Dalton Transactions

PAPER

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Cite this: DOI: 10.1039/c8dt02444h

Received 14th June 2018, Accepted 2nd August 2018 DOI: 10.1039/c8dt02444h rsc.li/dalton

Introduction

After the fortuitous and beneficial discovery of the antitumor effects of cisplatin, a wide pool of Pt(n) complexes were proposed and successfully used as anticancer drugs.¹ Initially, the two *cis*-coordinating leaving groups, which activate the Pt(n) complex towards DNA binding, and the neutral character of the Pt(n) complexes were defined as key features for the antiproliferative effects.² Unfortunately, the labile character of the two coordination sites causes, instead, multiple adverse cytotoxic

Anionic cyclometalated Pt(II) and Pt(IV) complexes respectively bearing one or two 1,2-benzenedithiolate ligands[†]

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Novel anionic cyclometalated Pt(III) square-planar complexes NBu₄[(C^N)Pt^{II}(S^S)], containing 2-phenylpyridine H(PhPy), 2-(2,4-difluorophenyl)-pyridine H(F₂PhPy) and benzo[*h*]quinoline H(Bzq), respectively, as a cyclometalated ligand and the dianionic 1,2-benzenedithiolate (Thio)^{2–} fragment as an (S^S) ligand, were synthesised. By the simple addition of an equivalent of (Thio)^{2–} to the NBu₄[(C^N)Pt^{II}(Thio)] complexes, octahedral anionic NBu₄[(C^N)Pt^{IV}(Thio)₂] analogues were obtained, representing, to the best of our knowledge, the first examples of Pt(IV) anionic cyclometalated complexes. The molecular structures of the obtained complexes in the case of the NBu₄[(Bzq)Pt^{II}(Thio)] and the NBu₄[(Bzq)Pt^{IV}(Thio)₂] complexes were confirmed by single crystal X-ray diffraction analysis. Furthermore, the electrochemical and photophysical properties of the two series of Pt(III) and Pt(IV) newly synthesised complexes were studied and DFT and TD-DFT calculations were performed in order to comprehensively investigate the displayed behaviour. All Pt(III) and Pt(IV) complexes show intense luminescence in the solid state, with remarkable enhancement of the emission quantum yields, proving to be excellent examples of aggregation-induced emission systems.

effects.³ In an attempt to prevent undesirable effects and also to extend the therapeutic window, 'rule-breaking' $Pt(\pi)$ antitumor complexes were synthesised and tested.⁴ For instance, recent examples include di- and trinuclear cationic $Pt(\pi)$ complexes⁵ or photoactivated-porphyrin,⁶ curcumin,⁷ catecholate⁸ and photocaging⁹ $Pt(\pi)$ complexes, thus reaching the so-called 4th generation of platinum drugs.

On the other hand, cyclometalated d⁸ Pt(π) complexes [(C^N)Pt^{II}(X^Y)], where H(C^N) is the cyclometalated ligand and (X^Y) is the ancillary ligand completing the metal coordination sphere, are becoming well studied as anticancer drugs and bio-imaging probes,^{10,11} displaying phosphorescence properties in solution and in the solid state.^{12,13} Moreover, Pt(π) luminescent complexes are successfully employed in organic light-emitting,^{14,15} photochromic and water-splitting devices,^{16,17} chemosensors,¹⁸ photocatalysis¹⁹ and optical limiters.²⁰

Depending on the nature of the ancillary (X^Y) ligands completing the coordination sphere of the cyclometalated Pt(II) complexes [(C^N)Pt^{II}(X^Y)], neutral or ionic species may be prepared.¹² Since the luminescence properties of Pt(II) complexes are mainly determined by the chemical nature of the coordinated ligands, it is, nevertheless, useful to remember that the whole metal coordination sphere is a non-innocent player.^{21–23} In particular, with regard to the overall formal

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[†]Electronic supplementary information (ESI) available: Calculated geometrical structures and parameters of **1,2a-c** complexes, graphical representation of the highest occupied and lowest unoccupied MOs for the **1,2a,b** complexes, cyclic voltammetry traces of **1,2a-b** and scan rate dependency for each complex. CCDC 1848424 and 1848700. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt02444h

Paper

charge within the reported and studied $[(C^N)Pt^{II}(X^Y)]$ species, anionic Pt(II) complexes have received much less attention. Indeed, due to the greater availability of neutral or monoanionic (X^Y) ligands, a wide number of cationic and neutral luminescent Pt(II) complexes are reported, containing mostly X⁻, CN⁻ or bis-cyclometallated ligands.²⁴⁻³² Complexes containing (X^Y) aromatic dianionic bidentate ligands are even rarer. In this context, we recently reported on the use of bidentate catecholate (O^O) and orotate (O^N) ligands to access a novel series of anionic Pt(u) complexes that present high luminescence both in solution and in the solid state (Chart 1).³³ Unfortunately, due to their chemical nature, these ligands offer few opportunities for further functionalisation, precluding the introduction of suitable substituents necessary to tune, through electronic effects on the metal centre, the luminescence properties of the resulting [(C^N) $Pt^{II}(X^{Y})^{-}$ anionic complexes.

Due to the poor stability, in the deprotonated form, of the Pt(u) complexes bearing catecholate (O^O) derivatives,^{34,35} we decided to explore other di-anionic ancillary ligands in the synthesis of new anionic platinum species. In particular, knowing that 1,2-benzenedithiole H_2 (Thio) has been already used in the synthesis of Pt(u) anionic complexes,³⁶ we report herein the possibility of using this type of aromatic (S^S) ligand, as a probe ligand to extend its reactivity towards the formation of Pt(u) and Pt(v) new anionic complexes.

It is worth noting that there is growing interest in obtaining tetracoordinated Pt(II) cytotoxic complexes *in situ* from the intracellular reduction of kinetically more stable hexacoordinate Pt(IV) complexes.^{37–44} These Pt(IV) prodrugs can display additional selectivity in photodynamic therapy or in photoactivated chemotherapy since they can be triggered through photoactivation directly within the neoplastic cells, limiting the undesired cytotoxic effects.¹ In this context, Pt(IV) complexes absorbing at high wavelengths are highly interesting due to their better tissue penetration features.⁴⁵ Therefore, by including within the coordination sphere of Pt(IV) prodrugs, for instance, cyclometalating ligands, their redox and spectral



Chart 1 Molecular structure of anionic Pt(μ) luminescent complexes NBu₄[(C^N)Pt(Cat)] and NBu₄[(C^N)Pt(Ort)].³⁴



Chart 2 Molecular structures of the synthesised Pt(II) square-planar (1a-c) NBu₄[(C^N)Pt^{II}(Thio)] and Pt(IV) octahedral NBu₄[(C^N)Pt^{IV}(Thio)₂] (2a-c) cyclometalated complexes, bearing the dianionic form of the H₂(Thio) ligand(s).

properties may be finely tuned, hence improving their biological activity.^{46–48} Despite this motivation, very little attention was devoted so far to cyclometalated Pt(IV) complexes, which may display luminescence, an important feature for monitoring their potential antitumor activity. Until now, the only Pt(IV) cyclometalated emitters already reported are mono,⁴⁹ bis^{50,51} and tris⁵²-cyclometalated neutral or cationic complexes.⁵³

We present herein a series of novel anionic square-planar complexes of the general formula $NBu_4[(C^N)Pt^{II}(S^S)]$ (1a–c in Chart 2) and their anionic octahedral $NBu_4[(C^N)Pt^{IV}(S^S)_2]$ (2a–c in Chart 2) derivatives, bearing 2-phenylpyridine H(PhPy), 2-(2,4-difluorophenyl)-pyridine H(F₂PhPy), and benzo [h]quinoline H(Bzq), respectively, as a cyclometalated ligand and the (Thio)^{2–} fragment as an (S^S) dianionic ligand.³⁶

The octahedral Pt(IV) anionic complexes **2a–c** were directly obtained upon the reaction of one equivalent of H_2 (Thio) with the anionic Pt(II) complexes **1a–c** (Chart 2) through oxidation and addition reactions. Even though octahedral anionic Ir(III) complexes bearing the Thio ligand have been reported,⁵⁴ to the best of our knowledge, complexes **2a–c** are the first examples of Pt(IV) cyclometalated anionic complexes reported until now in the literature. All Pt(II) and Pt(IV) complexes show notable luminescence in the solid state, proving to be excellent examples of aggregation-induced emission systems.

