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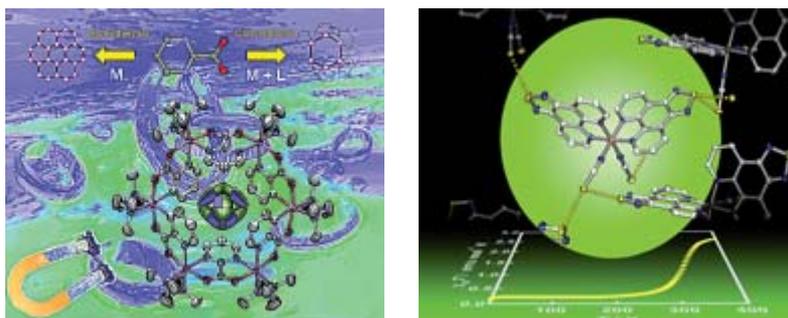
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# Crystal structure of (RBzPy)_n[Ni(4-pedt)_2] salts engineering by pyridine ring arrangements‡

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Two new salts (p-NO_2BzPy)_2 [Ni(4-pedt)_2] and p-BrBzPy [Ni(4-pedt)_2] [BzPy=benzylpyridinium, 4-pedt = 1-(pyridine-4-yl)- ethylene-1,2-dithiolate] were prepared and characterized by X-ray diffraction and magnetic measurements. The paramagnetic salt p-BrBzPy [Ni(4-pedt)_2] displays strong pair antiferromagnetic interactions.

## Introduction

Square planar transition metal bis(dithiolene) complexes have attracted research interest for more than 30 years as building blocks for conducting and magnetic molecular materials, due to their rich redox behaviour and favourable solid state interactions.[1] They also offer the advantage that depending on the oxidation state and on the transition metal they can be either diamagnetic or paramagnetic with different magnetic moments.

Asymmetrically substituted dithiolenes have been less studied despite also providing interesting properties,[2] namely for magnetic materials[3] and optoelectronics.[4] Recently we reported the preparation and characterization of monoanionic bis-(dithiolene) complexes of nickel, copper and gold using an asymmetrically pyridine substituted ligand, the 4-pedt = 1-(pyridine-4-yl)-ethylene-1,2-dithiolate][5] previously also used to prepare the Au complex.[6] Aiming at better understanding of the role of the nickel anion with this ligand versus the role of a cation with proved the ability to promote specific supramolecular solid state structures, we decided to study salts of [Ni(4-pedt)_2] with benzylpyridinium cations. The benzylpyridinium cations are known to favour the segregated stacking of cations and anions in the solid state, and can therefore be used to induce different molecular interactions associated with specific magnetic behaviour.[7]

In this paper we describe the preparation and characterization of [Ni(4-pedt)_2] complexes with two benzylpyridinium salts (Scheme 1). Despite the anaerobic conditions used to prepare both salts, the p-NO_2BzPy[+] cation leads to a dianionic diamagnetic salt while the p-BrBzPy[+] cation leads to a monoanionic paramagnetic salt that presents strong antiferromagnetic pair interactions.

## Results and discussion

### (p-NO_2BzPy)_2[Ni(4-pedt)_2] (1) and (p-BrBzpy)[Ni(4-pedt)_2] (2)

The X-ray structure analysis of (p-NO_2BzPy)_2[Ni(4-pedt)_2] (1) reveals that this compound crystallises in the monoclinic system, space group P2_1/c. An ORTEP diagram of salt 1 is represented in Fig. 1a). Its crystal structure consists of centrosymmetric dianions [Ni(4-pedt)_2]^{2-} and (p-NO_2BzPy)^+ cations forming pairs via an inversion centre. The Ni atom presents the usual square planar coordination, with the average Ni–S distances (2.180(1) Å) within the usual range reported for other Ni dianionic dithiolene complexes.[8] These distances are significantly larger than those previously reported for the monoanionic species[5] and for the p-BrBzPy salt 2 (see below). The salt 1 is the first compound of the dianionic complex [Ni(4-pedt)_2]. As in other Ni bisdithiolene complexes we observe that the dianionic complex in 1 presents Ni–S bonds slightly longer than the monoanionic one in 2.[5] The angle between the pyridine ring mean plane and the metallocycle mean plane in the dianionic [Ni(4-pedt)_2]^{2-} unit is about 10.35(6)°, significantly smaller than that previously found in the monoanionic complex [13.14–33.56°][5] as well as in 2 [20.42°]. This smaller angle is probably related to a significant π–π interactions between the pyridine anion rings and benzyl cation rings.

