



HAL
open science

Cyclometallated Platinum(II) Complexes Featuring an Unusual, *CN*-Coordinating Pyridyl-pyridylidene Ligand and L X Coligands: Synthesis, Structures and Dual Luminescence Behavior

Julien Montagu, Geoffrey Gontard, J a Gareth Williams, Jamal Moussa

► **To cite this version:**

Julien Montagu, Geoffrey Gontard, J a Gareth Williams, Jamal Moussa. Cyclometallated Platinum(II) Complexes Featuring an Unusual, *CN*-Coordinating Pyridyl-pyridylidene Ligand and L X Coligands: Synthesis, Structures and Dual Luminescence Behavior. European Journal of Inorganic Chemistry, 2023, 10.1002/ejic.202300487 . hal-04226665

HAL Id: hal-04226665

<https://hal.sorbonne-universite.fr/hal-04226665v1>

Submitted on 3 Oct 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Excellence in Chemistry Research

Announcing our new flagship journal

- Gold Open Access
- Publishing charges waived
- Preprints welcome
- Edited by active scientists



Meet the Editors of *ChemistryEurope*



Luisa De Cola

Università degli Studi
di Milano Statale, Italy



Ive Hermans

University of
Wisconsin-Madison, USA



Ken Tanaka

Tokyo Institute of
Technology, Japan

Cyclometallated Platinum(II) Complexes Featuring an Unusual, C[^]N-Coordinating Pyridyl-pyridylidene Ligand and LX Coligands: Synthesis, Structures and Dual Luminescence Behavior

Julien Montagu,^[a] Geoffrey Gontard,^[a] J. A. Gareth Williams,^[b] and Jamal Moussa^{*[a]}

Thanks to an unusual protodemethylation reaction, a series of luminescent cyclometallated platinum(II) complexes can be prepared, which incorporate a rare NC-chelating, pyridyl-pyridylidene ligand, in combination with OO-coordinating acetylacetonate (acac) or NO-coordinating 2-picolinate (pic) or 8-hydroxyquinolate. The acac and pic complexes show unusual dual emission in a frozen glass.

A series of cyclometallated platinum(II) complexes incorporating a rare, N[^]C-chelating, pyridyl-pyridylidene ligand are described, in which the coordination sphere is completed by two chlorides

or an LX co-ligand, namely OO-coordinating acetylacetonate (acac), or N[^]O-coordinating 2-picolinate (pic) or 8-hydroxyquinolate. The acac and pic complexes have been structurally characterized in the solid state by single-crystal X-ray diffraction. These two complexes display red phosphorescence in the solid state at room temperature. In a frozen glass at 77 K, all four complexes show two broad emission bands that span much of the visible spectrum, apparently from two unequilibrated excited states.

Introduction

Cyclometallated platinum(II) complexes with 2-phenylpyridine (ppy) derivatives, or related aryl-heterocycles acting as C[^]N chelates, have been the focus of intense investigations over the past two decades, owing to their often outstanding photo-physical and electrochemical properties. For example, many have been studied in the context of triplet-harvesting agents for the emissive layer of OLEDs, or as bioimaging agents amenable to time-resolved detection procedures.^[1] Such complexes generally feature the bidentate cyclometallating ligand in combination with various co-ligands such as OO-coordinating β -diketonates like acac;^[2] N[^]O-coordinating ligands like 2-picolinate^[3] or occasionally 8-hydroxyquinolate;^[4] C[^]A[^]C-chelating N-heterocyclic carbenes (NHCs);^[5] or a pair of monodentate ligands such as acetylides^[6] or thiolates, for instance.^[7]

Even though the first carbene complexes of transition metals date back to early reports by the groups of Öfele,^[8] Wanzlick^[9] and Lappert,^[10] it was only after the landmark paper by Arduengo *et al.*^[11] that NHC ligands emerged as a unique class of strong σ -donors, providing complexes with an exceptional stability and stereoelectronic tunability. Recently, platinum(II) complexes with polydentate-NHC-based imidazolylidene ligands have proven to be excellent candidates for some optoelectronic applications.^[12] In contrast to the extensive reports and applications of transition metal complexes with imidazolylidene-based ligands,^[13] however, 2- and 4-pyridylidenes have scarcely been investigated. Pyridylidenes are isomers of pyridines with one carbene center either in position 2- or 4- of the pyridyl ring (*e.g.*, structure 2 in Scheme 1); they are highly reactive species not isolated to date. They have been shown to be even better σ -donors than imidazolylidenes in metal complexes, whilst also acting as good π -acceptors (in contrast to Arduengo-type NHCs). This combination of properties should render them potentially attractive for promoting phosphorescence in transition metal complexes,^[14] yet reports of metal pyridylidene complexes are very limited due to the lack of obvious synthetic procedures.^[15] Only one example of a luminescent platinum(II) complex of such ligands has been reported to date by the group of Chi *et al.* in parallel to our work.^[16]