Results and discussion

Synthetic procedures and crystallography

The novel anionic Pt(n) cyclometalated complexes **1a–c** (Chart 2) were synthesised starting from the respective cycloplatinated precursors **I–III** by adapting an already reported procedure.³³ Complexes bearing cyclometalated PhPy (**1a**) or F₂PhPy (**1b**) were prepared starting from a mononuclear intermediate, obtained by microwave assisted synthesis, as previously reported,⁵⁵ while for complex **1c** incorporating a benzo [*h*]quinoline (Bzq) fragment, a chloro-bridged binuclear cycloplatinated precursor was used (Scheme 1).⁵⁶



Scheme 1 Synthesis of the anionic Pt(II) complexes 1a-c. Reagents and conditions: (i) I–II: MW, 250 W, 110 °C, 3 min, III: 2-ethoxyethanol/water 3/1, N₂, reflux, 48 h; (ii) NBu₄OH, methanol, r.t. 12 h, N₂.

The treatment of **I–III** with an equimolar amount of the $H_2(Thio)$ ligand in basic media (NBu₄OH) afforded the anionic square-planar Pt(II) complexes NBu₄[(C^N)Pt^{II}(Thio)] (**1a–c**) in moderate to high yields (Scheme 1). While the synthesis and the NMR and photophysical data of complex **1a** were previously reported by González-Herrero and co-workers,³⁶ the newly synthesised **1,2b–c** complexes were characterised by ¹H-NMR, ¹³C-NMR, FT-IR, ESI-MS and elemental analysis.

The coordination of the $(Thio)^{2-}$ fragment to the Pt(II) center in the **1a-c** series was confirmed by using the ¹H-NMR spectra through the absence at 3.79 ppm of the two acidic protons of H₂(Thio) and by the presence of the aliphatic signals associated with the NBu₄⁺ counterion and, in the case of **1c**, confirmed by single crystal X-ray diffraction studies. Indeed, suitable lamellar red crystals of **1c** were obtained from the slow evaporation of an ethanol solution. As shown in Fig. 1, the Pt(II) anion of complex **1c** is built up by a slightly distorted square planar Pt(II) centre, bis-chelated by the C-deprotonated Bzq ligand and the $(Thio)^{2-}$ anion. The bond distances and angles are reported in Table 1.

The structural data of complex **1c** can be compared with the only reported crystal structure of an analogous Pt(n) anionic derivative, containing PhPy as a cyclometalated ligand and a different dithiolate ligand.⁵⁷ The most evident difference is related to the "bite" angles within the metallated rings, being 0.8° larger in the case of CCCNPt, and 1.5° smaller in SCCSPt, in the Pt(n) anion of **1c** compared with the literature analogues. Although the bond lengths around the metal ion are all within the expected values for Pt–N, Pt–C and Pt–S bond distances, with the Pt–S bond *trans* to the coordinated carbon atom longer than the other bonds, they are all slightly different from those observed in the analogous derivatives of the literature (Pt–N and Pt–C being longer and Pt–S shorter than the corresponding literature reported values).

The $Pt(\pi)$ anion of **1c** shows an overall planar structure, characterised by a torsion angle between the best mean planes passing through the two metallated rings of $177.7(1)^{\circ}$. As a consequence, significant intramolecular contacts involving the coordinated S atoms are found, with Pt–S···H distances mostly equal between each other at 2.85 Å. In the 3D crystalline packing, weak C–H···S intermolecular contacts are found



Fig. 1 Molecular structure of the Pt(II) anion of complex **1c** with atomic numbering scheme (ellipsoids at the 30% level) (a), its repetition in 3D packing showing the C-H···S (b) and the C-H··· π weak intermolecular contacts (c).

Table 1 Selected bond length (Å) and angles (°) of 1c and 2c complexes

	1c	2c
Pt-N(1)	2.068(5)	2.140(5)
Pt-C(7)	2.023(5)	2.117(7)
Pt-S(1), S(3)	2.2803(18)	2.343(2), 2.377(2)
Pt-S(2), S(4)	2.3055(18)	2.420(3), 2.369(2)
C(7)-Pt-N(1)	81.6(2)	80.9(3)
S(1) - Pt - S(2), S(3), S(4)	88.89(7)	91.32(8), 89.17(7), 89.75(7)
S(2)-Pt-S(4)		88.92(8)
S(3) - Pt - S(4)		178.91(6)
C(7) - Pt - S(1), S(3)	94.15(14)	94.3(2), 91.3(2)
N(1) - Pt - S(1), S(3)	175.70(15)	175.2(2), 90.6(2)
C(7) - Pt - S(2), S(4)	176.46(13)	173.9(2), 88.8(2)
N(1)-Pt-S(2), S(4)	95.36(16)	93.4(2), 90.4(2)

between laterally interacting Pt(II) anions $[H(15)\cdots S(2)^i 2.99 \text{ Å}, C(15)\cdots S(2) 3.81(1) \text{ Å}, C(15)-H(15)\cdots S(2) 149^\circ, i = x - 1/2, -y + 1/2, +z - 1/2], as shown in Fig. 1b, being the overall supramole$ cular architecture built up with a strict segregation of undulating anionic and cationic layers.

Indeed, no overlap between anionic moieties is found, preventing, then, the observation of π - π stacking interactions or any contact involving the Pt(π) ion. The only type of contact involving the aromatic faces of anions is of C-H… π weak interactions, however characterised by discrete long distances between donors and acceptors (Fig. 1c).

By treating complexes **1a–c** with an equivalent of H_2 (Thio) under very mild conditions (r.t., oxygen atmosphere), Pt(v)

complexes 2a-c (Chart 2) were obtained in good yields. The coordination of a second molecule of H₂(Thio) and the consequent formation of the Pt(IV) complexes were confirmed by ¹H and ¹³C-NMR spectroscopy. A downfield shift is observed for the signals relative to the hydrogen atoms of the Pt(IV) 2a-c complexes compared to the Pt(II) 1a-c precursors. Such difference is particularly evident for the signal associated with the hydrogen atom in alfa position to the N donor atom involved in the cyclometalation, for which a ca. 0.5 ppm downfield shift is registered in the ¹H-NMR spectra. Moreover, the MS analyses of the complexes, carried out via direct infusion in the positive mode, showed the presence of an ion at m/z 242.2, corresponding to the NBu₄⁺ counterion. The MS analyses of the complexes, carried out via direct infusion in the negative mode, showed, instead, an isotope cluster, centered at m/z 488.7 (1a), 524.8 (1b), and 512.7 (1c) due to the natural abundances, and corresponding to [(C^N)Pt(Thio)]⁻ and, respectively, 628.7 (2a), 664.8 (**2b**), and 652.8 (**2c**) for the [(C^N)Pt(Thio)₂]⁻ anion.