The p-NO_2BzPy^+ cation in 1 adopts a slightly unusual geometry, with the benzyl and the pyridine rings making dihedral angles of 86.87(6)° and these rings make dihedral angles with the reference plane N3-C25-C26, of 75.67(3) and 17.64(3)°,
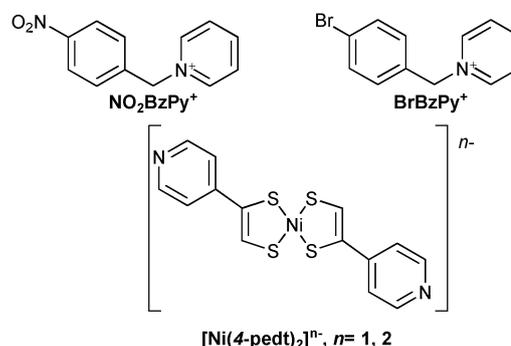
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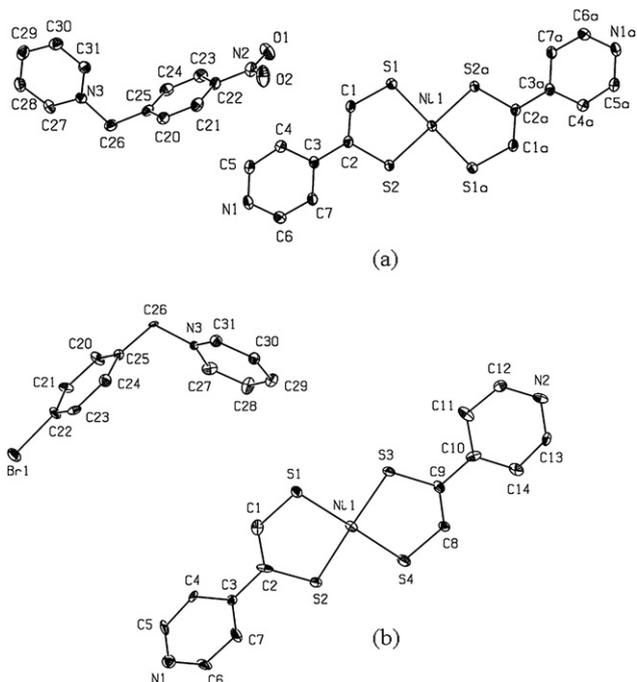
Scheme 1

**Fig. 1** ORTEP diagram of compound **1** (a) and **2** (b) drawn at the 40% probability level and showing the atomic numbering scheme. H atoms were omitted for clarity. #a = 2 − x, −y, 2 − z.

respectively (Fig. 2a), the later value being unusually small. The *p*-NO$_2$BzPy$^+$ cations are related by an inversion centre forming pairs in a P4AE (parallel fourfold aryl embrace),[9] where the pyridine and the benzyl rings are parallel at a ring centroid distance of 4.96(1) Å, allowing a π–π interaction, C30···C30 #g at 3.245(3) Å (#g = −x, −y, 1 − z) (Table 1) between the pyridine rings. The arrangement in the cation pair in this crystal structure is different from all other salts of this cation reported so far. This could be related to the above referred unusual small dihedral angle between the reference plane N3–C25–C26 and the pyridine ring. This unusual cation geometry conformation is due to the fact that the benzyl ring of the cation is not very far from being parallel to the pyridine ring of the anion (22.05(9)°), at a ring centroid distance of 4.04(8) Å, allowing a π–π interaction as denoted by the short contact C6···C21 #a at 3.348(3) Å (Table 1). The most similar case described in literature is *p*-NO$_2$BzPy[Ni(bdt)$_2$] where the dihedral angle between the reference plane N3–C25–C26 and the benzyl ring is 41.6°.[10] Also,

in this salt, it is possible to observe a π–π interaction between anions and cations, in this case between the pyridine cation and the benzene anion rings (dihedral angle 7°), at a ring centroid distance of 3.65°Å.

