, S(3)···H(14) (#c) 2.883 Å (c# = −*x*, +*y* − 1/2, −*z* + 1/2). The layers are connected along *c* by hydrogen bonds C(6)–H(6)···N(2) (#d) 2.491 Å (#d = −*x* + 1/2, −*y* + 2, *z* + 1/2), C(12)–H(12)···N(1) (#e) 2.537 Å (#e = *x*, −*y* + 1/2 + 1, *z* + 1/2) and C(1)–H(1)···N(1) (#f) 2.687 Å (#f = −*x*, −*y* + 2, −*z* + 1) between the more rotated pyridine groups.

Complex **3** crystallises in the triclinic system, space group *P$\bar{1}$* (see Table 2). The asymmetric unit comprises two independent [Au(4-pedt)$_2$] units, two sodium ions located in general independent positions with an occupation factor of 0.5 and two PF$_6$ anions units with the phosphorus atoms located on an inversion center. In one of the PF$_6$ units (P1) the fluorine atoms appear disordered over two positions (0.68 and 0.32). Fig. 4 shows the molecular structure of **3**. The [Au(4-pedt)$_2$] units adopts a square-planar coordination geometry and a *trans* configuration. The central core of the dithiolene units, constituted by the gold atom, the four sulfur atoms and the four carbon atoms, is essentially planar (rms deviation of fitted atoms are 0.0353 and 0.0303 Å for [Au1(4-pedt)$_2$] and [Au2(4-pedt)$_2$], respectively). Important bond lengths within the AuS$_2$C$_2$

Table 2
Bond lengths in monoanionic and neutral complexes [M(4-pedt)$_2$], M = Au and Ni.

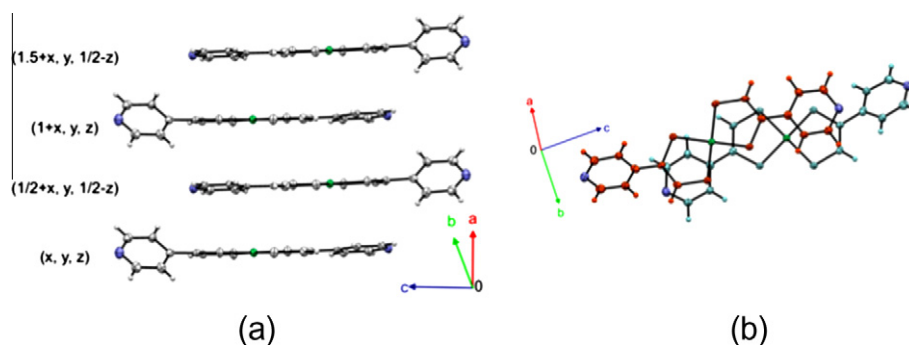| Complex	Ni–S	C–S	C=C	Ref.
[Ni(4-pedt)$_2$]^0	2.123(2)–2.138(2)	1.668(8)–1.695(7)	1.389(10)–1.410(10)	This work
[Ni(4-pedt)$_2$]$^-$	2.1293(5)–2.159(6)	1.713(2)–1.742(2)	1.351(3)–1.364(3)	[28]
[Au(4-pedt)$_2$]$_2$NaPF$_6$	2.250(6)–2.302(5)	2.250(6)–2.302(5)	1.23(3)–1.36(3)	This work
[Au(4-pedt)$_2$]$^-$	2.3053(11)–2.3183(13)	1.735(5)–1.771(4)	1.33(6)–1.345(6)	[28]