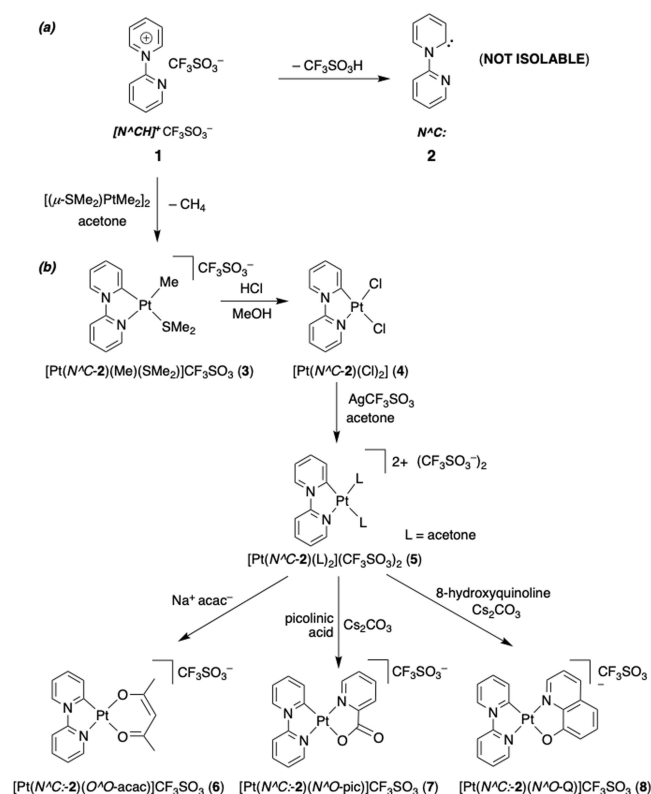
In the course of our recent investigations in the area of luminescent organometallic materials,^[17] the platinum complex [Pt(Me)(N[^]C:-2)(SMe₂)]CF₃SO₃ (**3**) caught our attention (Scheme 1). It was first reported by Bercaw *et al.* in 2004, who prepared it from the proligand **1** as shown in Scheme 1.^[18] We used it to prepare Pt(II) complexes of ligand **2** (not isolated in pure form) in which the coordination sphere is completed by the methyl group and either a triphenylphosphine or triphenylphosphinine ligand, through displacement of the Me₂S. The phosphinine compound exhibited red phosphorescence at 77 K

[a] J. Montagu, G. Gontard, Dr. J. Moussa
Institut Parisien de Chimie Moléculaire
UMR 8232, Sorbonne Université
4 Place Jussieu 75252 Paris (France)
E-mail: jamal.moussa@sorbonne-universite.fr

[b] Prof. J. A. G. Williams
Department of Chemistry
Durham University
South Road, Durham, DH1 3LE (UK)

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/ejic.202300487>

© 2023 The Authors. European Journal of Inorganic Chemistry published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.



Scheme 1. (a) The $N^A C^-$ -coordinating pyridylidene ligand **2** (not isolable) derived from proligand $[N^A CH]^+$. (b) Synthetic route to the new bis-bidentate complexes **6**, **7**, and **8** via the dichloro complex **4**.

that was found to emanate from a phosphinine-based intraligand excited state with a lifetime of around 90 μ s. Although the emission was quenched at room temperature, the compound was the first reported example of a luminescent pyridylidene platinum complex.^[19]

We were intrigued to explore other Pt(II) complexes featuring ligand **2**, but in combination with bidentate ligands in place of the two monodentate ligands used previously, in the hope of improving the luminescence properties. We describe here the synthesis, characterization and photoluminescence properties of three such complexes of the form $Pt(N^A C-2)(LX)$, namely **6**, **7**, and **8** in Scheme 1. To this end we have prepared the novel complex $[Pt(N^A C-2)(Cl)_2]$ (**4**) that proved to be the cornerstone to obtain the target compounds $[Pt(N^A C-2)(OO-acac)]CF_3SO_3$ (**6**), $[Pt(N^A C-2)(N^A O-pic)]CF_3SO_3$ (**7**) and $[Pt(N^A C-2)(N^A O-Q)]CF_3SO_3$ (**8**).

Results and Discussion

The treatment of the parent complex $[Pt(Me)(N^A C-2)(SMe_2)]CF_3SO_3$ (**3**) with a slight excess of aqueous hydrochloric acid in methanol at room temperature gave the novel complex **4** in good yield, which is the important precursor to the target complexes (see Experimental Section for procedural details and full characterization of new compounds). One may note the relative stability of the pyridylidene center under acidic

conditions, which is probably helped by the immediate precipitation of the target compound **4**. The complex was obtained as a crystalline solid and it was only characterized spectroscopically by infrared and by elemental analysis. Attempts to record 1H -NMR in non-strongly coordinating solvents such as acetone or acetonitrile failed due to very poor solubility in these solvents. 1H -NMR data recorded in $DMSO-d_6$ were not accurate since equilibrated displacement of the chloro ligands by this solvent occurs easily.

We then sought to use this new compound as a precursor to the target bis-bidentate complexes. The treatment of **4** with two equivalents of silver triflate in acetone led to precipitation of AgCl and a species – not isolated – that can be assumed to be **5**, in which the coordination sphere of the Pt(II) is completed by two weakly coordinated acetone ligands. Such an approach follows well-established precedent in some of our previous work on cyclometallated chloro-complexes of platinum(II), rhodium(III) and iridium(III).^[20] Addition of sodium acetylacetonate then led to the complex **6** through the simple displacement of the acetone ligands by the bidentate acac. Similarly, the treatment of **5** with 2-picolinic acid (picH) or 8-hydroxyquinoline (HQ), in the presence of cesium carbonate as a base, led to **7** and **8** respectively, in good yields. In principle, two isomers are possible for complexes **7** and **8**, according to whether the pyridine rings in the two bidentate ligands are disposed *trans* or *cis* to one another. 1H -NMR data shows that only one isomer is formed, confirmed by crystallography in the case of **7** (see below), namely that with the pyridine rings *trans* to one another, and the oxygen atom *trans* to the carbene. The compounds are sparsely soluble in acetonitrile and butyronitrile, in which they are stable for several days.