In the crystal supramolecular cations motif, the *p*-NO$_2$BzPy$^+$ units are arranged EF (edge-to-face) along *c*, P4AE within the pair of the units and OFF (offset face to face) along *b* (Fig. 3a).

The crystal structure of **1** can be viewed as consisting of segregated mixed columns of pairs of cations alternating with an anion along the *b* axis. The parallel columns align along the *c* axis giving rise to parallel layers of mixed columns (Fig. 4). Magnetic measurements performed on this compound show that, as expected, the Ni dianionic complex is diamagnetic.

The *p*-BrBzPy[Ni(4-pedt)$_2$] (**2**) salt crystallises in the monoclinic system, space group *P*2$_1$/*n*. An ORTEP diagram of salt **2** is represented in Fig. 1b). Its crystal structure consists of [Ni(4-pedt)$_2$]$^-$ anions and (*p*-BrBzPy)$^+$ cations forming pairs *via* an inversion centre. The Ni atom presents the usual square planar coordination, the average Ni–S bond length (2.143(3) Å) and the bond distances and angles in the 4-pedt ligand being in good agreement with the values found in other Ni monoanionic dithiolate complexes with this same ligand.[5] The angles between the pyridine group planes and the NiS$_4$C$_4$ plane in the monoanionic [Ni(4-pedt)$_2$]$^-$ unit are 19.7(2) and 20.4(4)°.
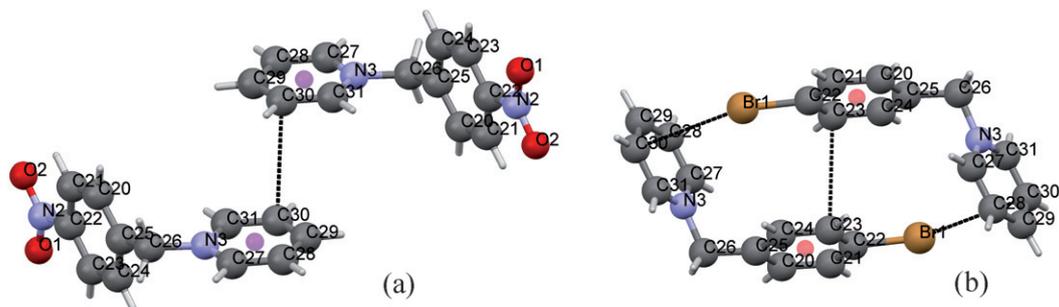


**Fig. 2** Details showing: (a) the *p*-NO$_2$BzPy cation pair in **1**; (b) the *p*-BrBzPy cation pair in **2**.
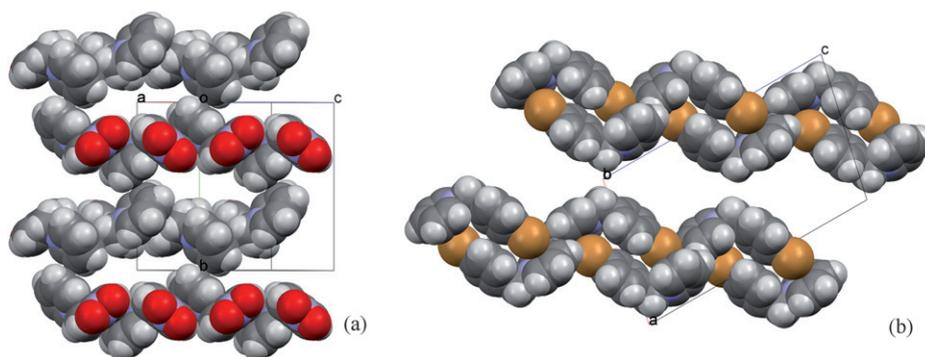
**Fig. 3** Partial view showing the crystal supramolecular cationic motif of: (a) *p*-NO$_2$BzPy$^+$ units in **1**; (b) *p*-BrBzPy$^+$ units in **2**.