Suitable single crystals of **2c** were obtained from a methanol/diethyl ether solution and the crystal structure is shown in Fig. 2. The experimental molecular structure of **2c** confirms the oxidation of the metal centre of the Pt(n) derivative **1c**. The Pt(nv) anion shows a slightly distorted octahedral geometry, with the cyclometalated ligand and two S atoms of the different chelated (Thio)^{2–} anions in the square basal plane of the Pt(nv) coordination sphere. All bond distances are found, as expected, to be slightly longer than those found in **1c** and comparable with other (C^N)Pt^{IV} compounds,^{47,51} retaining the differences between the Pt–S distances due to the *trans* carbon effect (Table 1). The "bite angles" within the cyclometallated rings are comparable with those found in **1c**.



Fig. 2 Molecular structure of the Pt(IV) anion of complex 2c with atomic numbering scheme (ellipsoids at the 30% level) (a); views showing the OFF primary embrace formed within the metal anion dimers, P4AE secondary aryl embrace (with the centroid–centroid and CH/ π distances), and the weak interactions between the cations and the anion dimers (b, c).

In the 3D crystal packing of 2c, the anions are arranged in centrosymmetric pairs as shown in Fig. 2b, according to the description of the crystal supramolecular motifs formed by Mextended planar aromatic complexes.58 The primary motif between the pyridine aryl surface of the Bzq ligands is of the offset face-to-face (OFF) type (Fig. 2b). The π - π stacking interactions between the pyridine rings within the primary supramolecular motif are characterised by an interplanar distance, displacement angle and horizontal displacement of 3.49 Å, 25.4° and 1.6 Å, respectively. Due to the octahedral geometry around the metal ion, each molecule in the OFF dimer is part of the secondary motif P4AE (parallel four-fold aryl embrace), being the aromatic ring of the Thio ligands facing the OFF motif. Indeed, the edge-to-face (EF) motifs are formed by C-H··· π interactions. Within the dimer, the interactions between anions are reinforced by C-H...S contacts, due to the orthogonal facing of the dithiolate ligands with the aromatic rings of the OFF motif [H(3)...S(4)ⁱ 2.99 Å, C(3)...S(4) 3.87(1) Å, C(3)-H(3)···S(4) 159°, i = -x + 1, -y, -z]. The anion dimers are surrounded by cations, weakly interacting via C-H··· π and C-H...S interactions with the extruding fragments from the OFF motif Thio ligands (Fig. 2c).

Electrochemistry and DFT calculations

All the structures of Pt(n) and Pt(n) complexes have been fully optimised. The calculated geometries together with a table listing the optimised bond lengths and angles compared with the data from experiments are reported in the ESI in Fig. ESI1 and Table ESI1,† respectively. The DFT geometrical parameters fit well with the experimental values, being deviations due to the crystal packing that imposes different arrangements with respect to the gas phase.

The electrochemical properties and the calculated values of the HOMO and LUMO energies for **1a–c** and **2a–c** complexes are reported in Table 2. The electrochemical properties were investigated by cyclic voltammetry in 0.1 M NBu₄BF₄ dichloromethane electrolytic solutions, using a Pt disk as a working electrode, a Pt wire as a counterelectrode and an Ag wire as a *pseudo*-reference electrode and ferrocene (Fc) was added in an equimolar amount as an internal reference. The HOMO levels were estimated from the oxidation potentials taking into account –4.8 eV for the HOMO energy level of Fc.⁵⁹

No reduction waves were observed within the investigated potential window (down to -0.9 V vs. SCE).

The Pt(π) and Pt(π) complexes display for the two first oxidation processes similar behaviour. The cyclic voltammograms of the [(Bzq)Pt^{II}(Thio)]⁻/[(Bzq)Pt^{IV}(Thio)₂]⁻ couple, obtained at a 100 mV s⁻¹ scan rate, are shown in Fig. 3 as a couple, while the data relative to complexes **1a,b** and **2a,b** are reported in Fig. ESI4.† The first observed oxidation wave for both Pt(π) and Pt(π) complexes displays a complete irreversible character and presents a current intensity corresponding to a bi-electronic process. It is noteworthy that these Pt(π) and Pt(π) anions are easily oxidised with an oxidation potential lower than that of ferrocene. The second oxidation process, of a mono-electronic nature, is either irreversible for the Pt(π) complexes or quasi-

Table 2 Electrochemical data relative to complexes 1a-c and 2a-c. Scan rate: 100 mV s⁻¹. Irr. = irreversible wave and calculated energy values of the HOMO and LUMO frontier orbitals and gaps

	$E_{\mathrm{ox}}^{1\ a}\left(\mathrm{V}\right)$	E_{ox}^{2} a (V)	E_{ox}^{3} ^{<i>a</i>} (V)	$HOMO^{b}$ (eV)	$HOMO^{c}$ (eV)	$LUMO^{c}(eV)$	HOMO–LUMO gap ^{c} (eV)
1a [(PhPy)Pt ^{II} (Thio)] ⁻	-0.29 (Irr.)	+0.13 (Irr.)	_	-4.51	-4.18	-1.49	2.69
$1b [(F_2PhPy)Pt^{II}(Thio)]^-$	–0.25 (Irr.)	+0.29 (Irr.)		-4.55	-4.35	-1.61	2.74
1c [(Bzq)Pt ^{II} (Thio)] ⁻	–0.28 (Irr.)	+0.20 (Irr.)		-4.52	-4.17	-1.72	2.45
$2a [(PhPy)Pt^{iv}(Thio)_2]^-$	–0.09 (Irr.)	+0.32 (Irr.)	+0.54 (Irr.)	-4.71	-4.38	-1.47	2.91
$2b [(F_2PhPy)Pt^{IV}(Thio)_2]^-$	-0.13 (Irr.)	+0.39 (Irr.)	+0.59 (Irr.)	-4.67	-4.52	-1.57	2.94
$2c [(Bzq)Pt^{IV}(Thio)_2]^{-1}$	-0.10 (Irr.)	+0.33 (Irr.)	+0.57 (Irr.)	-4.70	-4.38	-1.68	2.90

^{*a*} Oxidation and reduction potentials are reported *vs.* Fc/Fc⁺ redox couple standard oxidation potential. ^{*b*} Estimated from the oxidation potential. ^{*c*} Calculated.



Fig. 3 Cyclic voltammetry of 1c, $[(Bzq)Pt^{II}(Thio)]^-$ (red curve), and 2c, $[(Bzq)Pt^{IV}(Thio)_2]^-$ (black curve). Scan rate 100 mV s⁻¹.

reversible for the Pt(rv) complexes, while a third reversible mono-electronic oxidation is only observed for the Pt(rv) complexes. All oxidation potentials are roughly identical within each series suggesting the weak contribution of the cyclometalated ligand to the HOMO energy level. However, the two first common oxidation processes between Pt(II) and Pt(rv) complexes are shifted in a potential of *ca.* 200 mV, the Pt(II) complexes being more easily oxidised than their Pt(IV) analogues. This observed difference is due to the entirely different coordination sphere of the Pt(IV) complexes with respect to their Pt(II) analogues. The oxidation of the metal centre in Pt(π) neutral or ionic complexes has been usually reported at high potential values (*i.e. ca.* +0.5 V with respect to Fc/Fc⁺).^{29,33,60} It is therefore remarkable that the introduction of a Thio ligand within the coordination sphere of the Pt(π) metal center drastically decreases the oxidation potential.