X-ray Structural Analysis

Single crystals of **6** and **7** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into acetonitrile solutions of the two complexes. The structural features agree with the spectroscopic data. The platinum center in compound **6** is confirmed to be chelated by the bidentate $N^A C^-$ ligand **2** and *OO*-coordinating acac (Figure 1). The molecule is almost perfectly planar around the platinum center with a dihedral angle of $9.0(1)^\circ$ between the two ligands. Molecules pack in layers, in a head-to-tail arrangement, and the distance of $3.221(1)$ Å between Pt centers in nearest adjacent molecules is indicative of Pt...Pt interactions. These do not extend to a further layer, however, as the next-nearest Pt is too far, at $4.465(1)$ Å.

Unfortunately, because of the random orientation of the $N^A C^-$ ligand **2**, the positions of the nitrogen and cyclometalated carbene cannot be distinguished, prohibiting any deductions as to the Pt–N, Pt–O and Pt–C bond distances and angles.

The bis-bidentate coordination by the $N^A C^-$ ligand **2** and $N^A O$ -coordinating picolinate is confirmed in compound **7**, with the oxygen atom *trans* to the carbene (Figure 1). The structure shows the coordinated oxygen atom to be *trans* located to the carbene center of the pyridylidene ring. Pt–O ($2.076(3)$ Å) and

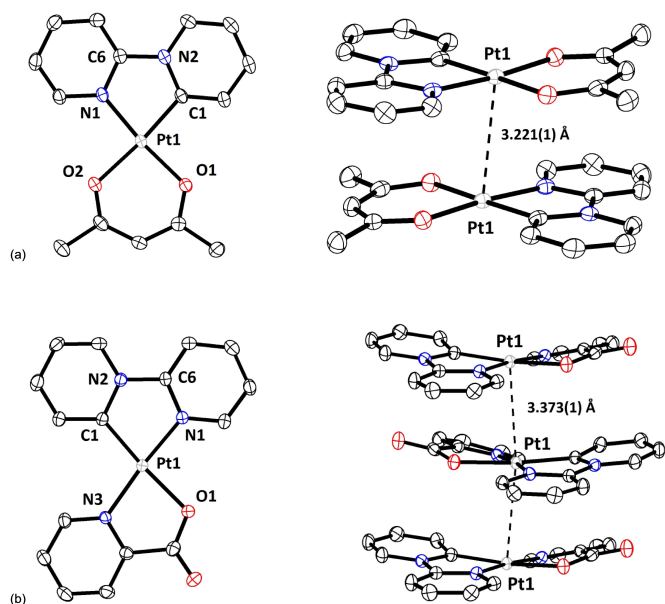


Figure 1. Molecular structures of the cations, and the packing arrangement with neighboring cations, in (a) $[\text{Pt}(\text{N}^{\wedge}\text{C}-2)(\text{O}-\text{O}-\text{acac})]\text{CF}_3\text{SO}_3$ (**6**) and (b) $[\text{Pt}(\text{N}^{\wedge}\text{C}-2)(\text{N}^{\wedge}\text{O}-\text{pic})]\text{CF}_3\text{SO}_3$ (**7**).

Pt–N ((1.997(3) and 2.047(3) Å) bond distances are in line with those found in related cyclometalated platinum(II) compounds. The Pt–C_{pyridylidene} bond distance ($d_{\text{Pt1}-\text{C1}} = 1.973(4)$ Å) is among the shortest Pt–C bonds in related compounds. The bond angles around the platinum(II) center and in the chelating ligands are in the normal range of similar compounds reported in the literature. One striking feature is the bond angle around the carbene atom ($\text{C2}-\text{C1}-\text{N2} = 115.0(4)^\circ$), which is significantly smaller than the expected value of 120° , indicating the pyridylidene nature of the ligand. The distance of 3.373(1) Å between Pt centers in adjacent, head-to-tail-disposed molecules is again indicative of Pt...Pt interactions. On the other hand, in this case, the complexes are distorted away from planarity, with a tilting of the aromatic ligands relative to one another (dihedral angle of $18.1(1)^\circ$), such that no clear-cut π - π interaction appears.

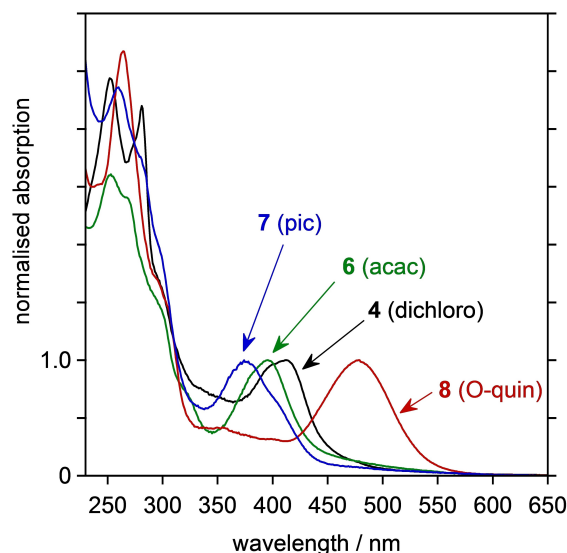


Figure 2. UV–Visible absorption spectra of complexes **4**, **6**, **7**, and **8** in acetonitrile solution at 295 K.

Absorption and Emission Properties

The UV–visible spectra of the three cationic, bis-bidentate complexes **6**, **7**, and **8** were recorded as the triflate salts in acetonitrile solution at 295 K, together with the charge-neutral dichloro complex **4**. The spectra are shown in Figure 2, normalized to λ_{max} at the lowest-energy absorption band to aid comparison between them. Absorption and photoluminescence data are summarised in Table 1.