Fig. 2. Views of stacks of [Ni(4-pedt)$_2$] units in **1**; (a) parallel to the central molecular plane; (b) overlap mode of [Ni(4-pedt)$_2$] units.
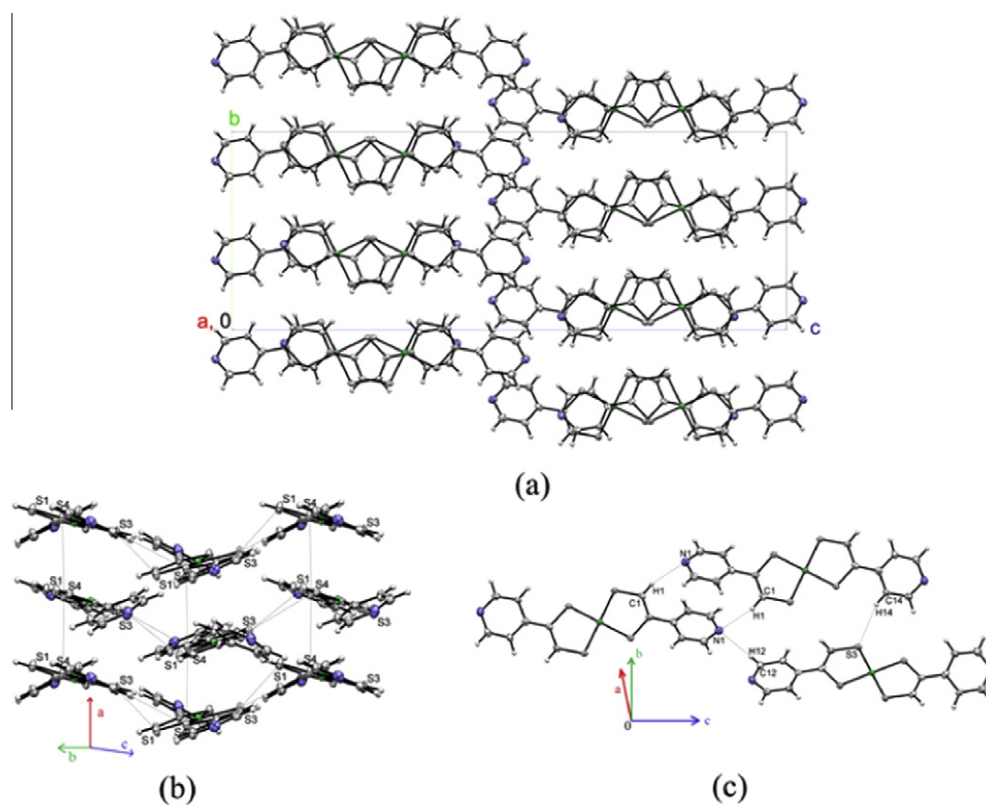

Fig. 3. Crystal structure of **1**; (a) view along the stacking axis *a*; (b and c) partial views emphasizing the intrastack and interstack contacts.

metallocycle are collected in Table 3. The average Au–S bond lengths are in good agreement with values found in other Au neutral bisdithiolene complexes [39–44]. The usual trends upon oxidation are observed, the Au–S bond distance remains essentially constant while the shortening of the C–S bond and the concurrent lengthening of the C=C double bond reflects the localization of the electron density on the dithiolene moieties which upon oxidation adopt a more dithioketonic structure.

In the molecular structures of the monoanionic [Au(4-pedt)$_2$]$^-$ complexes previously reported the two pyridine rings were found clearly rotated out of the dithiolene core with angles in the range 21.83(13)–33.44(17)° [28]. In **3** the pyridine rings are significantly less rotated with dihedral angles of 10.35(45), 5.57(47), 5.69(69) and 5.26(75)° for [Au1(4-pedt)$_2$] and [Au2(4-pedt)$_2$], respectively.

