Inorg. Chem. **2008**, *47*, 7166−7176

Inorganic Chemistry
Article

New Water Soluble and Luminescent Platinum(II) Compounds, Vapochromic Behavior of [K(H_2O)][Pt(bzq)($CN)_2$], New Examples of the Influence of the Counterion on the Photophysical Properties of d^8 Square-Planar Complexes

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Received February 12, 2008

This work describes the synthesis of compounds [Pt(C∧N)($NCMe)_2$]ClO_4 (C∧N = 7,8-benzoquinolinato (bzq), 2-phenylpyridinato (ppy)) and their use as precursors for the preparation of the cyanido complexes [Pt(C∧N)($CN)_2$]$^-$, which were isolated as the potassium, [K(H_2O)][Pt(C∧N)($CN)_2$] [C∧N = bzq (**3a**), ppy (**4a**)], and the tetrabutylammonium, NBu_4[Pt(C∧N)($CN)_2$] [C∧N = bzq (**5**), ppy (**6**)], salts. The difference in the cation has an influence on the solubility, color, and emission properties of these compounds. Compounds **5** and **6** are yellow and soluble in organic solvents, while the potassium salts are also soluble in water and exhibit two forms: the water-containing [K(H_2O)][Pt(C∧N)($CN)_2$] [C∧N = bzq (**3a**), ppy (**4a**)] complexes and the anhydrous ones K[Pt(C∧N)($CN)_2$] [C∧N = bzq (**3b**), ppy (**4b**)], the former being strongly colored [red (**3a**) or purple (**4a**)] and the latter being yellow. Compounds **3a** and **4a** transform reversibly into the yellow, **3b** and **4b**, compounds upon desorption/ reabsorption of water molecules from the environment. The red solid, **3a**, also exhibits vapochromic behavior when it is exposed to volatile organic compounds, the shortest response times being those observed for methanol and ethanol. UV−vis and emission spectra of all compounds were recorded both in solution and in the solid state. In methanol solution, the difference in the cation causes no differences in the absorption nor in the emission spectra, which is as expected for the monomer species. However, in the solid state, the differences are notable. For both the red (**3a**) and purple (**4a**) compounds, a prominent absorption, which has maxima at about 550 nm and is responsible for their intense colors, as well as a structureless emission at $\lambda > 700$ nm that suffers a significant red-shift upon cooling, are due to ^{1,3}MMLCT (= metal−metal-to-ligand charge transfer) [dσ^*(Pt) → π^*(C∧N)] transitions characteristic of linear-chain platinum complexes with short Pt···Pt contacts. Time-dependent density-functional theory calculations on complex **5** and the X-ray diffraction study on compound [K($OCMe_2)_2$][Pt(ppy)($CN)_2$] (**4c**) are also included.

Introduction

Vapochromic compounds are potentially useful in chemical-sensing applications because they exhibit pronounced and reversible changes of color and emission in the presence of volatile organic compounds (VOCs).[1–23]

Increasing attention is being paid to stacked square-planar d^8 complexes because some of them have proved to be effective as vapochromic materials[7,24–36] and have been incorporated into electronic components for chemical vapor sensing applications. In the chemistry of Pt(II), vapochromism is known mainly in a series of stacked

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10.1021/ic800265q CCC: $40.75

double salts, $[Pt(CNR)_4][M(CN)_4]$ (M = Pt, Pd; R = alkyl, aryl),[7,24–27,30–34] in which anions and cations are stacked in an alternate way. Extensive studies on these double salts have been performed by Mann and co-workers and conclude that solvent sorption alters their crystal lattice, affecting the Pt···Pt/Pd interactions and hence the emissive excited state. The list also includes the neutral complexes, $[PtCl_2L]$ (L = 2,2′-bpy; 6,6′-Me_2-bpy; 5,5′-Me_2bpy; 4,4′-Me_2bpy],[28] $[Pt(CN)_2(5,5'(CH_3)_2\text{-}2,2'\text{-bpy})]$,[29] $[Pt(CNR)_2(CN)_2]$,[9] and $[(C{\wedge}N{\wedge}C)_2Pt_2(\mu\text{-dppm})]$ ($C{\wedge}N{\wedge}C{-}H_2$ = 2,6-di-(2′-naphthyl)-pyridine, dppm = bis(diphenylphosphino)methane),[37] and the simple Pt(II) salts consisting of stacked monomers or dimers with non-metal-containing counterions:[14–16] $[Pt(Me_2bzimpy)Cl]X$ (Me_2bzimpy = 2,6-bis-(N-methylbenzimidazol-2-ylpyridine; X = Cl, PF_6),[14] $[Pt(Nttpy)Cl](PF_6)_2$ (Nttpy = 4′-(p-nicotinamide-N-methylphenyl-2,2′:6′2′′-terpyridine),[15] $[Pt_2(bpy)_2(pyt)_2](PF_6)_2$ (pyt = pyridine-2-thiolate)[10] $[(^tBu_2\text{-bpy})Pt(C{\equiv}CR)_2]$ (R = C_5H_4N, C_6F_5).[13]

Square-planar complexes of Pt(II)-containing π-conjugated ligands (diimines; terpyridines; and C∧N, N∧N∧C, or N∧C∧N-cyclometallated groups) display strong and interesting luminescence properties due to excited states derived from ligand charge (LC) and metal-to-ligand charge-transfer (MLCT) transitions.[35,38–54] With sterically undemanding ligands, these complexes are essentially flat, and the monomers can interact one with another through $\pi\cdots\pi$ or Pt···Pt interactions, which lead to a red-shifted phosphorescence derived from $^3\pi\pi^*$ and ^{3}MMLCT excited states.[38] Stacked square-planar diimine or terpyridine Pt(II) complexes with relatively short metal···metal distances (3−3.5 Å) are well-known because of their strong colors and red emissions, both of which are assigned to the MMLCT [$d\sigma^* \rightarrow \pi^*$] transition in which the highest occupied molecular orbital (HOMO; $d\sigma^*$) comes from the Pt···Pt interaction and the lowest unoccupied molecular orbital (LUMO; π^*) is located mainly on the conjugated aromatic ligand.[38] Their absorption and emission maxima are strongly dependent on the metal···metal separation and are extremely sensitive to the environment (crystallization solvent, temperature, counterion nature, etc.).[24,28,55–62] In some cases, as in the aforementioned, these compounds behave as vapochromic materials because they are able to incorporate solvent molecules to the lattice in a reversible way, with important changes in the packing interactions and in the nature of absorption and emission.

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Bearing these ideas in mind, we focused our attention on the synthesis of anionic Pt(II) cyanido complexes containing 7,8-benzoquinolinato (bzq) and 2-phenylpyridinato (ppy) as π-conjugated ligands, and we studied the effect of the counterion on the packing interactions and photophysical properties. In this paper, we report the new strongly colored and water-soluble compounds $[K(H_2O)][Pt(C{\wedge}N)(CN)_2]$ [C∧N: 7,8-benzoquinolinato (bzq) (**3a**), 2-phenylpyridinato (ppy) (**4a**)], which transform reversibly into the yellow ones $K[Pt(C{\wedge}N)(CN)_2]$ [C∧N: bzq (**3b**), ppy (**4b**)] upon the desorption/reabsorption of water molecules. Compound **3a** shows a vapochromic response when it is exposed to different VOCs. The analogous and non-vapochromic tetrabutylammonium salts, NBu_4 $[Pt(C{\wedge}N)(CN)_2]$ [C∧N: bzq (**5**), ppy (**6**)], have also been prepared and included for comparison.

Experimental Section

General Procedures and Materials. Elemental analyses were carried out in a Perkin-Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (Nujol mulls between polyethylene plates in the range 350−4000 cm^{-1}). ^{1}H NMR spectra were recorded on Varian Unity-300 and Bruker-400 spectrometers, using tetramethylsilane as a standard reference. Mass spectral analyses were performed with a VG AustoSpec instrument. Conductivity measurements were performed in acetonitrile solutions (5×10^{-4} M) with a Philips PW 9509 conductimeter. UV−visible spectra were obtained on a Unicam UV4 spectrophotometer. For diffuse-reflectance−UV measurements, the spectrophotometer was equipped with a Spectralon RSA-UC-40 Labsphere integrating sphere. Emission and excitation spectra were obtained on a Fluorolog FL-3-11 spectrofluorimeter. Lifetime measurements were performed with a Fluromax phosphorimeter for lifetimes shorter than 10 μs and with an IBH Datastation HUB 5000F for lifetimes higher than 10 μs.

KCN was purchased from Panreac; $AgClO_4$,[63] $[\{Pt(bzq)(\mu\text{-}Cl)\}_2]$ (**A**),[64] and $[\{Pt(ppy)(\mu\text{-}Cl)\}_2]$ (**B**)[65] were prepared as described elsewhere.