The general form of the spectra of **4**, **6** and **7** is similar, with strong absorption bands at $\lambda < 350$ nm, evidently arising from π - π^* transitions in the ligands. The lowest-energy band, at $\lambda > 370$ nm, extends into the visible region for each complex, accounting for their pinkish colors. There is no such low-energy band in either the proligand **1** or acacH or picH, and the transition(s) responsible for it are accordingly attributed to the introduction of low-energy, charge-transfer states upon metalation. Such bands are typical for more conventional cyclometalated complexes based on aryl-heterocycles like ppy, where

Table 1. Absorption (in MeCN at 295 K) and photoluminescence data (in solid state at 295 K and in butyronitrile at 77 K) of complexes **4**, **6**, **7**, and **8**.

	complex 4	complex 6	complex 7	complex 8
Absorption	413 (4.99)	395 (5.50)	407 [†] (3.72)	478 (7.22)
$\lambda_{\text{max}}/\text{nm}$	302 [†] (7.66)	302 [†] (7.42)	374 (6.27)	350 [†] (3.03)
$(\epsilon/10^3 \text{ M}^{-1}\text{cm}^{-1})$	280 (15.7)	253 (14.4)	298 [†] (3.39)	298 [†] (11.8)
	252 (17.2)		262 (20.9)	263 (26.4)
Emission solid 295 K	665 [65]	625 [30]	668 [90]	–
$\lambda_{\text{max}}/\text{nm}$ [τ/ns]				
Emission PrCN 77 K	470, 494	462, 490	474 [8.0]	450, 469
$\lambda_{\text{max}}/\text{nm}$ [$\tau/\mu\text{s}$]	[6.6]	[10]	608 [2.6]	[7.0]
		644 [1.6]		614, 666 [†] [22]

[†] denotes a “shoulder” in the spectra rather than a well-defined band.

[‡] indicates no emission detectable.

they typically have mixed $d_{Pt}|\pi_{N/C} \rightarrow \pi^*_{M/C}$ character.^[2c, 21] In the present instance, the energy of the band appears to decrease in the order $7 > 6 > 4$, at least based on the increasing λ_{max} values. The higher excited-state energy of the pic-containing complex **7** versus the acac analogue **6** is consistent with, for example, $Ir(N^{\wedge}C-ppy)_2(N^{\wedge}O-pic)$ versus $Ir(N^{\wedge}C-ppy)_2(OO-acac)$,^[22] where the [small] difference is interpreted in terms of the slightly more electron-withdrawing nature of pic stabilising the occupied metal orbitals. For Pt(ppy) analogues, however, the values for acac and pic are similar to one another.^[23]

The spectrum of complex **8** is quite distinct from the other three in that the lowest-energy band is greatly displaced into the visible region, with $\lambda_{max} = 478$ nm. The value is typical of the ILCT transition of hydroxyquinoline itself in its metal complexes, including in $Pt(N^{\wedge}O-Q)_2$ ^[24] and $Pt(N^{\wedge}C-ppy)(N^{\wedge}O-Q)$,^[4a] and it seems likely to be the case here too. In other words, the highest-occupied orbitals are probably based on the Q ligand rather than on the metal or $N^{\wedge}C$ ligand.

None of the complexes displayed detectable photoluminescence in air-equilibrated or deoxygenated acetonitrile solution at room temperature (see Experimental Section for details of the spectrometer used). On the other hand, solid state (powdered) samples of **4**, **6** and **7** display weak red emission upon excitation at 400 nm, with broad, structureless bands in their spectra: $\lambda_{max} = 625$ nm for **6** and around 660 nm for **4** and **7** (Figure 3). Given the short Pt...Pt contacts within pairs of molecules observed in the crystals of **6** and **7** (which are significantly shorter than the value of around 3.5 Å where low-energy excimer and aggregate states can come into play^[25]), it is very likely that this solid-state emission arises from bimolecular states that span two molecules. The temporal decay of emission approximates to a single exponential, giving lifetimes in the range of 30–90 ns (shown in Figure 3). Coupled with the weak nature of the emission (the solid-state PLQY values are estimated to be around 1%), we can tentatively conclude that the radiative rate constants are of the order of 10^5 s⁻¹. Values of that order are too small to be fluorescence, but are quite typical of phosphorescence from brightly-emitting

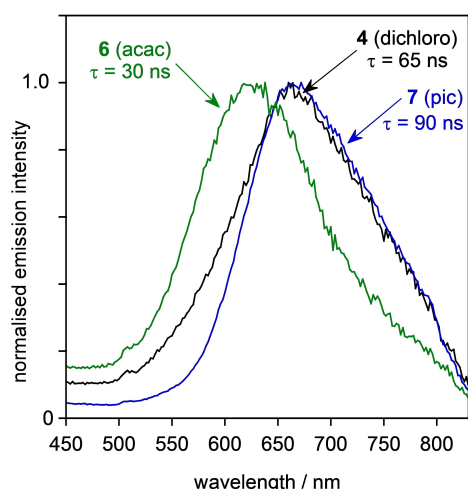


Figure 3. Photoluminescence spectra of complexes **4**, **6**, and **7** in the solid state at 295 K, upon excitation at 400 nm.

cyclometallated Pt(II) complexes, where the formally forbidden $T_1 \rightarrow S_0$ process is facilitated by efficient spin-orbit coupling induced by the metal.^[26] The relative weakness of the emission in the present instance may thus be largely due to severely competitive non-radiative decay processes. The lack of room-temperature emission in solution then reflects even more efficient non-radiative decay under those conditions, and the fact that the aggregates probably do not form in significant amounts in solution at accessible concentrations.

