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Neutral and cationic palladium(II) and platinum(II) complexes of 2,2'-dipyridylamine with saccharinate: Syntheses, spectroscopic, structural, fluorescent and thermal studies

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ABSTRACT

Four palladium(II) and platinum(II) complexes of 2,2'-dipyridylamine (dpya) with saccharinate (sac), *cis*-[Pd(dpya)(sac)₂]·H₂O (**1**), *cis*-[Pt(dpya)(sac)₂]·H₂O (**2**), [Pd(dpya)₂](sac)₂·2H₂O (**3**) and [Pt(dpya)₂] (sac)₂·2H₂O (**4**), have been synthesized and characterized by elemental analysis, IR, NMR, TG-DTA and X-ray diffraction. In **1** and **2**, the metal ions are coordinated by two N-bonded sac ligands, and two nitrogen atoms of dpya, resulting in a neutral square-planar coordination sphere, while in **3** and **4**, the metal ions are coordinated by two sac counter-ions. The mononuclear species of **1** and **2** interact each other through weak intermolecular N-H···O, C-H···O and $\pi \cdot \cdot \pi$ interactions to form a three-dimensional network, while the ions of **3** and **4** are connected by N-H···N and OW-H···O hydrogen bonds into one-dimensional chains. On heating at 250 °C, the solid cationic complexes of **3** and **4** convert to corresponding anhydrous neutral complexes of **1** and **2** after elimination of a dpya ligand. In addition, all complexes **1–4** are luminescent at room temperature and their emissions seem to be attributed to the MLCT fluorescence.

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1. Introduction

Saccharin (sacH, also named 1,1-dioxo-1,2-benzothiazol-3-one or *o*-benzosulfimide) is a well-known artificial sweetener and readily deprotonates in solutions, forming the corresponding saccharinate anion (sac). Owing to the presence of the imino, carbonyl and sulfonyl donor sites, sac acts as a mono-, bi- or tridentate polyfunctional ligand and coordinates many transition metal ions, forming complexes from mononuclear species to coordination polymers. The earlier work in this field has been comprehensively reviewed by Baran and Yilmaz [1].

2,2'-Dipyridylamine (dpya) is an aromatic amine. It behaves as a neutral or monoanionic ligand. The NH group is usually not involved in coordination because of geometrical constraints and the two pyridine rings are flexible in their coordination to metal centers, leading to different coordination modes such as monodentate, chelating bidentate and bridging tridentate [2–7]. In recent years, palladium(II) and platinum(II) complexes of dpya have received increasing attention and have been investigated due to their use as potential anticancer agents [8–12].

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Only three metal complexes of sac with dpya have been reported in recent years [13-15]. The dpya ligand acts in a bidentate chelating fashion in these complexes. In $[Cu(dpya)(sac)_2(H_2O)]$ [13,14], one sac is N-bonded, while the other is O-bonded, whereas in $[Cd(dpya)_2(sac)(H_2O)](sac) H_2O$ [15], two sac anions act as a ligand and a counter-ion, but in [Hg(dpya)(sac)₂] [15], both sac ligands are N-coordinated. On the other hand, palladium(II) and platinum(II) complexes of sac are rare and only a few complexes have been reported [16-19]. As part of our continuing study of metal complexes of sac, we have recently reported the palladium(II) and platinum(II) complexes of sac with 2,2':6',2"-terpyridine (terpy) [20] and 2,2'-bipyridine (bpy) [21]. In the present work, we report the synthesis, characterization and crystal structures of new palladium(II) and platinum(II) complexes of dpya containing sac. The new complexes are classified into two groups such as neutral complexes, *cis*-[Pd(dpya)(sac)₂]·H₂O (**1**) and *cis*-[Pt(dpya)- $(sac)_2$ H_2O (2), and cationic complexes, $[Pd(dpya)_2](sac)_2 H_2O$ (3) and $[Pt(dpya)_2](sac)_2 \cdot 2H_2O$ (4). In complexes 1–4, the dpya ligand behaves as a bidentate chelating ligand. However, both sac anions in the neutral complexes coordinate the metal(II) ions, while these sac anions in the cationic complexes are present as counter-ions, remaining in the outside coordination sphere. Furthermore, the luminescent and thermal properties of these complexes have also been studied.





