

Spectroscopic, structural and DFT studies of luminescent Pt(II) and Ag(I) complexes with an asymmetric 2,2'-bipyridine chelating ligand



İsmail Yılmaz^a, Nursel Acar-Selçuki^b, Simon J Coles^c, Fatih Pekdemir^d,
Abdurrahman Şengül^{d,*}

^a Department of Chemistry, Faculty of Sciences, Karabük University, 78050 Karabük, Turkey

^b Department of Chemistry, Faculty of Science, Ege University, 35100, Bornova, Izmir, Turkey

^c UK National Crystallography Service, School of Chemistry, Faculty of Engineering and Physical Sciences, University of Southampton, Southampton, SO17 1BJ, UK

^d Department of Chemistry, Faculty of Arts and Sciences, Zonguldak Bülent Ecevit University, 67100 Zonguldak, Turkey

ARTICLE INFO

Article history:

Received 26 June 2020

Revised 3 September 2020

Accepted 15 September 2020

Available online 16 September 2020

Keywords:

Bipyridine

Platinum

Silver

Luminescence

X-ray structures

DFT studies

ABSTRACT

A new unsymmetrically substituted 2,2'-bipyridine ligand, 5-methyl-5'-carbomethoxy-2,2'-bipyridine (L) was isolated from the dry distillation of the copper(II) complex, *mono-aqua-bis(trans-5-methyl-pyridine-2-carboxylato-N,O)copper(II)*. The ligand was fully characterized. The spectroscopic and single-crystal X-ray diffraction (SCXRD) studies of the coordination compounds of the ligand with platinum(II) and silver(I); *cis*-Pt(L)Cl₂ (**1**) and [Ag(L)₂]PF₆ (**2**), respectively are reported. In **1**, the Pt centre coordinates to tertiary N atoms of the ligand and two chloride ions to form a neutral square-planar coordination sphere, while in **2**, the Ag(I) centre is coordinated by two ligands through N atoms to generate a cationic flattened tetrahedron geometry in which two mean planes intersect each other at 50.93°. The pyridine rings are nearly coplanar as revealed by the torsion angle of N2-C7-C6-N1 1.32(5)°. In both complexes, L acts as a chelating ligand through pyridyl N atoms. In **1**, the molecular units are stacked in a head-to-tail fashion with a Pt...Pt separation of 3.5 Å. Supramolecular self-assembly of the molecular units by extensive intermolecular contacts through C-H...Cl and C-H...O between the adjacent units results in an infinite two-dimensional flattened-out herringbone structure in the crystalline state. In **2**, the molecular units are interconnected with each other by C-H...O contacts between the adjacent units running parallel to each other. Both complexes are fluorescent in solution and have emission maxima in the UV-Vis regions, which is a very important property for optoelectronic applications. DFT (density functional theory) and TD-DFT (time-dependent-DFT) calculations were performed at B3LYP/6-311+G(d,p)/LANL2DZ level to explore structural, electronic, and spectroscopic properties to compare with the experimental results. The molecular orbitals (MOs) were carried out with DFT at the same level.

© 2020 Elsevier B.V. All rights reserved.

1. Introduction

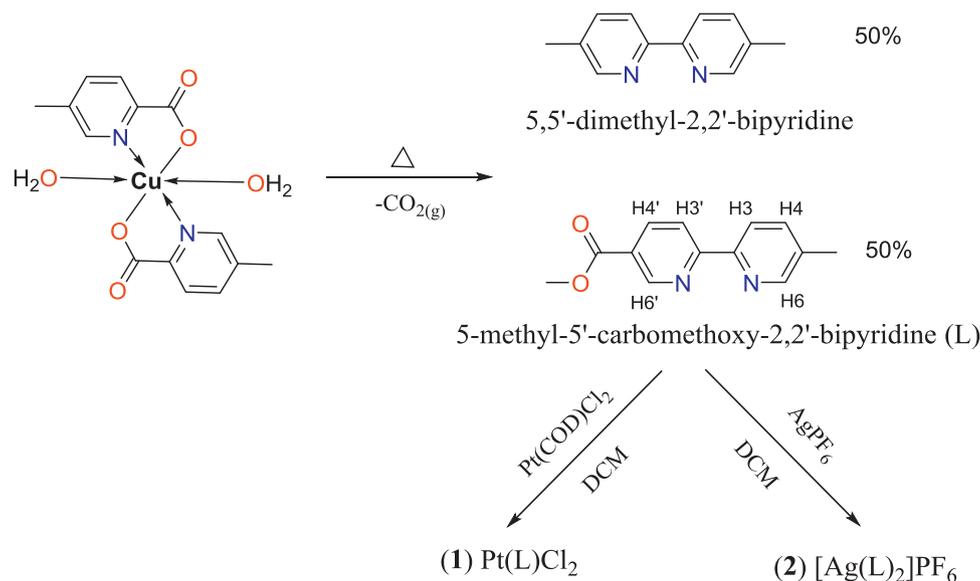
Luminescent compounds are of current interest due to their promising applications in chemical sensors, photochemistry, and electroluminescent devices [1–7]. Metal complexes of *N*-heterocycles derived from 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) and 2,2':6',2''-terpyridine (terpy) are widely used luminophores. The optical properties of these compounds can be easily tuned by changing the nature of its substituents, protonation, and also metal complexation [8]. It has previously been shown that the presence of substituents at 5,5'-positions of 2,2'-

bipyridine causes a significant red-shift of the emission maximum akin to that of the protonated ligand [8]. The main interactions in these molecules occur by an intramolecular charge-transfer (ICT) between the donor (D) and acceptor (A) functionalities, thereby tuning the optical properties [9]. The bpy derivatives are very promising candidates as a fluorescent probe, a property that is associated with the orbital energy of the lowest unoccupied molecular orbital (LUMO) of pyridine [9]. As both a σ -donor and π -acceptor ligand, 2,2'-bipyridine derivatives form very stable metal complexes due to the formation of a five-membered ring [10]. Depending on the metal centre, 2,2'-bipyridines adopt diverse coordination geometries such as square-planar (SP), tetrahedral, and octahedral coordination geometries [10]. The syntheses of luminophores based on the 5,5'-disubstituted-2,2'-bipyridine

* Corresponding author.

E-mail address: sengul@beun.edu.tr (A. Şengül).

derivatives have been reviewed previously [11]. The coordination compounds of a bpy derivative incorporating different substituents at 5,5'-positions with different metal ions (Pt^{II} as d^8 and Ag^{I} as d^{10} ion) usually generate subtly different electronic structure and symmetry, and thus potentially give rise to tunable optical and photonic properties as reported for the analogous compounds [12]. The significant efforts on both computational and experimental studies on the asymmetric 2,2'-bipyridine derivatives [12] have stimulated us to employ DFT and TD-DFT calculations to estimate the frontier molecular orbitals (FMOs) and natural bond orbital (NBO) of these compounds. It is noteworthy that the coordination chemistry of silver(I) is very rich, showing the adoption of a wide variety of coordination geometries [13]. This rich coordination behaviour of silver(I) can be accounted for by the lack of stereochemical preference of a d^{10} configuration and the weak nature of the silver-ligand bond [14]. $\text{Ag}(\text{I})$ complexes with bpy type ligands emit weak photoluminescence at low temperatures due to intra-ligand emission [14]. Since the most intense electronic transition of bpy skeleton is polarized along with the 5,5'-positions [15], the platinum(II) complexes formed with these luminophores would be very interesting. The platinum(II) complexes with α -diimine ligands are well-known to show triplet metal-to-ligand charge-transfer ($^3\text{MLCT}$) lowest excited states [16]. Moreover, the electron-withdrawing carbomethoxy substituents on the bpy have been reported to lead to a redshift of the MLCT band [16]. Studies showed that to promote luminescence in platinum(II) complexes, the lowest-lying excited state is supposed to be a ligand-centred or charge-transfer state [17]. The electronic and spectroscopic properties of four-coordinate planar platinum(II) complexes very much depend on intermolecular, metal-metal, and also π - π interactions [18]. Herein we therefore explore the ligating properties of 5-methyl-5'-carbomethoxy-2,2'-bipyridine (L) with platinum(II) and silver(I) for the first time (Scheme 1). The corresponding metal complexes, **1** and **2** have been synthesized in the crystal form and characterized by UV-Vis, luminescence, FT-IR, ^1H NMR, mass and elemental analysis methods. The SCXRD analysis reveals that, despite the same chelating mode adopted by L in these complexes, the metal centres present different geometries. Both complexes and the ligand exhibit strong emission in the UV-Vis region. These luminescent compounds at room temperature presumably have potential usages in electro-optical devices [19–21].