DFT calculations were performed in order to elucidate the frontier orbital localisation and the obtained results were compared with the experimental data obtained from cyclic voltammetry. Due to the strong similarity, molecular orbital plots generated through static density functional theory calculations for the geometry-optimized singlet ground states are shown only for the **1c** and **2c** complexes in Fig. 4. The graphical representation of MOs for **1a,b** and **2a,b** complexes can be found in Fig. ESI2 and 3 of the ESI.[†]

Computations are able to very well reproduce the energies of the HOMO for all the investigated complexes (Table 2) and predict the LUMO energies as well as the HOMO–LUMO gaps. As can be deduced from the MOs' plot, the HOMO are mainly localised on the Thio ligands and the LUMO on the cyclometalating ligands for each investigated complex.

Photophysics and TD-DFT analysis

Compounds 1a–c. The optical properties of the anionic cyclometalated $NBu_4[(C^N)Pt^{II}(Thio)]$ **1a–c** were investigated in DMSO solution and in the solid state at 298 K.



Fig. 4 Graphical representation of the highest occupied and lowest unoccupied MOs for the (a) 1c and (b) 2c complexes.

The absorption spectra of **1a–c** were simulated with timedependent density functional theory (TD-DFT), modelling the solvent as a uniform medium considering the DMSO's dielectric constant. The computed TD-DFT singlet excitation energies, oscillator strengths, and wavelengths as well as the orbital transitions are reported in Table ESI2.[†]

In all the Pt(n) square-planar complexes the seven highest occupied molecular orbitals are denoted to be mainly Thio/ metal in character, even if to the HOMO – 5 and HOMO – 3 the C^N ligands provide a significant contribution and to the HOMO – 2 the main contribution comes from the metal center. The seven lowest unoccupied orbitals, instead, are calculated to be almost exclusively located on the C^N fragments with a limited contribution of the metal, except LUMO + 5, which has a relevant contribution from the (Thio)^{2–} ligand.

The experimental spectra of the Pt(n) square-planar complexes are in good agreement with the calculated spectral profiles. The electronic absorption spectra of **1a–c** in DMSO solution at 298 K are reported in Fig. 5 and the numerical data are summarised in Table 3. Based on the theoretical calculations (Table ESI2†), the intense absorption bands in the UV range correspond to the transitions of mixed contributions mainly from the metal centre and $(Thio)^{2-}$ towards the cyclometalating ligand.

A very broad band is observed at lower energy ($\lambda > 400$ nm), assigned on the basis of a comparison with previously reported anionic Pt(S^S) complexes^{36,61} and of the theoretical calculations to mixed MLCT/LLCT transitions from the metal and the dithiolate fragment to the C^N ligands. A slight blue shift of the lower energy absorption band results in **1b** relative to **1a**, due to the introduction of two electron-withdrawing substituents on the phenyl ring of the cyclometalated fragment, while in the case of **1c**, a significant bathochromic shift is observed. The latter, as confirmed by calculations, can be explained taking into account the extended aromatic system of the Bzq ligand compared to the PhPy ligand, which leads to a shift of the LUMO at lower energies (Table ESI2†), with the consequent decrease of the HOMO–LUMO energy gap.

All **1a–c** compounds are weakly luminescent in DMSO solution at 298 K. The emission spectra display broad and structureless bands in the yellow-red region (Fig. 6), with an emission quantum yield value of 0.30%, 0.18% and 0.15%, respectively. The goodness of the emission is highlighted by the excitation spectra (Fig. ESI6–8†). In a deaerated solution, an enhancement of the luminescence quantum yield was



Fig. 5 Electronic absorption spectra of 1a-c in DMSO solution at 298 K.



Fig. 6 Emission spectra of 1a-c in DMSO solution (1×10^{-5} M) at 298 K (excitation wavelength: 485, 480 and 525 nm, respectively).

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Compound	Absorption, $\lambda_{max}/nm \left(\epsilon/M^{-1} \text{ cm}^{-1}\right)$	Emission, $\lambda_{\rm max}/{\rm nm}$	Ф (%)	Lifetime, $\tau(\alpha)/\text{ns}(\%)$	$\Phi^{a}\left(\% ight)$	Lifetime ^{<i>a</i>} , $\tau(\alpha)/\text{ns}(\%)$
1a	282(38 245)-312(sh)-348(5553)-485(8208)	645	0.30	32.7 (4.33) 187.7 (95.67)	0.60	2143.8 (6.54) 4952.1 (93.46)
1b	281(51723)-313(sh)-343(9480)-480(10814)	649	0.18	17.6 (3) 214.4 (97)	2.2	1969.2 (9.80) 3895.8 (90.20)
1c	301(sh)-330(5859)-350(5570)-415(4299)- 480(3605)-525(4343)	690	0.15	93.6 (54.65) 233.6 (45.35)	0.92	174.5(12.58) 2281.2(87.42)
2a	306(12385)-331(12079)-387(sh)-465(510)	648	0.06	6.1 (12.74) 185.3 (87.26)	0.21	215.7 (1.54) 2980.1 (98.46)
2b	300(16728)-320(13955)-389(sh)-465(699)	650	0.05	7.9 (4.18) 207.3 (95.82)	0.61	713.4 (15.70)
2c	282(28 634)-338(9776)-375(4566)-465(568)	630, 678, 748	0.05	8.4 (30.60) 152.4 (69.40)	0.13	168.9 (33.46) 1661.8 (66.54)

^a Deaerated solution.

observed, highlighting the quenching of the emissive state by molecular oxygen (Table 3).

With regard to the excited-state decays of all complexes, the fitting procedure gave invariably better results by using a biexponential function. As previously reported for relative complexes, this can be attributed to the presence of aggregation phenomena even at very low concentrations.³³ The sensitivity to molecular oxygen and the decay lifetimes in the microsecond range (Table 3) confirm the triplet nature of the emissive state.

All **1a–c** compounds are emissive in the solid state at 298 K. The emission spectra are very similar in shape to those in DMSO solution, with maxima largely hypsochromic shifted (Fig. 7). It is noteworthy that in the solid state with respect to the solution, a remarkable enhancement of the emission quantum yield was observed reaching values respectively for **1a–c** of 38%, 35% and 25% (Table 4). As highlighted in the 3D crystalline packing of **1c** no π – π stacking interactions or any contact involving the Pt(π) centres is observed between the anionic moieties, confirming that π – π and/or Pt–Pt interactions between adjacent anionic molecules are not the key factor of the aggregation-induced emission effect.⁶²

Analogously to previously reported Pt(n) complexes, the increase of the emission quantum yield may be attributed to the physical constraint and to the more rigid local environment experienced in the crystalline state.⁶³ The C–H···S and C–H··· π intermolecular contacts between laterally interacting Pt(n) anions contribute to stiffen the conformation of the



Fig. 7 Emission spectra of **1a**–**c** in the solid state (excitation wavelength: 485, 480 and 525 nm, respectively).

molecules, strengthening the enhancement of their lumine-
scence efficiency. The excited-state decays of all the investi-
gated compounds gave longer lifetime values with respect to
those measured in solution (Table 4). This result is consistent
with the increased emission quantum yield values of the solid
samples with respect to the solution, confirming that the more
rigid environment favours the radiative deactivation of the
excited states.