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2. Experimental

2.1. Materials and measurements

[M(dpya)Cl₂] was prepared according to the literature methods (M = Pd^{II} [9] and Pt^{II} [9,22]). Other chemicals were purchased and used without further purification. Elemental analyses for C, H, and N were performed using a Costech elemental analyser. UV-Vis spectra were measured on a Shimadzu 1700UV spectrophotometer using 1×10^{-5} M DMSO/water solutions (1:1) in the 200-800 nm range. IR spectra were recorded on a Thermo Nicolet 6700 FT-IR spectrophotometer as KBr pellets in the frequency range 4000-400 cm⁻¹. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercuryplus spectrometer. Thermal analysis curves (TG and DTA) were obtained from a Seiko Exstar TG/DTA 6200 thermal analyser in a flowing air atmosphere with a heating rate of 10 K min⁻¹ using a sample size of 5–10 mg and platinum crucibles. Excitation and emission spectra of 1×10^{-3} M DMSO/ water solutions (1:1) were recorded at room temperature with a Varian Cary Eclipse spectrophotometer equipped with a Xe pulse lamp of 75 kW.

2.2. Synthesis of the palladium(II) and platinum(II) complexes

Complexes **1** and **2** were synthesized by the following method. AgNO₃ (1 mmol, 0.17 g) was added to a suspension of $[M(dpya)Cl_2]$ (0.5 mmol) in water (200 ml) and then, this suspension was refluxed for 6 h. After cooling to room temperature, the precipitate of AgCl was removed by filtering through Celite paste to obtain a clear solution. The filtrate was concentrated to 25 ml and followed by the addition of Na(sac)·2H₂O (1 mmol, 0.24 g) and stirred at 60 °C for 30 min. As soon as the addition of Na(sac)·2H₂O, a polycrystalline yellow precipitate was formed. The final suspension was cooled to room temperature and filtered off to remove the yellow solid $[M(dpya)(sac)_2]\cdot H_2O$ (**1** for Pd^{II} and **2** for Pt^{II}). The polycrystalline yellow powders were recrystallized from a mixture of water and DMSO (1:1).

For the synthesis of complexes **3** and **4**, a suspension of $[M(dpya)Cl_2]$ (0.5 mmol) in water (50 ml) was mixed with a solu-

Table 1

Crv	vstallo	graphic	data	and	structure	refinement	for	1-4	1
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tion of dpya (1 mmol) in methanol (10 ml) and this suspension was set to reflux overnight. Then, the resulting solution was filtered off and mixed with a 5 ml aqueous solution of Na(sac)·2H₂O (1 mmol, 0.24 g). This solution was stirred at 60 °C for 2 h and evaporated to about 10 ml. Well shaped yellow crystals of $[M(dpya)_2](sac)_2$ ·2H₂O (**3** for Pd^{II} and **4** for Pt^{II}) were obtained within a day.

2.2.1. [Pd(dpya)(sac)₂]·H₂O (1)

Yield 86%. M.p. 280–290 °C (decomp.). Anal. Calc. for $C_{24}H_{19}N_5O_7S_2Pd$: C, 43.7; H, 2.9; N, 10.6. Found: C, 43.5; H, 3.2; N, 10.7%. ¹H NMR (400 MHz, DMSO- d_6): δ 11.41 (s, 1H, NH), 8.22–8.20 (d, 2H, H⁶ and H^{6'}), 8.01–7.97 (t, 2H, H⁵ and H^{5'}), 7.78–7.69 (m, 8H, H^{sac}), 7.40–7.38 (d, 2H, H³ and H^{3'}), 7.14–7.11 (t, 2H, H⁴ and H^{4'}). ¹³C NMR (400 MHz, DMSO- d_6): δ 165.60, 150.10, 149.56, 142.36, 142.03, 133.44, 133.27, 130.97, 123.68, 120.21, 119.83, 114.77. (Solid KBr pellet): v (cm⁻¹) 3569m v(OH), 3484sb v(OH), 3296w v(NH), 3243w, 3194m, 3136w, 3087m v(CH), 3028m v(CH), 2923w v(CH), 2848w v(CH), 1659vs v(CO), 1590s v(CN), 1530m, 1479vs v(C=C), 1436w v(C=C), 1420w, 1338w v_s (CNS), 1294vs v_{as} (SO₂), 1248s v_{as} (SO₂), 1175vs v_s (SO₂), 1161vs v_s (SO₂), 1125m, 1058w, 1025w, 967s v_{as} (CNS), 903w, 874w, 778s, 754s, 678m, 596s, 565m, 535s.