Scheme 1. Synthetic pathway for the compounds.

2. Experimental

2.1. Materials and instruments

All chemicals were obtained from commercial sources and used without further purification unless otherwise stated. Elemental analysis data were performed on a LECO CHNS analyser (for C, H, N). ^1H NMR spectra were recorded on a Bruker DPX-400, 400 MHz High Performance Digital FT-NMR. Chemical shifts of ^1H is reported in parts per million (ppm) relative to tetramethylsilane (TMS). Chemical shifts are given in ppm relative to TMS as an internal standard in $\text{DMSO}-d_6$ as a solvent, the coupling constants J are given in Hz and spectra were recorded in parts per million (ppm). The IR spectra were recorded as ATR on a Perkin-Elmer FT-IR 100 spectrometer in the range of $4000\text{--}400\text{ cm}^{-1}$. The APCI-MS mass studies were carried out on LC/MS Agilent 1100 MSD mass spectrometer. The ESI-MS studies were performed on a Thermo Finnigan LCQ Deca quadrupole ion trap mass spectrometer (Thermo Finnigan, San Jose, CA). UV-Vis absorption spectra were performed at room temperature on a Carry VinUV 100 Bio, Varian spectrophotometer from the range of $200\text{--}600\text{ nm}$, and the samples were in DMSO solution. Emission spectra at room temperature were collected in the wavelength range of $300\text{--}600\text{ nm}$ by using a Perkin Elmer LS55 Fluorescence Spectrometer.

2.2. Crystal structure determination

Single crystals of the compounds suitable for X-ray diffraction were grown from acetonitrile solution at room temperature by slow evaporation. The data was collected on a Bruker Nonius KappaCCD diffractometer with an Apex2 detector situated at the window of an FR591 rotating anode generator with $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) selected by a confocal max-flux focusing mirror. The sample was kept at a temperature of $120(2)\text{ K}$. The lattice parameters were refined by least-squares based on all reflections with $F^2 > 2\sigma(F^2)$. Integration of intensities, correction for Lorentz and polarization effects, and cell refinements were performed using Bruker Nonius COLLECT software [22]. The structures were solved by direct methods using SHELXS-97 [23] and refined by a full-matrix least-squares procedure using the program SHELXL [24] within the Olex2 software package [25]. All hydrogen atoms were constrained to idealised positions and refined using a riding

Table 1
Crystal data and structure refinement.

	1	2
Empirical formula	C ₁₃ H ₁₂ Cl ₂ N ₂ O ₂ Pt	C ₂₆ H ₂₄ AgF ₆ N ₄ O ₄ P
Formula weight	494.24	709.34
Temperature/K	120.15	120.15
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /c	P2/c
a/Å	9.1229(2)	11.4692(4)
b/Å	17.9189(4)	8.1247(2)
c/Å	8.9761(2)	16.0726(4)
α/°	90	90
β/°	105.7300(10)	114.326(2)
γ/°	90	90
Volume/Å ³	1412.39(6)	1364.73(7)
Z	4	2
ρ _{calc} /g/cm ³	23.241	17.260
μ/mm ⁻¹	10.311	0.879
F(000)	923.4	710.9
Crystal size/mm ³	0.18 × 0.08 × 0.01	0.2 × 0.2 × 0.2
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2θ range for data collection/°	6.08 to 55.1	7.32 to 55
Index ranges	-11 ≤ h ≤ 11, -23 ≤ k ≤ 22, -11 ≤ l ≤ 10	-14 ≤ h ≤ 14, -10 ≤ k ≤ 10, -20 ≤ l ≤ 20
Reflections collected	15268	16153
Independent reflections	3189 [R _{int} = 0.0383, R _{sigma} = 0.0314]	3131 [R _{int} = 0.0343, R _{sigma} = 0.0291]
Data/restraints/parameters	3189/0/178	3131/0/220
Goodness-of-fit on F ²	1.042	1.052
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0385, wR ₂ = 0.0914	R ₁ = 0.0321, wR ₂ = 0.0755
Final R indexes [all data]	R ₁ = 0.0420, wR ₂ = 0.0944	R ₁ = 0.0366, wR ₂ = 0.0780
Largest diff. peak/hole / e ⁻ Å ⁻³	7.54/-1.20	0.70/-0.75

model. The PF₆ counter ion in **2** is disordered over two sites due to the symmetry of the space group (site ratio = 50:50). Details of crystal data, data collection, structure solution, and refinement for the structures of **1** and **2** are given in Table 1.

2.3. Computational details

Geometry optimizations in the gas phase and solution were performed using Gaussian09 software [26]. Gaussview 5.0 visual software [27] was used to obtain images for molecular structures, UV-Vis absorption spectra, and molecular orbitals of the investigated systems. Ground-state optimizations were carried out with Density Functional Theory (DFT) [28] using the hybrid B3LYP functional (B3: Becke's three-parameter nonlocal exchange functional [29,30] LYP: Lee-Yang-Parr's correlation function [31]) together with the 6-311+G(d,p) basis set and with LANL2DZ basis set [32] (latter only for metals). Frequency analysis confirmed that the optimized structures are true minima. Calculations in solution were carried out using acetonitrile (ACN) and dimethylsulfoxide (DMSO) as solvents with the Polarizable Continuum Model (PCM) [33,34]. The theoretical UV-Vis absorption spectra were obtained using the time-dependent DFT (TD-DFT) method at the same level as used in DFT optimizations to compare with the experimental UV-Vis absorption spectra. The first 80 singlet excited states for each system were used in vertical excitation calculations.

2.4. Synthesis of 5-methyl-5'-carbomethoxy-2,2'-bipyridine (**L**)

The preparation methods were previously reported for the analogous compound, 5,5'-dimethyl-2,2'-bipyridine, in reference [35]. The ligand, 5-methyl-5'-carbomethoxy-2,2'-bipyridine was obtained by using the same synthetic method which yielded a mixture of two different products as revealed by the ¹H NMR studies. The pyrolysis of the copper(II) complex, *mono*-aqua-*bis*(*trans*-5-methyl-pyridine-2-carboxylato-*N,O*)copper(II) requires very high temperature, so the evolving gases may lead to react with the radicals of the reagent to yield a different product at such an elevated temperature and pressure in the reaction vessel. The pre-

cursor copper(II) complex was placed in a pyrolysis vessel and heated at an elevated temperature until all of the product sublimed on the cold finger of the sublimation apparatus. The product was scratched and washed down into the beaker with acetone. The white precipitate was obtained by slow evaporation at room temperature. The preliminary ¹H NMR investigation of the crude product showed that it is a (1:1) mixture of the symmetrically substituted 5,5'-dimethyl-2,2'-bipyridine and the unsymmetrically substituted 5-methyl-5'-carbomethoxy-2,2'-bipyridine (**L**) as shown in Scheme 1. The ligand was isolated from the mixture by column chromatography eluted with dichloromethane-hexane (1:1 v/v), and successive crystallisation from the solution yielded the pure product (~7%). m.p. 423 K. IR (ATR, ν/cm⁻¹): 3449sb, 3051w, 2951w, 2913vw, 1717 vs, 1597s, 1553m, 1469s, 1435s, 1372m, 1294vs, 1246w, 1219w, 1196m, 1115vs, 1054vw, 1029m, 960w, 844m, 813vw, 787m, 748m, 652m, 604vw, 506vw. ¹H-NMR (dms_o-d₆, δ_{ppm}): 9.07 (s, 1H, H6'), 8.50 (d, J = 0.6 Hz 1H, H6), 8.41 (d, J_{4',3'} = 8.3 Hz, 1H, H4'), 8.35 - 8.34 (m, 1H, H3'), 8.27 (d, J_{3,4} = 8.1 Hz, 1H, H3), 7.73 (d, J_{4,3} = 8.1 Hz, 1H, H4), 3.83 (s, 3H, OCH₃), 2.31 (s, 3H, CH₃). ¹³C-NMR (dms_o-d₆, δ_{ppm}): 165.9 (C=O), 159.5 (C2'), 152.5 (C2), 150.4 (C6'), 149.8 (C6), 137.9 (C4'), 137.6 (C4), 134.5 (C5'), 125.4 (C5), 121.5 (C3'), 120.3 (C3), 52.3 (OCH₃), 18.4 (CH₃). MS (APCI, m/z): 228.0 (100%) (**L**). Anal. Calc for C₁₃H₁₂N₂O₂: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.31; H, 4.88; N, 11.96%.