In this structure the pyridine nitrogen atoms are coordinating the sodium ions at relatively short sodium–nitrogen distance of
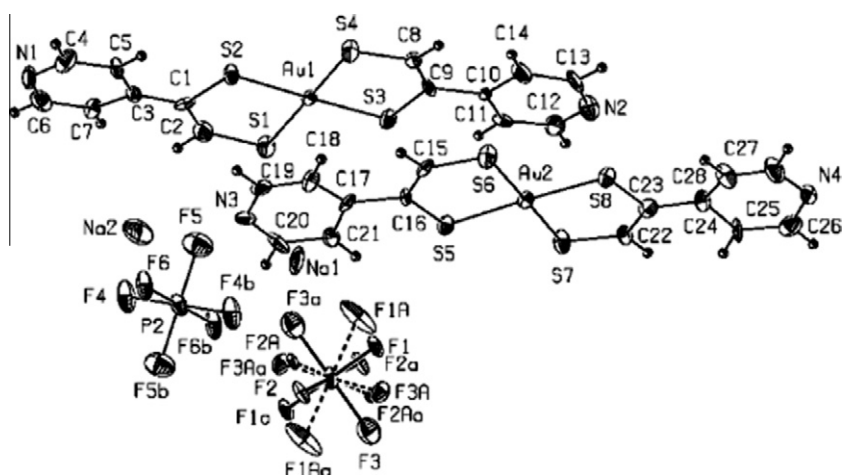
Fig. 4. ORTEP diagram of **3** with atomic displacement parameters drawn at the 40% probability level and the atomic numbering scheme.

Table 3
Selected contacts in the crystal structure of **3**.

Inter stack-short contacts	d (Å)
S7···S3[a]	3.550
S6···S2[b]	3.588
S1···C25[a]	3.452
S4···C26[c]	3.469
S7···C4[d]	3.310
S7···C5[d]	3.408
Na2···Na2[e]	4.093

[a] $1 - x, 1 - y, 2 - z$.
[b] $-x, 1 - y, 1 - z$.
[c] $x, y, -1 + z$.
[d] $x, y, 1 + z$.
[e] $1 - x, 2 - y, 1 - z$.

2.824 and 2.711 Å. The coordination of sodium ions in this compound is quite unusual. In addition to the nitrogen, hydrogen and fluorine atoms the coordination is complemented by one sulfur and three carbon short contacts Na(1)···S(1) (#a) 3.331 Å (a# = $1-x$, $+1 - y$, $2 - z$) and Na(1)···C(23) (#b) 3.905 Å, Na(1)···C(24) (#b) 3.809 Å, Na(1)···C(25) (#b) 3.964 Å, in case of Na1 and by sodium and carbon short contacts in case of Na2, Na(2)···Na(2) (#c) 4.093 Å (c# = $1 - x$, $+2 - y$, $1 - z$), Na(2)···C(6) (#c) 3.759 Å and Na(2)···C(7) (#c) 3.272 Å, (see Fig. S1 for a detailed drawing of sodium ions coordination). The coordination of alkaline ions by nitrogen atoms has already been observed on other substituted bisdithiolate complexes [25,45–48], but only one, based on [Au(btdt)$_2$] (btdt = 2,1,3-benzenethiadiazole-5,6-dithiolate) leading to a polymeric coordination network [49]. However to the best of our knowledge, this is the first report of N coordination based on a neutral gold–dithiolene complex.

The crystal structure of **3** consists in a layer of slipped stacks along *a* of dithiolene neutral gold units intercalating PF$_6^-$ and Na$^+$ ions (this last one in half occupied positions) acting as frame regulators (Fig. 5(a)). In the stacks there are two different [Au(4-pedt)$_2$] complexes with three overlap modes depicted in Fig. 6. The distances between the average plane of the [Au(4-pedt)$_2$] complexes for each overlap mode are also presented in Fig. 6 and present similar values (3.50, 3.570 and 3.560 Å). However the distance between the Au atoms varies significantly due to the different overlap modes: 6.579, 4.095 and 4.063 Å for the superposition modes (a), (b) and (c), respectively. In the stacks there are no short contacts (Fig. 5(b)) and all S or C contacts are well above the sum of

the Van der Walls radii (Table S1). Shorter contacts between the dithiolene units are however between adjacent stacks (Table 3 and Fig. 5(c)).