Compounds 2a–c. Few studies on the excited state properties of Pt(rv) complexes are reported in the literature^{49,51,64} and no examples of anionic Pt(rv) compounds have been reported to date.

Analogously to $Pt(\pi)$ complexes, similar TD-DFT calculations were carried out on complexes **2a–c**.

For all complexes, electronic transitions calculated to be responsible for the lowest energy absorption band observed experimentally (see below) in the 425-525 nm region have negligible oscillator strengths. These transitions are due to excitations from the HOMO - 1 and HOMO to the LUMO in both 2a and 2b, while for 2c they correspond to excitations from the HOMO - 1 to the LUMO + 1 and from the HOMO to the LUMO + 1. As can be deduced from the MOs' plot reported for all the three Pt(IV) octahedral complexes (Fig. 4b for 2c and Fig. ESI3[†] for 2a-b) such transitions possess a predominantly LLCT character from the (Thio)²⁻ to the C^N ligand molecular orbitals. The more intense band experimentally observed between 280 and 400 nm can be considered as mixed-metal/ ligand-to-ligand CT due to the multiple comprised transitions and the localisation on both ligands and platinum metal center of the involved orbitals. The absorption spectra in DMSO solution of complexes $NBu_4[(C^N)Pt^{IV}(Thio)_2]$ 2a-c are shown in Fig. 8 and the data are included in Table 3.

Comparing the UV-vis spectra of **1a–c** compounds with their anionic hexacoordinate Pt(Iv) derivatives **2a–c**, it is evident that the change of the oxidation state of the platinum centre influences the absorption spectra of the complexes, as well as the band positions (Pt(II) complexes show red-shifted bands compared to their Pt(Iv) analogues) but also affects the values of the extinction coefficients, which in the case of the $NBu_4[(C^N)Pt^{IV}(Thio)_2]$ complexes are lowered with respect to the $NBu_4[(C^N)Pt^{II}(Thio)]$ series.

All the $NBu_4[(C^N)Pt^{IV}(Thio)_2]$ compounds exhibit very weak luminescence in DMSO solution at 298 K, arising from an excited state that is predominantly a LLCT state, mixed with

Compound	Emission, $\lambda_{\text{max}}/\text{nm}$	Φ (%)	$\begin{array}{c} \bullet \\ \bullet \end{array} \qquad \text{Lifetime, } \tau(\alpha)/\text{ns (\%)} \end{array}$		Lifetime, $\tau(\alpha)/ns$ (%)	
1a	605	38	_		1882.7	
1b	600	35	—		2883.9	
1c	653	25	—		2974.1	
2a	534, 596	10	λ_{em} 534	6.5 (72.80) 60.3 (27.20)	λ_{em} 596	10.3 (38.22) 117.1 (61.78)
2b	521, 621	10	λ_{em} 521	5.9	λ_{em} 621	85.5 (15.67) 563.4 (84.33)
2c	522, 618	5	λ_{em} 522	5.7	$\lambda_{ m em}$ 618	37.9 (13.46) 504.2 (86.54)

Table 4 Photophysical data of solid samples



Fig. 8 Electronic absorption spectra of 2a-c in DMSO solution at 298 K.



Fig. 9 Emission spectra of 2a-c in DMSO solution (1 × 10^{-5} M) at 298 K (excitation wavelength 465 nm).

a MLCT character. The emission spectra (Fig. 9) show unstructured bands in the visible region, very similar in shape and energy to those of the NBu₄[(C^N)Pt^{II}(Thio)] series and the reported excitation spectra (Fig. ESI6–8†) confirm the emission. The emission quantum yields in an aerated solution of *ca.* 0.05% are one order of magnitude lower compared with the values of the analogous Pt(II) complexes (Table 3).

This behaviour is in agreement with the literature reports concerning the detrimental effect of the oxidation state of the metal center, with emission quantum yields for the $NBu_4[(C^N)Pt^{IV}(Thio)_2]$ series significantly lower than those of the $NBu_4[(C^N)Pt^{II}(Thio)]$ series.^{65,66}

The quenching of the luminescence from molecular oxygen is indicated by the increase of the emission quantum yield and lifetime values under deaerated conditions, without any significant difference within the series (Table 3).

All **2a–c** compounds are luminescent in the solid state at 298 K displaying, with respect to the solution, a marked enhancement of the emission quantum yield up to values of 10%, 10% and 5%, respectively (Table 4). The emission spectra show bands in the range of 475–725 nm and in particular, two spectral zones can be identified (Fig. 10): a first zone at higher energy, which includes the 475–575 nm range, and a second



Fig. 10 Emission spectra of 2a-c in the solid state (excitation wavelength 465 nm).

one at longer wavelength, which includes the 575-725 nm range. For all the samples the decay lifetimes were measured in each defined spectral zone and the recorded values are reported in Table 4. The obtained results show for the first zone excited-state lifetimes values in the nanosecond range, while for the second one, lifetimes of hundreds of nanoseconds were measured. The emission peak at higher energy probably originates from an excited state generated by π - π interactions between the ligand fragments of neighboring Pt(IV) complex molecules, whereas the emission peak at lower energy is tentatively attributed to phosphorescence from an excited state involving the metal centre.^{67,68} It is noteworthy, comparing the emission bands of 2a-c, that the spectral shapes of 2b and 2c are similar rather than that of 2a. In particular, in the case of the complexes bearing F₂PhPy and Bzq as the cyclometalating ligands, both the spectral zones are well defined and are of similar intensities, whereas in the case of the PhPy complex the predominant contribution of the peak to higher energy with respect to the second one is evident. The parallelism between 1b and 1c is also highlighted from the obtained lifetime values, very similar in 1b and 1c, slightly different in the complex bearing the PhPy cyclometalated ligand.

Conclusions

Normalized Emission Intensity (a. u.)

A series of novel anionic cyclometalated Pt(II) square-planar complexes NBu₄[(C^N)Pt^{II}(Thio)], bearing a (C^N) cyclometalated ligand and the 1,2-benzenedithiolate (Thio)^{2–} fragment as a (S^S) dianionic ligand, were synthesised. Through combined addition and oxidation processes, an equivalent of (Thio)^{2–} is easily added to the square-planar NBu₄[(C^N) Pt^{II}(Thio)₂] complexes, leading to the formation of the corresponding octahedral NBu₄[(C^N)Pt^{IV}(Thio)₂] anionic complexes.

The molecular structure of the obtained complexes was confirmed by X-ray single crystal diffraction on NBu₄[(Bzq) Pt^{II}(Thio)] and, respectively, NBu₄[(Bzq)Pt^{IV}(Thio)₂] Pt(II) and Pt(IV) complexes. While no π - π stacking or metallophilic interactions were observed for square-planar Pt(II) complexes, π - π stacking interactions between the pyridine rings within the

primary supramolecular motif of the octahedral Pt(IV) complexes are observed.

The electrochemical and photophysical properties of the two series of Pt(II) and Pt(IV) newly synthesised complexes were determined and the obtained data are discussed through DFT and TD-DFT calculations. Low oxidation potentials were observed for the Pt(II) and Pt(IV) complexes, compared to the literature data, while no reduction waves were registered in the investigated potential window. The HOMO and LUMO resulted mainly localised on the (Thio) and (C^N) ligands, respectively, for both the NBu₄[(C^N)Pt^{II}(Thio)] and NBu₄[(C^N)Pt^{IV}(Thio)₂] series. This localisation of the frontier orbitals may afford the separate energy tuning of the HOMO/LUMO levels, by further functionalisation of the (C^N) and, respectively, the (Thio) ligands. The photophysical properties may be thus potentially modulated towards higher emission in solution.