2.5. Synthesis of dichloro(5-methyl-5'-carbomethoxy-2,2'-bipyridine)platinum(II) (**1**)

The ligand (0.010 g, 0.040 mmol) and Pt(COD)Cl₂ (0.032 g, 0.040 mmol) in 10 ml of DCM was set to reflux for 24 h. The resulting orange solution was evaporated to dryness. The crude product was dissolved in methanol and filtered to remove unreacted Pt(COD)Cl₂. The solid was recrystallized from acetonitrile to give orange crystals suitable for X-ray analysis. IR (KBr, ν/cm⁻¹): 3448sb, 3097vw, 3050w, 3007vw, 2955w, 2366vw, 2341vw, 1718vs, 1609m, 1475m, 1430s, 1380m, 1338w, 1306vs, 1276vs, 1191w, 1156m, 1130s, 1054w, 1009w, 954w, 906vw, 871w, 845m, 834m,

Table 2
Selected FT-IR spectral data for L, **1** and **2**.^a

	L	1	2
$\nu(\text{CH})$	3051w	3050w	3047vw
$\nu(\text{CH})$	2951w	2955w	2951w
$\nu(\text{CO})$	1717vs	1718vs	1717vs
$\nu(\text{CC, CN})$	1597s, 1552m, 1469s, 1435s	1609m, 1475m, 1430s	1598s, 1558m, 1472m, 1436s

^a Frequencies in cm^{-1} . vs = very strong; s = strong; m = medium; w = weak; vw = very weak.

775m, 740m, 713vw, 695vw, 580vw, 474m, 416w. ¹H NMR (dmsd-*d*₆, δ_{ppm}): 10.01 (d, $J_{6',4'} = 1.7$ Hz, 1H, H6'), 9.34 (s, 1H, H6), 8.81 (dd, $J_{4',3'} = 8.4$, $J_{4',6'} = 1.8$ Hz, 1H, H4'), 8.66 (d, $J_{3',4'} = 8.5$ Hz, 1H, H3'), 8.60 (d, $J_{3,4} = 8.3$ Hz, 1H, H3), 8.31 (d, $J_{4,3} = 8.9$ Hz, 1H, H4), 3.98 (s, 3H, OCH₃), 2.55 (s, 3H, CH₃). MS (APCI, *m/z*): 493.45 [M⁺].

2.6. Synthesis of

bis(5-methyl-5'-carbomethoxy-2,2'-bipyridine)silver(I) hexafluorophosphate (2)

A solution of L (0.031 g, 0.134 mmol) in DCM (20 cm³) was treated with AgPF₆ (0.032 g, 0.126 mmol) in ACN (20 cm³) under dry nitrogen in the dark (the reaction flask was covered with aluminium foil) and stirred at room temperature for 3h. The mixture was then set to reflux for 1h to yield a homogenous solution. After cooling down the solution to room temperature, the filtrate was allowed to stand at room temperature in the dark to afford amber colour crystals suitable for X-ray diffraction. 0.054 g (60%). IR (KBr, ν/cm^{-1}): 3047vw, 2951w, 2360m, 1717vs, 1653m, 1598m, 1558m, 1541m, 1507m, 1472m, 1436m, 1374m, 1294s, 1196w, 1115s, 1030w, 966vw, 844m, 787m, 747m, 652w, 517vw, 419w. ¹H NMR (dmsd-*d*₆, δ_{ppm}): 9.20 (d, $J_{6',4'} = 1.5$ Hz, 1H, H6'), 8.62 (s, 1H, H6), 8.56-8.51(m, 2H, H4' and H3'), 8.42 (d, $J_{3,4} = 8.2$ Hz, 1H, H3), 7.94 (dd, $J_{4,3} = 8.2$, $J_{4,6} = 1.6$ Hz, 1H, H4), 3.93 (s, 3H, OCH₃), 2.42 (s, 3H, CH₃). ¹³C-NMR (dmsd-*d*₆, δ_{ppm}): 165.3 (C=O), 157.9 (C2'), 152.1 (C2), 151.7 (C6'), 150.0 (C6), 138.9 (C4'), 138.5 (C4), 135.5 (C5'), 125.4 (C5), 122.1 (C3'), 120.9 (C3), 53.1 (OCH₃), 18.3 (CH₃). MS (ESI, *m/z*): 564.85 [AgL₂], 352.56 [AgL+H₂O]

3. Results and discussion

3.1. Spectroscopic characterization of L, **1**, and **2**

The ligand was obtained in low yield as described in the experimental part. The final product, 5-methyl-5'-carbomethoxy-2,2'-bipyridine (L) was characterized by mass spectrometry (Fig. S1), ¹H NMR (Fig. S2), ¹³C NMR (Fig. S3), and ATR-IR (Fig. S4), respectively. The selected FT-IR data for L, **1** and **2** are collected in Table 2. The IR (Fig. S4) shows the characteristic bands for aromatic CH at 3051 cm⁻¹ and aliphatic CH at 2951 cm⁻¹. The stretching band at 1717 cm⁻¹ can easily be assigned to the C=O group. The ligand was fully characterized by ¹H NMR, in which the methyl and the carboxymethyl appeared at 2.31 and 3.83 ppm, respectively (Table 3). Thus, the presence of four singlet protons in the aromatic region (*vide supra*) confirms the structure. This was further supported by the ¹³C NMR (Fig. S3), which shows as expected thirteen carbon

Table 4
UV-Vis absorption (1×10^{-5} M) and fluorescence emission of L, **1**, and **2** in DMSO.

Compound	λ_{max} , nm (log ϵ , L mol ⁻¹ cm ⁻¹)	λ_{ex} , nm	λ_{em} , nm
L	245 (4.33), 307 (4.89)	320	384.5, 431.5
1	265 (4.98), 329 (4.57), 338 (4.58)	350	380.5, 449.5
2	257 (4.61), 301(5.00)	310	378.5, 441.5

atoms (see the experimental part for the assignment). Two of these are in the aliphatic region due to methyl resonance at 23.87 ppm and OCH₃ at 52.32 ppm, others are observed in the aromatic region as expected. The ligand was further characterized by mass spectrometry, where the molecular ion appeared at *m/z* 228.0, and confirms the molecular formula.

The platinum(II) complex (**1**) was also fully characterized. The IR spectrum (Fig. S5) is similar to that of the ligand (Table 2). In the ¹H NMR (Fig. S6), the corresponding methyl and methoxy groups appear at 2.53 and 3.98 ppm, respectively. These two signals show very small downfield shifts compared to those of the free ligand (Table 3). However, the corresponding aromatic protons are significantly shifted downfield. This is clearly due to the coordination of the ligand to the platinum centre, which acts as a Lewis acid to withdraw electron density from the ligand. The molecular ion peak (Fig. S7) was observed in the mass spectrum at *m/z* 493.4 [M⁺] (calculated for C₁₃H₁₂N₂O₂Cl₂Pt *m/z* = 493.9), identical to the theoretical value calculated for the molecular structure. This peak can be detected in the mass data but is absent in the spectrum range due to the chemical ionization method, which afforded a highly fragmented spectrum. In the spectrum, the de-fragmented ligand and the PtCl₂ moieties can be easily noticed at *m/z* = 227.0 and 265.2, respectively. The complex was also characterized by single-crystal X-ray diffraction (*vide infra*).

Coordination of a silver(I) ion with the ligand surprisingly afforded a mononuclear cationic complex (**2**), which was also characterized by IR, ¹H NMR, and mass spectrometry. The IR spectrum (Fig. S8) is very similar to that of the ligand (Table 2). In the ¹H NMR (Fig. S9) the methyl and methoxy group are observed as a singlet at 2.4 and 3.9 ppm, respectively. The corresponding four aromatic protons have a resonance between 9.2 and 8.3 ppm, showing almost the same pattern of the free ligand with an insignificant downfield shift (Table 3).

The complex (**2**) was further characterized by mass spectrometry (Fig. S10), in which the molecular ion peak was observed at *m/z* 564.7 (calculated for C₂₆H₂₄N₄O₄Ag *m/z* = 564.0) which is consistent with the theoretical molecular weight of the cation [Ag(L)₂]⁺.

