New NHC cycloplatinated compounds. Significance of the cyclometalated group on the electronic and emitting properties of bis-cyanide compounds

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ABSTRACT

Compounds NBu4[Pt(C^A/B/C)(CN)2] (HC^A = 1-(4-ethoxycarbonyl)phenyl)-3-methyl-1H-imidazol-2-ylidine 1, HC^B = 1-(4-cyanophenyl)-3-methyl-1H-imidazol-2-ylidine 2, HC^C = 1-(3,5-dichlorophenyl)-3-methyl-1H-imidazol-2-ylidine 3) and NBu4[Pt(C^A/B/C)(CN)2] (1-3) were synthesized by addition of KCN (or K13CN) to freshly prepared species [Pt(C^A/B/C)(NCCH3)2]ClO4 in a 2:1 M ratio. Single crystal X-ray structures of 1-3 showed the absence of intermolecular π-π and Pt-Pt interactions. The 195Pt{1H} NMR data of 1-3 were obtained and compared with those of the related compounds NBu4[Pt(C^A/N)(CN)2] (C^N = benzoquinolate, bzq; phenylpyridinate, ppy). They indicate that the electronic density on the Pt center is larger for NBu4[Pt(C^A/B/C)(CN)2](C^A/B/C)(CN)2, which has been proved through NBO charge distribution analysis. Compounds 1 and 2 resulted to be rather good blue-emitters with their emissions arising mainly from 3IL ^N(NHC) excited states with little 3MLCT [5d(Pt)→π*(NHC)] character. The emission of 2 in PMMA film render PLQY (Φ) of 70% and Commission Internationale de L’Eclairage (CIE) coordinates (0.15, 0.19) highly close to the optimal ones for blue emitters (0.15, 0.19).

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1. Introduction

Organometallic compounds of Pt(II) containing cyanide as ligand are known since a long time. The cyanide is typically bonded through the C atom; the π-back bonding from the platinum to the cyanide (CN-) orbitals strengthens the Pt-CN bond and the robustness of the compounds [1,2]. Many of these complexes exhibit very good luminescent properties [3–13] due to the strong field nature of the CN- ligand, which raises the energy of the corresponding d-d excited state (MC) then precluding fast non radiative deactivation and/or photo reactions. Really well known are the vapochromic and vapoluminescent stacked double salts (DCS) [Pt(CNR)2][M(CN)4] (M = Pt, Pd; R = alkyl, aryl), reported by Mann and co-workers [14–17]. Experimental work has demonstrated that stronger field and π-acidic ligands, such as CN- enhance the strength of the Pt…Pt interactions [18–20], as in DCS and in many neutral cyanide complexes such as [Pt(CNR)2(CN)2](R = 1-C3H7 [21], p-C6H4-C2H5 [22,23], CNBu2 [24]) or [Pt(CNR)2(N-N)](N = bpy [6,7], i-biq [8,9], phen [10]). When the complexes contain also non bulky π-conjugated systems such as diimines or C,N-cyclometalated ligands, π-π interactions add to the Pt…Pt ones as the major forces to determine the supramolecular structures [9,10,25,26]. As result, square-planar Pt(II) complexes exhibit intense colors and orange-red luminescence due to 3MLCT (metal-metal-to-ligand charge transfer) [dσ*(Pt)2 → π*(L)] and/or ππ* excimeric low-energy excited states in rigid media, which strongly depends on the extent of such interactions [6–10,27,28]. In this work we reported the neutral compounds [Pt(bzq-CN)(CNR)] [R = Bu, Xyl, 2-Np] [4], and the anionic complexes [Pt(CN)2(CNR)] (C^N = benzoquinolate, bzq; phenylpyridinate, ppy) [13]. The later were isolated as the potassium and the tetrabutylammonium salts. The key effect of the counterion on the photophysical properties of these compounds is evident since

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2. Experimental

2.1. Materials and instrumentation

$^{1}H$, $^{13}C(H)$, $^{195}Pt(H)$ NMR spectra were recorded on a Bruker Avance 400 and 300 MHz instrument using the standard references: tetramethylsilane (Si(H)$_3$)$_4$ for $^{1}H$ and $^{13}C$ and Na$_2$PtCl$_6$ in D$_2$O for $^{195}Pt$. Coupling constant, $J$, is given in Hz and assignments are based on $^{1}H$-1H COSY and $^{1}H$-$^{13}C$ HSQC and HMBC experiments. Infrared spectra were recorded on a Bruker IFS 55 spectrometer with a Smart iTR ATR accessory and 500–4000 cm$^{-1}$ (neat solids). Mass spectra were acquired using the Microflex matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) Bruker or an Autoflex III MALDI-TOF Bruker instruments. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS analyzer. UV–visible spectra were recorded on a Unicam UV4 spectrophotometer. Diffuse reflectance UV–vis (DRUV) spectra were recorded on a Thermo Electron corporation evolution 600 spectrophotometer equipped with a Praying Mantis integrating sphere. The solid samples were homogeneously diluted with silica. The mixtures were placed in a homemade cell equipped with quartz window. Steady-state photoluminescence spectra were recorded on a Jobin-Yvon Horiba Fluorolog FL-3-11 Tau 3 spectrophotometer. Photoluminescence lifetimes were recorded with a Fluoromaxphosphorimeter accessory containing a UV xenon flash tube. Nanosecond lifetimes were recorded with a Datastare HUB-B.