Synthesis of $[Pt(bzq)(NCMe)_2]ClO_4$ (1). $AgClO_4$ (208.1 mg, 1 mmol) was added to a stirred suspension of **A** (410 mg, 0.50 mmol) in NCMe (100 mL). After stirring at room temperature for 7 h in the dark, the mixture was filtered through celite and the resulting solution evaporated to dryness. The addition of Et_2O (30 mL) to the residue gave pure **1** as an orange solid. Yield: 530 mg, 96%. Elem anal. calcd (%) for $C_{17}ClH_{14}N_3O_4Pt$: C, 36.80; H, 2.52; N, 7.57. Found: C, 37.07; H, 2.29; N, 7.60. IR (Nujol, cm^{-1}) ν: 2360 (m, NCMe), 2340 (m, NCMe), 2297 (m, ν_{st}(C−N), NCMe), 1625 (m), 1574 (m), 1087 (vs, ν_3 ClO_4^-), 831 (s), 769 (m), 624 (s, ν_4 ClO_4^-). Λ_M (124.3 Ω cm^{-1}, solution 5×10^{-4} M in NCMe). ^{1}H NMR (293 K, CD_3CN, 400 MHz, ppm): δ 8.80 (dd, H_2, $^3J_{H2-H3} = 5.4$ Hz; $^4J_{H2-H4} = 1.2$ Hz, $^3J_{Pt-H} = 47.3$ Hz), 8.56 (dd, H_4, $^3J_{H4-H3} = 8.2$ Hz, $^4J_{H4-H2} = 1.2$ Hz), 7.87 (H_5, ν_A), 7.74 (H_6, ν_B, $^3J_{H5-H6} = 8.6$ Hz), 7.74 (m, H_7), 7.60 (dd, H_3, $^3J_{H3-H4} = 7.8$ Hz, $^3J_{H3-H2} = 5.4$ Hz), [7.56−7.49] (m, 2 H, H_8, H_9), 2.69 (s, 3 H, CH_3CN), 1.99 (s, 3 H, CH_3CN).

Synthesis of $[Pt(ppy)(NCMe)_2]ClO_4$ (2). Complex **2** was prepared in the same way as **1**, with $AgClO_4$ (382.6 mg, 1.843 mmol) and **B** (710 mg, 0.923 mmol), yielding **2**,with a yellow color. Yield: 965 mg, 98%. Elem anal. calcd (%) for $C_{15}ClH_{14}N_3O_4Pt$: C, 33.94; H, 2.65; N, 7.91. Found: C, 33.84; H, 2.43; N, 7.52. IR ν: 2340 (m, NCMe), 2324 (m, NCMe), 2296 (m, ν_{st}(C−N), NCMe), 1612 (m), 1586 (m), 1094 (s, ν_3 ClO_4^-), 758 (s), 749 (s), 624 (s, ν_4 ClO_4^-). Λ_M (123.0 Ω cm^{-1}, solution 5×10^{-4} M in NCMe).^{1}H NMR (293 K, CD_3CN, 400 MHz, ppm): δ 8.62 (ddd, H_2, $^3J_{H2-H3} = 5.8$ Hz; $^4J_{H2-H4} = 1.4$ Hz, $^4J_{H2-H5} = 0.6$ Hz, $^3J_{Pt-H2} = 46.1$ Hz), 8.08 (ddd, H_4, $^3J_{H4-H5} = 8.2$ Hz; $^3J_{H4-H3} = 7.4$ Hz, $^4J_{H4-H2} = 1.4$ Hz), 7.88 (d, H_5, $^3J_{H5-H4} = 8.2$ Hz), 7.59 (dd, H_6, $^3J_{H6-H7} = 7.5$ Hz, $^4J_{H6-H8} = 1.7$ Hz), 7.35 (dd, H_9, $^3J_{H9-H8} = 7.5$ Hz; $^4J_{H9-H7} = 1.3$ Hz,$^3J_{Pt-H9} = 47.4$ Hz), 7.32 (ddd, H_3, $^3J_{H3-H4} = 7.4$, $^3J_{H3-H2} = 5.8$ Hz, $^4J_{H3-H5} = 1.6$ Hz), 7.07 (td, H_7, $^3J_{H7-H8} = {}^3J_{H7-H6} = 7.5$ Hz, $^4J_{H7-H9} = 1.3$ Hz), 7.01 (td, H_8, $^3J_{H8-H7} = {}^3J_{H8-H9} = 7.5$ Hz, $^4J_{H8-H6} = 1.7$ Hz), 2.62 (s, 3 H, CH_3CN), 1.99 (s, 3 H, CH_3CN).

Synthesis of $[K(H_2O)][Pt(bzq)(CN)_2]$ (3a). KCN (116.8 mg, 1.794 mmol) was added to a stirred suspension of $[Pt(bzq)(NCMe)_2]ClO_4$ (497.6 mg, 0.897 mmol) in MeOH (60 mL) at room temperature. After 1 h, the mixture was concentrated to 10 mL, kept at −30 °C for 2 h, and filtered through celite. The resulting solution was evaporated to dryness, and diethyl ether (20 mL) was added to the residue to give pure **3a** as a red solid. Yield: 351.2 mg, 78%. Elem anal. calcd (%) for $C_{15}H_{10}KN_3OPt$: C, 37.34; H, 2.09; N, 8.71. Found: C, 36.88; H, 2.33; N, 8.86. IR: $\tilde{\nu}$ (cm^{-1}): 3400 (vs, H_2O), 2121(vs, C≡N), 2102 (vs, C≡N). 1654 (m, H_2O), 1618 (s), 1569 (m), 821 (vs), 816 (vs), 750 (s). Negative FAB-MS (*m*/*z*): 425 $[Pt(bzq)(CN)_2]^-$. ^{1}H NMR (293 K, CD_3COCD_3, 400 MHz, ppm): δ 9.62 (dd, H_2, $^3J_{H2-H3} = 5.2$ Hz; $^4J_{H2-H4} = 1.4$ Hz, $^3J_{Pt-H} = 32.0$ Hz), 8.58 (dd, H_4, $^3J_{H4-H3} = 8.0$ Hz, $^4J_{H4-H2} = 1.4$ Hz), 8.29 (dd, H_9, $^3J_{H9-H8} = 7.0$ Hz, $^4J_{H9-H7} = 1.0$ Hz, $^3J_{Pt-H9} = 46.0$ Hz), 7.82 (H_5, ν_A), 7.68 (H_6, ν_B, $^3J_{H5-H6} = 8.4$ Hz), 7.68 (m, H_3), 7.60 (dd, H_7, $^3J_{H7-H8} = 8.0$ Hz, $^4J_{H7-H9} = 1.2$ Hz), 7.50 (dd, H_8, $^3J_{H8-H7} = 8.0$ Hz, $^3J_{H8-H9} = 7.0$ Hz).

Synthesis of $[K(H_2O)][Pt(ppy)(CN)_2]$ (4a). Complex **4a** was synthesized in a similar way to **3a**, using KCN (123.1 mg, 1.891 mmol) and $[Pt(ppy)(NCMe)_2]ClO_4$ (502 mg, 0.945 mmol) and yielding **6a**, with a purple color. Yield: 325 mg, 72%. Elem anal. calcd (%) for $C_{13}H_{10}KN_3OPt$: C, 34.06; H, 2.20; N, 9.16. Found: C, 33.62; H, 2.18; N, 8.70. IR: $\tilde{\nu}$ (cm^{-1}): 3400 (vs, H_2O), 2113 (s, C≡N), 2093 (vs, C≡N), 1628 (m, H_2O), 1610 (s), 1586 (m), 1567 (w), 784 (w), 745 (s). Negative FAB-MS (*m*/*z*): 401 $[Pt(ppy)(CN)_2]^-$. ^{1}H NMR (293 K, CD_3COCD_3, 400 MHz, ppm): δ 9.41 (dd, H_2, $^3J_{H2-H3} = 5.9$ Hz; $^4J_{H2-H4} = 0.4$ Hz, $^3J_{Pt-H2} = 30.6$ Hz), 8.12 (dd, H_9, $^3J_{H9-H8} = 7.0$ Hz, $^4J_{H9-H7} = 0.8$ Hz, $^3J_{Pt-H9} = 48.2$ Hz), 8.02 (m, H_4), 7.93 (d, H_5, $^3J_{H5-H4} = 8.0$ Hz), 7.62 (d, H_6, $^3J_{H6-H7} = 7.0$ Hz), 7.29 (t, H_3, $^3J_{H3-H4} = {}^3J_{H3-H2} = 5.9$ Hz), 7.07 (tm, H_8, $^3J_{H8-H7} = {}^3J_{H8-H9} = 7.0$ Hz), 7.01 (t, H_7, $^3J_{H7-H8} = {}^3J_{H7-H6} = 7.0$ Hz).