The UV-Vis and luminescence spectra of L, **1**, and **2** were measured in DMSO at room temperature (Fig. 1) and the data are listed in Table 4. The ligand displays a very strong absorption band at 307 nm that is assigned to $\pi \rightarrow \pi^*$ transitions. The UV-Vis spectrum of **2** displays $\pi \rightarrow \pi^*$ transitions at 301 nm with similar vibrational progression but undergoes a blue shift, while in that of **1** the high energy band at 265 nm is very intense, having shoulder at around 300 nm which is more pronounced and comparatively blue-shifted. In **1**, significantly low energy absorption bands observed at around 328-338 nm and a weak absorption band at 400 nm are assigned to a combined metal-to-ligand (ML) and intra-ligand (IL) charge transfer (CT) transitions [36].

Table 3
¹H NMR chemical shifts (with respect to TMS) for L, **1** and **2** in DMSO-*d*₆.^a

	H6'	H6	H4'	H3'	H3	H4	OCH ₃	CH ₃
L	9.07(s)	8.50(d)	8.41(d)	8.35-8.34(m)	8.27(d)	7.73(d)	3.83(s)	2.31(s)
1	10.01(d)	9.34(s)	8.81(dd)	8.66(d)	8.60(d)	8.31(d)	3.98(s)	2.55(s)
2	9.20(d)	8.62(s)	8.56-8.51(m)		8.42(d)	7.94(dd)	3.93(s)	2.42(s)

^a s = singlet; d = doublet; dd = doublet of doublet; m = multiplet.

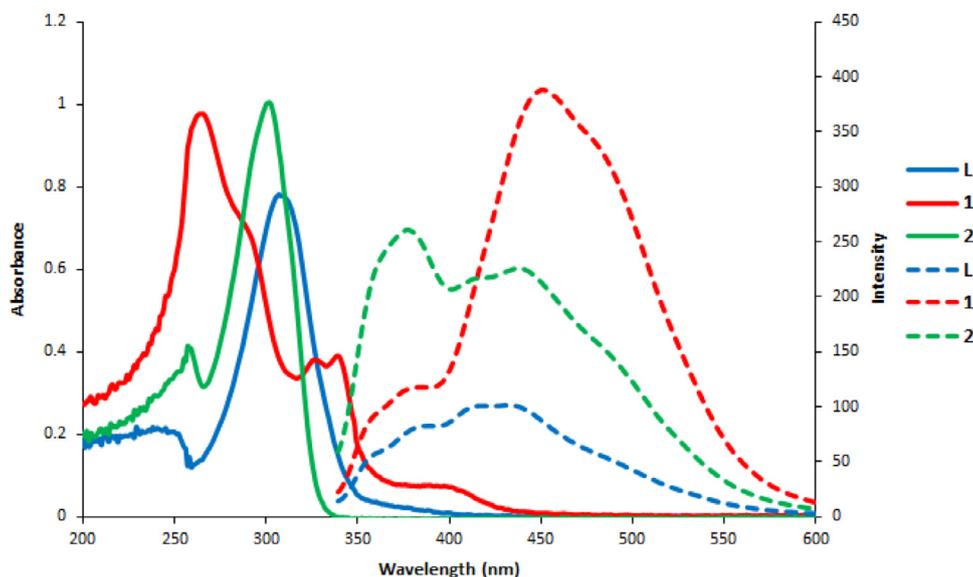


Fig. 1. UV-Vis absorption and fluorescence emission of L, **1**, and **2** in DMSO. (solid line: electronic absorption, dashed line: fluorescence emission).

The ligand and the corresponding metal complexes are luminescent in DMSO solution at room temperature. The emission maxima data are summarised in Table 4. The emission energies of the ligand and the complexes parallel the shifts observed in the absorption spectra. Interestingly, all compounds have very similar emission spectra (Fig. 1). The intensity of the emissions decreases in the order $\mathbf{1} > \mathbf{2} > \mathbf{L}$ as shown in Fig. 1. The enhancement of the luminescence of the metal complexes may be attributed to the ligation of L to the metal centres, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiation-less decay [37,38]. On the other hand, the emission bands centred between 380 and 600 nm for all compounds, the platinum(II) complex (**1**) exhibits the most red-shifted emission ($\lambda_{\text{max}} \approx 450$ nm), while that of the silver(I) (**2**) and L are very similar. Their emissions seem to originate mainly from $\pi \rightarrow \pi^*$ (L) intra-ligand (IL) excited states. 292 (3590)

3.2. Structural analyses

The details of the crystal data collection and refinement of complexes **1** and **2** are summarized in Table 1. Selected bond distances and angles for both metal complexes are collected in Table 5. A thermal ellipsoid plot of **1** with the atom numbering scheme as shown in Fig. 2, indicates that the Pt(II) ion exhibits a square-planar geometry, completed by two nitrogen atoms from the chelating ligand L, (through the N1 and N2 positions) and two chloride ligands. The platinum atom in **1** deviates by 0.67(7) Å from the best plane of the PtN₂Cl₂ chromophore. There is a small distortion from the ideal square planar geometry, as revealed by the narrowing of the N2–Pt1–N1 angle to 80.4(2)°, similar to analogous compounds [39,40]. The mean plane of the chromophore PtN₂Cl₂ makes angles with the ligand rings, namely [N2–C13–C10–C9–C8–C7] and [N1–C6–C5–C4–C2–C1], 8.71 (4) and 9.03(4)°, respectively. The torsion angle, N2–C7–C6–N1 1.32(5)° shows a deviation of the pyridine rings from the planarity, as observed in the Pt(bpy)Cl₂ [41]. The deviation from ideal square planar geometry may be due to C–H...Cl interactions between the coordinated chloride ligands and the hydrogen atoms of L (Fig. 3). These interactions form a linear chain along the c-axis, while a 2-dimensional zig-zag layer is generated along the b axis via C–H...O hydrogen bonds (Fig. 3). The overall packing is stabilized by weak C–H...Cl interactions [42]. The molecules are stacked in a head-to-tail fash-

Table 5
Selected bond lengths [Å] and angles [°].

1						
Pt1	Cl2	2.3053(17)	C11	Pt1	Cl2	89.53(6)
Pt1	C11	2.2985(17)	N1	Pt1	Cl2	174.81(17)
Pt1	N1	2.008(6)	N1	Pt1	C11	95.13(17)
Pt1	N2	2.004(6)	N2	Pt1	Cl2	94.91(17)
N1	C6	1.357(9)	N2	Pt1	C11	175.32(17)
N1	C1	1.345(9)	N2	Pt1	N1	80.4(2)
C13	C10	1.398(10)	C6	N1	Pt1	115.2(5)
C13	N2	1.337(9)	C1	N1	Pt1	125.4(5)
C5	C6	1.384(10)	C1	N1	C6	119.4(6)
C5	C4	1.405(10)	N2	C13	C10	122.3(6)
C6	C7	1.474(9)	C5	C6	N1	121.4(6)
C2	C1	1.394(10)	C7	C6	N1	114.3(6)
C2	C4	1.373(10)	C2	C1	N1	122.5(6)
C2	C3	1.511(11)	N2	C7	C6	114.2(6)
C10	C9	1.396(10)	N2	C7	C8	121.8(6)
C10	C11	1.492(10)	C12	O1	C11	115.5(6)
C9	C8	1.386(10)	O1	C11	C10	111.5(6)
C8	C7	1.383(9)	O2	C11	C10	123.1(7)
C7	N2	1.359(9)	O2	C11	O1	125.5(7)
O1	C11	1.317(9)	C13	N2	Pt1	125.7(5)
O1	C12	1.461(9)	C7	N2	Pt1	115.3(4)
O2	C11	1.193(9)	C7	N2	C13	118.9(6)
2						
Ag1	N1	2.2541(17)	N1'	Ag1	N1	140.42(9)
Ag1	N2	2.4060(19)	N2'	Ag1	N1	141.15(7)
O2	C11	1.203(3)	N2	Ag1	N1	71.47(7)
O1	C11	1.337(3)	N2	Ag1	N1'	141.15(7)
O1	C12	1.449(3)	N2'	Ag1	N2	94.15(9)
N1	C1	1.343(3)	C12	O1	C11	115.23(18)
N1	C6	1.346(3)	C1	N1	Ag1	121.28(14)
C4	C2	1.386(3)	C6	N1	Ag1	119.51(14)
C4	C5	1.380(4)	C6	N1	C1	119.18(18)
N2	C7	1.348(3)	C7	N2	Ag1	114.42(14)
C9	C8	1.380(3)	C13	N2	Ag1	126.84(15)
C9	C10	1.384(3)	C13	N2	C7	118.64(19)
C1	C2	1.391(3)	C2	C1	N1	123.8(2)
C2	C3	1.504(3)	C5	C6	N1	120.3(2)
C5	C6	1.396(3)	C7	C6	N1	117.46(18)
C6	C7	1.489(3)	C6	C7	N2	117.12(19)
C7	C8	1.393(3)	C8	C7	N2	121.1(2)
C10	C13	1.386(3)	C10	C13	N2	123.6(2)
C10	C11	1.494(3)	O1	C11	O2	124.2(2)
N2	C13	1.332(3)	C10	C11	O2	124.2(2)
			C10	C11	O1	111.62(18)