Even if the new anionic species are not highly emissive in solution, a notable increase of the emission quantum yields is observed in the crystalline solid state, attributable, at least in the case of the Pt(n) derivatives, to restricted the rotational motion associated with a more rigid local environment experienced. Furthermore, the Pt(n) complexes showed more intense absorption and high luminescence intensity compared to the analogous Pt(nv) complexes. However, no emission quenching is observed in the case of the Pt(nv) derivatives, in which it seems that intermolecular interactions play a key role in retaining the property.

With respect to the catecholate Pt(II) anionic complexes previously reported,³³ the newly synthesised $NBu_4[(C^N)Pt^{II}(Thio)]$ species present red shifted absorption and emission either in solution or in the solid state. It is noteworthy that the emission quantum yields of the novel complexes are also overall higher compared to their previously prepared analogues, either in DMSO solution or in the solid state.

In conclusion, the NBu₄[$(C^N)Pt^{IV}(Thio)_2$] species are, to the best of our knowledge, the first examples of Pt(iv) anionic cyclometalated complexes. Since, as evidenced by electrochemical and DFT studies, the LUMO is mainly localised on the C^N ligands, by properly modifying the cyclometalating ligand, the reduction potentials of the Pt(iv) complexes may be tuned towards more positive values, potentially leading to a novel generation of Pt(iv) prodrugs.

Experimental

Materials and methods

All commercially available chemicals were purchased from Aldrich Chemical Co. and Alfa Aesar and were used without further purification. Microwave reactions were performed using a CEM Discover Synthesis Unit (CEM Corp., Matthews, NC). This instrument consists of a continuous focused microwave power delivery system with operator-selectable power output (0–300 W). IR spectra (KBr pellets) were recorded on a PerkinElmer Spectrum One FT-IR spectrometer. ¹H and ¹³C-NMR spectra were recorded on a Bruker WH-300 spectrometer in deuterated solvents with TMS as an internal standard. Elemental analyses were performed with a PerkinElmer 2400 CHNS/O analyzer. Melting points were examined with a Leica DMLP polarising microscope equipped with a Leica DFC280 camera and a CalCTec (Italy) heating stage.

Mass spectra were obtained using an AB Sciex API 2000 mass spectrometer equipped with a turbo ion spray ionization source in the positive or negative mode [ion spray voltage (IS) 4500 V; curtain gas 20 psi, temperature 300 °C, ion source gas (1) 30 psi, ion source gas (2) 40 psi, declustering and focusing potentials 50 and 400 V, respectively] through the direct infusion (5 μ L min⁻¹) of a solution containing the appropriate compound dissolved in MeOH (20 μ g mL⁻¹).

X-ray crystallography

The X-ray data for derivatives **1c** and **2c** were obtained at room temperature on a Bruker-Nonius X8 Apex CCD area detector equipped with graphite monochromator and Mo-K α radiation ($\lambda = 0.71073$ Å). The data were processed through the SAINT⁶⁹ reduction and SADABS⁷⁰ absorption software. The structure was solved by standard Patterson methods through the SHELXTL-NT⁷¹ structure determination package and refined by full-matrix least squares based on F^2 . In general, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as idealized atoms riding on the respective carbon atoms with C–H bond lengths appropriate to the carbon atom hybridization.

In the case of complex 2c, two carbon atoms of one of the butyl chains in the $[NBu_4]^+$ cation are found disordered in two positions, with the occupancy factor fixed at 0.5. Therefore C(40) and C(41) atoms have been refined isotropically.

The details of the data and structure refinements are given in Table 5.

Table 5 Details of data collection and structure refinements for complexes 1c and 2c

1c	2c
C35H48N2S2Pt	$C_{41}H_{47}N_2S_4Pt$
755.96	755.64
0.18 imes 0.15 imes 0.09	$0.38 \times 0.27 \times 0.12$
Monoclinic	Monoclinic
$P2_1/n$	$P2_1/n$
9.088(5)	10.456(6)
24.031(13)	22.287(13)
15.593(9)	18.723(11)
95.02(3)	102.58(3)
3393(3)	4258(4)
298	298
4	4
1.480	1.398
4.284	3.520
2.143-27.25	2.141 - 24.904
38 960	37 484
7450, 0.043	7777, 0.082
5021	5822
361	431
0.0371	0.0517
0.0910	0.0982
1.016	1.117
	$\begin{array}{c} {\rm 1c} \\ {\rm C}_{35}{\rm H}_{48}{\rm N}_2{\rm S}_2{\rm Pt} \\ 755.96 \\ 0.18 \times 0.15 \times 0.09 \\ {\rm Monoclinic} \\ P2_1/n \\ 9.088(5) \\ 24.031(13) \\ 15.593(9) \\ 95.02(3) \\ 3393(3) \\ 298 \\ 4 \\ 1.480 \\ 4.284 \\ 2.143-27.25 \\ 38960 \\ 7450, 0.043 \\ 5021 \\ 361 \\ 0.0371 \\ 0.0910 \\ 1.016 \end{array}$

CCDC 1848424 (1c) and 1848700 (2c)[†] contain the supplementary crystallographic data for this paper.

Electrochemistry

Electrochemical measurements were carried out by cyclic voltammetry, performed with an Autolab potentiostat-galvanostat controlled by the NOVA 1.1 software. A conventional 3 mL three-electrode cell was employed, with a Pt wire as a counterelectrode, an Ag wire as a pseudo-reference electrode and a Pt disk as a working electrode. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as a supporting electrolyte and the experiments were performed in a dry and degassed (Ar) dimethylformamide solution.

Photophysics

Spectrofluorimetric grade DMSO was used for the photophysical investigations in solution without further purification. A PerkinElmer Lambda 900 spectrophotometer was employed to obtain the UV/Vis absorption spectra, using quartz cuvettes of 1 cm path length. Steady-state emission and excitation spectra were recorded on a Horiba Jobin Yvon Fluorolog 3 spectrofluorimeter, equipped with a Hamamatsu R-928 photomultiplier tube. The luminescence quantum yields of the samples in solution were determined using the optical dilution method⁷² using Ru(bpy)₃Cl₂ in an air-equilibrated water solution as a reference standard ($\phi = 0.028$).⁷³

Solutions were degassed by bubbling argon into quartz cells prior to measurements. The emission quantum yields of the solid samples were obtained by means of a 102 mm diameter integrating sphere coated with Spectralon® and mounted in the optical path of the spectrofluorimeter using, as an excitation source, a 450 W xenon lamp coupled with a double-grating monochromator for selecting wavelengths. With regard to the solid state measurements, samples were prepared by placing a given amount of powder between two quartz slides and standardising the layer. Time-resolved measurements were performed using time-correlated singlephoton counting (TCSPC) on the Fluorolog-3 apparatus. NanoLED pulses centered at 484 nm (FWHM < 200 ps with a 1 MHz repetition rate) were used as the excitation source and fixed directly on the sample chamber at 90° to a single-grating emission monochromator (2.1 nm mm⁻¹ dispersion; 1200 grooves per mm). Data analysis was performed using the commercially available DAS6 software (HORIBA Jobin Yvon IBH).