The *p*-BrBzPy$^+$ cation in **2** adopts a standard geometry, with the pyridine and the benzyl rings making dihedral angles of 80.1(3)° and these rings make dihedral angles with the reference plane N3–C25–C26, of 61.7(7) and 70.7(9)°, respectively (Fig. 2b). The *p*-BrBzPy$^+$ cations are arranged in pairs in a P4AE (parallel fourfold aryl embrace),[9] where the pyridine and the benzyl groups are parallel at a ring centroid distance of 5.1(1) Å, allowing a π–π interaction, C23···C23#g at 3.29(2) Å (#g = 2 − x, 2 − y, 1 − z) (Table 2) between the benzyl rings, at variance with the cation pair in **1**, where the π–π interactions were found between the pyridine rings. The P4AE packing motif of the cation pair in **2** is similar to other salts of this cation.[11]

The anions in **2** are arranged in layers parallel to (*b, a + c*) (Fig. 5). Each anion is connected with tree neighbours through one short S4···S4#f contact at 3.609(4) Å (#f = 2 − x, 2 − y, −z) only 1% above the van der Waals radii sum and two contacts between a pyridine ring and a hydrogen atom of the metalocycle, N1···H8#e and C5···H8#e at 2.72 Å and 2.86 Å, respectively, (e# = −1/2 + x, 1.5 − y, −1/2 + z). Therefore the anion layer can be seen essentially as a 2D network of dimers (Fig. 5b). The anionic layers alternate with cation layers which are interconnected by several anion cation short contacts listed in Table 2.

**Table 2** Short contacts in the crystal structure of **2**

| Anion–cation | d/Å |
| --- | --- |
| H26B···S4$^a$ | 2.77 |
| N3···N1$^b$ | 3.01(1) |
| C31···N1$^b$ | 3.02(1) |
| H24···C9$^c$ | 2.87 |
| H24···C10$^c$ | 2.85 |
| H31···Ni1$^c$ | 2.70 |
| H21···C10$^d$ | 2.88 |
| H21···C14$^d$ | 2.86 |
| Anion–anion | |
| H8···N1$^e$ | 2.72 |
| H8···C5$^e$ | 2.86 |
| S4···S4$^f$ | 3.609(4)$^h$ |
| Cation–cation | |
| Br1···C30$^g$ | 3.53(1) |
| C23···C23$^g$ | 3.29(2) |

$^a$ 2.5 − x, 1/2 + y, 1/2 − z. $^b$ 3 − x, 2 − y, 1 − z. $^c$ 1/2 + x, 1.5 − y, 1/2 + z. $^d$ 1/2 + x, 2.5 − y, 1/2 + z. $^e$ −1/2 + x, 1.5 − y, −1/2 + z. $^f$ 2 − x, 2 − y, −z. $^g$ 2 − x, 2 − y, 1 − z. $^h$ 1% above the van der Waals radii sum.

In the crystal supramolecular cations motif the *p*-BrBzPy$^+$ units are OFF (offset face-to-face) along the (*b, a + c*) plane and P4AE in the pair of the units. (Fig. 3b).
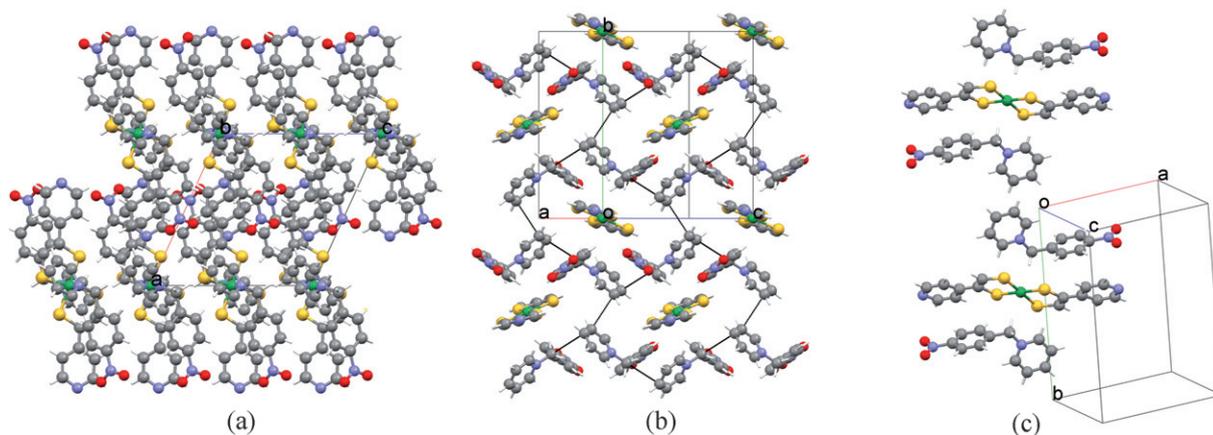