No emission could be detected from complex **8** in the solid state at room temperature. Given the large red-shift in the lowest-energy absorption band of **8** compared to **5**–**7**, it is possible that the emission of **8** lies too far into the near-infrared, where the photomultiplier is very inefficient, and/or its emission is simply too weak to detect using the available equipment.

Apparently, then, severely competitive non-radiative decay processes must be responsible for the lack of detectable emission in solution. Such processes may be suppressed to some extent in the more rigid environment of the solid, allowing emission to be observed.

At 77 K, under dilute conditions in a butyronitrile glass, all four complexes are photoluminescent (Figure 4b). Complexes **4**, **6** and **7** show a band or bands centered between 450 and 500 nm, but **6** and **7** also show a second band at longer wavelength, around 600–650 nm. As the feature in common in these three complexes is the $Pt(N^{\wedge}C)$ unit, we tentatively assign

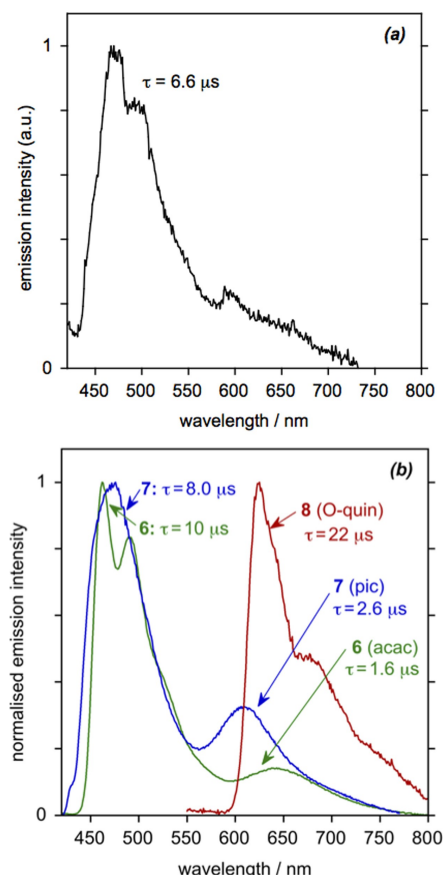


Figure 4. Photoluminescence spectra of (a) complex **4** and (b) complexes **6**, **7**, and **8** in butyronitrile glass at 77 K, upon excitation at 390 nm.

the higher-energy band to an excited state associated with this moiety (i.e., $d_{Pt}|\pi_{NC} \rightarrow \pi^*_{MC}$) with the other possibly due to an unequilibrated excited state involving the acac or pic units (e.g., $d_{Pt}|\pi_{NC} \rightarrow \pi^*_{OO}/\pi^*_{NO}$). We note that the relative intensity of the lower-energy band increases with increasing λ_{ex} (see Supporting Information, Figures S1, 2), an observation that is at least consistent with (though not proof of) such an assignment. The intensity ratio of the bands is independent of concentration (within the accessible range limited by solubility), probably ruling out the possibility that one of the bands is due to the formation of aggregates of the type found in the solid state. The lifetimes of the bands are of the order of microseconds (Figure 4 and Table 1), which would be consistent with phosphorescence from triplet states promoted by the metal, with non-radiative decay processes greatly suppressed compared to room temperature. The quinoline complex **8** shows only one emission band, at low energy, with evidence of a vibrational progression of approx. 1300 cm^{-1} and a rather longer lifetime, which may be indicative of an excited state based largely on the quinoline unit.

Conclusions

In this paper we reported the synthesis of cycloplatinated complexes containing an unusual $N^{\wedge}C$: pyridyl-pyridylidene ligand and three different LX-coordinating coligands. We have established a potentially versatile synthetic strategy to access such species via the intermediary of the dichloro complex. Preliminary photoluminescence results reveal some of the complexes to be phosphorescent in the solid state and at low temperature, where dual emission is observed. This new class of complexes might lead to the discovery of further novel luminophores with interesting photophysical properties.

Experimental Section

General procedures: All experimental procedures were carried out under an argon atmosphere by using Schlenk tube techniques. Solvents were dried and distilled under argon by standard procedures. All reagents obtained from commercial sources were used as received. Compound $[N^{\wedge}CH]CF_3SO_3$ (**1**) and $[Pt(Me)(N^{\wedge}C:2)(SMe_2)]CF_3SO_3$ (**3**)^[18] were prepared according to literature procedures. The 1H and ^{19}F -NMR spectra were recorded in CD_3CN using a Bruker Avance 300 NMR spectrometer at 300.13 MHz and 121.45 MHz respectively. Because of poor solubility, accurate ^{13}C -NMR data could not be obtained. IR spectra were recorded on a Bruker Tensor 27 equipped with an ATR Harricks apparatus. UV-visible absorption spectra were recorded on a Biotek Instruments Uvikon XS spectrometer operated with LabPower software. Emission spectra in the solid state were acquired on an Edinburgh Instruments OB920 spectrometer, equipped with a red-sensitive Hamamatsu R928 photomultiplier tube thermoelectrically cooled to $-20\text{ }^\circ\text{C}$. Emission was recorded at 90° to the excitation source, and spectra were corrected for the spectral response of the detector. The emission spectra at 77 K were recorded in 4 mm diameter tubes held within a liquid-nitrogen-cooled quartz Dewar, using a Jobin Yvon Fluoromax-2 spectrometer, also equipped with an R928 detector.

The luminescence lifetimes were measured on the former instrument by time-correlated single-photon counting, for $\tau < 10\ \mu\text{s}$, using an

EPL405 pulsed-diode laser as excitation source (405 nm excitation, pulse length of 60 ps, repetition rate 20 kHz, or faster for shorter lifetimes). The emission was detected at 90° to the excitation source, after passage through a monochromator. Lifetimes at $77\text{ K} \geq 10\ \mu\text{s}$ were recorded using the same detector operating in multichannel scaling mode, following excitation with a microsecond pulsed xenon lamp.