Synthesis of $NBu_4[Pt(bzq)(CN)_2]$ (5). KCN (0.2638 g, 4.052 mmol) was added to a stirred suspension of $[Pt(bzq)(NCMe)_2]ClO_4$

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(1.1240 g, 2.026 mmol) in MeOH (60 mL). After 1 h at room temperature, the mixture was filtered through celite, and the resulting solution was evaporated to dryness. NBu_4ClO_4 (692.7 mg, 2.025 mmol) and acetone (60 mL) were added to the residue. After stirring for 1 h, the suspension was filtered through celite, the solution was evaporated to dryness, and the residue was treated with H_2O (3 × 40 mL). The remaining solid was filtered, dried (110 °C), and recrystallized from CH_2Cl_2/Et_2O to give pure **5** as a bright yellow solid. Yield: 988.5 mg, 73%. Elem anal. calcd (%) for $PtC_{31}H_{44}N_4$: C, 55.76; H, 6.64; N, 8.38. Found: C, 55.63; H, 6.47; N, 8.45. IR: $\tilde{\nu}$ (cm^{-1}): 2120 (vs, C≡N), 2107 (vs, C≡N), 1615 (m), 1566 (m), 880 (s, NBu_4^+), 861 (s), 789 (s). Negative FAB-MS (*m*/*z*): 425 $[Pt(bzq)(CN)_2]^-$. ^1H NMR (293 K, CD_3COCD_3, 400 MHz, ppm): δ 9.68 (dd, H_2, $^3J_{H2-H3} = 4.8$ Hz; $^4J_{H2-H4} = 1.2$ Hz, $^3J_{Pt-H2} = 31.4$ Hz), 8.57 (dd, H_4, $^3J_{H4-H3} = 8.0$ Hz, $^4J_{H4-H2} = 1.2$ Hz), 8.35 (dd, H_9, $^3J_{H9-H8} = 7.0$ Hz, $^4J_{H9-H7} = 0.4$ Hz, $^3J_{Pt-H9} = 46.0$ Hz), 7.82 (H_5, ν_A), 7.68 (H_6, ν_B, $^3J_{H5-H6} = 8.8$ Hz), 7.69 (m, H_3), 7.6 (dd, H_7, $^3J_{H7-H8} = 7.0$ Hz, $^4J_{H7-H9} = 0.4$ Hz), 7.50 (t, H_8, $^3J_{H8-H7} = {}^3J_{H8-H9} = 7.0$ Hz), 3.44 (m, 8 H, CH_2, NBu_4^+), 1.80 (m, 8 H, CH_2, NBu_4^+), 1.41 (m, 8 H, CH_2, NBu_4^+), 0.95 (t, $^3J_{H-H} = 7.3$ Hz, 12 H, CH_3, NBu_4^+).

Synthesis of $NBu_4[Pt(ppy)(CN)_2]$ (6). Complex **6** was synthesized in a similar way to **5**, using KCN (276.0 mg, 4.238 mmol), $[Pt(ppy)(NCMe)_2]ClO_4$ (1.1250 g, 2.119 mmol), and NBu_4ClO_4 (724.4 mg, 2.118 mmol). Yield: 1.1918 g, 88%. Elem anal. calcd (%) for $PtC_{29}H_{44}N_4$: C, 54.10; H, 6.88; N, 8.70. Found: C, 53.95; H, 6.95; N, 8.47. IR: $\tilde{\nu}$ (cm^{-1}): 2122 (vs, C≡N), 2110 (vs, C≡N) 1604 (s), 1581 (m), 1560 (m), 885 (m, NBu_4^+), 778 (s), 745 (m). Negative FAB-MS (*m*/*z*): 401 $[Pt(ppy)(CN)_2]^-$. ^1H NMR (293 K, CD_3COCD_3, 400 MHz, ppm): δ 9.47 (ddd, H_2, $^3J_{H2-H3} = 5.8$ Hz; $^4J_{H2-H4} = 1.8$ Hz, $^5J_{H2-H5} = 0.8$ Hz, $^3J_{Pt-H2} = 30.4$ Hz), 8.18 (dd, H_9, $^3J_{H9-H8} = 7.2$ Hz, $^4J_{H9-H7} = 1.4$ Hz, $^3J_{Pt-H9} = 48.8$ Hz), 8.01 (ddd, H_4, $^3J_{H4-H5} = 8.0$ Hz, $^3J_{H4-H3} = 7.2$ Hz, $^4J_{H4-H2} = 1.8$ Hz), 7.92 (dd, H_5, $^3J_{H5-H4} = 8.0$ Hz, $^4J_{H5-H3} = 1.2$ Hz), 7.61 (dd, H_6, $^3J_{H6-H7} = 7.2$ Hz, $^4J_{H6-H8} = 1.4$ Hz), 7.29 (ddd, H_3, $^3J_{H3-H4} = 7.2$ Hz, $^3J_{H3-H2} = 5.8$ Hz, $^4J_{H3-H5} = 1.2$ Hz), 7.07 (td, H_8, $^3J_{H8-H7} = {}^3J_{H8-H9} = 7.2$ Hz, $^4J_{H8-H6} = 1.4$ Hz), 7.01 (td, H_7, $^3J_{H7-H8} = {}^3J_{H7-H6} = 7.2$ Hz, $^4J_{H7-H9} = 1.4$ Hz), 3.45 (m, 8 H, CH_2, NBu_4^+), 1.81 (m, 8 H, CH_2, NBu_4^+), 1.42 (m, 8 H, CH_2, NBu_4^+), 0.96 (t, $^3J_{H-H} = 7.3$ Hz, 12 H, CH_3, NBu_4^+).

Computational Details. The computational method used was density functional theory (DFT) with the B3LYP exchange-correlation functional,[66–68] using the Gaussian 03[69] program package. The basic set used was the LanL2DZ effective core potential for the platinum atom, and 6-31G(d,p) for the remaining atoms. Compound **5** was optimized as an isolated molecule from the solid-state geometry at the DFT level of theory. The time-dependent density-functional theory (TD-DFT) calculation was carried out using the polarized continuum model approach implemented in the Gaussian 03 software.

Table 1. Crystal Data and Structure Refinement for Complex $[K(OCMe_2)_2][Pt(ppy)(CN)_2]$ (**4c**)

empirical formula	$C_{19}H_{20}KN_3O_2Pt$
fw	556.57
cryst size (mm)	0.39 × 0.32 × 0.12
temperature (K)	100(1)
cryst syst	orthorhombic
space group	*Pbca*
a (Å)	8.6678(2)
b (Å)	16.9658(5)
c (Å)	27.9597(7)
V (Å^3), *Z*	4536.7(18)
Z	8
d_{calcd} (g cm^{-3})	1.798
μ (mm^{-1})	7.044
θ range (deg)	3.93−25.07
no. of reflns collected	23065
no. of unique reflns	3635, $R_{int} = 0.0419$
final *R* indices ($I > 2\sigma(I)$)[a]	$R_1 = 0.0297$, $wR_2 = 0.0729$
R indices (all data)	$R_1 = 0.0346$, $wR_2 = 0.0759$
GOF[b] on F^2	1.054

[a] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{0.5}$; $R1 = \sum||F_o|F_c||/\sum|F_o|$. [b] Goodness of fit $= [\sum w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{0.5}$.

X-Ray Structure Determination of $[K(OCMe_2)_2][Pt(ppy)(CN)_2]$ (4c). Crystal data and other details of the structure analysis are presented in Table 1. A single crystal was mounted on a quartz fiber in a random orientation and held in place with fluorinated oil. Data collection was performed at 100 K on a Oxford Diffraction Xcalibur CCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) with a nominal crystal-to-detector distance of 5.0 cm. Unit cell dimensions were determined from the positions of 17 973 reflections from the main data set. A set of data was collected on the basis of ω-scans runs. The diffraction frames were integrated and corrected for absorption using the CrysAlis RED package.[70] Lorentz and polarization corrections were applied.

The structure was solved by direct methods. All refinements were carried out using the SHELXL-97 program.[71] All non-hydrogen atoms of the complex were refined with anisotropic displacement parameters. The hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to 1.2 times the U_{iso} values of their respective parent atoms (1.5 times for the methyl H atoms). Full-matrix least-squares refinement of the model against F^2 converged to the final residual indices given in Table 1.