2.2. X-ray structure determinations

Single crystals of 1, 2 and 3 were obtained by slow diffusion of non-anhydrous n-hexane (1, 3) or diethyl ether (2) into a saturated CH$_2$Cl$_2$ (1, 3) or CHCl$_3$ (2) solutions of them. The crystal data, data collection parameters, and structure solution and refinement details for the crystal structures determined are summarized in Table 1. Crystals were mounted at the end of quartz fibers. Data collections were carried out on an Oxford Diffraction Xcalibur diffractometer using graphite monochromated MoK$_\alpha$ radiation (0.71073 Å). The sample temperature was controlled using an Oxford Diffraction Cryostream cooling device (100/2 K). The diffraction frames were integrated and corrected from absorption by using the Crysalis RED program [41]. Structure solution, followed by full-matrix least-squares refinement (all data) was performed using SHELX [42] under the WinGX package [43].

All non-hydrogen atoms were refined with anisotropic displacement parameters and refined without positional constraints, except as noted below. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U(eq) value of the atoms they are linked to (1.5 times for methyl groups). In the structure of 1, some atoms of one of the NBu$_4^+$ cations are found to be disordered and they were refined with partial occupancies 0.505 and 0.70/0.3. Constrains in both C-C distances and the thermal ellipsoid parameters were used for these atoms. Because compound 1 exhibits two molecules of complex in the asymmetric unit, a selection of bond distances and angles of the second molecule appears listed in Table S1.

2.3. Computational methods

Density functional calculations were performed using the M06 [44] hybrid density functional under the Gaussian 09 package [45]. The SDD pseudopotential and associated basis set [46] was used for platinum, and the 6-31G* [47,48] basis set was used for all other atoms. Geometry optimizations for $S_0$ and $T_1$ states were performed under no symmetry restrictions with the implemented Gaussian 09 package, using initial coordinates of models derived from X-ray data. Atomic coordinates (x, y, z) for the optimized structures of 2 and 3 are collected in the Table S2–S5. ArgusLab and GaussView5 program packages were used for analysis and graphic representation of molecular structures and orbitals. The time-dependent density-functional (TD-DFT) calculations were also carried out in the presence of dichloromethane using the polarizable continuum model (PCM) implemented Gaussian 09 package. Mulliken population analysis was carried out using Gaussian 09 package for interpretation purposes. ArgusLab, Molekel, Gaussian and GaussView5 program packages were used for analysis and graphic representation of molecular structures and orbitals. Atomic charges were calculated by using the NBO analysis option as incorporated in Gaussian 09.

2.4. Synthesis and characterization

NBu$_4^{+}$[Pt(C$^\equiv$A/C)(CN)$_2$]$_2$(1), KCN (30.4 mg, 0.46 mmol) was added to a freshly prepared suspension of [Pt(C$^\equiv$A/C)(NCH$_3$)$_2$]ClO$_4$ with a nanoLED controller and software DS6. The nanoLEDs employed for lifetime measurements were of 340 nm. The lifetime data were fitted using the Jobin-Yvon software package and the Origin Pro 8 program. Quantum yields were measured using the Hamamatsu Absolute PL Quantum Yield Measurement System C11347–11. PL films were prepared by drop-casting solutions 5 wt % complex in PMMA (10$^{-2}$ M, CH$_2$Cl$_2$) onto a quartz slide and allowing the solvent to evaporate.
a pure white solid. Yield: 106.7 mg, 67%. Elemental analysis Calcd (%) for C32H45N6PtO6: C 51.85, H 6.60, N 12.51; found: C 51.48, H 6.96, N 12.50. IR (ATR, cm⁻¹): v = 2212, 2111 (m, CN), 1696 (s, CO₂Et). 1H NMR (400 MHz, CD₂Cl₂): δ = 8.74 (d, J₉-H₂ = 1.9, J₇-H₁ = 55.7, 1H, H₂), 7.78 (dd, J₃-H₁ = 8.1, 1H, H₂), 7.34 (d, Jₙ-H₁ = 2.0, 1H, H₂), 7.09 (d, J₉-H₁ = 10.0, 1H, H₂), 6.92 (d, H₂), 4.36 (q, J₃-H₁ = 7.1, 2H, CH₂ (OEt)), 4.16 (s, 3H, NMe₂), 3.28 (m, 8H, CH₂, NBu₄), 1.66 (m, 8H, CH₂, NBu₄), 1.41 (m, 11H, CH₃, NBu₄ and CH₃ (OEt)), 0.99 (t, J₃-H₁ = 7.1, 12H, CH₃, NBu₄), 13C[¹H] NMR plus HMBC and HSQC (101 MHz, CD₂Cl₂, rt (T) 193 K (1)): δ = 172.2 (s, C₁), 167.8 (s, COO), 152.8 (s, C₁), 143.1 (s, C₁), 141.5 (s, J₇-C = 64.8, C₁), 136.4 (s, J₇-C = 46.1, J₇-Pt = 840, 13Ctrans-Caryl), 134.5 (s, J₇-Pt = 1037, 13Ctrans-Caryl), 128.0 (s, C₂), 126.8 (s, C₂), 122.4 (s, J₇-Pt = 67.9, C₂), 115.2 (s, J₇-Pt = 391.2, C₂), 110.1 (s, J₇-C₁O = 249, C₁O, 61.0 (s, CH₂ (OEt)), 59.5 (s, CH₂ NBu₄), 39.4 (s, C₃), 24.6 (s, CH₂ NBu₄), 20.2 (s, CH₂ NBu₄), 14.8 (s, CH₂ (OEt)), 14.0 (s, CH₂ NBu₄), 1.35¹⁹⁵Pt{¹H} NMR (64.3 MHz, CD₂Cl₂, 293 K): δ = 4534.57. MS (MALDI-): m/z 476.0 [M⁺].