Computational details

Ground-state electronic structure calculations of synthesised **1a–c** and **2a–c** complexes have been performed using the density functional theory level of theory employing the GAUSSIAN09⁷⁴ software package. The functional used throughout this study is the hybrid three-parameter B3LYP, consisting of a non-local hybrid exchange functional as defined by Becke's three-parameter equation⁷⁵ and the non-local Lee–Yang–Parr correlation functional.⁷⁶

Dresden effective core potential⁷⁷ was used in conjunction with its split valence basis set. The standard triple- ζ quality 6-311G** basis set of Pople was employed for the rest of the atoms, except S atoms. For the descriptions of such atoms, indeed, a larger basis set 6-311+G*, including diffuse functions, was adopted. Vibrational analysis for each optimized structure was performed to determine its minimum point nature. The 20 and 20 lowest singlet and triplet excited states of the closed shell complexes were calculated within the time dependent DFT (TDDFT)⁷⁸ formalism, adopting the same computational protocol used for geometry optimizations. To estimate the possible response of the electronic structure due to solvation, the solvent was modeled by the integral equation formalism polarizable continuum model (IEFPCM),⁷⁹ which corresponds to a linear response in equilibrium and nonequilibrium solvation, and in the geometry optimization of excited and ground states, respectively. A dielectric constant of 47.24 was used in order to take into account the influence of the solvent, DMSO, used in the experiments.

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Syntheses

General procedure for the synthesis of I–III precursors. The I–III precursors were prepared by the reaction of the K₂PtCl₄ salt with the appropriate cyclometalating ligand, as previously reported.³³

General procedure for the synthesis of complexes 1a–c. Cycloplatinated precursor complexes I–III were suspended in 15 mL of methanol and treated with a 1 M methanol solution of NBu₄OH. Once the solution became clear, H_2 (Thio) was added and the reaction mixture was stirred at room temperature for 12 h under nitrogen. The solution was concentrated and the formed precipitate was filtered off, washed with diethyl ether and ethyl acetate and dried under vacuum.

1a. Intermediate complex I (150 mg, 0.28 mmol) was treated with 2.2 eq. (0.61 mL) of NBu₄OH 1 M and 1.1 eq. of H_2 (Thio) (35 μ L, 0.31 mmol).

Red solid; yield 71% (144 mg); m.p. 195 °C.

¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 9.28 (dd, J_{Pt-H} = 32.8 Hz, J_{H-H} = 5.4 Hz, 1H), 8.01 (dd, J_{Pt-H} = 34.1 Hz, J_{H-H} = 7.1 Hz, 1H), 7.78–7.73 (m, 2H), 7.56 (d, J_{H-H} = 4.9 Hz, 1H), 7.49 (d, J_{H-H} = 2.9 Hz, 1H), 7.35 (d, J_{H-H} = 3.7 Hz, 1H), 7.07–7.02 (m, 1H), 6.95–6.90 (m, 1H), 6.61 (m, 2H), 6.44–6.40 (m, 1H), 2.91–2.85 (m, 8H), 1.23–1.19 (m, 8H), 1.04–1.02 (m, 8H), 0.75–0.69 (m, 12H); ¹³C (75 MHz, CDCl₃, 25 °C, TMS): δ = 167.13, 157.85, 149.80, 148.86, 144.54, 143.39, 135.93, 134.21, 130.48, 130.09, 128.71, 123.34, 121.18, 121.15, 120.20, 119.89, 118.39, 57.33, 24.30, 19.76, 13.98; FT-IR (KBr, cm⁻¹): 2960, 2934, 2872, 1599, 1564, 1473, 1438, 1401, 1284, 1098, 981, 825, 737, 568; elemental analysis calculated (%) for C₃₃H₄₈N₂PtS₂ (731.96): C 54.15, H 6.61, N 3.83 found C 54.45, H 6.53, N 3.43; MS (ESI⁻, direct infusion) m/z = 488.7 (100% [(PhPy)Pt(Thio)]⁻); MS (ESI⁺, direct infusion) m/z = 242.2 (100% [NBu₄]⁺).

1b. Intermediate complex **II** (100 mg, 0.16 mmol) was treated with 2.2 eq. (0.36 mL) of NBu₄OH 1 M and 1.1 eq. of H_2 [Thio] (21 µL, 0.18 mmol).

Red solid; yield 73% (92 mg); m.p. 125 °C.

¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 9.32 (dd, J_{Pt-H} = 36.9 Hz, J_{H-H} = 4.8 Hz, 1H), 8.06 (d, J_{H-H} = 7.6 Hz, 1H), 7.78–7.77 (m, 1H), 7.55 (d, J_{H-H} = 8.5 Hz, 1H), 7.44–7.38 (m, 2H), 6.94 (t, J = 5.7 Hz, 1H), 6.64-6.61 (m, 2H), 6.52-6.45 (m, 1H), 3.03-2.97 (m, 8H), 1.31-1.29 (m, 8H), 0.80-0.75 (m, 12H); ¹³C (75 MHz, CDCl₃, 25 °C, TMS): δ = 164.09 (d, $J_{^{13}C-F}$ = 15 Hz), 166.00 (d, $J_{^{13}C-F}$ = 10 Hz), 163.98 (d, $J_{^{13}C-F}$ = 11 Hz), 162.83, 159.88 (d, $J_{^{13}C-F}$ = 15 Hz), 149.78, 148.26, 146.89, 144.41, 136.52, 130.38, 128.60, 122.29 (d, $J_{^{13}C-F}$ = 19.9 Hz), 121.85, 120.47, 120.20, 115.05 (d, $J_{^{13}C-F}$ = 13.7 Hz), 96.88 (t, $J_{^{13}C-F}$ = 27.9 Hz), 57.98, 23.85, 19.27, 13.50; FT-IR (KBr, cm⁻¹): 2958, 2934, 2872, 1600, 1580, 1476, 1437, 1415, 1097, 756, 732; elemental analysis calculated (%) for C₃₃H₄₆F₂N₂PtS₂ (767.94): C 51.61, H 6.04, N 3.65 found C 51.91, H 6.05, N 3.43; MS (ESI⁻, direct infusion) $m/z = 524.8 \ (100\% \ [(F_2PhPy)Pt(Thio)]^-); MS \ (ESI^+,$ direct infusion) $m/z = 242.2 (100\% [Bu_4N]^+)$.

1c. Intermediate complex III (200 mg, 0.24 mmol) was treated with 1.6 eq. (45 μL , 0.39 mmol) of H_2[Thio] and 3.8 eq. (0.93 mL) of NBu_4OH 1 M.

Red solid; yield 71% (238 mg); m.p. 216 °C.

¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 9.40 (dd, J_{Pt-H} = 32.5 Hz, J_{H-H} = 5.3 Hz, 1H), 8.16 (d, J_{H-H} = 8.1 Hz, 1H), 8.04 (dd, J_{Pt-H} = 33.2 Hz, J_{H-H} = 7.4 Hz, 1H), 7.66 (d, J_{H-H} = 8.0 Hz, 1H), 7.48–7.22 (m, 4H), 7.31–7.30 (m, 1H), 7.24–7.22 (m, 1H), 6.56–6.53 (m, 2H), 2.73–2.66 (m, 8H), 1.03–0.95 (m, 8H), 0.75–0.72 (m, 8H), 0.51–0.46 (m, 12H); ¹³C (75 MHz, CDCl₃, 25 °C, TMS): δ = 157.18, 156.32, 148.79, 147.70, 144.47, 141.41, 134.84, 133.99, 130.84, 130.47, 129.95, 129.47, 128.68, 126.99, 122.72, 121.17, 120.36, 119.99, 119.15, 58.20, 23.88, 19.22, 13.45; FT-IR (KBr, cm⁻¹): 2957, 2927, 2871, 1628, 1617, 1481, 1413, 1381, 1096, 1239, 834, 737, 718; elemental analysis calculated (%) for C₃₅H₄₈N₂PtS₂ (755.98): C 55.61, H 6.40, N 3.71 found C 55.70, H 6.57, N 3.90; MS (ESI⁺, direct infusion) *m*/*z* = 242.2 (100% [NBu₄]⁺).