Results and Discussion

Synthesis and Characterization of the Starting Materials $[Pt(C{\wedge}N)(NCMe)_2]ClO_4$ [$C{\wedge}N$ = bzq (1), ppy (2)]. Compounds **1** and **2** were prepared by treatment of the corresponding dinuclear chlorido compound $[\{Pt(C{\wedge}N)(\mu\text{-}Cl)\}_2]$ [$C{\wedge}N$ = bzq (**A**), ppy (**B**)] with $AgClO_4$ in a 1:2 molar ratio in NCMe. After removing the AgCl, compounds **1** (orange color) and **2** (yellow color) were obtained from their corresponding solutions as analytically pure solids (see

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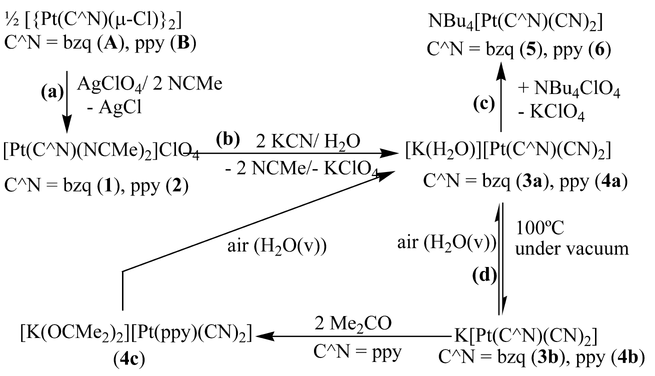
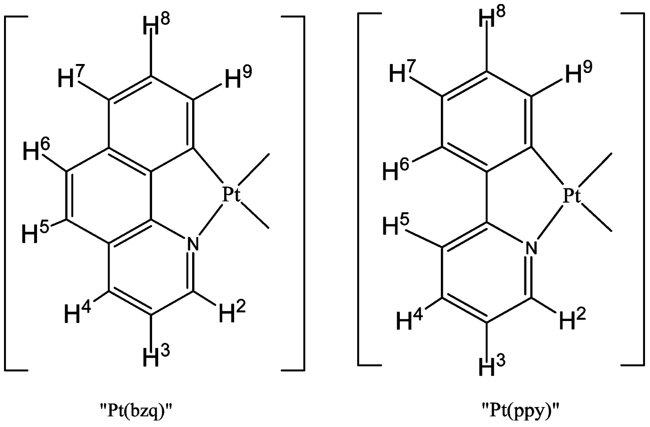
Scheme 1



Scheme 2. Numerical Scheme for NMR Purposes



Scheme 1a and the Experimental Section). Their IR spectra show absorptions corresponding to the perchlorate ion (Td),[72] N-coordinated acetonitrile molecules in a cis disposition,[73,74] and several absorptions due to the C∧N groups, in agreement with their stoichiometry. They show low solubility and stability in common organic solvents, except in acetonitrile, in which they were characterized by NMR spectroscopy (see Scheme 2 and the Experimental Section). They behave in acetonitrile solution as 1:1 electrolytes.[75] These compounds were used as starting materials in the synthesis of the cyanido derivatives described in the following.

Synthesis and Characterization of the Cyanido Compounds [K(H$_2$O)$_x$][Pt(C∧N)(CN)$_2$] [x = 1, C∧N = bzq (3a), ppy (4a)]; x = 0, C∧N = bzq (3b), ppy (4b)] and NBu$_4$[Pt(C∧N)(CN)$_2$](C∧N = bzq (5), ppy (6)). Compounds [K(H$_2$O)][Pt(C∧N)(CN)$_2$] [C∧N: bzq (**3a**), ppy (**4a**)] were prepared by the addition of KCN in a 2:1 molar ratio to a suspension of the corresponding compound [Pt(C∧N)(NCMe)$_2$]ClO$_4$ [C∧N = bzq (**1**), ppy (**2**)] in aqueous methanol (see Scheme 1b and the Experimental Section). Addition of the equimolar amount of NBu$_4$ClO$_4$ to "in situ" freshly prepared solutions of **3a** and **4a** in acetone yields complexes NBu$_4$[Pt(C∧N)(CN)$_2$] [C∧N: bzq (**5**), ppy (**6**)] (see Scheme 1c and the Experimental Section). Compound **6** had already been synthesized previously by Kvam and Songstad from [Pt(ppy)(en)]Cl.[76,77]

The difference in cation nature causes considerable changes in the solubility and also in the color of these solids. Hence, the potassium compounds are red (**3a**) or purple (**4a**) and soluble in water, methanol, and acetone but are insoluble in dichloromethane or chloroform; by contrast, the tetrabutylammonium salts (**5** and **6**) are yellow and soluble in methanol, acetone, dichloromethane, or chloroform but insoluble in water. The IR spectra of complexes **3a**, **4a**, **5**, and **6** show, in all cases, two ν_{CN} absorptions around 2110 cm^{-1} and 2120 cm^{-1}, as expected for two terminal CN$^-$ ligands in a cis arrangement.[78] The presence of water in compounds **3a** and **4a** is evident from the strong absorptions observed at about 3400 cm^{-1}.[79] In solution, their FAB$^-$ mass spectra show peaks due to the corresponding anion [Pt(C∧N)(CN)$_2$]$^-$ (100%) regardless of the cation nature, as also happens with the signals that are due to the corresponding C,N-cyclometallated ligand[43,44,65,80,81] (see Scheme 2 and the Experimental Section) observed in their ^{1}H NMR spectra in acetone-d_6 at 293 K. Additionally, the ^{1}H NMR spectra of **3a** and **4a** in dry acetone-d_6 show one signal at about 2.9 ppm (2 H) due to free water, and those of **5** and **6** show the signals due to the NBu$_4$$^+$cation. Thermal gravimetric analysis (TGA) for complex **3a** shows two stages in the range of 40−140° due to the total loss of one water molecule (total weight loss: calcd/found (%), 3.73/3.83), the first stage at 70 °C (weight loss 3.38%) and the second one at 127 °C (weight loss 0.45%). Similar behavior was observed for complex **4a** (total weight loss: calcd/found (%), 3.93/3.95), the first stage at 92 °C (weight loss 3.51%) and the second at 122 °C (weight loss 0.44%).

The 1.0 equivalent of H$_2$O present in the red (**3a**) and purple (**4a**) potassium compounds can be removed when they are heated in the oven at 110 °C (or gently heated under a vacuum), to give the yellow solids K[Pt(C∧N)(CN)$_2$] [C∧N: bzq (**3b**), ppy (**4b**)] (Figure 1). The absence of water in **3b** and **4b** can be proved by IR and ^{1}H NMR in dry acetone-d_6. When solid samples of **3b** and **4b** are exposed to the air, they undergo a change of color from yellow to red (**3**) or purple (**4**) within seconds because they pick up water molecules again to regenerate compounds **3a** and **4a**, respectively (see Scheme 1d). In spite of this, the anhydrous species (**3b**, **4b**) can be stored under an argon atmosphere or under a vacuum for several months without decomposition. These processes, in which compounds **3** and **4** take in or lose water molecules, are completely reversible and easily perceptible given the dramatic color change (Figure 1).

Unfortunately, no good-quality crystals of **3a** or **4a** could be obtained for X-ray purposes. In an attempt to

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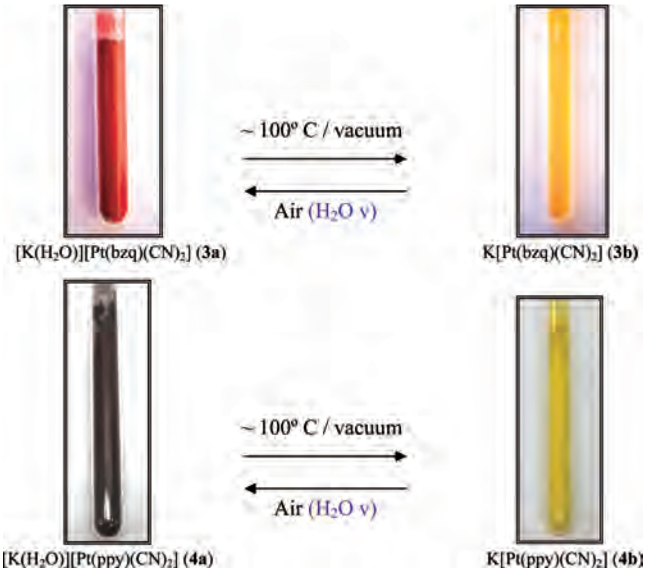

Figure 1. Solids **3a**, **3b**, **4a**, and **4b**.

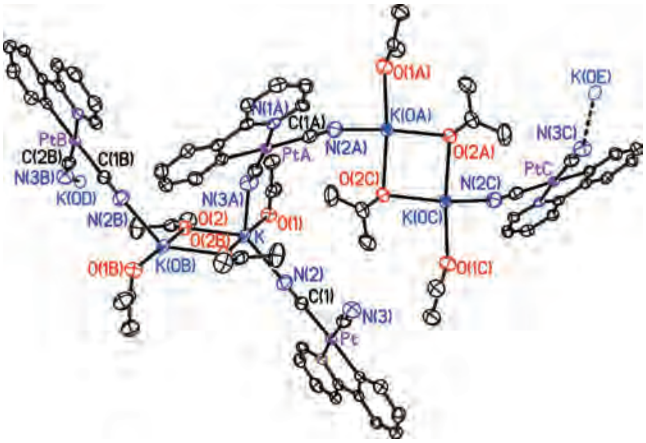

Figure 2. X-ray structure of **4c**.

obtain crystals of **4b** by the slow diffusion of dry *n*-hexane into a solution of **4b** in dry acetone at −30 °C under an argon atmosphere, crystals of compound $[K(OCMe_2)_2][Pt(ppy)(CN)_2]$ (**4c**) suitable for X-ray diffraction studies were obtained (Figure 2, Table 2). This is a hybrid inorganic−organometallic coordination polymer, in which the organometallic anions $[Pt(ppy)(CN)_2]^-$ are interconnected in a network built together by the countercation $[\{K(OCMe_2)(\mu\text{-}OCMe_2)\}_2]^+$.