NBu₄[Pt(C≡C≡B)(CN)₂] (2). Compound 2 was synthesized following the same procedure used for 1 but using B (107.3 mg, 0.13 mmol), AgClO₄ (53.9 mg, 0.26 mmol), KCN (34.2 mg, 0.52 mmol) and NBu₄ClO₄ (85.2 mg, 0.22 mmol). 2 was obtained as a white solid. Yield: 98.8 mg, 59%. Elemental analysis Calcd (%) for C₉₂H₄₅N₆PtClO₄: C 51.85, H 6.60, N 12.51; found: C 51.48, H 6.96, N 12.50. IR (ATR, cm⁻¹): v = 2218, 2111 (m, CN), 1696 (s, CO₂Et). 1H NMR (400 MHz, CD₂Cl₂): δ = 8.40 (d, J₉-H₂ = 1.6, J₇-H₁ = 54.8, 1H, H₂), 7.37 (dd, J₉-H₁ = 8.1, 1H, H₂), 7.30 (d, J₇-H₁ = 2.1, 1H, H₂), 7.08 (d, J₉-H₁ = 9.8, 1H, H₂), 6.91 (d, 1H, H₂), 4.13 (s, 3H, H₃), 3.24 (m, 8H, CH₂, NBu₄), 1.64 (m, 8H, CH₂, NBu₄), 1.42 (m, 8H, CH₂, NBu₄), 0.98 (t, J₉-H₂ = 7.3, 12H, CH₂, NBu₄). ¹H NMR plus HMBC and HSQC (101 MHz, CD₂Cl₂): δ = 172.0 (s, C₁), 152.2 (s, C₁), 144.2 (s, C₂), 143.4 (s, J₇-Pt = 65.7, C₇), 135.4 (d, J₂-C = 4.6, J₇-Pt = 850, 13Ctrans-Caryl), 133.9 (d, J₉-Pt = 1044, 13Ctrans-Caryl), 129.0 (s, C₂), 125.5 (s, J₇-Pt = 26.4, C₁), 120.5 (s, C₇-C), 115.1 (s, J₉-Pt = 37.0, C₂), 110.5 (s, J₉-Pt = 24.0, C₁₀), 109.2 (s, J₉-Pt = 61.1, C₈), 59.4 (s, CH₂ NBu₄), 59.2 (s, J₉-Pt = 21.3, C₈), 24.4 (s, CH₂ NBu₄), 20.1 (s, CH₂ NBu₄), 13.8 (s, CH₂ NBu₄), 1.91 (s, CH₂ NBu₄), 1.35¹⁹⁵Pt{¹H} NMR (64.3 MHz, CD₂Cl₂, 293 K): δ = −4534.57. MS (MALDI-): m/z 429.0 [M⁺].