2.2.2. $[Pt(dpya)(sac)_2] \cdot H_2O(2)$

Yield 80%. M.p. 307–318 °C (decomp.). *Anal.* Calc. for $C_{24}H_{19}N_5O_7S_2Pt$: C, 38.5; H, 2.6; N, 9.4. Found: C, 38.2; H, 2.9; N, 9.7%. ¹H NMR (400 MHz, DMSO-*d*₆): δ 11.36 (s, 1H, NH), 8.35–8.12 (d, 2H, H⁶ and H^{6'}), 7.95–7.85 (t, 2H, H⁵ and H^{5'}), 7.83–7.60 (m, 8H, H^{sac}), 7.35–7.14 (d, 2H, H³ and H^{3'}), 7.14–6.90 (t, 2H, H⁴ and H^{4'}). ¹³C NMR (400 MHz, DMSO-*d*₆): δ 165.25, 150.32, 146.85, 142.20, 141.38, 133.18, 133.01, 131.66, 123.80, 120.41, 119.98, 116.07. (Solid KBr pellet): v (cm⁻¹) 3448sb v(OH), 3297w, 3195m v(NH), 3137w, 3079m v(CH), 3022m v(CH), 2920w v(CH), 1652vs v(CO), 1591m v(CN), 1532m, 1485vs v(C=C), 1435w v(C=C), 1339w v_s (CNS), 1305vs v_{as} (SO₂), 1177vs v_s (SO₂), 1160vs v_s (SO₂), 1129s, 1058w, 969s v_{as} (CNS), 758s, 677s, 595vs, 566s, 525m.

Complex	1	2	3	4
Formula	$C_{24}H_{19}N_5O_7S_2Pd$	$C_{24}H_{17}N_5O_6S_2Pt$	$C_{34}H_{30}N_8O_8S_2Pd$	C34H30N8O8S2Pt
М	659.96	730.64	849.18	937.87
T (K)	295(2)	295(2)	295(2)	295(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	ΡĪ	ΡĪ	$P2_1/c$	P21/c
a (Å)	9.8338(7)	9.6972(7)	11.0900(5)	11.0789(4)
b (Å)	9.7194(6)	9.9176(9)	12.8646(5)	12.8623(3)
c (Å)	13.3028(8)	13.2449(10)	16.1348(7)	16.1324(6)
α (°)	87.173(5)	85.926(6)	90	90
β (°)	85.591(5)	86.758(6)	131.338(2)	131.393(2)
γ (°)	81.862(6)	81.811(7)	90	90
$V(Å^3)$	1253.98(14)	1256.24(17)	1728.35(13)	1724.59(10)
Ζ	2	2	2	2
D_{calcd} (g cm ⁻³)	1.748	1.929	1.632	1.806
$\mu ({\rm mm}^{-1})$	0.963	5.802	0.723	4.255
F(0 0 0)	664	708	864	928
θ Range (°)	1.54-26.50	2.08-26.50	2.31-26.50	2.31-26.50
Index range	$-12 \leqslant h \leqslant 12$,	$-12 \leqslant h \leqslant 12$,	$-13 \leqslant h \leqslant 13$,	$-13 \leqslant h \leqslant 13$,
	$-12 \leqslant k \leqslant 12, -16 \leqslant l \leqslant 16$	$-12 \leqslant k \leqslant 12, -16 \leqslant l \leqslant 16$	$-16 \leqslant k \leqslant 16$, $-20 \leqslant l \leqslant 20$	$-16 \leqslant k \leqslant 16$, $-20 \leqslant l \leqslant 20$
Reflections collected	18 366	12 239	18 825	22 372
Data/parameters	5198/358	5145/343	3578/247	3570/248
Goodness-of-fit (GOF) on F^2	1.060	1.051	1.048	1.068
$R_1 [I > 2\sigma]$	0.0425	0.0716	0.0349	0.0204
wR ₂	0.1059	0.1416	0.0751	0.0489



Scheme 1. Synthesis of complexes 1-4.