The organometallic anion is a slightly distorted square-planar complex of Pt(II) containing one 2-phenylpyridinato and two C-bonded cyanido ligands. The narrow N(1)−Pt−C(3) bite angle [80.6(2)°] and the $Pt-N_{C\wedge N}$,[44,45,65,80,82] $Pt-C_{C\wedge N}$, and $Pt-C_{C\equiv N}$ bond distances are all in the range of those observed in platinum complexes with C∧N cyclometallated[44,45,65,80,82] and cyanido[9,27,83–88] ligands. The two cyanido ligands of a platinum unit "$Pt(ppy)(CN)_2$" are each N-bonded to a different potassium atom to give a supramolecular structure. Each bridging cyanido groups exhibits different K−N bond lengths (2.677(5) Å, 2.709(5)Å) and C−N−K bond angles (164.3(4)° and 147.2(4)°). The K−N bond lengths are much shorter than those described in cyanidometalate complexes connected by potassium cations, as $[KCr(CN)_6]^{2-}$,[89] $[KCu(bpm)(CN)_2]$ (bpm = bipyrimidine),[90] $[KFe(CN)_6]^{2-}$,[91] $K[Fe(CN)_3(CO)_3]$,[92] $\{K(DMF)_2Cu(CN)_2\}_\infty$,[93] and $[(Me_2PhSi)_3CCu(CN)K]_4$.[94]

The potassium ions show a distorted *bpt* coordination environment formed by two N atoms from the bridging cyanido groups, and three O atoms from the acetone molecules (one terminal and two bridging ones). All K−O[95] bond lengths are in the range of those found in potassium compounds with acetone as a ligand. No noticeable difference in the K−Ot (terminal acetone) and K−Ob (bridging acetone) bond distances is observed, as occurs in other complexes containing acetone in these two coordination modes.[96,97]

The presence of acetone in the crystal lattice of **4c** was clearly proved by FTIR[79] on a single crystal (Figure 3). Its spectrum shows one absorption at ca. 1700 cm^{-1} assigned to ν_{CO} of the acetone. The FTIR spectrum of the same sample upon exposure to air for 2 min shows the absence of this absorption and the presence of a broad absorption in the 3300−3500 cm^{-1} range corresponding to the ν_{OH} of water molecules. There is full agreement between this FTIR spectrum and that of **4a** in powder, which indicates that the replacement of acetone by water molecules takes place in the solid state.

Photophysical Properties of the Cyanido Compounds 3a, 4a, 3b, 4b, 5, and 6 and TD-DFT Calculations. The UV−vis absorption spectra of compounds $[K(H_2O)][Pt(C\wedge N)(CN)_2]$ [C∧N = bzq (**3a**), ppy (**4a**)] and $NBu_4[Pt(C\wedge N)(CN)_2]$ (C∧N = bzq (**5**), ppy (**6**)) in methanol solution are represented in Figure 4; the data are summarized in Table 3. The absorption study on compound **6** was reported earlier by Kvam and co-workers[42,98] but is included

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Table 2. Structural Data for $[K(OCMe_2)_2][Pt(ppy)(CN)_2]$(**4c**)[a]

Bond Lengths [Å]					
Pt−C(1)	2.019(5)	Pt−C(2)	1.959(5)	Pt−C(3)	2.041(5)
Pt−N(1)	2.069(4)	K−O(1)	2.658(4)	K−N(2)	2.677(5)
K−O(2)	2.685(4)	K−O(2B)	2.788(4)	K−N(3A)	2.709(5)
K−K(0B)	3.907(2)				
Bond Angles [deg]					
C(2)−Pt−C(1)	89.5(2)	C(2)−Pt−C(3)	94.9(2)	C(1)−Pt−N(1)	95.1(2)
C(3)−Pt−N(1)	80.6(2)	N(2)−K−O(2)	134.2(1)	O(1)−K−N(2)	86.7(1)
O(1)−K−O(2)	97.6(1)	O(2)−K−N(3A)	95.9(1)	N(2)−K−N(3A)	128.5(2)
O(1)−K−N(3A)	98.9(1)	O(1)−K−O(2B)	171.8(1)	N(2)−K−O(2B)	92.3(1)
O(2)−K−O(2B)	88.9(1)	N(3A)−K−O(2B)	75.3(1)	N(2)−C(1)−Pt	179.5(5)
C(1)−N(2)−K	164.3(4)	N(3)−C(2)−Pt	178.8(5)	C(2)−N(3)−K(0A)	147.2(4)
K−O(2)−K(0B)	91.1(1)				

[a] Symmetry transformations used to generate equivalent atoms: (A) $x + 1/2, -y + 3/2, -z + 1$; (B) $-x - 1, -y + 1, -z + 1$.

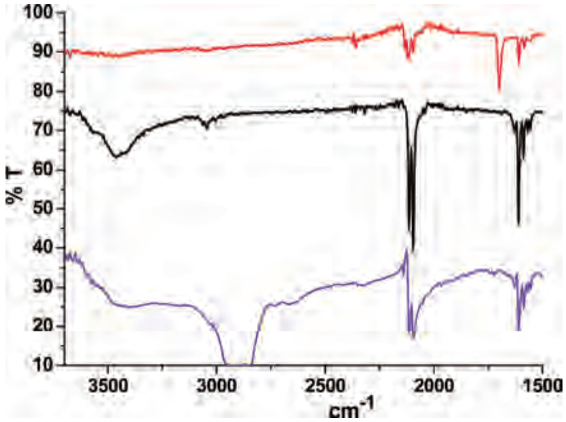

Figure 3. IR spectra of a crystal of $[K(OCMe_2)_2][Pt(ppy)(CN)_2]$(**4c**) (red —), the crystal of **4c** upon exposure to air; black —), and the crystal of **4a** (powder; blue —).

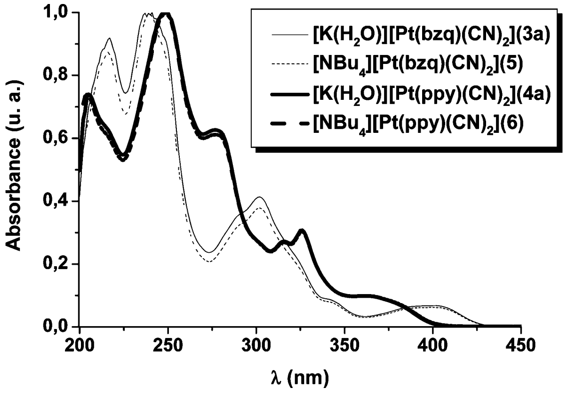

Figure 4. Normalized UV−visible absorption spectra of **3a**, **4a**, **5**, and **6** in methanol (10^{-4} M) at 298 K.

here for comparison. The UV−vis spectra in solution of compounds containing the same C∧N ligand (C∧N = bzq, **3a** and **5**; C∧N = ppy, **4a** and **6**) are identical, indicating that in a methanol solution the absorptions do not depend on the cation or the presence of water in the solid lattice. In agreement with previous assignments in analogous platinum complexes based on cyclometalated C∧N aromatic rings,[42,45,48,49,80,98–102] it seems plausible to assign the high-energy absorptions [$\lambda < 350$ nm (**3a**, **5**, C∧N = bzq), $\lambda < 340$ nm (**4a**, **6**, C∧N = ppy)] to a metal-perturbed ligand-centered transition (^{1}LC $\pi-\pi^*$) of the C∧N ligands, since the free ligands (H-bzq, Hppy) show LC transitions at $\lambda < 300$ nm under the same conditions,[101] and the less intense transitions at lower energy to spin-allowed, metal-to-ligand charge transfer transitions (^{1}MLCT). An alternative assignment of these low-energy bands as transitions of the type {[5d(Pt)][6p$_z$(Pt), π^*(C≡N)} is not favored since mononuclear Pt^{II} cyanido derivatives as *trans*-$[Pt(PCy_3)_2(CN)_2]$,[84] *trans*-$[Pt(P(n\text{-}Bu_3))_2(CN)_2]$,[103] or $[Pt(CN)_4]^{2-}$[104] do not absorb strongly at $\lambda > 300$ nm.

Taking into account that the auxiliary ligands in these kinds of complexes can alter the energy of the MO and therefore the transition energy, TD-DFT calculations were made. The B3LYP DFT calculations essentially reproduce the experimental structure of complex **5**, giving an overall picture of the valence orbitals (see the Supporting Information). The relative compositions of the different energy levels in terms of composing fragments are reported in Table 4. As can be seen, the HOMO is mainly formed by similar contributions of Pt(5d$_\pi$) (40%) and bzq π (45%) orbitals, with a smaller one due to the CN$^-$ ligands (14%), and the LUMO is largely located at the bzq site. Thus, it seems unambiguous that the lowest-energy absorption is better assigned to LC [π(C∧N) → π^*(C∧N)] transitions mixed with MLCT in character (see Figure 5, Table 5). By analogy, in complexes **3a** (C∧N = bzq) and **4a** and **6** (C∧N = ppy), the lowest-energy absorptions can be tentatively assigned to the same kind of transition.