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3. Results and discussion

3.1. Synthesis and characterization of compounds NBu₄[Pt(C≡C≡B)(CN)₂] (3). Compound 3 was synthesized following the same procedure used for 1 but using C (164.4 mg, 0.18 mmol), AgClO₄ (76.7 mg, 0.37 mmol) and NBu₄ClO₄ (120 mg, 0.35 mmol). 3 was obtained as a white solid. Yield: 118.2 mg, 45%. Elemental analysis Calcd (%) for C₉₂H₄₅N₆PtClO₄: C 51.85, H 6.60, N 12.51; found: C 51.48, H 6.96, N 12.50. IR (ATR, cm⁻¹): v = 2218, 2111 (m, CN). ¹H NMR (400 MHz, CD₂Cl₂) δ = 7.13 (d, J₉-H₂ = 2.0, 1H, H₂), 7.03 (d, J₉-H₂ = 1.9, J₇-H₁ = 14.8, 1H, H₂), 6.85 (d, J₉-H₂ = 1.9, 1H, H₂), 4.05 (s, 3H, H₃), 3.18 (m, 8H, CH₂ NBu₄), 1.57 (m, 8H, CH₂ NBu₄), 1.34 (m, 8H, CH₂ NBu₄), 0.89 (t, J₉-H₂ = 7.3, 12H, CH₂, NBu₄). ¹H NMR plus HMBC and HSQC (101 MHz, CD₂Cl₂): δ = 170.2 (s, C₁), 151.5 (s, Caryl), 146.54 (s, Caryl), 143.35 (s, Caryl), 131.8 (d, J₇-C = 7.1, J₇-Pt = 1025, 13Ctrans-Caryl), 130.7 (d, J₉-Pt = 892, 13Ctrans-Caryl), 130.2 (s, Caryl), 126.4 (s, J₉-Pt = 27.7, Caryl), 122.9 (s, J₃-Pt = 27.0, C₇), 115.0 (s, J₉-Pt = 35.4, C₂), 109.9 (s, J₉-Pt = 25.0, C₁₀), 59.5 (s, CH₂ NBu₄), 39.7 (s, J₉-Pt = 20.9, C₈), 24.6 (s, CH₂ NBu₄), 20.3 (s, CH₂ NBu₄), 14.0 (s, CH₂ NBu₄), 1.35¹⁹⁵Pt{¹H} NMR (64.3 MHz, CD₂Cl₂, 293 K): δ = −4498.50. MS (MALDI-): m/z 472.8 [M⁺].
After 2 h of reaction, the exchange of the cation was accomplished by reaction of the residue with 1 equiv. of NBu₄ClO₄ in acetone (see Scheme 1 path c). The work-up of the reactions and the subsequent recrystallization of the solids afforded the corresponding compounds NBu₄[Pt(C=C*A/B/C)(CN)₂(C=C*A₁,C*C*B₂,C*C*C₃)] as pure solids in good yields (45–67%).

These compounds were fully characterized through different techniques (see Experimental Section and SI). Two absorptions in the range of 2125–2107 cm⁻¹ were observed in the IR spectra of compounds 1–3, as expected from the cis configuration of two inequivalent cyanide ligands [13,49]. Compound 1 presents an additional absorption at 1696 cm⁻¹ attributed to the (C=O) bond in the ethoxycarbonyl fragment [29], while the nitrile group in 2 is responsible of an absorption band at 2218 cm⁻¹ [50]. The $^1$H NMR spectra of 1–3, showing the expected resonances for the NHC moiety and the NBu₄⁺ cation with intensity ratio according to their stoichiometry and the $^{195}$Pt{¹H} NMR spectra (see Fig. S4), showing a singlet at ca. –4500 ppm, confirmed the purity of these compounds.

X-ray diffraction studies on a single-crystal of each, 1, 2 and 3 show mononuclear anionic complexes, in which the Pt atom exhibits a distorted square-planar environment due to the small bite angle of the cyclometalated ligand [C(1)-Pt-C(6) angle of ca. 79°] (Fig. 1, Table 2 and S1).

Bond distances and angles in the Pt(C=C*) metallacycle are similar to those found in other cyclometalated NHC complexes [11,12,30,50,51]. The Pt-C and C-N bond lengths of the two CN ligands, are similar one to another, as expected from the not much different trans influence of the two carbon atoms of the C=C* ligand [50]. They are also similar to those observed in other bis-cyanide complexes [3,49].

The complex anions of both, 1 and 2 adopt a zig-zag arrangement in a layer, with the NBu₄⁺ cations intercalated between each two layers, thus avoiding π-π and Pt···Pt interactions among them (see Fig. 2). In compound 3, the presence of water molecules from the crystallization solvent allow the formation of hydrogen interactions between one molecule of water and four complex anions through two O-H···NC (ca. 2.2 Å) and two C-H···O interactions (ca. 2.4 Å) (see Fig. 3 a). On the other hand, the chlorine atoms in the phenyl ring allow the molecules to arrange themselves...
than 19 Hz, while the coupling constant in the trans compounds $K_{13CN}$, in order to get more spectroscopic details about this kind of compound.

### 3.2. 13C{1H} and 195Pt{1H} NMR data and discussion

Compounds $\text{NBu}_4[\text{Pt}(\text{C}_3\text{N})\text{CN}]_2$ (1′–3′) were prepared following the same method as that used for 1–3, but using $\text{K}^{13}\text{CN}$, in order to get more spectroscopic details about this kind of species. As can be seen in Table 3, the similarity of $\Delta \delta$ and $\Delta \epsilon$ in compounds 1 and 2 (1′ and 2′) confirmed, once again, the rather similar electronic properties of the cyclometalated NH ligands.

The $^{13}C${1H} NMR spectra of 1′–3′ shows two doublets flanked by platinum satellites (see Table 3, Experimental Section and Figs. S1–S3 in SI), as expected for the two inequivalent cyanides. The $J_{\text{Pt-13C}}$ values for trans-$^{(13}\text{CN}\text{Caryl})$ are of the same order than those corresponding to trans-$^{(12}\text{CN}\text{Caryl})$ for $[\text{Pt}(\text{C3N})(\text{CN})_2]^{-}$ (C N = ppy, bzz). The $J_{\text{Pt-13C}}$ values for trans-$^{(13}\text{CN}\text{C})$ are a little bigger than those of trans-$^{(12}\text{CN}\text{Caryl})$ but clearly smaller than those of the trans-$^{(13}\text{CN}\text{N})$ in complexes $[\text{Pt}(\text{C3N})(\text{CN})_2]^{-}$ (C N = ppy, bzz), in agreement with the high trans influence of the carbenic atom [50]. The $J_{\text{Pt-13C}}$ values for the trans-$^{(13}\text{CN}\text{C})$ in all the three compounds, 1′–3′, undergoes small variations of no more than 19 Hz, while the coupling constant in the trans-$^{(12}\text{CN}\text{Caryl})$ arrangement present greater differences (up to 52 Hz) depending on the substituent at the cyclometalated (aryl) fragment.