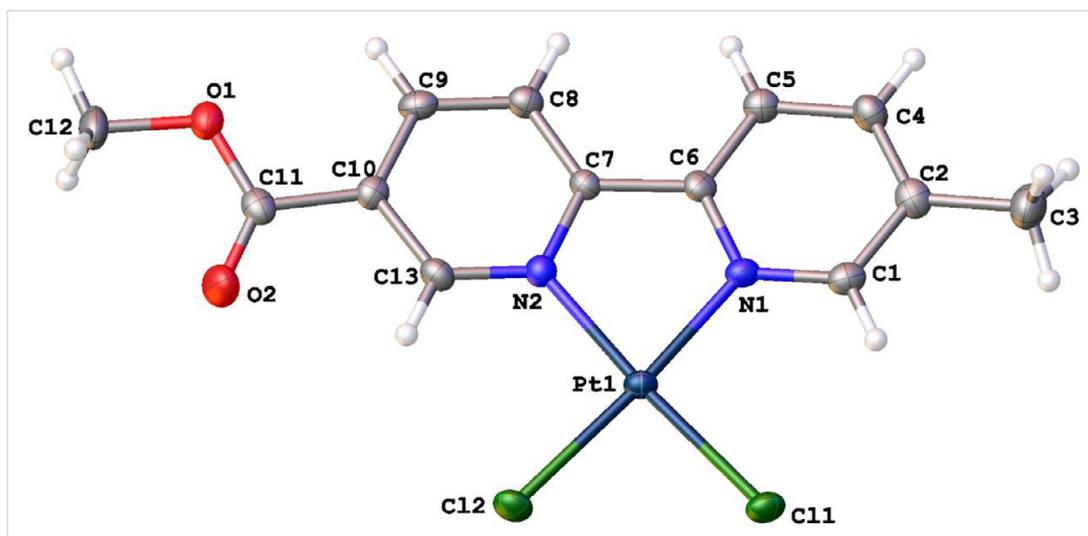


Fig. 2. Molecular structure of **1** with the atom labeling scheme.

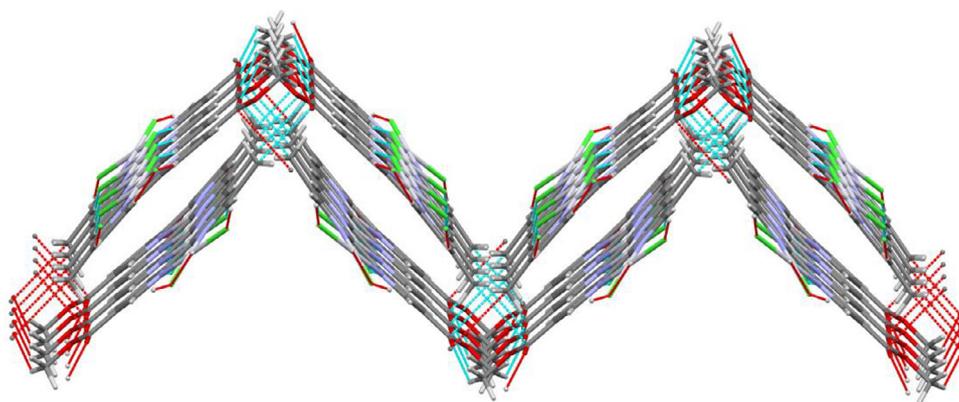


Fig. 3. The packing and significant intermolecular interactions formed in the structure of **1**.

ion akin to the related platinum(II) complexes with terpy ligands [40,43–46]. The Pt⋯Pt separation of 3.509 Å again reflects similarity with those of platinum(II) complexes and indicates the intermolecular π - π interactions [40]. As shown by the previous investigations on the platinum(II) linear-chain systems, their electronic and photoluminescence properties strongly depend on the intra-chain metal separation [45]. The Pt–N bond distances of 2.007(6) and 2.004(6) Å, and the Pt–Cl bond distances of 2.299(1) and 2.305(5) Å are in the expected range and can be compared to those of the related platinum(II) complexes in the literature [39,47,48].

A perspective view of **2** is shown in Fig. 4. The asymmetric unit of **2** is built up of an $[\text{Ag}(\text{L})_2]^+$ cation and a PF_6^- anion. In the cation, the silver(I) ion is coordinated by two ligands through the nitrogen atoms in a chelating fashion to form an MN_4 chromophore. The coordination around the Ag(I) ion can be best described as a flattened tetrahedron geometry as depicted in Fig. 4. The four Ag–N bond distances in **2** show a disparity with two short [2.254(4) Å for Ag–N(1)] and two long [2.406(5) Å for Ag–N(2)] bonds and agree with those reported in the literature [49,50]. The N–Ag–N bite angles for the chelate ring(s) have an average value of 61.68°. The angle between the two mean planes for each ligand is 50.93°. A torsion angle of 90° is expected for a perfect tetrahedron, whereas a torsion angle of 0° is expected for a square-planar arrangement. Thus, the present case can be best described as a flattened tetrahedron. The pyridine rings in the chelating ligands are almost coplanar with an insignificant deviation of 3.41°

from the mean plane, as expected from the analogous ligand system [43].

3.3. Computational results

The ground-state, gas-phase optimized structures of **1** and **2** for ACN and DMSO are given in Fig. S11 at the B3LYP/6-311+G(d,p) level with a LANL2DZ basis set on the metals. Compound **1** has a planar geometry, however, the 2,2'-bipyridine ligands almost form a perpendicular angle (O2–Ag–O2: 86.99° in the gas phase, 82.97° in DMSO) in compound **2**. Additionally, the Pt centre is square-planar whereas the Ag centre adopts a distorted tetrahedral structure. The experimental and the calculated bond distances and bond angles are listed in Table S1 and Table S2 for comparison. Figures S12 and S13 provide a better overall understanding of all the differences in distances and angles. The experimental and calculated values are generally similar for planar compound **1**. However, the Ag–N distance is slightly larger in both gas phase and solution compared to the crystal structure in compound **2**.

As for the angles, the largest difference (deviation) between the experimental and the computational values is 32.95° measured for the N2'–Ag1–N2 bond angle in DMSO. The dihedral angle between pyridine rings is nearly 10.87° in the gas phase and 13.01° in DMSO (N2–C7–C6–C5). It is highly probable that these differences are a result of a more dense and compact structure in the crystal form due to the presence of neighbouring molecules and the attractive

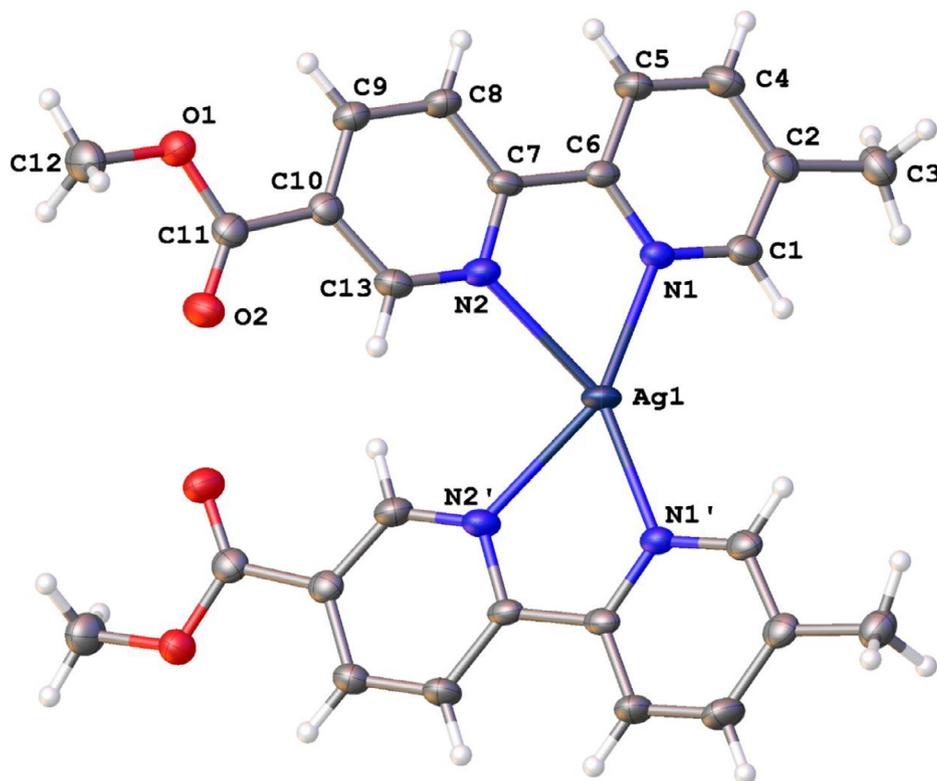


Fig. 4. Molecular structure of **2** with the atom labeling scheme. The counter ion was omitted for clarity.

interaction between them compared to the single molecules used for the calculations in the gas phase and solution.