As more extensive aromaticity in the bzq ligand with respect to ppy lowers the π^* energy level, a red shift is observed for the lower-energy MLCT/LC transition of complexes **3a** and **5** (C∧N = bzq) with respect to those of **4a** and **6** (C∧N = ppy).[49]

The UV−vis absorption spectra of compounds $[K(H_2O)][Pt(C∧N)(CN)_2]$ [C∧N = bzq (**3a**), ppy (**4a**)] in a water solution (10^{-4} M; Table 3, Figure 6) when compared to those in methanol show the expected solvatochromism of the low energy band in agreement with its MLCT character.

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Table 3. Absorption Data for Compounds **3**−**6** at Room Temperature

compound	absorption /nm (10^3 ε/M^{-1}cm^{-1})
[K(H$_2$O)][Pt(bzq)(CN)$_2$] (**3a**)	217 (39.9), 241 (43.4), 291 sh (15.6), 302 (18), 320 sh (10.5), 340 (4), 389 (2.9), 402 (3) (MeOH) 216 (34.3), 234 (41.5), 245 (29.2), 287 sh (17.3), 295 (18.2), 334 sh (3.1), 361 (3.9), 376 (4.4) (H$_2$O) 308, 402, 548 (solid)
K[Pt(bzq)(CN)$_2$] (**3b**)	316, 400 (solid)
[NBu$_4$][Pt(bzq)(CN)$_2$] (**5**)	216 (36.4), 239 (41.7), 248 sh (36.5), 291 (13.6), 302 (15.7), 318 sh (9.8), 341 (3.3), 389 (2.5), 401 (2.6) (MeOH) 330, 358, 410 (solid)
[K(H$_2$O)][Pt(ppy)(CN)$_2$](**4a**)	243 (27.7), 270 (23), 313 (8.7), 321 (8.6), 350 (3.4), 365 sh (2.8) (MeOH) 205 (28.6), 215 (24.5), 249 (38.7), 278 (24.2), 316 (10.5), 326 (11.9), 362 (3.8), 378 h (2.9) (H$_2$O) 330, 564 (solid)
K[Pt(ppy)(CN)$_2$] (**4b**)	200−420 (solid)
[NBu$_4$][Pt(ppy)(CN)$_2$] (**6**)	204 (25.1), 214 sh (21), 249 (33.9), 277 (20.8), 312 (9.1), 326 (10.3), 362 (3.3), 379 sh (2.6) (MeOH) 340, 382, 444 (solid)

Table 4. Population Analysis (%) for Complex NBu$_4$[Pt(bzq)(CN)$_2$] (**5**)

MO	Pt	CN	bzq
L+ 2	5	2	93
L+ 1	3	1	96
LUMO	3	1	96
HOMO	40	14	45
H-1	94	3	3
H-2	53	35	12
H-3	36	55	9
H-4	19	21	60
H-5	10	61	29

In the solid state, the differences are notable (Table 3). For both the red (**3a**) and purple (**4a**) compounds, a prominent absorption is observed at room temperature with maxima at 548 nm (**3a**) and 564 nm (**4a**), which is completely absent in their solution spectra and also in the spectra of the yellow solids **3b**, **4b**, **5**, and **6**, as can be seen in Figure 7 (compounds **4a**, **4b**, and **6**) and the Supporting Information (compounds **3a**, **3b**, and **5**). This absorption is assigned to ^{1}MMLCT [dσ*(Pt) → π*(C∧N)], and it is the responsible for the intense color showed by compounds **3a** and **4a**, characteristic of linear-chain platinum complexes with short Pt···Pt contacts (3.0 − 3.5 Å).[28,57,59,105,106]

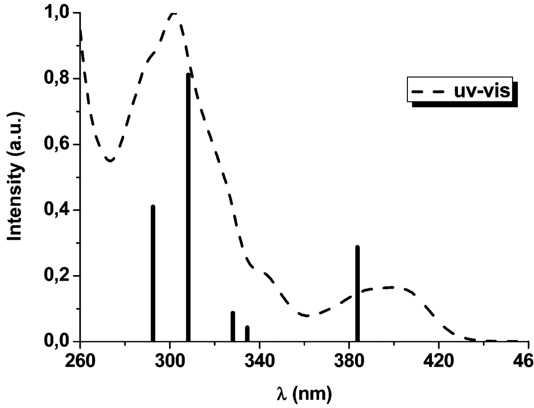

Figure 5. Calculated absorption spectrum (bars) of [Pt(bzq)(CN)$_2$]$^-$ in methanol and experimental UV−visible spectrum of **5** in methanol (10^{-4} M) at 298 K.

Table 5. TD-DFT Singlet Excitation Calculations for Complex NBu$_4$[Pt(bzq)(CN)$_2$](**5**) in Methanol

transition	contribution	o.s.	λexc (calc.)/nm
HOMO → LUMO	91%	0.0575	383.63
H-2 → LUMO	98%	0.0108	334.54
H-1 → LUMO	56%	0.0205	328.10
HOMO → L+1	−35%		
H-1 → LUMO	30%	0.1916	308.15
HOMO → L+1	49%		
H-5 → LUMO	56%	0.082	292.44
H-3 → LUMO	22%		
H-1 → L+1	14%		

Emission and Excitation Spectra. Complexes **3a**, **4a**, **5**, and **6**[42,98] exhibit luminescence in methanol solution at room temperature. At 77 K (Figure 8), in a rigid matrix of methanol, all of them show a vibronically structured emission

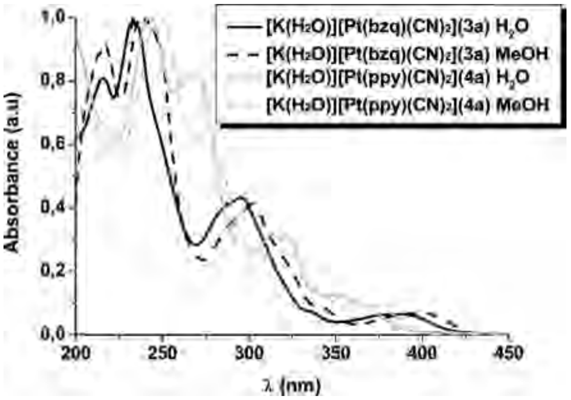

Figure 6. Normalized UV−visible absorption spectra of **3a** and **4a** in solution (10^{-4} M) at 298 K.

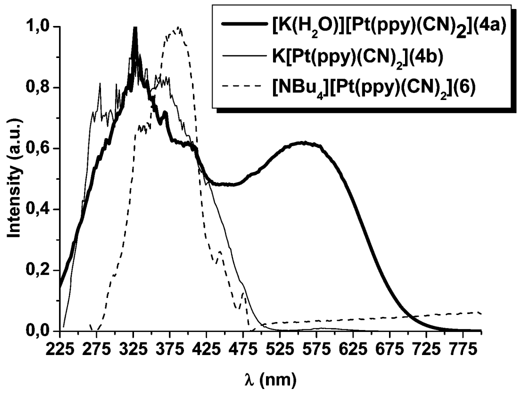

Figure 7. Normalized diffuse reflectance UV−visible spectra of **4a**, **4b**, and **6** in the solid state at 298 K.

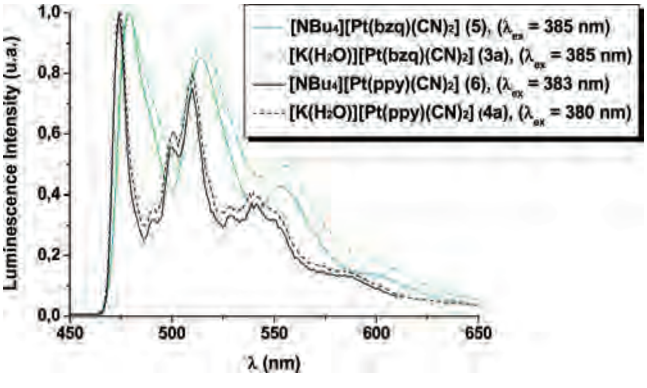

Figure 8. Normalized emission spectra in methanol at 77K of **3a**, **4a**, **5**, and **6**.