Concerning the $^{195}\text{Pt}${1H} NMR data, it deserves to be mentioned the great upfield shift of the $^{195}\text{Pt}$ resonances of 1′–3′ compared with those of the cyclometalated compounds $\text{NBu}_4[\text{Pt}(\text{C3N})(\text{CN})_2]$ (C N = ppy, bzz) (Table 3), suggesting a bigger electronic density on their Pt centers. Additional information on this matter was inferred from the NBO charge distributions analysis on these compounds, which were calculated at the DFT/M06/SDD/6-31G* level of theory in solution of dichloromethane (Table 3). As a result of the four $\sigma$-C atoms bonded to the platinum center and the anionic nature of the complexes, the atomic charges on the platinum centers of 2 and 3 present negative values (−0.095 and −0.087), but not the platinum centers of the related anionic derivatives $\text{NBu}_4[\text{Pt}(\text{C3N})(\text{CN})_2]$ (C N = ppy, bzz), which still keep a positive atomic charge of +0.03. Nonetheless, this is in accordance with the trend observed for the $^{195}\text{Pt}$ chemical shifts, and can be explained in terms of the bigger donor ability of C C with respect to C N, in part due to the lower electronegativity of the C atom with respect to the N one.

### 3.3. Optical properties and theoretical calculations of $\text{NBu}_4[\text{Pt}(\text{C}_3\text{A/B/C})(\text{CN})_2]$

Absorption spectra and DFT calculations. Absorption data are summarized in Table 4 and represented in Fig. 4 (left) and Fig. S5 in SI. As can be seen, solutions (10$^{-4}$ M) of all the three compounds 1–3 in dichloromethane show strong absorption bands in the high energy (HE) region at $\lambda < 300$ nm ($\epsilon > 10^4$ M$^{-1}$ cm$^{-1}$), commonly assigned to singlet intraligand ($^1$IL) transitions of the cyclometalated NH ligand. They show as well an intense absorption at $\lambda \sim 320$ nm ($\epsilon \approx 10^4$ M$^{-1}$ cm$^{-1}$) and their lowest-energy one at ca. 340 nm ($\epsilon \approx 10^3$ M$^{-1}$ cm$^{-1}$), with just little blue-shift of the absorption bands of 3 with respect to those of 1 and 2. As inferred from the similar absorption spectra, 1 and 2 are a new example of the similarities of the electronic features of the cyclometalated NH ligands CO$_2$Et-C-C* (C C=O) and NC-C-C* (C B=O).

In all the three compounds 1–3, the lowest energy absorption obey Beer's Law, suggesting that in each case it corresponds to a transition in the molecular species with no significant aggregation in concentration up to 5×10$^{-4}$ M (see Fig. S6 in SI). Besides, the UV–vis spectra of powdery solid samples (Fig. S7) show no significant differences with those observed in dichloromethane solution.

DFT and TD-DFT calculations were carried out in CH$_2$Cl$_2$ solution for compounds 2 and 3 (see Fig. 4, right), Tables 5 and 6, and Tables S2 and S3 in SI). For compound 1 we assumed similar results than for 2, since the cyclometalated NH ligands C C=O and C B=O have already demonstrated their similar electronic properties [30,52]. On one hand, the highest occupied molecular orbitals (HOMOs) are mainly built from $\pi$ orbitals of the NH ligand and $\pi$ orbitals of the platinum center in all cases, with a very small contribution of $\pi$ orbitals of the CN$^-$ ligands (5–6%). On the other hand, the lowest unoccupied molecular orbitals (LUMOs) still show a small contribution of the ancillary ligands (5–9%) but differ from the HOMOs in the distribution of the electronic density between Pt.

![Fig. 2. Molecular packing view of 1 (a) and 2 (b).](image-url)
and both halves of the NHC ligand. For both the two compounds, the lowest-energy absorption calculated ($S_1$) in dichloromethane solution corresponds mainly to the HOMO to LUMO transition (>-95%) and therefore, it can be mainly attributed to a 1MLCT [$\pi$ (NHC) $\rightarrow$ $\pi^*$ (NHC)] transition but, with some little 1MLCT [5d(Pt) $\rightarrow$ $\pi^*$ (NHC)] character in 2.