Table 3

2.2.3. $[Pd(dpya)_2](sac)_2 \cdot 2H_2O(3)$

Yield 85%. M.p. 330-338 °C (decomp.). Anal. Calc. for C34H30N8O8S2Pd: C, 48.1; H, 3.6; N, 13.2. Found: C, 48.4; H, 3.4; N, 13.5%. ¹H NMR (400 MHz, DMSO-*d*₆): δ 11.65 (s, 2H, NH), 8.20–8.17 (m, 4H, H⁶ and H⁶), 8.09–8.03 (m, 4H, H⁵ and H⁵), 7.77–7.53 (m, 8H, H^{sac}), 7.47–7.41 (d, 4H, H³ and H^{3'}), 7.14–7.08 (m, 4H, H⁴ and H^{4'}). ¹³C NMR (400 MHz, DMSO- d_6): δ 165.57, 154.82, 150.06, 147.82, 142.30, 137.94, 132.04, 131.47, 122.96, 120.23, 119.60, 116.24. (Solid KBr pellet): v (cm⁻¹) 3385sb v(OH),

3293sb	v(NH),	3130w,	3071w	v(CH),	2981w	v(CH),	2901w
1650vs	v(CO),	1626vs	v(CO),	1585vs	v(CN),	1534m,	1472vs
v(C=C),	1435m	v(C=C), 1	417w, 13	358w, 13	338w v _s (CNS), 12	70s v _{as} (-
SO ₂), 1	251s v _a	s(SO ₂), 1	168vs v	s(SO ₂),	1155vs	$v_{\rm s}({\rm SO}_2)$,	1119w
1053w,	1025w,	968m v _a	s(CNS), 9	52m, 90	03w, 78	7m, 765s	, 745m
675m, 6	637w, 60	5m, 543i	m, 461w.				

2.2.4. [Pt(dpya)₂](sac)₂·2H₂O (4)

Selected FT-IR spectral data for 1-4.ª

1

Yield 80%. M.p. 350-360 °C (decomp.). Anal. Calc. for C₃₄H₃₀N₈O₈S₂Pd: C, 43.5; H, 3.2; N, 12.0. Found: C, 43.7; H, 3.0;

3

4

Table 2				
Electronic and	photoluminescence	spectral	data ^a for	1-4.

Compounds	UV–Vis (λ/nm) $(\epsilon/dm^3 mol^{-1} cm^{-1})$	Excitation (λ/nm)	Emission (λ/nm)
dpya	270 (27 080) 317 (16 700)	336	353
Na(sac)	273 (2022)	285	429
1	257 (22 286) 301 (13 576)	323	373
2	245 (74 020) 306 (13 209) 423 (6812)	330	383
3	253 (20 391) 300 (19 504)	325	410
4	249 (35 752) 306 (19 380)	324	386

Assignment v(OH) 3569m, 3448sb 3385sb 3571sb, 3484sb 3415sb v(NH)3296w 3195m 3293w 3305w v(CH) 3087m-3097m-3071w, 3064w-2848w 2920w 2981w 2846w v(CO) 1659 1650

2

v(CO)	1659vs	1652vs	1650vs, 1626vs	1655vs, 1641vs
$v_{\rm s}(\rm CNS)$	1338w	1339w	1338w	1326s
$v_{as}(SO_2)$	1294vs,	1305vs,	1270s, 1251s	1266vs,
	1248s	1258vs		1247vs
$v_{\rm s}({\rm SO}_2)$	1175vs,	1177vs,	1168vs,	1152vs
	1161vs	1160vs	1155vs	
$v_{as}(CNS)$	967s	969s	968m	954s

^a Frequencies in cm⁻¹. b = broad; m = medium; w = weak; vw = very weak; vs = very strong; s = strong.

N, 11.9%. ¹H NMR (400 MHz, DMSO- d_6): δ 11.54 (s, 2H, NH), 8.13– 8.08 (m, 4H, H⁶ and H^{6'}), 7.87–7.84 (dd, 4H, H⁵ and H^{5'}), 7.65–7.53 (m, 8H, H^{sac}), 7.51–7.47 (d, 4H, H³ and H^{3'}), 7.16–7.11 (m, 4H, H⁴ and H^{4'}). ¹³C NMR (400 MHz, DMSO- d_6): δ 168.20, 152.30, 150.24, 145.69, 142.83, 135.23, 132.05, 131.49, 122.96, 121.04, 119.60, 115.65. (Solid KBr pellet): v (cm⁻¹) 3571sb v(OH), 3415sb v(OH), 3305w v(NH), 3191w, 3135w, 3064w v(CH), 2958w v(CH), 2846w v(CH), 1655vs v(CO), 1641vs v(CO), 1585vs v(CN), 1535s, 1480vs v(C=C), 1439m v(C=C), 1420w, 1376s, 1326s v_s (CNS), 1266vs v_{as} (SO₂), 1247vs v_{as} (SO₂), 1152vs v_s (SO₂), 1124vs, 1054w, 1034m, 954s v_{as} (CNS), 895w, 827s, 787m, 768vs, 679s, 659m, 603vs, 543s, 472w, 446w.