Some of the selected parameters of the molecule calculated with the B3LYP functional, including the sum of electronic energies with thermal free energies ($E_{\text{elec}} + \Delta G$) and total electronic energies with zero-point energy corrections ($E_{\text{elec}} + \text{ZPE}$, Hartree) in the gas phase and solvents are given in Table S3. When the dielectric constant of the medium is increased, the dipole moment of the molecule is also increased and the molecule is more stable at room temperature (negative ΔE and $\Delta \Delta G$).

The frontier molecular orbitals and energy gaps of **1** and **2** in DMSO were shown in Fig. 5. As seen from the figure, the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) are localized in different parts of the molecules. While the HOMO is localized mostly on the chlorine and Pt atoms, the LUMO is localized on π -antibonding orbitals in compound **1**. The HOMO is localized on the d orbitals of Ag and nonbonding electrons on N for compound **2**. The LUMO is also localized on the bpy rings as in compound **1**. The value of the energy separation between the HOMO and LUMO is 2.64 eV and 4.31 eV for **1** and **2** respectively.

The B3LYP/6-311+G(d,p)/LANL2DZ level was used in TD-DFT calculations to obtain the absorption wavelengths and excitation energies for the first 80 singlet excited states (from S_0 to S_{80}). Fig. S14 shows the calculated UV-Vis absorption spectrum for **1** in DMSO. The selected electronic transitions and the corresponding orbitals for the compound are displayed in Table S4 and Fig. S15 respectively.

There are three charge transfer types observed for compound **1**: metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), and charge transfer from the chlorine atoms to the pyridine rings (CT). The $S_0 \rightarrow S_3$ transition (405 nm) has intramolecular charge transfer from the chlorine atoms to the bpy rings between the HOMO-2 and the LUMO orbitals. Additionally, it

has MLCT from the Pt to the bpy rings (MLCT1). It appears approximately at 400 nm in experimental spectrum.

The maximum oscillator strength peak at 329.5 nm displays a local excitation of bpy rings (LE3) with $\pi-\pi^*$ character (Fig. S14, experimental peak value is 265 nm). The transition at 302 nm has LE3 between the HOMO-2 and the LUMO+2. The S_{13} transition has also CT1 and MLCT1 at 302 nm. In the calculated spectrum, there is an additional absorption at 277 nm, which has the transition from the HOMO-5 of chlorine atoms to the LUMO+2 of d orbitals on Pt (LMCT2: ligand-to-metal charge transfer). The S_{19} transition displays local excitation for chlorine atoms (LE2) at 277 nm. At wavelengths below 250 nm, $\pi-\pi^*$ character of the absorption peaks for the local excitation for bpy ring (LE3) causes a slight increase in oscillator strength.

Fig. S16 shows the calculated UV-Vis absorption spectrum for **2** in DMSO. The selected electronic transitions and the corresponding orbitals for the compound are displayed in Table S5 and Fig. S17 respectively. Unlike **1**, the electronic transitions for **2** are mostly concentrated on MLCT from Ag to bpy rings (MLCT1). The S_1 transition at 382.5 nm mainly consists of MLCT1 character from the highest occupied molecular orbital (HOMO Ag) to the lowest unoccupied molecular orbital of the bpy rings (LUMO bipyridine). However, it is not observed in the experimental results because of its weak oscillator strength. The maximum peak at 318.4 nm displays a $\pi-\pi^*$ transition from the HOMO-2 of the bpy to the LUMO of the bpy rings. It is consistent with 307 nm in experimental spectrum. Both MLCT1 and local excitation of bpy (LE2) were observed at wavelengths below 269 nm.

The molecular electrostatic potential relates to the electronic density and also emphasizes its molecular shape, charge distribution, and the positive, negative, and zero electrostatic potential regions. MEPS analysis enables the identification of electron donor and electron acceptor regions that are particularly useful for understanding intramolecular and intermolecular interactions. Such

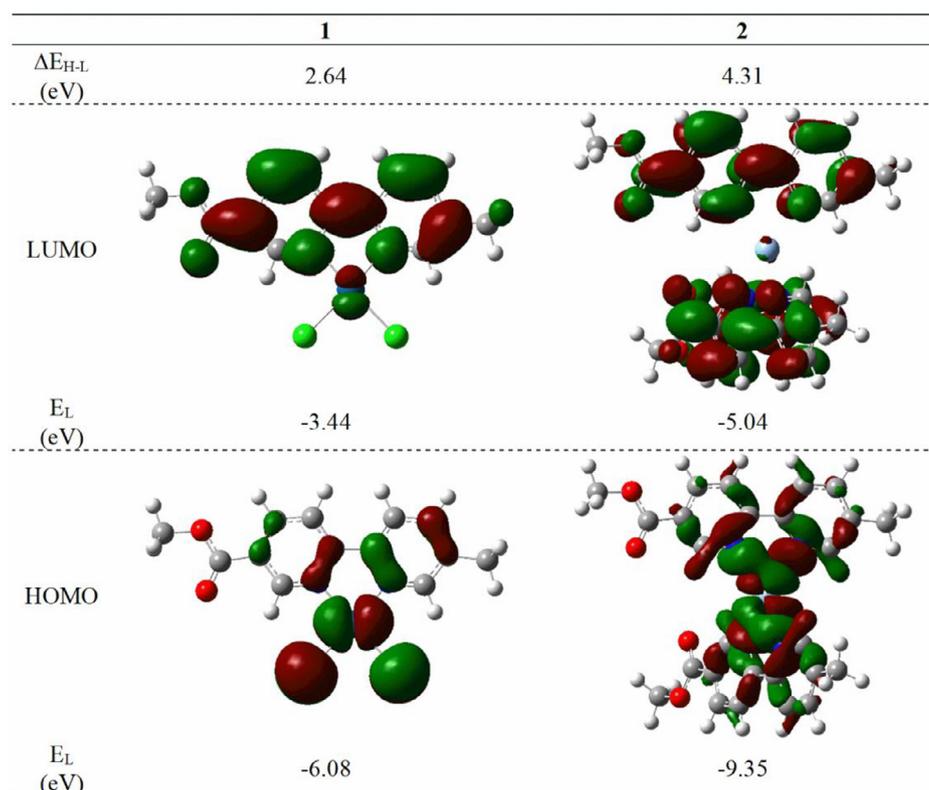


Fig. 5. Frontier orbital energies (E_H , E_L) and energy gaps (ΔE_{H-L}) of investigated compounds at B3LYP/6-311+G(d,p)/LANL2DZ level in DMSO (orbitals were generated using Gaussview with an isovalue of 0.02).

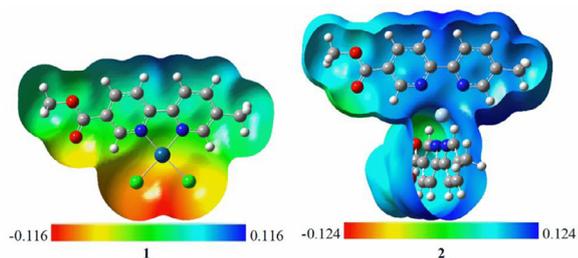


Fig. 6. Map of the molecular electrostatic potential surface for **1** and **2** in DMSO calculated at B3LYP/6-311+G(d,p)/LANL2DZ level. Colours represent electron density: red, electron-rich; yellow, slightly electron-rich region; green, neutral; light blue, slight electron deficiency; blue, electron deficiency; isovalue is 0.02.

visual analysis for intermolecular interactions is consistent with those revealed by X-ray diffraction analysis. MEP was obtained at the B3LYP/6-311+G(d,p)/LANL2DZ level to investigate the nucleophilic or electrophilic region of the molecules examined. Fig. 6 shows the MEPS of **1** and **2** in DMSO (mapped in the range between -0.116 au and +0.116 a.u. for **1**; between -0.124 au and +0.124 a.u. for **2**). The total electron density was calculated using the Mulliken charge distribution. Different colours refer to different values of the electrostatic potentials. The negative charges are mostly localized on the electronegative Cl atoms as expected. Therefore, the electrophilic attack can occur through Cl atoms. On the other hand, compound **2** has mostly positively charged regions. Therefore, it is more susceptible to nucleophilic attack by other species.