Emission spectra. At room temperature, compounds 1–3 do not display luminescence in CH$_2$Cl$_2$ solution under UV light, even in an argon atmosphere, like in other discrete blue-emitting Pt(II) complexes; this kind of compounds show very often low or no emission in fluid solution due to thermal quenching processes via population of higher lying dd$^*$ states or exciplexes [11,30,31,35,36,52]. However, in rigid media like CH$_2$Cl$_2$ at 77K, solid state (298 K, 77 K) and PMMA films (5% weight) at room temperature in the low-lying absorption region ($\lambda$ : 320–350 nm), compounds 1 and 2 display a bright phosphorescent emission with maxima in the blue region ($\lambda_{\text{max}}$ : 450 nm) (see Table 7, Fig. 5 left for 2 and Fig. S8 for 1). The structured shape of these emission bands, with vibrational spacings [1200 - 1500 cm$^{-1}$] corresponding to the C=C/C=N stretches of the cyclometalated NHC ligand (C=C$^*$), suggests the involvement of them in their excited state. On the light of their spectral profiles, the absence of significant rigidochromism on going from 298 to 77 K [53], and the theoretical calculations, these emissions can be assigned mainly to a 3IL [$\pi$ (NHC) $\rightarrow$ $\pi^*$ (NHC)] excited states This assignment is as well in agreement with the large singlet-triplet splitting values [53,54] observed for this complexes (Exp. CH$_2$Cl$_2$ 77 K, $\Delta E_{S-T}$ = 0.69 eV 1, 0.68 eV 2; calculated $\Delta E_{S-T}$ = 0.65 eV, see Fig. S9). Phosphorescence from ligand centered excited states has been also reported for blue-emitting compounds such as (n-Bu$_4$N)[Pt(4,6-dFppy)(CN)$_2$]$_2$ [3], or [Pt(C)(acac)] [33,54]. However the measured emission lifetimes and theoretical calculations suggest some 3MLCT [5d(Pt) $\rightarrow$ $\pi^*$ (NHC)] character of the emission, in line with the closely related compounds, NBu$_4$[Pt(CN)$_2$(NHC)] (H$_2$NHC = 1-methyl-3-phenyl-1H-imidazolium and 1-methyl-3-phenyl-1H-benzimidazolium [11]. The absence of low-energy 3MMCT [d$^0$(Pt)$_2$ $\rightarrow$ $\pi^*$ (L)] and/or 3$^1\pi^*$ excimeric emission bands prove once more the key role of the counterion size on the emission properties of mononuclear Pt(II) complexes.

Compound 1 rendered moderate photoluminescent quantum

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**Table 3**  
Absorption data in 10$^{-4}$ M solution for compounds 1–3 at rt.

<table>
<thead>
<tr>
<th>Comp</th>
<th>$\lambda$ abs/nm ($10^5$ M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>245 (24.0), 252 (28.0), 258 (31.6), 275 (17.0), 293 (10.3), 305 (7.5), 324 (7.7), 342 (3.1) CH$_2$Cl$_2$</td>
</tr>
<tr>
<td></td>
<td>240 (16.3), 250 (24.3), 273 (14.6), 290 (7.9), 303 (5.5), 320 (5.8), 338 (2.1) MeOH</td>
</tr>
<tr>
<td></td>
<td>245 (11.6), 252 (13.1), 259 (15.0), 277 (7.9), 294 (4.2), 305 (3.3), 326 (3.3), 344 (1.7) THF</td>
</tr>
<tr>
<td>2</td>
<td>249 (29.1), 255 (32.9), 273 (15.7), 291 (10.9), 304 (7.2), 323 (7.8), 342 (3.3) CH$_2$Cl$_2$</td>
</tr>
<tr>
<td></td>
<td>252 (31.9), 270 (15.0), 284 (10.9), 291 (9.2), 302 (6.1), 319 (7.5), 317 (2.7) MeOH</td>
</tr>
<tr>
<td></td>
<td>256 (29.5), 275 (19.5), 291 (13.5), 303 (8.9), 324 (7.1), 330 (5.8), 343 (3.4) THF</td>
</tr>
<tr>
<td>3</td>
<td>246 (19.9), 253 (24.5), 265 (15.3), 286 (8.8), 309 (5.6), 320 (6.5), CH$_2$Cl$_2$</td>
</tr>
<tr>
<td></td>
<td>251 (22.6), 264 (18.4), 282 (14.5), 305 (5.3), 317 (4.7) MeOH</td>
</tr>
<tr>
<td></td>
<td>246 (17.9), 252 (21.1), 265 (12.7), 287 (6.9), 293 (6.2), 306 (5.0), 319 (5.6), 326 (5.2), 335 (3.7) THF</td>
</tr>
</tbody>
</table>