2.3. X-ray crystallography

The intensity data of the complexes **1–4** were collected using a STOE IPDS 2 diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97 program [23]. All non-hydrogen atoms were found from the difference Fourier map and refined anisotropically. The crystals of complex **2** were extremely small ($0.04 \times 0.08 \times 0.012$ mm), which greatly influenced the quality of the data of this compound. Additionally, a rather high peak, which can be evaluated as the water O atom, remained as residue. Attempts to fix it as an O atom failed, however, due to



insufficient quality of the data for **2**. Hydrogen atoms bonded to C and N atoms were refined using a riding model, with C–H = 0.96–0.97 Å and N–H = 0.86–0.91 Å. The constraint $U_{iso}(H) = 1.2 U_{eq}(C$ and N) or 1.5 U_{eq} (methyl C) was applied. The water hydrogen atoms are refined freely. The details of data collection, refinement and crystallographic data are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and characterization

As shown in Scheme 1, a two-step reaction sequence was used to prepare new palladium(II) and platinum(II) complexes of sac. In the first step of the synthesis of bis(sac)palladium(II) and platinum(II) complexes, the chlorides of $[M(dpva)Cl_2]$ (M = Pt^{II} or Pd^{II}) were removed by AgNO₃ to obtain [M(dpya)(NO₃)₂] in solution and in the second step, the reaction of the $[M(dpya)(NO_3)_2]$ moiety with Na(sac) afforded the yellow solid complexes of [Pd(dpya) $(sac)_{2}$ ·H₂O (**1**) and [Pt(dpya)(sac)_{2}·H₂O (**2**). In the preparation of bis(dpya)palladium(II) and platinum(II) complexes, firstly $[M(dpya)Cl_2]$ was reacted with an excess of dpya and then, the addition of Na(sac) resulted in the formation of yellow solid complexes $[Pd(dpya)_2](sac)_2 \cdot 2H_2O(3)$ and $[Pt(dpya)_2](sac)_2 \cdot 2H_2O(4)$. As will be discussed in Section 3.4, on heating at around 250 °C for an hour, complexes 3 and 4 turn into the anhydrous complexes of 1 and 2, respectively. It is also observed that the anhydrous complexes obtained by the desolvation of 3 and 4 do not gain water of crystallization upon dispersion in water. All complexes are air-stable and obtained in high yields (over 80%). Complexes 1 and 2 are soluble in DMSO and DMF, while 3 and 4 are water-soluble.

The electronic spectra were measured using DMSO/water solutions of the ligands and their complexes. The free dpya displays two absorption bands in the UV region centered at 270 and 317 nm, and that of the free sac appears at 273 nm. These absorption bands are attributed to the π - π * transitions. The UV-Vis spectra of the complexes display a number of distinct bands at 257 and 301 nm for **1**, and 245, 306, 423 nm for **2**, 253, 300 nm for **3**, and 249, 306 nm for **4** (Table 2). The spectra of complexes **1**-**4** are dominated mainly by ligand-based strong transitions with considerable blue shifts.

Selected FT-IR spectroscopic data for complexes **1–4** are listed in Table 3. The broad and intense bands centered over 3400 cm⁻¹ are attributed to the v(OH) vibrations of the lattice water molecules. The NH stretching of the free dpya ligand appears at 3258 cm⁻¹ and in the complexes this band is observed in the frequency range 3250–3300 cm⁻¹ [24]. The sac moiety gives characteristic IR bands due to the presence of the carbonyl and sulfonyl groups. The sharp bands between 1625 and 1660 cm⁻¹ are due to the absorption of the carbonyl group. The asymmetric (v_{as}) and symmetric (v_s) stretchings of the SO₂ group are observed as two strong IR bands at ca. 1305–1245 and 1177–1150 cm⁻¹, respectively. Both v_{as} and v_s stretchings of the sulfonyl group are usually observed as two split bands. The v_s and v_{as} stretching modes of the CNS moiety of the sac ligands appear at ca. 1330 and 960 cm⁻¹, respectively.