Synthesis of $[Pt(N^{\wedge}C:2)(Cl)_2]$ (4**):** To a solution of compound **3** (103 mg, 0.18 mmol) in CH_3CN (20 ml) is added aqueous hydrochloric acid diluted in methanol (0.1 ml, 0.72 mmol). A red-brown solid precipitates immediately. The mixture is stirred for 30 minutes at room temperature and then volatiles removed under vacuum. The residue is washed with methanol (10 mL) and diethyl ether (2×20 ml). The purple-brown powder is dried under vacuum (81 mg, 79%).

IR (neat ATR Harricks, cm^{-1}) = $\nu(\text{Pt-Cl})$ 344; 318; 292; 267

Anal. Calcd for $C_{10}H_8Cl_2N_2Pt$ (422.1 $\text{g}\cdot\text{mol}^{-1}$): C, 28.45; H, 1.91; N, 6.64 Found: C, 28.56; H, 1.81; N, 6.54

Synthesis of $[Pt(N^{\wedge}C:2)(O\text{-}O\text{-}acac)]CF_3SO_3$ (6**):** AgOTf (52 mg, 0.20 mmol) in acetone (15 mL) is added to a suspension of complex **4** (40 mg, 0.096 mmol) in acetone (5 mL). The mixture is stirred for 10 minutes at room temperature to allow precipitation of silver chloride that is then filtered off through cotton and celite 521. The filtrate is directly added to solid sodium acetylacetonate (13 mg, 0.11 mmol). The mixture is stirred for two hours at room temperature and then solvent is removed under reduced pressure. The light brown solid obtained was washed with diethylether (2×20 mL) and dried under vacuum (53 mg, 92%).

Anal. Calcd for $C_{16}H_{15}F_3N_2O_5PtS_2H_2O$ (635.5 $\text{g}\cdot\text{mol}^{-1}$): C, 30.24; H, 3.01; N, 4.41 Found: C, 30.46; H, 3.42; N, 3.97

IR (neat ATR Harricks, cm^{-1}): $\nu(CF_3SO_3^-)$ 1271; 1026, $\nu(\text{Pt-O de Pt-acac})$ 471; 329; 1H NMR (300.13 MHz; DMSO- d_6): δ 9.57 (d, 1H), 9.09 (d, 1H), 8.59–8.67 (m, 2H), 8.15–8.24 (m, 2H), 7.95 (td, 1H), 7.86 (td, 1H), 5.88 (s, 1H), 2.19 (s, 3H), 2.17 (s, 3H); ^{19}F NMR: δ –79.3 (s)

Synthesis of $[Pt(N^{\wedge}C:2)(N^{\wedge}O\text{-}pic)]CF_3SO_3$ (7**):** This compound was prepared following procedure described for compound **6** using complex **4** (17 mg, 0.041 mmol) and AgOTf (24 mg, 0.093 mmol). The filtrate upon elimination of silver chloride was directly added to a mixture of solid 2-picolinic acid (6 mg, 0.046 mmol) and cesium carbonate (7 mg, 0.022 mmol). The isolated pink solid was dried under vacuum. (25 mg, 98%).

Anal. Calcd for $C_{17}H_{12}F_3N_3O_5PtS_2H_2O$ (640.5 $\text{g}\cdot\text{mol}^{-1}$): C, 31.88; H, 2.20; N, 6.56 Found: C, 31.73; H, 2.94; N, 6.31

IR (neat ATR Harricks, cm^{-1}): $\nu(C=O)$ 1662, $\nu(CF_3SO_3^-)$ 1253; 1026 1H -NMR (300.13 MHz; DMSO- d_6): δ 9.67 (d, 1H), 9.28 (d, 1H), 9.10 (d, 1H), 8.64–8.74 (m, 2H), 8.48 (t, 1H), 8.40 (d, 1H), 8.27 (t, 1H), 8.10 (d, 1H), 7.90–8.05 (m, 3H). ^{19}F -NMR: δ –79.3 (s)

Synthesis of $[Pt(N^{\wedge}C:2)(N^{\wedge}O\text{-}Q)]CF_3SO_3$ (8**):** This compound was prepared following procedure described for compound **6** using complex **4** (38 mg, 0.090 mmol), AgOTf (48 mg, 0.19 mmol) and 8-oxyquinolate as cesium salt (27 mg, 0.099 mmol). A dark red solid was obtained and dried under vacuum (48 mg, 82%).

Anal. Calcd for $C_{20}H_{14}F_3N_3O_4PtS$ (644.5 $\text{g}\cdot\text{mol}^{-1}$): C, 37.27; H, 2.19; N, 6.52 Found: C, 36.97; H, 2.51; N, 6.39.

IR (neat ATR Harricks, cm^{-1}): $\nu(CF_3SO_3^-)$ 1250; 1026 1H -NMR (300.13 MHz; DMSO- d_6): δ 9.20–9.25 (d, 1H), 8.96–8.97 (d, 1H), 8.73–8.79 (d, 1H), 8.40–8.50 (m, 2H), 8.00–8.07 (m, 2H), 7.87–7.91 (m, 1H), 7.77–7.79 (m, 1H), 7.61–7.65 (m, 1H), 7.51 (t, 2H), 7.09 (dd, 1H), 6.85 (dd, 1H) ^{19}F -NMR: δ –79.3 (s).