General procedure for the synthesis of complexes 2a–c. Anionic Pt(II) complexes 1a–c were suspended in 10 mL of methanol and treated with 1.1 eq. of H_2 (Thio). The reaction mixture was stirred at room temperature for 48 h. The solution was concentrated and the formed precipitate was filtered off, washed with diethyl ether and dried under vacuum.

2a. Complex 1a (50 mg, 0.07 mmol) was treated with 1.1 eq. of H_2 (Thio) (8 μ L, 0.08 mmol).

Orange solid; yield 58% (28 mg); m.p. 226 °C.

¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 9.8 (d, J_{H-H} = 4.9 Hz, 1H), 9.27 (d, J_{H-H} = 7.8 Hz, 1H), 7.90 (d, J_{H-H} = 7.4 Hz, 1H), 7.76–7.61 (m, 1H), 7.23–7.17 (m, 2H), 7.14–7.10 (m, 4H), 6.97 (d, J_{H-H} = 7.29 Hz, 1H), 6.92 (d, J_{H-H} = 7.68 Hz, 1H), 6.66–6.60 (m, 2H), 6.56–6.51 (m, 2H), 3.07–3.02 (m, 8H), 1.45–1.4 (m, 8H), 1.34–1.22 (m, 8H), 0.97–0.92 (m, 12H); ¹³C (75 MHz, CDCl₃, 25 °C, TMS): δ = 165.11, 161.11, 152.32, 148.04, 146.66, 145.86, 144.02, 142.23, 138.24, 132.36, 131.03, 128.67, 127.60, 127.58, 125.25, 124.78, 124.31, 122.43, 121.66, 121.58, 121.36, 120.78, 120.12; FT-IR (KBr, cm⁻¹): 2956, 2937, 2879, 1606, 1579, 1480 (s), 144 (s), 1415, 1099, 763, 733;

elemental analysis calculated (%) for $C_{39}H_{52}N_2PtS_2$ (872.19): C 53.71, H 6.01, N 3.21 found C 54.00, H 6.13, N 3.43; MS (ESI⁻, direct infusion) m/z = 628.7 (100% [(PhPy)Pt(Thio)₂]⁻); MS (ESI⁺, direct infusion) m/z = 242.2 (100% [NBu₄]⁺).

2b. Complex **1b** (50 mg, 0.07 mmol) was treated with 1.1 eq. of H_2 (Thio) (8 μ L, 0.07 mmol)

Orange solid; yield 57% (35 mg); m.p. 216 °C.

¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 9.83 (d, J_{H-H} = 5.1 Hz, 1H), 8.28 (d, J_{H-H} = 6.8 Hz, 1H), 7.93 (d, J_{H-H} = 8.5 Hz, 1H), 7.7-7.5 (m, 1H), 7.21-7.17 (m, 2H), 7.07 (d, J = 7.9 Hz, 1H), 6.95 (t, J = 7.8 Hz, 2H), 6.64–6.56 (m, 5H), 3.05–3.02 (m, 8H), 1.55-1.32 (m, 8H), 1.30-1.18 (m, 8H), 0.96-0.92 (m, 12H); ¹³C (75 MHz, CDCl₃, 25 °C, TMS): $\delta = {}^{13}$ C (75 MHz, CDCl₃, 25 °C, TMS): δ = 159.83 (d, $J_{^{13}C-F}$ = 81 Hz), 157.96 (d, $J_{^{13}C-F}$ = 112 Hz), 150.05, 143.41, 141.08, 140.08, 138.24, 134.09, 132.44, 123.79, 122.84, 122.78, 120.62, 119.64, 117.71, 117.25, 117.14, 116.85, 116.33, 110.02 (d, $J_{^{13}C-F}$ = 31 Hz), 107.52 (d, $J_{^{13}C-F}$ = 19 Hz), 99.25, 95.34 (d, $J_{^{13}C-F}$ = 38 Hz), 53.71, 19.40, 14.86, 9.05; FT-IR (KBr, cm⁻¹): 2961, 2873, 1599, 1578, 1479, 1440, 1414, 1401, 1295, 1271, 1244, 1099, 1066, 985, 879, 819, 736; elemental analysis calculated (%) for C₃₉H₅₀F₂N₂PtS₄ (908.17): C 51.58, H 5.55, N 3.08 found C 51.61, H 5.50, N 3.33; MS (ESI⁻, direct infusion) $m/z = 664.8 (100\% [(F_2PhPy)Pt(Thio)2]^-);$ MS (ESI⁺, direct infusion) $m/z = 242.2 (100\% [NBu_4]^+)$.

2c. Complex 1c (50 mg, 0.07 mmol) was treated with 1.1 eq. of H_2 (Thio) (8 µL, 0.07 mmol).

Yellow solid; yield 50% (30 mg); m.p. 206 °C.

¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 9.90 (d, J_{H-H} = 7.8 Hz, 1H), 8.30 (d, J_{H-H} = 7.8 Hz, 1H), 8.20 (d, J_{H-H} = 15.8 Hz, 1H), 7.8 (d, J_{H-H} = 15.6 Hz, 1H), 7.60–7.56 (m, 3H), 7.15–7.30 (m, 2H), 7.24–7.22 (m, 1H), 6.93 (d, J = 7.3 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 6.69-6.66 (m, 2H), 6.55-6.51 (m, 2H), 3.11-2.98 (m, 8H), 1.55-1.46 (m, 8H), 1.29-1.21 (m, 8H), 0.99-0.90 (m, 12H); ¹³C (75 MHz, CDCl₃, 25 °C, TMS): δ = 149.82, 145.64, 142.05, 141.76, 141.53, 141.29, 138.49, 134.52, 132.29, 129.95, 125.52, 125.03, 124.81, 123.88, 123.54, 123.35, 120.46, 118.47, 117.87, 116.99, 116.89, 116.79, 116.67, 116.08, 54.04, 19.27, 14.51, 9.14; FT-IR (KBr, cm⁻¹): 2958, 2933, 2871, 1621, 1480, 1442, 1414, 1379, 1098, 839, 738, 716; elemental analysis calculated (%) for C₄₁H₅₂N₂PtS₄ (896.21): C 54.95, H 5.85, N 3.13 found C 54.75, H 5.55, N 3.25; MS (ESI⁻, direct infusion) *m*/*z* = 652.8 (100% [(Bzq)Pt(Thio)₂]⁻); MS (ESI⁺, direct infusion) m/z =242.2 (100% $[NBu_4]^+$).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors are grateful to Dr Pierluigi Plastina (Department of Pharmacy, Health and Nutrition, University of Calabria) for the MS analyses and to Domenico Amico for the contribution to the syntheses. Part of this work was supported by the Ministero dell'Istruzione, dell'Università e della Ricerca through PON 2007/2013 ELIOTROPO (PON03PE_00092_2) and through MATERIA project (PONa3_00370).

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