**Fig. 4** Crystal structure of **1**, (a) viewed along the [010]; (b) partial view of one layer depicting short cation–cation contacts; (c) view of one mixed column.
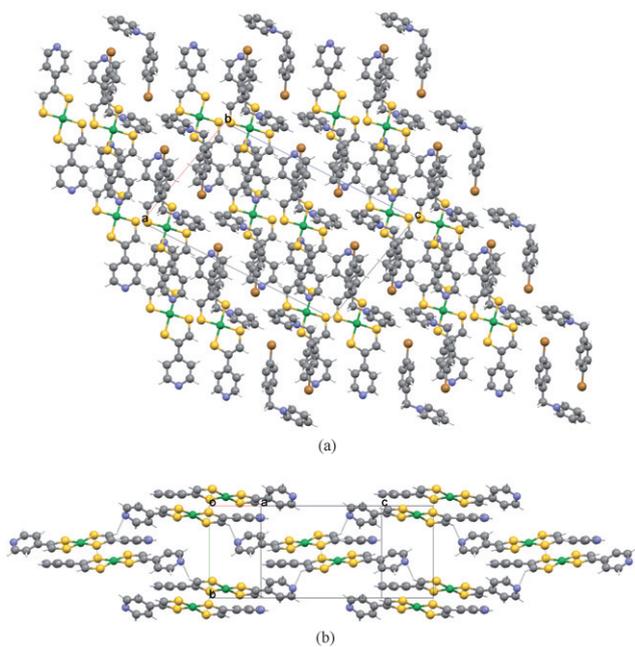
**Fig. 5** Crystal structure of BrBzPy[Ni(4-pedt)$_2$] (a) viewed along $b$; (b) partial view of anionic layers perpendicular to $b$.
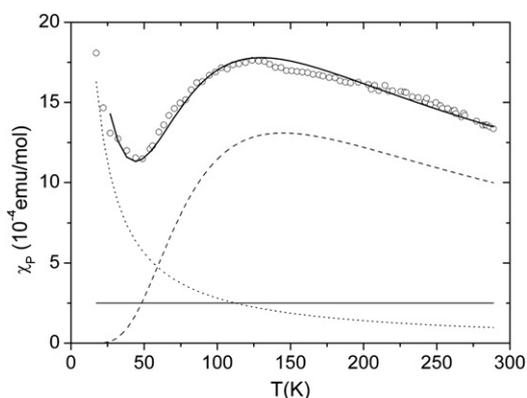


**Fig. 6** Paramagnetic susceptibility $\chi_P$ of **2** as a function of temperature. The thick solid line represents a fit with eqn (1); dotted line: Curie tail; dashed line: AF dimer contribution; thin solid line: TIP.

As expected for a monoanionic Ni dithiolene complex with a square planar coordination geometry, with $S = 1/2$, **2** was found to be paramagnetic. The paramagnetic susceptibility, $\chi_P$, of **2** obtained from magnetization measurements, after a correction for the diamagnetic contribution estimated from the Pascal constants as $-4.46 \times 10^{-4}$ emu mol$^{-1}$, is shown in Fig. 6. At room temperature the data correspond to an effective magnetic moment of 1.76 $\mu_B$, close to the calculated value, 1.78 $\mu_B$, for a system of independent spins with $S = 1/2$ and $<g> = 2.056$.[5] However, upon cooling there is a significant decrease of the effective magnetic moment denoting the presence of strong antiferromagnetic (AFM) interactions and the susceptibility goes through a broad maximum at ~120 K followed by a faster decrease towards a minimum at *ca* 45 K, finally followed by a low temperature increase.