Deposition Number(s) 1492966 (for **6**) and 1492967 (for **7**) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge

Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Supporting Information

The authors have cited additional references within the Supporting Information.^[27–30]

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

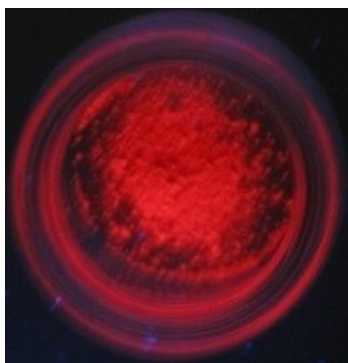
Keywords: carbenes · cyclometallated complexes · luminescence · platinum · pyridylidenes

- [1] a) M. C. Wong, V. W. W. Yam, *RSC Polymer Chemistry Series No. 2, Molecular Design and Applications of Photofunctional Polymers and Materials*, Cambridge, UK, 2012; b) M. D. Perez, P. I. Djurovich, A. Hassan, G. Y. Cheng, T. J. Stewart, K. Aznavour, R. Bau, M. E. Thompson, *Chem. Commun.* **2009**, 28, 4215; c) S.-W. Lai, C.-M. Che, *Top. Curr. Chem.* **2004**, 241, 27; d) H. Yersin, *Top. Curr. Chem.* **2004**, 241, 1; e) H.-F. Xiang, S.-W. Lai, P. T. Lai, C.-M. Che, *Phosphorescent Platinum(II) Materials for OLED Applications, in Highly Efficient OLEDs with Phosphorescent Materials*, ed. H. Yersin, Wiley-VCH, Weinheim, Germany, 2007; f) L. F. Gildea, J. A. G. Williams, *Iridium and platinum complexes for OLEDs, in Organic Light-Emitting Diodes: Materials, Devices and Applications*, ed. A. Buckley, Woodhead, Cambridge, 2013; g) M. Cocchi, J. Kalinowski, L. Murphy, J. A. G. Williams, V. Fattori, *Org. Electron.* **2010**, 11, 388.
- [2] a) J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau, M. E. Thompson, *Inorg. Chem.* **2002**, 41, 3055; b) P. I. Djurovich, D. Murphy, M. E. Thompson, B. Hernandez, R. Gao, P. L. Hunt, M. Selke, *Dalton Trans.* **2007**, 3763; c) M. Spencer, A. Santoro, G. R. Freeman, Á. Díez, P. R. Murray, J. Torroba, A. C. Whitwood, L. J. Yellowlees, J. A. G. Williams, D. W. Bruce, *Dalton Trans.* **2012**, 41, 14244; d) X. Yang, Z. Huang, J. Dang, C.-L. Ho, G. Zhou, W.-Y. Wong, *Chem. Commun.* **2013**, 49, 4406; e) F. Juliá, D. Bautista, J. M. Fernández-Hernández, P. González-Herrero, *Chem. Sci.* **2014**, 5, 1875.
- [3] a) X. Li, Y. Liu, J. Luo, Z. Zhang, D. Shi, Q. Chen, Y. Wang, J. He, J. Li, G. Lei, *Dalton Trans.* **2012**, 41, 2972; b) S.-B. Ko, J.-S. Lu, Y. Kang, S. Wang, *Organometallics* **2013**, 32, 599.
- [4] a) N. M. Shavaleev, H. Adams, J. Best, R. Edge, S. Navaratnam, J. A. Weinstein, *Inorg. Chem.* **2006**, 45, 9410; b) F. Niedermair, O. Kwon, K. Zojer, S. Kappaun, G. Trimmel, K. Mereiter, C. Slugovc, *Dalton Trans.* **2008**, 30, 4006.
- [5] a) T. Zou, C.-N. Lok, Y. M. E. Fung, C.-M. Che, *Chem. Commun.* **2013**, 49, 5423; b) H. Uesugi, T. Tsukuda, K. Takao, T. Tsubomura, *Dalton Trans.* **2013**, 42, 7396.
- [6] a) S. Fernández, J. Forniés, B. Gil, J. Gómez, E. Lalinde, *Dalton Trans.* **2003**, 82; b) J. Forniés, S. Fuertes, A. Martín, V. Sicilia, B. Gil, E. Lalinde, *Dalton Trans.* **2009**, 2224; c) J. R. Berenguer, Á. Díez, A. García, E. Lalinde, M. T. Moreno, S. Sánchez, J. Torroba, *Organometallics* **2011**, 30, 1646.
- [7] F. Juliá, P. G. Jones, P. González-Herrero, *Inorg. Chem.* **2012**, 51, 5037.
- [8] K. Öfele, *J. Organomet. Chem.* **1968**, 12, P42.
- [9] H.-W. Wanzlick, H.-J. Schönherr, *Angew. Chem. Int. Ed. Engl.* **1968**, 7, 141.
- [10] a) D. J. Cardin, B. Cetinkaya, M. F. Lappert, L. Manojlovic-Muir, K. W. Muir, *Chem. Commun.* **1971**, 400; b) P. J. Fraser, W. R. Roper, F. G. A. Stone, *J. Chem. Soc. Dalton Trans.* **1974**, 102.
- [11] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, 113, 361.
- [12] a) C. Cebrián, M. Mauro, *Beilstein J. Org. Chem.* **2018**, 14, 1459; b) H. Leopold, M. Tenne, A. Tronnier, S. Metz, I. Münster, G. Wagenblast, T. Strassner, *Angew. Chem. Int. Ed.* **2016**, 55, 15779; c) J. Kalinowski, V. Fattori, M. Cocchi, J. A. G. Williams, *Coord. Chem. Rev.* **2011**, 255, 2401.
- [13] a) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, 100, 39; b) O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, 109, 3445; c) W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, 41, 1290; d) L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Lapponnaz, V. César, *Chem. Rev.* **2011**, 111, 2705.