In the ¹H NMR spectra of complexes **1–4**, the NH proton appears as a singlet at δ = ca. 11.50 ppm, which was observed at δ = 9.50 ppm for [PdCl₂(dpya)₂] in CDCl₃ [25]. The pyridine protons appear as four signals in the range δ = 8.35–6.90 ppm, while the protons of sac are observed between 7.53 and 7.83 ppm as a multiplet (see Section 2.2). The signals of 3,3' H atoms of dpya in **1–4** shift to the lower frequency compared to those of the free dpya molecule, whereas those of 5,5' H atoms experience deshielding upon complexation. The proton resonances of coordinated sac rings in **1** and **2** slightly shift to the higher frequency compared to those of complexes 3 and 4 containing uncoordinated sac anions [20]. The signals of 13 C NMR are consistent with the structures of the metal complexes.

3.2. Description of crystal structures

The molecular structures of complex **1** and **2** are shown in Figs. 1a and 2, respectively. Selected bond distances and angles are listed in Table 4. Both complexes are isomorphous with a triclinic space group $P\bar{1}$. The structures of **1** and **2** consist of a lattice water molecule and neutral [M(dpya)(sac)₂] units, but the lattice water in **2** could not be fixed due to the data quality as explained in Section 2.3. The dpya ligand chelates the palladium(II) or platinum(II) ions via two pyridyl N atoms to form a six-membered ring. The squareplanar coordination around the metal(II) ions is completed by two N atoms of two sac anions at the *cis* positions, leading to a neutral



Fig. 2. Molecular structure of *cis*-[Pt(dpya)(sac)₂] (2). C–H hydrogen atoms were omitted for clarity. Note that a water molecule could not fixed due to the quality of the intensity data.

Table 4 Selected bond lengths (Å), angles (°) and hydrogen bonding geometry for 1 and 2. $^{\rm a}$

		1		2
M1-N1		2.033(3)		2.022(11)
M1-N2		2.017(3)		1.986(14)
M1-N4		2.031(3)		2.027(10)
M1-N5		2.031(3)		1.990(15)
N1-M1-N2		89.93(13)		90.8(5)
N1-M1-N4		177.98(13)		178.1(6)
N1-M1-N5		90.57(13)		90.2(5)
N2-M1-N4		91.38(13)		91.1(5)
N2-M1-N5		172.84(13)		174.1(5)
N4-M1-N5		87.93(13)		87.8(5)
$D{-}H{\cdot}{\cdot}{\cdot}A$	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
Hvdrogen bonds				
1				
01W-H1W05	0.86(13)	2.05(9)	2.834(10)	152(16)
01W-H2W01	0.85(15)	2.38(14)	3.090(13)	142(20)
N3−H3A· · · O4 ⁱ	0.86	1.99	2.740(4)	146
2				
N3–H3A \cdots O4 ⁱ	0.86	2.03	2.785(17)	146

^a Symmetry codes: (i) -x + 1, -y + 1, -z + 1.

coordination sphere (Figs. 1a and 2). The dpya ligand adopts a boat conformation and the dihedral angle between two py rings is $25.32(15)^{\circ}$ in **1**, and $24.77(13)^{\circ}$ in **2**. The coordination geometry

is slightly distorted from the perfect square-plane and the palladium(II) and platinum(II) ions are displaced from the coordination plane by 0.076(3) and 0.051(3) Å, respectively. In order to reduce



Fig. 3. (a) Molecular structure of [Pd(dpya)₂](sac)₂·2H₂O (3). C-H hydrogen atoms were omitted for clarity. (b) Packing of hydrogen-bonded chains of 3 viewed down a.



Fig. 4. Molecular structure of [Pt(dpya)₂](sac)₂·2H₂O (4). C-H hydrogen atoms were omitted for clarity.

steric hindrance, two sac ligands tend to be oriented to the coordination plane with the dihedral angles $73.12(14)^{\circ}$ and $86.70(12)^{\circ}$ in **1**, and $71.91(13)^{\circ}$ and $85.98(12)^{\circ}$ in **2**. The M–N(sac) distances are in close agreement with those reported in other palladium(II) and platinum(II) complexes with sac [17,18,20,21], while the M–N(dpya) bond distances are typical of those found in palladium(II) and platinum(II) complexes of the dpya ligand [9,11,12,22,26,27].

The problem with fixing of the water O in **2** makes it difficult to discuss the hydrogen bonding involving the water of crystallization, but as expected, the molecules of **2** show similar packing characteristics to those of **1**. The molecules of **1** are doubly bridged into dimers by the N-H···O hydrogen bonds involving the amine H atoms of dpya and the carbonyl O atoms of sac. The hydrogenbonded dimers are extended into a two-dimensional layer by $\pi(dpya)\cdots\pi(dpya)$ and $\pi(sac)\cdots\pi(sac)$ stacking interactions of 3.593(9) Å and 3.710(10) Å, respectively (Fig. 1b). Similarly, the plane-to-plane distances of $\pi(dpya)\cdots\pi(dpya)$ and $\pi(sac)\cdots\pi(sac)$ stacking interactions in **2** are 3.568(10) and 3.690(10) Å, respectively. The two-dimensional layers are further connected into a three-dimensional network by weak C-H···O hydrogen bonds (C···O = 3.02–3.47 Å).

