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Platinum(II) Complexes with Non-Innocent Ligands: Solid-Phase Synthesis, Redox Chemistry and Luminescence

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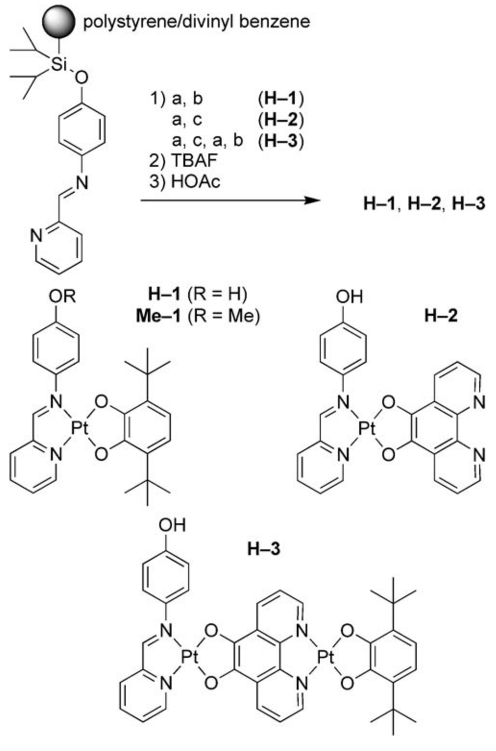
Describing the electronic structure of transition-metal complexes with open-shell ligands may not be a straightforward task in many cases; however, it is of fundamental importance for our understanding of their spectroscopic properties and their reactivity. Complexes with one potentially non-innocent ligand and a redox active central ion or complexes with two similar non-innocent ligands (e.g. catecholato/semiquinonato, amido/aminyl, α-diimine/α-diiminyl) have been extensively studied.[1,2]

Here, we report a phenol-substituted α-diimine ligand [4-(pyridine-2-ylmethylene)-amino]phenol (HO-N∩N′), which acquires a non-innocent character in conjunction with redox active catecholato/semiquinonato ligands (cat/sq) in platinum(II) complexes.

The diimine catecholato-platinum(II) complexes **H-1**, **H-2** and **H-3**, with HO-N∩N′ and 3,6-di-*tert*-butyl-catecholate as terminal ligands and 1,10-phenanthroline-5,6-diolate (O_2phen) as terminal/bridging ligands, were obtained by solid-phase synthesis.[3] For comparison reasons the methylated complex **Me-1** was prepared by solution methods (Scheme 1, for experimental details see Supporting Information). The principle of solid-phase synthesis of metal complexes as well as details of the ligand synthesis and its attachment to polystyrene/divinyl benzene support through a silyl ether linker has been reported by us.[3] The formation of immobilised platinum(II) complexes is indicated by an intense green colour of the resulting polymer. Liberation of the complexes from the support is achieved by cleaving the silyl ether with fluoride ions. The soluble anionic phenolate-substituted complexes 1^-, 2^- and 3^- produce bright turquoise solutions. Addition of acetic acid gives the deep green and poorly soluble neutral complexes **H-1**, **H-2** and **H-3**.[4] Complexes **H-1** and **H-2** possess two potentially (semi-)quinoid systems (*p*-iminoquinoid, *o*-quinoid), while **H-3** features three such building blocks (Scheme 1).



Scheme 1. Solid-phase synthesis of catecholatoplatinum(II) complexes **H-1**, **H-2** and **H-3**. a) Tris(norbornene)platinum(0); b) 3,6-di-*tert*-butyl-*ortho*-benzoquinone; c) 1,10-phenanthroline-5,6-dione. TBAF = tetra-*n*-butylammonium fluoride. HOAc = acetic acid.