Table 6. Emission Features for Complexes **3a**, **3b**, **4a**, **4b**, **5**, and **6**

compound		λ_{exc}/nm	λ_{em}/nm	τ /μs
[K(H_2O)][Pt(bzq)$(CN)_2$] **3a**	MeOH (298 K)	(330−345), (385−400)	470 (sh), 484 (max), 498, 517 (tail to 650)	
	MeOH (77 K)	344, 386, 405	480 (max), 515, 553 (tail to 650)	
	solid (298 K)	(370−600)	716	0.20
	solid (77 K)	(425−600)	755	
K[Pt(bzq)$(CN)_2$] **3b**	solid (298 K)	(370−450)	636	1.72
	solid (77 K)	(370−475)	640	
[NBu_4][Pt(bzq)$(CN)_2$] **5**	MeOH (298 K)	325, (385−401)	469 (sh), 484 (max), 498, 517 (tail to 650)	
	MeOH (77 K)	344, 386, 405	479 (max), 514, 553 (tail to 650)	
	solid (298 K)	(370−460)	491 (sh), 506 (max), 523, 561 (tail to 650)	173 (506)
	solid (77 K)	(370−455)	489 (max), 498, 526, 539 (sh), 568 (tail to 650)	
	CH_2Cl_2 (298 K)	339, 350 (sh), 392, 406	470 (sh), 484 (max), 498, 517 (tail to 650)	
	CH_2Cl_2 (77 K)	340, (380−406)	482 (max), 518, 559 (tail to 650)	
[K(H_2O)][Pt(ppy)$(CN)_2$] **4a**	MeOH (298 K)	325, 368, 385 (sh)	479, 512, 540 (sh) (tail to 650)	
	MeOH (77 K)	325, 364, 383 (sh)	474 (max), 491 (sh), 500(sh), 510, 530, 540, 550 (tail to 650)	
	solid (298 K)	(425−600)	745	0.12
	solid (77 K)	(450−625)	790	
K[Pt(ppy)$(CN)_2$] **4b**	solid (298 K)	(370−475)	636	2.41
	solid (77 K)	(370−425)	585	
[NBu_4][Pt(ppy)$(CN)_2$] **6**	MeOH (298 K)	328, 366, 382	479, 512, 538 (sh) (tail to 650)	
	MeOH (77 K)	325, 364, 383	474 (max), 491, 500, 510, 539 (tail to 650)	
	solid (298 K)	(370−455)	488 (sh), 517 (max), 547, 595 (tail to 650)	23
	solid (77 K)	(370−400)	486, 516 (max), 552, 589	24
	CH_2Cl_2 (298 K)	339, 368, 383	481, 515, 544 (sh) (tail to 650)	
	CH_2Cl_2 (77 K)	328, 365, 378	477 (max), 494, 504, 513, 544 (tail to 650)	

upon excitation at wavelengths between 370 and 460 nm, typical of monomer species containing the same "Pt(C∧N)" metallocycles;[98,42,45,65,107] the excitation frequency, the vibronic spacing (1370−1420 cm^{-1}), and the band shape are consistent with mixed ^{3}MLCT/^{3}LC transitions with a high ^{3}LC character of the emissive state. The results are summarized in Table 6.

The water-soluble potassium compounds (**3a**, **4a**) are also luminescent in water at low and room temperatures. The emission spectrum of **3a** (Figure 9) in water solution at 298 K depends on concentration. Excitation of a 5 × 10^{-5} M solution results in a high energy band similar to that obtained in methanol, that is assigned also to mixed ^{3}MLCT/^{3}LC emissive states and a low energy band (λ_{max} = 600 nm) whose intensity grows as the concentration is increased at the expense of the high energy band. However, upon cooling a 1 × 10^{-4} M solution at 77 K, only one symmetric structureless band with maxima at 578 nm is observed upon excitation in a wide range of λ's (370−490 nm). As can be seen in Figure 9, the excitation spectrum of the low energy band (595 nm) at 298 K resembles the absorption spectrum, being therefore attributed to excimeric $\pi\pi^*$ excited states[37] generated by the association of an excited molecule with a ground-state one (for **3a** at 298 K). However, at low temperatures (77 K), the excitation spectrum has a different profile which is suggestive of emission coming from the formation of ground-state aggregates. For complex **4a** (Figure 10), having the phenylpyridinato ligand, the low-energy emission only appears at low temperatures (77K), even at a higher concentration (1 × 10^{-3}M), thus indicating that this complex has a lesser tendency to form aggregates.

Concentration-dependent emission spectra have been previously observed in other compounds as [Pt(4,7-diphenyl-1,10-phenantroline)(CN)][108,109] and [Pt(bpy)(C≡CC_6H_4-2,2′-dipyridylamine$)_2$][110] and [Pt(phen)(C≡CC_6H_4−2,2′-dipyridylamine$)_2$].[110]

In the solid state, all complexes emit both at room temperature and at 77 K. The emission spectra at room temperature (Figure 11, Table 6) reveal important differences depending on the cation and on the presence or not of water in the lattice. For complexes **5** and **6**, the band shape and the exceptionally long lifetime of 173 μs (λ = 506 nm) are consistent with the emission from mixed ^{3}MLCT/^{3}LC excited states with a high ^{3}LC character characteristic of the monomer species as in fluid solution. At lower temperatures, the emission has a more structured shape, but its nature is the same. The longer emission lifetime observed for **5** compared to that of **6**, at each temperature, indicates the

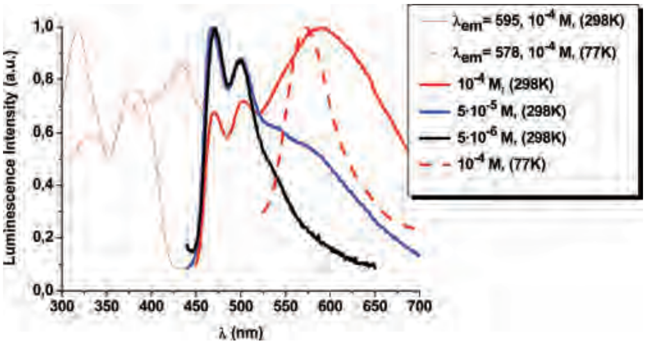

Figure 9. Normalized excitation and emission spectra of [K(H_2O)][Pt(bzq)$(CN)_2$] (**3a**) in H_2O.

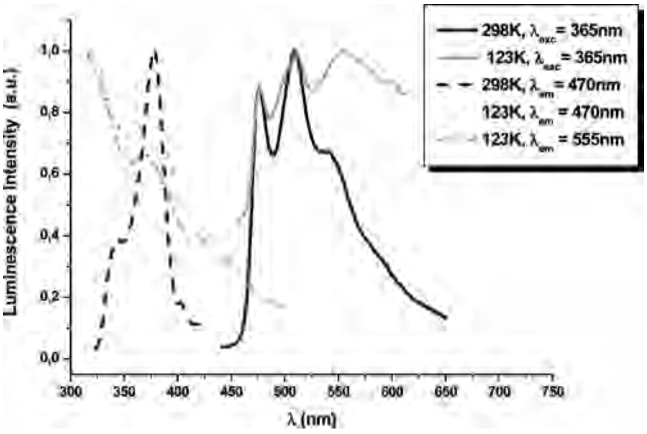

Figure 10. Normalized excitation and emission spectra of [K(H_2O)][Pt(ppy)$(CN)_2$] (**4a**) in water (10^{-3} M).

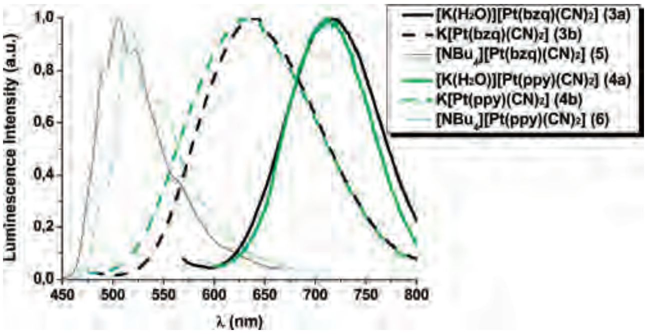

Figure 11. Normalized emission spectra in solid at 298 K of **3a** (λexc = 550 nm), **4a** (λexc = 550 nm), **3b** (λexc = 450 nm), **4b** (λexc = 450 nm), **5** (λexc = 370 nm), and **6** (λexc = 370 nm).

higher ^{3}LC character of the excited state,[43,45,49,82,111] as a result of the more extended π system of the bzq compared to ppy. The potassium derivatives, **3a**, **3b**, **4a**, and **4b**, reveal, both at room temperature and at 77 K, one broad structureless emission band, which is absent in methanol solution even at 77 K, and they do not depend on the excitation energy. Upon cooling to 77 K (Figure 12a and b, Table 5), the emissions of the anhydrous forms narrow slightly and undergo either no shift (**3b**) or a small shift to higher energy (**4b**), while the hydrated forms (**3a**, **4a**) suffer a significant red-shift in their emission maxima.