The molecular structures of complexes **3** and **4** are shown in Figs. 3a and 4, respectively, together with the atom numbering scheme. Selected bond distances and angles are listed in Table 5. X-ray analysis of complexes 3 and 4 indicates that they are isostructural and crystallize in the monoclinic crystal system (P2₁/ c). Both complexes are composed of a complex cation $[M(dpya)_2]^{2+}$ (M = Pd^{II} or Pt^{II}), two sac anions and two lattice water molecules. In the complex cation, the palladium(II) and platinum(II) ions are located on the inversion center and coordinated by two dpya ligands in a bidentate manner, forming a distorted square-planar geometry. Again, each dpya molecule shows a boat conformation. Contrary to 1 and 2, the sac anions in 3 and 4 do not coordinate the metal ions, but remain outside the coordination sphere as counter-ions. The Pd-N(dpya) and Pt-N(dpya) bond lengths are similar, being within the expected range for square-planar palladium(II) and platinum(II) complexes containing the dpya ligand [9.11.12.22.26.27].

Since complexes **3** and **4** are isostructural, they exhibit almost identical molecular packing interactions (see Table 5). Therefore, only packing of molecules of **3** is presented in Fig. 3b. In addition to electrostatic interactions, two sac anions located at either side of the complex cation interact with the cation via the N–H···N and are also doubly bridged by two water molecules leading to one-dimensional hydrogen-bonded chains running along the crystallographic *c* axis (Fig. 3b). It is interesting to note that no obvious

Table 5

Selected bond lengths (Å), angles (°) and hydrogen bonding geometry for ${\bf 3}$ and ${\bf 4.}^a$

		3		4
M1-N1 M1-N2 N1-M1-N2 N1-M1-N2 ⁱ		2.026(2) 2.016(2) 86.78(8) 93.22(8)		2.023(2) 2.016(2) 87.30(9) 92.70(9)
D−H···A	D–H (Å)	H⊷∙A (Å)	D· · ·A (Å)	$D-H\cdot\cdot\cdot A$ (°)
Hydrogen bonds 3 N3-H3AN4 ⁱⁱ O1W-H1WO3 ⁱⁱⁱ O1W-H2WO2 ^{iv}	0.86 0.83(8) 0.83(4)	2.13 2.06(8) 2.23(5)	2.907(3) 2.884(4) 3.047(5)	150 168(5) 167(6)
4 N3-H3A…N4 ⁱⁱ O1W-H1W…O3 ⁱⁱⁱ O1W-H2W…O2 ^{iv}	0.86 0.83(8) 0.84(5)	2.14 2.06(8) 2.23(5)	2.908(3) 2.885(4) 3.064(5)	148 173(6) 176(8)

^a Symmetry codes: (i) -x + 1, -y + 1, -z + 1; (ii) x, y, z - 1; (iii) -x + 1, y + 1/2, -z + 3/2; (iv) x, -y + 3/2, z - 1/2.



Fig. 5. Emission spectra of complexes **1–4** in DMSO/water solutions (1:1) at room temperature.

 π - π stacking interactions between the py rings of dpya or the phenyl rings of sac are present.

3.3. Photoluminescence

The photoluminescent spectra of the ligands and their complexes have been measured using DMSO/water solutions (1:1) at room temperature. The emission spectra of complexes 1-4 are illustrated in Fig. 5 and the excitation and emission data are listed in Table 2. All ligands and their complexes are weakly luminescent when excited at the absorption wavelengths in the range ca. 245-317 nm. However, the dpya ligand is highly emissive at 353 nm upon excitation at 336 nm. It was observed that the emission spectra of metal complexes are originated from the dpya ligand. The emission intensity of the complexes significantly decreases compared to that of the free dpya ligand, but the emission intensity of **2** is much higher than those of other three complexes. This enhancement in the emission intensity may be due to low-lying excited state orbitals of complex 2 [28]. Early studies showed that the emissions of manganese(II), zinc(II) and cadmium(II) complexes with dpya were attributed to the $\pi - \pi^*$ intraligand transitions, since upon complexation, the emissions of the metal complexes are not shifted compared to free dpya ligand [29-33]. However, in the present work, the emission energies of 1-4 are much lower than those of the free dpya, with the red-shifts varying from 50 to 85 nm (Table 2 and Fig. 5). These observations clearly indicate a metal-to-ligand charge transfer (MLCT) at the excited state [28,34].