4. Conclusion

This paper reports on, for the first time, the synthesis and characterization of unsymmetrically substituted 5-methyl-5'-carbomethoxy-2,2'-bipyridine (**L**) and also preparation and single-crystal X-ray structures of its metal complexes with silver(I) and platinum(II). All compounds are luminescent at room temperature and display low energy emission, which is very important for optoelectronic applications. Experimental and calculated structures have similar geometries. Calculated UV-Vis absorption spectra show that **2** has more MLCT than **1**. However, compound **1**, carrying a highly electronegative Cl atom, displays different charge transfers with both Pt and bpy; additionally, it shows absorption bands at longer wavelengths than 400 nm because of its smaller HOMO-LUMO energy gap. Molecular electrostatic potential calculations revealed that **1** has a nucleophilic nature whereas **2** behaves as an electrophile.

Declaration of Competing Interest

The authors declare no conflict of interest.

CRediT authorship contribution statement

İsmail Yılmaz: Investigation, Methodology, Validation. **Nursel Acar-Selçuki:** Data curation, Software, Visualization, Validation. **Simon J Coles:** Methodology, Formal analysis, Data curation. **Fatih Pekdemir:** Investigation, Validation. **Abdurrahman Şengül:** Conceptualization, Methodology, Validation, Resources, Data curation, Writing - original draft, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Acknowledgments

The authors are grateful to the Turkish Scientific and Technical Research Council [TBAG-2450 (104T060)] and also Zonguldak Bülent Ecevit University for grant 2007/3-13-02-01. The authors also wish to acknowledge the UK Engineering and Physical Sciences Research Council for funding the National Crystallography Service. Computer time provided by Fen Cluster (Ege University Faculty of Science) and TUBITAK ULAKBIM TRUBA Resources is gratefully acknowledged.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2020.129271.

References

- [1] C. Seward, J. Chan, D. Song, S. Wang, Anion dependent structures of luminescent silver(I) complexes, *Inorg. Chem.* 42 (2003) 1112–1120, doi:10.1021/ic020480q.
- [2] D. Paul Rillema, A.J. Cruz, C. Moore, K. Siam, A. Jehan, D. Base, T. Nguyen, W. Huang, Electronic and photophysical properties of platinum(II) biphenyl complexes containing 2,2'-bipyridine and 1,10-phenanthroline ligands, *Inorg. Chem.* 52 (2012) 596–607, doi:10.1021/ic301393e.
- [3] L.J. Grove, J.M. Rennekamp, H. Jude, W.B. Connick, A new class of platinum(II) vapochromic salts, *J. Am. Chem. Soc.* 126 (2004) 1594–1595, doi:10.1021/ja037783j.
- [4] T.J. Wadas, Q.-M. Wang, Y. Kim, C. Flaschenreim, T.N. Blanton, R. Eisenberg, Vapochromism and its structural basis in a luminescent Pt(II) terpyridine–nicotinamide complex, *J. Am. Chem. Soc.* 126 (2004) 16841–16849, doi:10.1021/ja047955s.
- [5] C. Cebrián, M. Mauro, D. Kourkoulos, P. Mercandelli, D. Hertel, K. Meerholz, C.A. Strassert, L. De Cola, Luminescent neutral platinum complexes bearing an asymmetric N⁺N⁺N ligand for high-performance solution-processed OLEDs, *Adv. Mater.* 25 (2013) 437–442, doi:10.1002/adma.201202123.
- [6] S.C.F. Kui, F.-F. Hung, S.-L. Lai, M.-Y. Yuen, C.-C. Kwok, K.-H. Low, S.S.-Y. Chui, C.-M. Che, Luminescent organoplatinum(II) complexes with functionalized cyclometalated C⁺N⁺C ligands: structures, photophysical properties, and material applications, *Chem. Eur. J.* 18 (2012) 96–109, doi:10.1002/chem.201101880.
- [7] T.-T. Yeh, J.-Y. Wu, Y.-S. Wen, Y.-H. Liu, J. Twu, Y.-T. Tao, K.-L. Lu, Luminescent silver metal chains with unusual μ -4-bonded 2,2'-bipyridazine, *Dalt. Trans.* (2005) 656–658, doi:10.1039/B416703A.
- [8] D.N. Kozhevnikov, O.V. Shabunina, D.S. Kopchuk, P.A. Slepukhin, V.N. Kozhevnikov, 5-Aryl-2,2'-bipyridines as tunable fluorophores, *Tetrahedron Lett.* 47 (2006) 7025–7029, doi:10.1016/j.tetlet.2006.07.111.
- [9] R. Bodapati, M. Sarma, A. Kanakati, S.K. Das, Asymmetrically substituted and π -conjugated 2,2'-bipyridine derivatives: synthesis, spectroscopy, computation, and crystallography, *J. Org. Chem.* 80 (2015) 12482–12491, doi:10.1021/acs.joc.5b02345.
- [10] S. Mazzucato, I. Fortunati, S. Scolaro, M. Zerbetto, C. Ferrante, R. Signorini, D. Pedron, R. Bozio, D. Locatelli, S. Righetto, D. Roberto, R. Ugo, A. Abbotto, G. Archetti, L. Beverina, S. Ghezzi, Two-photon absorption of Zn(II) octupolar molecules, *Phys. Chem. Chem. Phys.* 9 (2007) 2999–3005, doi:10.1039/B618709A.
- [11] C. Kaes, A. Katz, M. Wais Hosseini, Bipyridine: the most widely used ligand. A review of molecules comprising at least two 2,2'-bipyridine units, *Chem. Rev.* 100 (2000) 3553–3590, doi:10.1021/cr990376z.
- [12] H. Le Bozec, T. Renouard, Dipolar and non-dipolar pyridine and bipyridine metal complexes for nonlinear optics, *Eur. J. Inorg. Chem.* 2000 (2000) 229–239, doi:10.1002/(SICI)1099-0682(200002)2000:2<229::AID-EJIC229>3.0.CO;2-A.
- [13] A.G. Young, L.R. Hanton, Square planar silver(I) complexes: a rare but increasingly observed stereochemistry for silver(I), *Coord. Chem. Rev.* 252 (2008) 1346–1386, doi:10.1016/j.ccr.2007.07.017.
- [14] C.-J. Wang, Y.-Y. Wang, H. Wang, G.-P. Yang, G.-L. Wen, M. Zhang, Q.-Z. Shi, A novel silver(I) coordination polymer based on mixed ligands bpp and 2,2'-bipyridine-4,4'-dicarboxylate, *Inorg. Chem. Commun.* 11 (2008) 843–846, doi:10.1016/j.inoche.2008.04.013.
- [15] A. Kraft, A.C. Grimdale, A.B. Holmes, Electroluminescent conjugated polymers—seeing polymers in a new light, *Angew. Chemie Int. Ed.* 37 (1998) 402–428, doi:10.1002/(SICI)1521-3773(19980302)37:4<402::AID-ANIE402>3.0.CO;2-9.
- [16] V.M. Miskowski, V.H. Houlting, C. Ming Che, Y. Wang, Electronic spectra and photophysics of platinum(II) complexes with α -diimine ligands. Mixed complexes with halide ligands, *Inorg. Chem.* 32 (2002) 2518–2524, doi:10.1021/ic00063a052.
- [17] J.A. Gareth Williams, S. Develay, D.L. Rochester, L. Murphy, Optimising the luminescence of platinum(II) complexes and their application in organic light emitting devices (OLEDs), *Coord. Chem. Rev.* 252 (2008) 2596–2611, doi:10.1016/j.ccr.2008.03.014.
- [18] J. Ni, Y.-G. Wang, H.-H. Wang, Y.-Z. Pan, L. Xu, Y.-Q. Zhao, X.-Y. Liu, J.-J. Zhang, Reversible dual-stimulus-responsive luminescence and color switch of a platinum complex with 4-[(2-trimethylsilyl)ethynyl]-2,2'-bipyridine, *Eur. J. Inorg. Chem.* 2014 (2014) 986–993, doi:10.1002/ejic.201301329.
- [19] J. Zyss, *Molecular Nonlinear Optics: Materials, Physics, and Devices*, Academic press, 2013.
- [20] S.-Z. Zhan, F. Ding, X.-W. Liu, G.-H. Zhang, J. Zheng, D. Li, White light from blue fluorescence and sensitized yellow long-afterglow phosphorescence of o-terphenyl in its π -acid–base adduct with Ag₃Pz₃, *Inorg. Chem.* 58 (19) (2019) 12516–12520, doi:10.1021/acs.inorgchem.9b01911.
- [21] S.-Z. Zhan, W. Chen, W. Lu, J. Zheng, F. Ding, T. Feng, D. Li, Counteranion-triggered and excitation-dependent chemopalette effect in a supramolecular dual-emissive system based on Cu₃Pz₃, *Inorg. Chem.* 58 (2) (2019) 1081–1090, doi:10.1021/acs.inorgchem.8b02203.
- [22] B.V. Nonius, Collect Software, Nonius, Delft, The Netherlands, 1998.
- [23] G.M. Sheldrick, SHELXT—integrated space-group and crystal-structure determination, *Acta Crystallogr. Sect. C Struct. Chem.* 71 (2015) 3–8.
- [24] G.M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallogr. Sect. C Struct. Chem.* 71 (2015) 3–8.
- [25] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *OLEX2 J Appl Cryst* 42 (2009) 339.
- [26] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, H. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, *Gaussian 09 C.01*, Gaussian, Inc., Wallingford CT, 2009.
- [27] R.D. Dennington, T.A. Keith, J.M. Millam, in: *GaussView 5.0. 8*, Gaussian Inc., 2008, p. 340.
- [28] W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* 140 (1965) A1133–A1138, doi:10.1103/PhysRev.140.A1133.
- [29] A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys. Rev. A* 38 (1988) 3098–3100, doi:10.1103/PhysRevA.38.3098.
- [30] A.D. Becke, Becke's three parameter hybrid method using the LYP correlation functional, *J. Chem. Phys.* 98 (1993) 5648–5652, doi:10.1063/1.464913.
- [31] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* 37 (1988) 785–789, doi:10.1103/PhysRevB.37.785.
- [32] T.H. Dunning, P.J. Hay, *Methods of electronic structure theory*, in: *Mod. Theor. Chem.*, Plenum Press, New York, 1977, pp. 1–28, doi:10.1007/978-1-4757-0887-5_1.
- [33] J. Tomasi, B. Mennucci, E. Cancès, The IEF version of the PCM solvation method: an overview of a new method addressed to study molecular solutes at the QM ab initio level, *J. Mol. Struct. THEOCHEM* 464 (1999) 211–226, doi:10.1016/S0166-1280(98)00553-3.
- [34] J. Tomasi, B. Mennucci, R. Cammi, Quantum mechanical continuum solvation models, *Chem. Rev.* 105 (2005) 2999–3094, doi:10.1021/cr9904009.
- [35] C. Eller, B.W. Smucker, R. Kirgan, D.M. Eichhorn, D.P. Rillema, 5, 5'-Dimethyl-2, 2'-bipyridazine, *Acta Crystallogr. Sect. E* 60 (2004) o433–o434, doi:10.1107/S1600536804000881.
- [36] H.-M. Wen, Y.-H. Wu, Y. Fan, L.-Y. Zhang, C.-N. Chen, Z.-N. Chen, Spectroscopic and luminescence studies on square-planar platinum(II) complexes with anionic tridentate 3-bis(2-pyridylimino)isoindoline derivatives, *Inorg. Chem.* 49 (2010) 2210–2221, doi:10.1021/ic902019s.
- [37] L. Yi, L.-N. Zhu, B. Ding, P. Cheng, D.-Z. Liao, S.-P. Yan, Z.-H. Jiang, Six- and four-coordinated zinc(II) complexes exhibit strong blue fluorescent properties, *Inorg. Chem. Commun.* 6 (2003) 1209–1212, doi:10.1016/S1387-7003(03)00224-7.
- [38] G.-G. Luo, D.-L. Wu, L. Liu, S.-H. Wu, D.-X. Li, Z.-J. Xiao, J.-C. Dai, A novel 1D T5(0)A(2) water tape incorporated in the channel of the first 3D silver-suberate framework, *J. Mol. Struct.* 1014 (2012) 92–96, doi:10.1016/j.molstruc.2012.02.003.
- [39] R.-D. Schnebeck, E. Freisinger, F. Glahé, B. Lippert, Molecular architecture based on metal triangles derived from 2,2'-bipyridazine (Bpz) and EnMII (M = Pt, Pd), *J. Am. Chem. Soc.* 122 (2000) 1381–1390, doi:10.1021/ja991325.
- [40] E. Guney, V.T. Yılmaz, A. Sengül, O. Buyukgungor, Platinum(II) and palladium(II) saccharinato complexes with 2,2':6',2''-terpyridine: synthesis, characterization, crystal structures, photoluminescence and thermal studies, *Inorganica Chim. Acta* 363 (2010) 438–448, doi:10.1016/j.ica.2009.11.018.
- [41] V. Maheshwari, M. Carlone, F.R. Fronczek, L.G. Marzilli, Ligand and coordination-plane distortions in platinum(II) complexes of isomers of dimethyl-2,2'-bipyridine, *Acta Crystallogr. Sect. B* 63 (2007) 603–611, doi:10.1107/S0108768107027024.
- [42] T. Tian, I. Mutikainen, G.P. van Wezel, N. Aliaga-Alcalde, J. Reedijk, Chemical, structural and biological studies of cis-[Pt(3-AcPy)₂Cl₂], *J. Inorg. Biochem.* 103 (2009) 1221–1227, doi:10.1016/j.jinorgbio.2009.06.009.