Unfortunately, it was not possible to obtain good quality crystals of compound **2**, suitable for structure determination, which could enable to compare the differences and similarities of the two molecular packings, with and without the NaPF$_6$ acting as frame regulator. Compounds **2** and **3** are most probably isostructural, however the poor diffracting quality of the fine powder obtained for compound **2** did not allow the confirmation of this possibility.

At variance with several other neutral gold or nickel dithiolene complexes which may present metallic properties [16–20], single crystals of compounds **1** and **3** were found to be very poor semiconductors with room temperature electrical conductivity of 2×10^{-6} S/cm and 6×10^{-8} S/cm respectively. These results are not surprising in view of the absence of an extended bidimensional or tridimensional regular network of strong dithiolene–dithiolene interactions.

3.3. Magnetic properties

The neutral [Au(4-pedt)$_2$] complex in **2** and **3** is expected to be a radicalar species. Compound **3** was found to be EPR silent, but the X-band EPR spectrum of **2** as a powder at 77 K, presents a signal typical of a rhombic system indicative of a $S = 1/2$ ground state, shown in Fig. 7, with estimated $g_1 = 2.154$, $g_2 = 2.030$ and $g_3 = 1.944$.

Magnetic susceptibility measurements of compounds **2** and **3**, show a weak paramagnetic contribution following a Currie–Weiss law with Θ values of -7.8 and -4.2 K and effective magnetic moments of 0.5 and 0.37 μ_B/f.u., corresponding to 28.9% and 21.4% of $S = 1/2$ spins with $g = 2$, respectively. (see Fig. S2). The structure of **2** is not known, but in view of the multiple short contacts existing between the neutral complex units in **1** and **3** strong antiferromagnetic interactions are expected to occur in compounds **2** and **3**,. Under these circumstances the weak paramagnetism and the EPR signal observed should correspond to crystals defects of uncoupled [Au(4-pedt)$_2$] species.

3.4. The electronic optical absorption spectra

The neutral character of **1** is also confirmed by the electronic spectra which can provide a good indication on the neutral or anionic nature of the Ni–dithiolene complexes. A strong absorption
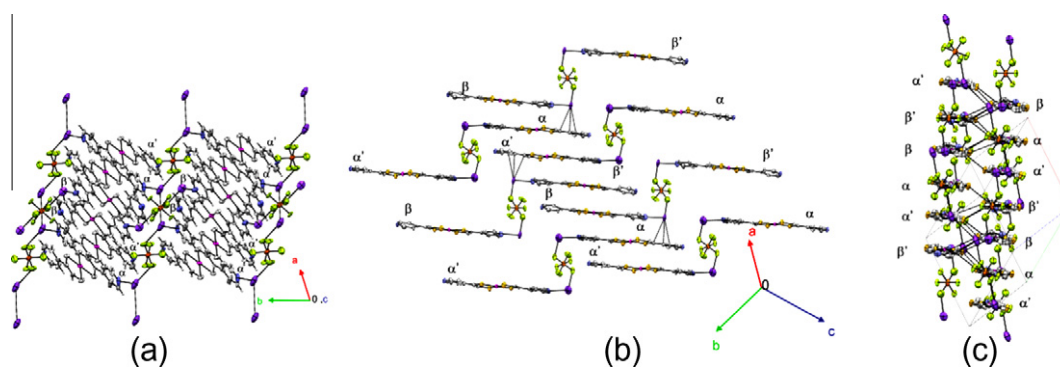
Fig. 5. Crystal structure of **3**; (a) viewed along the *c* axis; (b) partial view of columnar slipped stackings of dithiolene neutral gold units; (c) a pair of adjacent columns viewed along the long dithiolene axis.
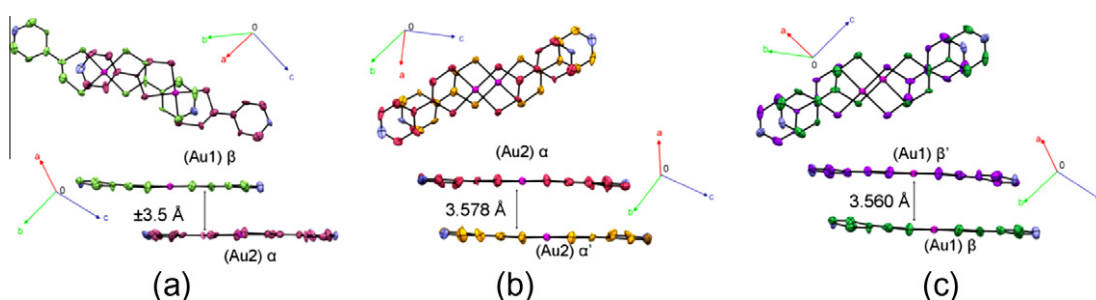