The band shape, lifetime, and thermal effects on emission in both hydrated compounds (**3a**, **4a**) are typical of MMLCT [$d\sigma^*(\mathrm{Pt}) \rightarrow \pi^*$] transitions in compounds with short Pt···Pt separations,[15,40,56,83,112] since investigations on Pt(II) linear-chain systems have demonstrated that, on cooling, a shortening of the Pt···Pt contacts between stacked complexes occurs, which results in a smaller HOMO−LUMO gap and a red-shift of the emission maxima.[55,56] The emissions observed in the spectra of the anhydrous forms (**3b**, **4b**) are consistent with the formation of aggregates in the ground state through $\pi-\pi$ interactions between adjacent monomers (see the Supporting Information, Figure S4), as observed for Pt(II) diimine; terpyridine; and C∧N, N∧N∧C, or N∧C∧N-cyclometalated complexes,[37,41,45,47,59,113–123] although the existence of Pt···Pt interactions cannot be completely ruled out, mainly for **3b** (298 K, 77 K) and **4b** at 298 K.

Hence, in these potassium derivatives, the change in the color from yellow (**3b** and **4b**) to red (**3a**) or purple (**4a**) due to the incorporation of water molecules into the lattice is accompanied by a red shift of the emission maxima, which reflects the shortening of the Pt···Pt separations. This behavior is just the opposite of that observed for the anhydrous red form of $[\mathrm{Pt(CN)_2(bpy)}]$ (bpy = 2,2′-bipyridine), which transforms to the yellow one, $[\mathrm{Pt(CN)_2(bpy)}]\cdot\mathrm{H_2O}$, by taking water molecules reversibly.[57,83,124] In this case, the presence of water molecules causes the change in the color from red to yellow, which is accompanied by a shift of the emission maxima [λ = 602 nm (red), 566 nm (yellow)] to a shorter wavelength as well as a lengthening of the Pt···Pt separations [3.35 Å (red); 3.33 Å and 4.68 Å (yellow)].[57]

Vapochromic Behavior of 3a. Thin films of the red potassium salt, **3a**, were exposed to a series of anhydrous VOCs at room temperature, including dichloromethane, methanol, ethanol, acetone, tetrahydrofuran, and acetonitrile. The solvent vapors were generated by slowly bubbling argon through a septum-capped flask containing the corresponding liquid.

Compound **3a** responds to all of these VOCs with the exception of dichloromethane, undergoing a pronounced change in color from red to yellow. The shortest response time is observed for methanol (~5 s), followed by ethanol (~10 s) or acetonitrile (~30 s), becoming longer for acetone (~ 2 min) and tetrahydrofuran (THF; ~45 min). In all cases, when vapor-exposed samples are left in the air or exposed to H_2O (v) (generated in the same way as the VOCs), they restore the original color (red) within seconds. The vapochromic response is fully reversible, and there was no change in behavior after repeated cycling of VOCs and H_2O (v) exposures.[125] However, the purple potassium salt, **4a**, does not show vapochromic behavior under the same conditions, perhaps because the water molecules are strongly bonded in the solid lattice, as was deduced from the TGA experiments.

Conclusions

The change of tetrabutylammonium by potassium as a counterion of the cyanidoplatinato complexes $[\mathrm{Pt(C{\wedge}N)(CN)_2}]^-$ (C∧N = bzq, ppy) allows the water-soluble organometallic compounds $[\mathrm{K(H_2O)}][\mathrm{Pt(C{\wedge}N)(CN)_2}]$ [C∧N = bzq (**3a**), ppy (**4a**)] to be prepared. They exhibit two forms: the water-containing $[\mathrm{K(H_2O)}][\mathrm{Pt(C{\wedge}N)(CN)_2}]$ [C∧N = bzq (**3a**), ppy (**4a**)] complexes and the anhydrous ones $\mathrm{K}[\mathrm{Pt(C{\wedge}N)(CN)_2}]$ [C∧N = bzq (**3b**), ppy (**4b**)], the former being strongly colored [red (**3a**) or purple (**4a**)] and the latter

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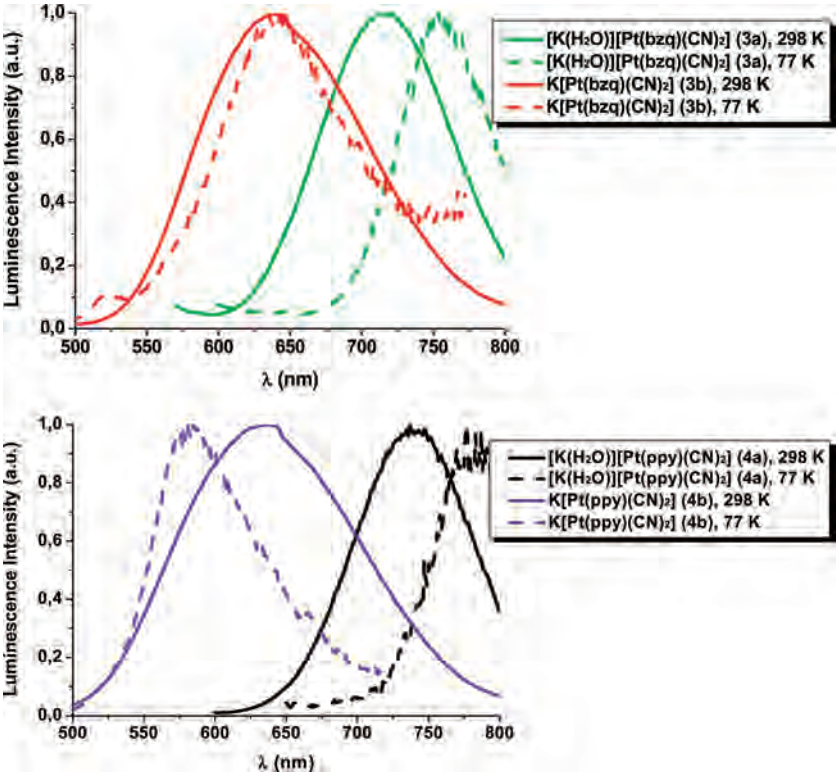

Figure 12. (a) Normalized emission spectra in solid of **3a** and **3b** at 298 K (—) and 77 K (---).b. Normalized emission spectra in solid of **4a** and **4b** at 298 K (—) and 77 K (---).

being yellow. Compounds **3a** and **4a** transform to **3b** and **4b** by heating at 110 °C for a while or by heating gently under a vacuum. Furthermore, **3b** and **4b** take up water molecules from the environment, regenerating the colored compounds within seconds, in a reversible way.

All of the potassium compounds are soluble and luminescent in a water solution at 298 and 77 K. In the solid state, both the red (**3a**) and purple (**4a**) solids show a prominent absorption at λ_{max} ca. 550 nm and one structureless emission band at $\lambda_{max} > 700$ nm that are typical of MMLCT [$d\sigma^*(Pt) \rightarrow \pi^*$] transitions in compounds with short Pt···Pt separations and that are absent in the yellow solids **3b**, **4b**, **5**, and **6**.

Hence, in these potassium derivatives, the change in color from yellow (**3b** and **4b**) to red (**3a**) or purple (**4a**) due to the incorporation of water molecules into the lattice is accompanied by a red shift of the emission maxima, which reflects the shortening of the Pt···Pt separations. This behavior is just the opposite of that observed for the anhydrous red form of [$Pt(CN)_2(bpy)$] (bpy = 2,2′-bipyridine) and the yellow one, [$Pt(CN)_2(bpy)$]·H_2O.

The red solid [$K(H_2O)$][$Pt(bzq)(CN)_2$] (**3a**) undergoes a pronounced change in its color, from red to yellow, when it is exposed to vapors of methanol, ethanol, acetonitrile, acetone, and THF but not of dichloromethane, with the response time observed for methanol being the shortest. Compound **3a** represents a new class of platinum(II) vapochromic compounds. Vapoluminescence studies on **3a** are in progress, and also the effect of different counterions on the structural and photoluminescent properties of these cyanido complexes.

Acknowledgment. This work was supported by the Spanish MEC (DGICYT)/FEDER Projects (CTQ2005-08606-C02-01 and CTQ2005-06807/BQU) and the Gobierno de Aragón (Grupo de Excelencia: Química Inorgánica y de los Compuestos Organometálicos).

Supporting Information Available: Drawing, table of atomic coordinates for the DFT-optimized structure of complex **5** and representative frontier orbitals for it. Crystallographic information file for the single-crystal structure determination of compound **4c**. Normalized diffuse reflectance UV−visible spectra of **3a**, **3b**, and **5** in the solid state at 298 K. Excitation spectra of **3b** and **4b** in the solid state and some experimental details about the preparation of samples for luminescence measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

IC800265Q

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(125) One of the reviewers suggested to us that the change of color **3a** from red to yellow upon exposure to VOCs could be due simply to the loss of water, but also to the absorption of organic vapors by the solid. We think that compound **3a** could absorb organic vapors, because the color of the exposed samples is not exactly the same as that of the anhydrous compound and because the changes take place under mild conditions; meanwhile, to remove the water from **3a** to get the anhydrous compound (**3b**), one needs to vacuum and/or heat the sample. However, we can't state this unambiguously because of the extremely sensitivity of all the samples towards humidity: if they are left in the air, they recover the color of the hydrated compound (red) within seconds, and we could not perform the IR or TGA on the exposed samples. The vapoluminescence study (in collaboration with other group) is in progress.