- [43] R.D. Gillard, A. Sengül, A. Oldroyd, Dimorphism in a 2,2':2''-terpyridyl compound, *Transit. Met. Chem.* 26 (2001) 339–344, doi:[10.1023/A:1007120731989](https://doi.org/10.1023/A:1007120731989).
- [44] A. Şengül, N. Karadayı, O. Büyükgüngör, N, N' -Bis[1-(pyrazin-2-yl)ethylidene]hydrazine, *Acta Crystallogr. Sect. C Cryst. Struct. Commun.* 60 (2004) o507–o508, doi:[10.1107/S010827010401220X](https://doi.org/10.1107/S010827010401220X).
- [45] A. Şengül, Crystal structure of nitrate(2,2',2''-terpyridyl)platinum(II) hydrogen dinitrate, [Pt(terpy)ONO₂][H(ONO₂)₂], *Turkish J. Chem.* 29 (2005) 571–578.
- [46] C.S. Angle, A.G. DiPasquale, A.L. Rheingold, L.H. Doerrer, Red and yellow solvates of chloro(2,2':6',2''-terpyridine)platinum(II) chloride and Pt...Pt interactions, *Acta Crystallogr. Sect. C* 62 (2006) m340–m342, doi:[10.1107/S010827010601924X](https://doi.org/10.1107/S010827010601924X).
- [47] R. Valiente, J.M. García-Lastra, P. García-Fernández, S. García-Revilla, O.S. Wenger, Red-to-yellow pressure-induced phase transition in Pt(bpy)Cl₂: spectroscopic study supported by DFT calculations, *Eur. J. Inorg. Chem.* 2007 (2007) 5735–5742, doi:[10.1002/ejic.200700060](https://doi.org/10.1002/ejic.200700060).
- [48] A. Sengül, Crystal and molecular structure of the yellow form of chloro(2,2':6',2''-terpyridine)platinum (II)chloride dihydrate, [Pt(terpy)Cl]Cl·2H₂O, *Turkish J. Chem.* 28 (2004) 667–672.
- [49] A. Şengül, W.-J. Wang, S.J. Coles, A novel dinuclear double-stranded helical complexes of bis(terdentate) N₄O₂ donor ligand with silver(I) and zinc(II) d¹⁰ metal ions, *Polyhedron* 28 (2009) 69–76, doi:[10.1016/J.POLY.2008.10.011](https://doi.org/10.1016/J.POLY.2008.10.011).
- [50] A. Sengul, O. Kurt, O. Buyukgungor, A 2D network silver coordination polymer with the multimodal ligand 2-pyrazyl methyl ketazine, *Struct. Chem.* 22 (2011) 925–929, doi:[10.1007/s11224-011-9778-z](https://doi.org/10.1007/s11224-011-9778-z).