The intense green colour of complexes **H-1**, **H-2** and **H-3** results from catecholato→diimine LLCT bands (Figure 1), similar to the analogous mono- and dinuclear complexes [Pt(O_2phen)(dbbpy)] and [Pt(dbbpy)(O_2phen)Pt(dbcat)] (dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine; dbcat = 3,5-di-*tert*-butyl-catecholato) prepared by Eisenberg.[5,6] The CT absorption bands are negatively solvatochromic (CH_2Cl_2/CH_3CN; **H-1**: 733/672 nm; **H-2**: 745/683 nm; **Me-1**: 740/

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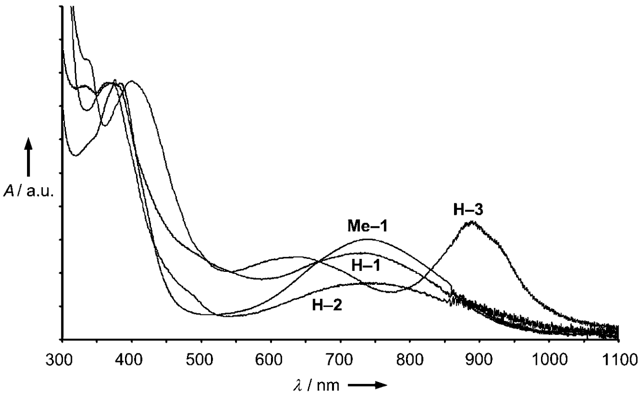


Figure 1. UV/Vis/NIR spectra of complexes **H-1**, **H-2**, **H-3** and **Me-1** in CH_2Cl_2.

672 nm). The dinuclear complex **H-3** displays two such catecholato→diimine LLCT bands, with the high-energy band being positively solvatochromic and the low-energy band being negatively solvatochromic (CH_2Cl_2/CH_3CN; 640/672 nm and 885/876 nm).

The extreme poor solubility of compounds **H-1**, **H-2** and **H-3** prevented recording of meaningful cyclic voltammograms that satisfy common standards. However, the methylated complex **Me-1** is soluble enough for CV experiments and is reversibly oxidised at 340 mV versus SCE in acetonitrile. The redox potential of **H-1** is estimated to be similar. Recently, Grinstaff and we reported the electrochemical and preparative oxidation of diiminecatecholatoplatinum(II) complexes to the respective *ortho*-benzosemiquinonatoplatinum(II) complexes.[7,8]

The preparative one-electron oxidation of **H-1**, **H-3** and **Me-1** was achieved by using silver(I) triflate (AgOTf) in CH_2Cl_2 (the redox potential of AgOTf is too low for **H-2**), resulting in the corresponding purple radical cations **H-1**$^{\cdot+}$, **H-3**$^{\cdot+}$ and **Me-1**$^{\cdot+}$, which are also rather insoluble. The radical cations display absorption bands typical for coordinated *ortho*-benzosemiquinonato radicals[7] at 460 (**H-1**$^{\cdot+}$), 489 (**H-3**$^{\cdot+}$) and 461 nm (**Me-1**$^{\cdot+}$) (see Figure 2 for the oxidation of **H-1** to **H-1**$^{\cdot+}$; for the pairs **H-3**/**H-3**$^{\cdot+}$ and **Me-1**/**Me-1**$^{\cdot+}$ see Supporting Information).

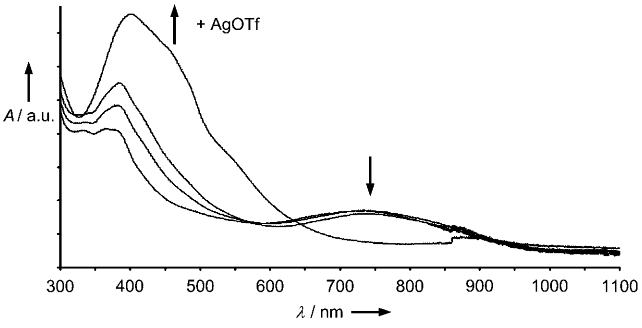


Figure 2. UV/Vis/NIR spectra during oxidation of **H-1** to **H-1**$^{\cdot+}$ with AgOTf in CH_2Cl_2.