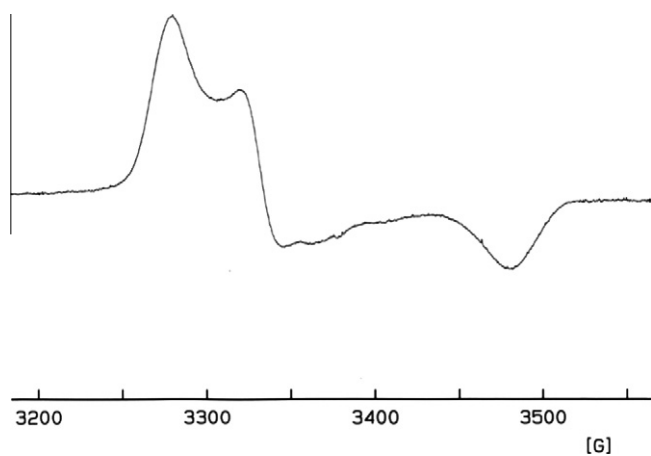**Fig. 6.** Overlap modes of [Au(4-pedt)$_2$] units in compound **3**.

Fig. 7. EPR spectrum of [Au(4-pedt)$_2$] in powder at 77 K.

band at the low energy region (near IR region) is characteristic of neutral complex, which shifts to a lower energy with less intensity in the monoanionic complex [50].

The electronic spectra of **1**, shown in Fig. 8, was recorded in THF solutions at ambient temperature and displays a strong absorbance bands in the region of 800–1000 nm at 800 nm, characteristic of neutral bis(dithiolene) nickel complexes generally assigned to π–π^* transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). As expected, the spectrum of the monoanionic [*n*-Bu$_4$N][Ni(4-pedt)$_2$] (also shown in Fig. 9) displays a less intense absorption band maximum in the NIR at lower energy, 925 nm. These results are in agreement with the observed on several other bis(dithiolene) nickel complexes [41,51–54].

The spectrum of **2**, shown in Fig. 9, was recorded at room temperature in DMF solution and exhibits a strong NIR absorbance