---

**Table 4**  
$^{195}$Pt$^1$H NMR data ($\delta$ ppm), J(Hz) in CD$_2$Cl$_2$ and calculated NBO charges on the Pt centers.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta^{195}$Pt</th>
<th>$\delta^{13}$CN$_{transC}$(or N)</th>
<th>$\delta^{13}$CN$_{transC}$</th>
<th>NBO charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBu$_4$[Pt(C=C$^*$)(CN)$_2$]</td>
<td>-4543</td>
<td>1345 (1037)</td>
<td></td>
<td>1364 (840)</td>
</tr>
<tr>
<td>NBu$_4$[Pt(C=C$^*$)(CN)$_2$]$_2$</td>
<td>-4498</td>
<td>1315 (1025)</td>
<td></td>
<td>1305 (892)</td>
</tr>
<tr>
<td>NBu$_4$[Pt(C=C$_2$)(CN)$_2$]</td>
<td>-4103</td>
<td>1155 (1424)</td>
<td></td>
<td>1442 (832)</td>
</tr>
<tr>
<td>NBu$_4$[Pt(bzq)(CN)$_2$]</td>
<td>-4072</td>
<td>148 (1418)</td>
<td></td>
<td>1453 (815)</td>
</tr>
</tbody>
</table>

a Performed at 193K
yield (PLQY, \(\Phi\)) at room temperature, both as neat powder (27%) and in PMMA film (17%), while compound 2 exhibits a more efficient emission (\(\Phi = 62\%\) as powder, 70% in PMMA film).

The CIE coordinates for 1 and 2 are represented in Fig. 5 right, being those for 2 (0.15, 0.19) highly close to the optimal ones for blue emitters (0.15, 0.15) [55]. The calculated radiative rate constants \(k_{\text{r}} = \Phi_{\text{PL}}/\tau\) at r.t. were in the order of \(10^4 \text{ s}^{-1}\) for complex 1 and \(10^5 \text{ s}^{-1}\) for 2. This difference suggests a higher LL character in the emission of 1 [31,11] and a more efficient spin-orbit coupling (SOC) for 2, the latter likely due to a higher contribution of the Pt \(6p_x\) orbital to the LUMO [11].

The moderate-good PLQYs, in solid state at r.t., are possible because of the moderate nonradiative rate constants \(k_{\text{nr}} = 1/\tau - \Phi_{\text{PL}}/\tau\) of \(-10^5 \text{ s}^{-1}\) for 1 and \(-10^5 \text{ s}^{-1}\) for 2. Since non-radiative deactivation seems unlikely because of the large energy gap between \(T_1\) and \(S_0\) (ca. 22000 cm\(^{-1}\)), according to the energy gap law [3], and the insignificant geometrical distortion of \(T_1\) from \(S_0\) (Fig. S10, Table S4), the \(k_{\text{nr}}\) values suggest the existence of thermal access to dd* states at room temperature, especially for compound 1 [56,57].

In spite of the strong field ligands bonded to platinum, the PLQYs of compounds 1 and 2 in PMMA films at r.t. are lower than the reported ones for [Pt(C \(C^6\)(acac))] (\(\Phi = 0.8-0.98\)) [33–36,38,51,58], [Pt(CX-L-L')] [CX = phenyl methyl imidazol; L-L' = carbazolyl pyridine, \(\Phi = 0.89\); CX = phenyl pyrazole; L-L' = carbazolyl pyridine, \(\Phi = 0.85\)] [55], or [Pt(C \(C^s\)(RpzH))\(A (A:\) ClO\(4\), PF\(6\), Rpz: 3,5-dmpz, 4-Mepz, \(\Phi = 1\)) [29]. For powder samples, the PLQYs at r.t. are very similar to the recently published by Kato et al., for NBu\(4_[Pt(CN)2(NHC)]\) (H2NHC \(=\) methyl-3-phenyl-1H-imidazolium and 1-methyl-3-phenyl-1H-benzimidazolim [11].

The photoluminescent properties of these complexes seem to be strongly affected by the different substituents on the cyclometalated fragment. Then, compound 3 resulted to be emissive just at 77 K (see Table 7). It exhibits a structured emission, \(^3\text{IL} \rightarrow \pi^*(\text{NH})\) in nature, as much in rigid matrix of CH\(2\)Cl\(2\) as in the solid state on the light of its spectrum profile (see Fig. S11) and the theoretical calculations. The absence of luminescence at room temperature could be explained by the existence of thermally accessible higher lying nonradiative dd\* excited states and additionally, to the large distortion of the \(T_1\) from the \(S_0\) state (see Fig. S10 and Tables S3 and S5), which enlarge the temperature-independent nonradiative decay rate constant [56,57].

The emission bands of compounds NBu\(4_[Pt(C\(C^s\)(NHC))\(CN)2])\) in rigid matrix of CH\(2\)Cl\(2\) appeared shifted to higher energies with respect to those of NBu\(4_[Pt(CN)2(NHC)]\) (CN = bzu, ppy) [13], which highlight the effect of the cyclometalated group on them (Fig. 6).

The analysis of the composition and energy of the FOs (HOMO and LUMO) for these compounds agree with the experimental data. The presence of the electron withdrawing groups in the cyclometalated fragment lowers the energy of the HOMO but the carbenic fragment raises more the energy of the LUMO in the C \(C^+\) derivatives with respect to those in the C N ones (see Table S6 in SI), enlarging their HOMO LUMO gap and then shifting their emission to the blue region of the visible spectrum.

The blue-shift of the emissions of these C \(C^+\) compounds with respect to NBu\(4_[Pt(ppy)(CN)2])\) is even bigger than the one got in (NBu\(4_[Pt(4,6-dFppy)(CN)2])\) (4,6-dFppy = 4,6′-difluorophenyl).