The antiferromagnetic interactions are certainly mediated by the S4···S4#f contacts previously referred to in the structure description, which are responsible for the formation of dimers. In view of the crystal structure where the anions are arranged in layers of dimers it is tempting to fit the susceptibility data to eqn (1) where in addition to a temperature independent term and a low temperature Curie contribution there is a Bleaney–Bowers contribution of antiferromagnetically coupled dimers:

$$\chi_P = A + \frac{Ng^2\mu_B^2}{3kT}x + (1-x)\frac{Ng^2\mu_B^2}{3kT}\left[1 + \frac{1}{3}\exp\left(\frac{-J}{kT}\right)\right]^{-1} \quad (1)$$

where $N$ is the Avogadro number, $g$ the Landé factor, $\mu_B$ the Bohr magneton, and $k$ the Boltzman constant.

As shown in Fig. 6 a fair agreement with experimental data above 20 K was obtained, considering $g = 2.06$[5] and with $A = 2.4(1) \times 10^{-4}$ emu mol$^{-1}$, $x = 0.052(1)$ and $J/k = -232(2)$ K. The temperature independent contribution $A$ is relatively small and may correspond to a true TIP contribution or most likely to experimental or diamagnetic contribution errors. The observed Curie tail corresponds to about 5% of the paramagnetic $S = 1/2$ impurities or defects.

Although the dimer S4···S4#f contacts are certainly responsible for the AFM coupling in dimers, since they involve equivalent atoms and they are dominant, other interanion magnetic interactions may arise mediated by the other interanion contacts.

## Experimental

### General materials and methods

All manipulations were carried out under anaerobic conditions, unless stated otherwise. Whenever required, the solvents were dried according to the standard literature procedures,[12] 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.[13,14]

Elemental analyses of the compounds isolated in these studies were performed at ITN analytical services using an EA 110 CE Instruments automatic analyzer.

### Synthesis of the complexes

($p$-NO$_2$BzPy)$_2$[Ni(4-pedt)$_2$]: on a round-bottom Schlenk flask, the 4-(4-pyridyl)-1,3-dithiol-2-one (0.200 g, 1.02 mmol) was added to a freshly prepared sodium methoxide solution (0.048 g, 2.04 mmol, 10 cm$^3$) and stirred for 1 h. A solution of NiCl$_2$.6H$_2$O (0.12 g, 0.52 mmol) in methanol (10 cm$^3$) was added to the dark red mixture and allowed to stir for another hour. $p$-NO$_2$BzPyBr (0.336 g, 1.02 mmol) in methanol (10 cm$^3$) was carefully added to the mixture, without stirring. The flask was closed and stored overnight at 4 °C. The solid was recovered by filtration, affording dark brown powder and crystals, which were suitable for X-ray diffraction. The product was recrystallised from acetonitrile/isopropyl ether (0.198 g, 47%). (Found: C, 54.72; H, 3.39; N, 9.98; S, 16.15. Calc. For C$_{38}$H$_{32}$N$_6$NiO$_4$S$_4$: C, 55.41; H, 3.92; N, 10.20; S, 15.57%).

*p*-BrBzPy[Ni(4-pedt)$_2$]: on a round-bottom Schlenk flask, the 4-(4-pyridyl)-1,3-dithiol-2-one (0.200 g, 1.02 mmol) was added to a freshly prepared sodium methoxide solution (0.048 g, 2.04 mmol, 10 cm$^3$) and stirred for 1 h. A solution of NiCl$_2$.6H$_2$O (0.12 g, 0.52 mmol) in methanol (10 cm$^3$) was added to the dark red mixture and allowed to stir for another hour. *p*-BrBzPyBr (0.302 g, 1.02 mmol) in methanol (10 cm$^3$) was carefully added to the mixture, without stirring. The flask was closed and stored for some days at 4 °C. The solid was recovered by filtration, affording a dark brown powder and crystals, which were suitable for X-ray diffraction. The product was recrystallised from acetonitrile/isopropyl ether (0.204 g, 63%). (Found: C, 48.60; H, 3.62; N, 6.55; S, 18.35. Calc. for C$_{26}$H$_{21}$BrN$_3$NiS$_4$: C, 48.62; H, 3.30; N, 6.54; S, 19.97%).