band at 1443 nm which is not expected on the corresponding monoanionic complex. However when a solution of the monoanionic complex [*n*-Bu$_4$N][Au(4-pedt)$_2$] was prepared on DMF the spectrum exhibits the same strong NIR absorption band. This may be due to the fact that the solution of the monoanionic salt was prepared under air, and in the oxygen presence the neutral compound is formed on the solution which easily dissolves it. Using a different solvent, where only the monoanionic salt is soluble it is possible to obtain a spectrum of the monoanionic complex. Indeed using THF as a solvent the strong NIR absorbance band at 1443 nm was no more visible. As expected only the monoanionic species presents absorption bands in the UV–Vis region, below
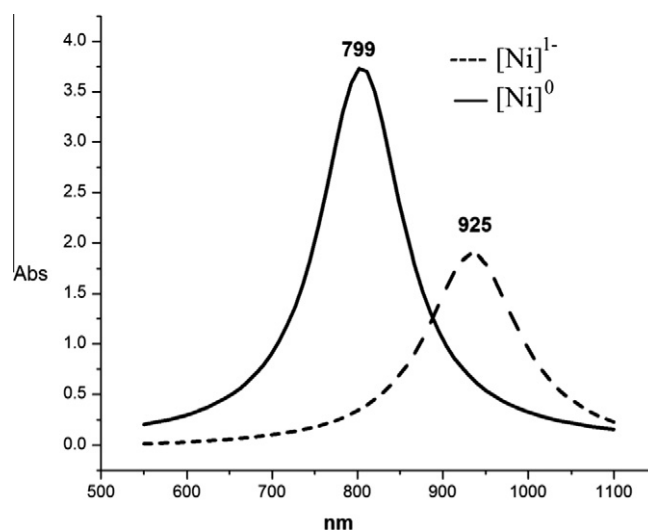

Fig. 8. Electronic spectra of neutral nickel complex **1** (black) and [*n*-Bu$_4$N] [Ni(4-pedt)$_2$] (dashed line) in THF solution.

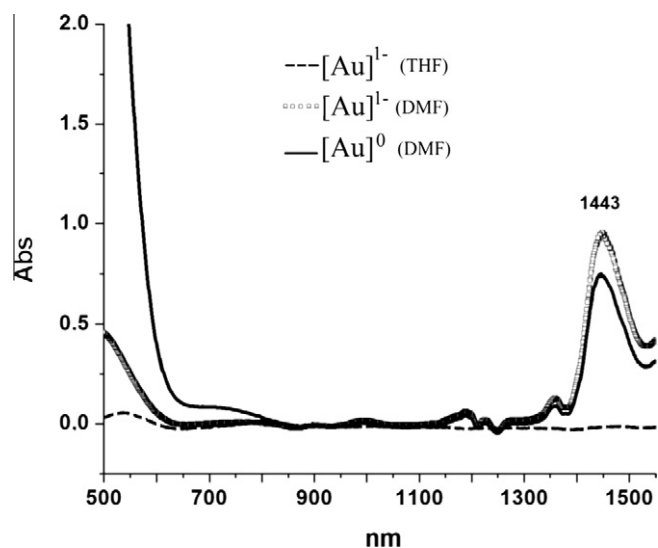**Fig. 9.** Electronic spectra of neutral gold complex **2** (black), monoanionic [*n*-Bu$_4$N] [Au(*4*-pedt)$_2$] (squares) both in DMF solution and [*n*-Bu$_4$N] [Au(*4*-pedt)$_2$] (dashed line) in THF solution.

500 nm generally assigned to *d–d* transition. This behavior in agreement with the observed on other bis(dithiolene) gold complexes [40,41,53,55–57].

4. Conclusions

In conclusion the Ni and Au bis(dithiolene) complexes based on the 4-pedt ligand were prepared in their neutral state enlarging the still reduced number of bisdithiolene complexes that have been characterized in a neutral state. The ability of theses complexes to coordinate other ions was demonstrated by the nitrogen coordination of sodium ions on the [Au(*4*-pedt)$_2$]$_2$ NaPF$_6$ salt. None of the compounds based on these neutral complexes appears to be a good electrical conductor which is ascribed to the absence of an extended and regular network of strong dithiolene–dithiolene interactions. The magnetic susceptibility of the compounds based on the neutral gold complex is dominated by strong antiferromagnetic interactions.

Acknowledgements

Appendix A. Supplementary data

CCDC 863875 and 863876 contain the supplementary crystallographic data for [Ni(*4*-pedt)$_2$] and [Au(*4*-pedt)$_2$]$_2$NaPF$_6$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/con-ts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.03.024.

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