- [14] E. Stander-Grobler, O. Schuster, G. Heudenyrych, S. Cronje, E. Tosh, M. Albrecht, G. Frenking, H. G. Raubenheimer, *Organometallics* **2010**, 29, 5821.
- [15] a) Z. Zhou, S. Chen, Y. Hong, E. Winterling, Y. Tan, M. Hemming, K. Harms, K. N. Houk, E. Meggers, *J. Am. Chem. Soc.* **2019**, 141, 19048; b) S. Tang, N. von Wolff, Y. Diskin-Posner, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2019**, 141, 7554; c) B. J. Coe, M. Helliwell, S. Sanchez, M. K. Peers, N. S. Scrutton, *Dalton Trans.* **2015**, 44, 15420; d) T. L. Lam, J. Lai, R. R. Annapureddy, M. Xue, C. Yang, Y. Guan, P. Zhou, S. L.-F. Chan, *Inorg. Chem.* **2017**, 56, 10835.
- [16] C.-H. Tseng, M. A. Fox, J.-L. Liao, C.-H. Ku, Z.-T. Sie, C.-H. Chang, J.-Y. Wang, Z.-N. Chen, G.-H. Lee, Y. Chi, *J. Mater. Chem. C* **2017**, 5, 1420.
- [17] a) A. Hassoun, A. Benchohra, O. Khaled, D. Seghouane, J. Moussa, *Monatsh. Chem.* **2020**, 151, 799; b) D. Amelot, A. Hassoun, L. M. Chamoreau, H. Amouri, J. Moussa, *Edelweiss Chem Sci J* **2019**, 1, 24; c) J. Moussa, K. Haddouche, L. M. Chamoreau, H. Amouri, *Dalton Trans.* **2016**, 45, 12644; d) J. Moussa, L. M. Chamoreau, H. Amouri, *RSC Adv.* **2014**, 4, 11539.
- [18] a) J. S. Owen, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2004**, 126, 8247; b) N. A. Piro, J. S. Owens, J. E. Bercaw, *Polyhedron* **2004**, 23, 2797.
- [19] J. Moussa, G. Freeman, J. A. G. Williams, L.-M. Chamoreau, P. Herson, H. Amouri, *Eur. J. Inorg. Chem.* **2016**, 761.
- [20] a) J. Moussa, A. Loch, L.-M. Chamoreau, A. Degli Esposti, E. Bandini, A. Barbieri, H. Amouri, *Inorg. Chem.* **2017**, 56, 2050; b) J. Moussa, T. Cheminel, G. R. Freeman, L.-M. Chamoreau, J. A. G. Williams, H. Amouri, *Dalton Trans.* **2014**, 43, 8162; c) B. Matt, J. Moussa, L.-M. Chamoreau, C. Afonso, A. Proust, H. Amouri, G. Izzet, *Organometallics* **2012**, 31, 35.
- [21] a) P. J. Hay, *J. Phys. Chem. A* **2002**, 106, 1634; b) A. Vleck, S. Zalis, *Coord. Chem. Rev.* **2007**, 251, 258; c) D. Daniel, *Top. Curr. Chem.* **2016**, 368, 377; d) D. L. Rochester, S. Develay, S. Zalis, J. A. G. Williams, *Dalton Trans.* **2009**, 1728.
- [22] J. Frey, B. F. E. Curchod, R. Scopelliti, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin, E. Baranoff, *Dalton Trans.* **2014**, 43, 5667.
- [23] a) J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau, M. E. Thompson, *Inorg. Chem.* **2002**, 41, 3055; b) M. Ebina, A. Kobayashi, T. Ogawa, M. Yoshida, M. Kato, *Inorg. Chem.* **2015**, 54, 8878.
- [24] R. Ballardina, M. T. Indelli, G. Varani, C. A. Bignozzi, F. Scandola, *Inorg. Chim. Acta* **1978**, 31, 1423.
- [25] a) L. C. Sukpattanacharoen, P. Kumar, Y. Chi, N. Kungwan, D. Escudero, *Inorg. Chem.* **2020**, 59, 18253; b) P. Pander, A. Sil, R. J. Salthouse, C. W. Harris, M. T. Walden, D. S. Yufit, J. A. G. Williams, F. B. Dias, *J. Mater. Chem. C* **2022**, 10, 15084; c) R. J. Salthouse, P. Pander, D. S. Yufit, F. B. Dias, J. A. G. Williams, *Chem. Sci.* **2022**, 13, 13600.
- [26] H. Yersin, A. F. Rausch, R. Czerwieniec, T. Hoffbeck, T. Fischer, *Coord. Chem. Rev.* **2011**, 255, 2622.
- [27] A. Altomare, G. Casciarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, 26, 343.
- [28] C. Giacovazzo et al., *J. Appl. Crystallogr.* **1999**, 32, 115.
- [29] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, 64, 112.
- [30] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, 32, 837.

Manuscript received: August 1, 2023
Revised manuscript received: August 18, 2023
Accepted manuscript online: August 22, 2023
Version of record online: ■■■, ■■■

RESEARCH ARTICLE

Dear Author, please provide a TOC text (about three short sentences, which summarize the content of your article). This text will appear together with the TOC figure on the first pages of the online issue, if your article will become part of this issue.



*J. Montagu, G. Gontard, Prof. J. A. G. Williams, Dr. J. Moussa**

1 – 7

Cyclometallated Platinum(II) Complexes Featuring an Unusual, C[^]N-Coordinating Pyridyl-pyridylidene Ligand and LX Coligands: Synthesis, Structures and Dual Luminescence Behavior