---

Table 6

<table>
<thead>
<tr>
<th>States</th>
<th>(\lambda_{\text{ex}}) (calc./nm)</th>
<th>o.s.</th>
<th>Transition (% contribution)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>342.50</td>
<td>0.0031</td>
<td>H (\rightarrow) L (95%)</td>
<td>(^3\text{IL} \rightarrow \pi^*(\text{NH}))</td>
</tr>
<tr>
<td>S2</td>
<td>315.56</td>
<td>0.0276</td>
<td>H-2 (\rightarrow) L (98%)</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>303.06</td>
<td>0.1746</td>
<td>H-1 (\rightarrow) L (94%)</td>
<td></td>
</tr>
<tr>
<td>[Pt(C (C^s))(CN)2)](2)</td>
<td>327.33</td>
<td>0.0113</td>
<td>H (\rightarrow) L (97%)</td>
<td>(^3\text{IL} \rightarrow \pi^*(\text{NH}))</td>
</tr>
<tr>
<td>[Pt(C (C^s))(CN)2)](3)</td>
<td>298.98</td>
<td>0.0431</td>
<td>H-2 (\rightarrow) L (99%)</td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>293.42</td>
<td>0.1705</td>
<td>H-1 (\rightarrow) L (92%)</td>
<td></td>
</tr>
</tbody>
</table>

---

Fig. 4. Absorption spectra of compounds 1–3 in CH\(2\)Cl\(2\) (10\(^{-4}\) M) (left). FOs of compounds 2 and 3 calculated in CH\(2\)Cl\(2\) solution (right).
pyridinate) (λem = 459 nm in neat power) in which the electron withdrawing fluorine atoms attached in the 4 and 6 position stabilize the HOMO with respect to the non-fluorinated ppy [3].

4. Conclusions

In this paper we reported the synthesis, characterization and emissive properties of new anionic platinum (II) complexes containing strong field ligands such as cyclometalated N-heterocyclic carbenes and cyanides: NBu4[Pt(C\(\text{C}^*\text{A/B/C})(\text{CN})_2]\. The upfield shift of the \(^{195}\text{Pt}\{^1\text{H}\} \text{NMR signals of 1 and 3 with respect to those of the cyclometalated compounds NBu4[Pt(C\(\text{N})(\text{CN})_2]} (\text{C\(\text{N}\) = ppy, bzq}), and the NBO charge distributions analysis confirmed the bigger donor ability of C\(\text{C}^*\) with respect to C\(\text{N}\). In their crystal structures, the bulky cations (NBu_4^+) appear intercalated between each two layers of complexes, then avoiding Pt-Pt interactions among them. This fact has an evident effect on the photoluminescent properties of these compounds, since in rigid media their emissions come from excited states corresponding to isolated molecules, mainly \(^3\text{IL}[\pi(\text{NHC}) \rightarrow \pi^*(\text{NHC})]\) in nature, with some little \(^3\text{MLCT}[5\text{d}(\text{Pt}) \rightarrow \pi^*(\text{NHC})]\) character in complexes 1 and 2.

The analysis of the composition and energy of the FOs (HOMO and LUMO) showed that in these C\(\text{C}^*\) derivatives the HOMO is stabilized but the LUMO is destabilized to a larger extent with respect to the FOs of the analogous C\(\text{N}\) complexes. As result, their HOMO LUMO gap is larger and their emission is shifted to the blue region of the visible spectrum with respect to them.

The luminescent properties of the reported new compounds are strongly affected by the substituent on the cyclometalated fragment, R = CO_2Et, CN or Cl. In this sense, compound 2 (R = CN) shows the most efficient emission with \(\Phi \) of 70% in PMMA film and CIE coordinates of (0.15, 0.19), highly close to the optimal ones for blue emitters.

<table>
<thead>
<tr>
<th>Table 7</th>
<th>Emission data for complexes 1, 2 and 3.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Medium (T/K)</strong></td>
<td><strong>(\lambda_{\text{ex}}) (nm)</strong></td>
</tr>
<tr>
<td>1</td>
<td>PMMA^a (298)</td>
</tr>
<tr>
<td></td>
<td>Solid (298)</td>
</tr>
<tr>
<td></td>
<td>Solid (77)</td>
</tr>
<tr>
<td></td>
<td>CH_2Cl_2(77)</td>
</tr>
<tr>
<td>2</td>
<td>PMMA^a (298)</td>
</tr>
<tr>
<td></td>
<td>Solid (298)</td>
</tr>
<tr>
<td></td>
<td>Solid (77)</td>
</tr>
<tr>
<td></td>
<td>CH_2Cl_2(77)</td>
</tr>
<tr>
<td>3</td>
<td>Solid (77)</td>
</tr>
<tr>
<td></td>
<td>CH_2Cl_2(77)</td>
</tr>
</tbody>
</table>

^a\ = 5% w/w; \nb\ = measured at the \(\lambda_{\text{max}}\); \nc\ = \(10^{-3}\)M; same results were found at \(10^{-5}\)M.