3.4. Thermal decomposition

The thermal stability and thermal decomposition behaviors of complexes **1–4** were studied by TG and DTA at the atmosphere of air in the temperature range 25–900 °C. The TG and DTA curves are illustrated in Fig. 6 and the thermoanalytical data are presented in Table 6. In general, all complexes dehydrate in the range of 35–160 °C. Then, the endothermic elimination of the dpya ligands takes place and it is followed by the highly exothermic decomposition of the sac moiety. It is clearly observed that the dehydration temperatures of the cationic complexes (**3** and **4**) are significantly higher than those of the neutral complexes (**1** and **2**). This may be



Fig. 6. DTA and TG curves of 1–4.

Table 6Thermoanalytical data for 1–4.

	Stage	Temperature range (°C)	DTA _{max} (°C) ^a	Mass loss (%) ^b	Solid residue
1	1	38–78	58 (+)	2.2 (2.7)	[Pd(dpya)(sac) ₂]
	2	284–410	404 (-)	78.7 (78.8)	PdO
	3	794–816	807 (+)	2.3 (2.3)	Pd
2	1	34–95	54 (+)	2.6 (2.4)	[Pt(dpya)(sac) ₂]
	2	308–409	390 (–)	70.9 (71.5)	Pt
3	1	100–158	135 (+)	4.4 (4.2)	[Pd(dpya) ₂](sac) ₂
	2	170–245	206 (+)	19.1 (20.1)	[Pd(dpya)(sac) ₂]
	3	332–434	427 (-)	63.4 (63.1)	PdO
	4	782–795	789 (+)	1.7 (1.9)	Pd
4	1	100–130	118 (+)	4.0 (3.8)	[Pt(dpya) ₂](sac) ₂
	2	207–241	231 (+)	17.4 (18.3)	[Pt(dpya)(sac) ₂]
	3	350–488	470 (-)	58.8 (57.2)	Pt

^a (+) and (–) donate endothermic and exothermic processes.

^b Calculated values are given in parentheses.

due to the presence of strong ion-dipole interactions involving the water molecules and the ions in **3** and **4**, in addition to other supramolecular interactions as discussed above. The end product for the palladium(II) complexes is PdO, which decomposes to metallic Pd over ca. 780 °C, while the platinum(II) complexes directly produce metallic Pt.

The most important observation is that the cationic complexes of **3** and **4** turn into corresponding neutral complexes of **1** and **2** at around 250 °C. The solid complexes formed at that temperature are thermally stable up to 285 °C for **1** and 330 °C for **2**. This is shown as a plateau in the TG curves (Fig. 6). In a separate experiment, complexes **3** and **4** were heated at 250 °C for an hour. The solid polycrystalline decomposition products were characterized by elemental analysis, IR and NMR techniques, and shown to be high purity anhydrous **1** and **2**. These results clearly show that **1** and **2** can readily be synthesized from **3** and **4** by a solid-state decomposition followed by an inter-conversion mechanism, in which two sac counter-ions become involved in coordination with palladium(II) or platinum(II) subject to the removal of a bidentate dpya ligand (see Scheme 1).

4. Conclusions

In this study, two neutral complexes, *cis*- $[Pd(dpya)(sac)_2]\cdotH_2O$ (**1**) and *cis*- $[Pt(dpya)(sac)_2]\cdotH_2O$ (**2**), and two cationic complexes, $[Pd(dpya)_2](sac)_2\cdot 2H_2O$ (**3**) and $[Pt(dpya)_2](sac)_2\cdot 2H_2O$ (**4**), have been synthesized and characterized by various techniques including elemental analysis, IR, NMR and crystallography. The neutral complexes contain two N-coordinated sac ligands, while in the cationic complexes sac acts as a counter-ion. On heating at around 250 °C, the solid cationic complexes **3** and **4** transform to the corresponding solid neutral complexes **1** and **2** after elimination of a dpya ligand. The solid-state decomposition of the cationic complexes can be used as an alternative method for the preparation of the neutral complexes. All complexes are fluorescent due to MLCT transitions.

5. Supplementary material

CCDC 767469, 767470, 767471 and 767472 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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