### X-Ray crystallography

X-Ray diffraction experiments were performed on a Bruker AXS APEX CCD area detector X-ray diffractometer equipped with an Oxford Cryosystems low-temperature device at 150 K in the $\omega$ and $\varphi$ scans mode. A semiempirical absorption correction was carried out using SADABS.[15] Data collection, cell refinement and data reduction were performed with the SMART and SAINT programs.[16] The structures were solved by direct methods using SIR97[17] and refined by full-matrix least-squares methods with the SHELXL97[18] program using the winGX software package.[19] 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.† Molecular graphics were prepared using ORTEP3[20] and Mercury 1.4.2.[21]

### Magnetic measurements

Magnetic measurements: Measurements of polycrystalline samples (10–15 mg) in gelatin capsules were performed in 2 magnetic systems, a 7 Tesla S700X SQUID (Cryogenic Ltd.) and a 12 Tesla Maglab 2000 System (Oxford Instruments) with a DC extraction technique, over the temperature range 1.6–300 K.

## Conclusions

Two new salts (*p*-NO$_2$BzPy)$_2$ [Ni(4-pedt)$_2$] and *p*-BrBzPy [Ni(4-pedt)$_2$] were prepared and characterized. For the first time the dianionic Ni complex with this ligand was obtained as a salt with the *p*-NO$_2$BzPy$^+$ cation. This is probably a consequence of the low solubility of this salt, compared with *p*-BrBzPy$^+$ and other

cations previously used that prevented further oxidation of the complex.

The crystal structures of these two salts are quite distinct. In the dianionic salt there are mixed columns of anion and cation pairs, while the monoanionic salt presents alternated layers of pairs of anions and layers of cation pairs.

While the (*p*-NO$_2$BzPy)$_2$ [Ni(4-pedt)$_2$] was found to be diamagnetic with $S = 0$, the paramagnetic salt *p*-BrBzPy [Ni(4-pedt)$_2$] presents strong antiferromagnetic pair interactions.

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† **Crystallographic data for (*p*-NO$_2$BzPy)$_2$[Ni(4-pedt)$_2$]:** C$_{38}$H$_{32}$N$_6$NiOS$_4$, M = 823.65 g mol$^{-1}$, monoclinic, space group $P2_1/c$, $a = 11.8506(7)$ Å, $b = 14.3634(7)$ Å, $c = 11.4282(7)$ Å, $\beta = 114.2380(10)°$, $V = 1773.77(17)$ Å$^3$, $Z = 2$, $D_c = 1.542$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 0.835 mm$^{-1}$, 12 272 reflections measured, 3364 unique, final $R(F^2) = 1.026$ using 3364 reflections with $I > 2.0\sigma(I)$, $R(I > 2.0\sigma(I)) = 0.0324$, $T = 150(2)$ K. CCDC 725672. **Crystallographic data for *p*-BrBzPy[Ni(4-pedt)$_2$]:** C$_{26}$H$_{21}$BrN$_3$NiS$_4$, $M = 642.32$ g mol$^{-1}$, monoclinic, space group $P2_1/n$, $a = 13.053(5)$ Å, $b = 9.318(3)$ Å, $c = 21.376(5)$ Å, $\beta = 102.602(11)°$, $V = 2537.3(15)$ Å$^3$, $Z = 4$, $D_c = 1.681$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 2.691 mm$^{-1}$, 7587 reflections measured, 3972 unique, final $R(F^2) = 0.848$ using 3972 reflections with $I > 2.0\sigma(I)$, $R(I > 2.0\sigma(I),) = 0.0770$, $T = 150(2)$ K. CCDC 725673.

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