The EPR spectra (see Supporting Information) of **H-1**$^{\cdot+}$, **H-3**$^{\cdot+}$ and **Me-1**$^{\cdot+}$ in THF at room temperature display isotropic signals with g values around 2.00 and hyperfine splitting constants to the platinum isotope $^{195}Pt(I={}^1/_2, 34\,\%)$ $A_{iso}(^{195}Pt) = 26$, 21 and 30 G, respectively, and to two protons $A_{iso}(2\times{}^1H) = 3.8$, 3.7and 4.0 G, respectively, which is fully compatible with analogous *ortho*-benzosemiquinonatoplatinum(II) complexes.[7,8]

In comparison with the EPR data of **H-1**$^{\cdot+}$ and **Me-1**$^{\cdot+}$, the experimental data of **H-3**$^{\cdot+}$ suggest that the radical character is mainly localised at the terminal cat/sq ligand in favour the bridging O_2phen ligand, which is also in accordance with the redox potentials of the respective ligands. DFT calculations[9] (B3LYP/LANL2DZ, for details see Supporting Information) additionally substantiate this delineation of **H-3**$^{\cdot+}$. The most prominent geometrical differences between **H-3** and **H-3**$^{\cdot+}$ are located at the terminal catecholatoplatinum(II) fragment. In particular, the Pt–O bond lengths of **H-3**$^{\cdot+}$ are elongated and the terminal ligand acquires a symmetrical semiquinoid structure. NBO analyses suggest that electron density at the platinum ions and at the O_2phen bridging ligand remains almost constant, while it is reduced by 0.65 at the terminal cat/sq ligand. The spin density (Mulliken analysis) is largely localised at the terminal cat/sq ligand (94 %). The hyperfine splitting constants estimated by DFT methods ($A_{iso}(^{195}Pt) = 16.0$ G and $A_{iso}(^1H) =$ 3.2 and 3.7 G); these results additionally support the proposed description of the radical cation **H-3**$^{\cdot+}$ as *ortho*-benzosemiquinonato complex.

Thus, **H-1**, **H-2**, **H-3** and **Me-1** as well as the oxidised complex cations **H-1**$^{\cdot+}$, **H-3**$^{\cdot+}$ and **Me-1**$^{\cdot+}$ are fully compatible with characterised $[Pt^{II}(cat/sq)(diimine)]$ compounds reported so far. However, in addition to the redox-active cat/sq ligands, **H-1**, **H-2** and **H-3** feature an acidic phenol substituent at the α-diimine-ligand. Deprotonation of **H-1**, **H-2** and **H-3** using the phosphazene base P_1-*t*Bu[10] furnishes the bright turquoise diamagnetic complex anions **1**$^-$, **2**$^-$ and **3**$^-$, respectively, which were already observed during the solid-phase synthesis (vide supra). De- and reprotonation is fully reversible as judged by UV/Vis spectroscopy (Figure 3). Deprotonation results in a hypochromic shift of the catecholato→diimine LLCT bands[11] from 733 to 570 nm (**H-1**/**1**$^-$), from 745 to 580 nm (**H-2**/**2**$^-$) and from 640 to 574 nm (**H-3**/**3**$^-$) in CH_2Cl_2. The low-energy LLCT band of **H-3** is shifted bathochromically from 885 to 1313 nm (CH_2Cl_2, **3**$^-$). The absorption bands of the anions are only weakly solvatochromic (CH_2Cl_2/CH_3CN; **1**$^-$: 570/580 nm; **2**$^-$: 580/587 nm; **3**$^-$: 574/580 nm). As expected, the UV/Vis/NIR spectrum of **Me-1** is unaffected by the presence of bases.

In analogy to known catecholatoplatinum(II) complexes[5–7,12] the neutral complexes **H-1**, **H-2**, **H-3** and **Me-1** are non-luminescent at room temperature in fluid solution. Likewise, the phenol-substituted α-diimine ligand and its conjugate base HO-N∩N′/[O-N∩N′]$^-$ and the known dichloroplatinum(II) complex $[PtCl_2(HO\text{-}N\cap N')]$ (**H-4**) and its conjugate base $[PtCl_2(O\text{-}N\cap N')]^-$ (**4**$^-$) do not emit under these conditions.[3b]

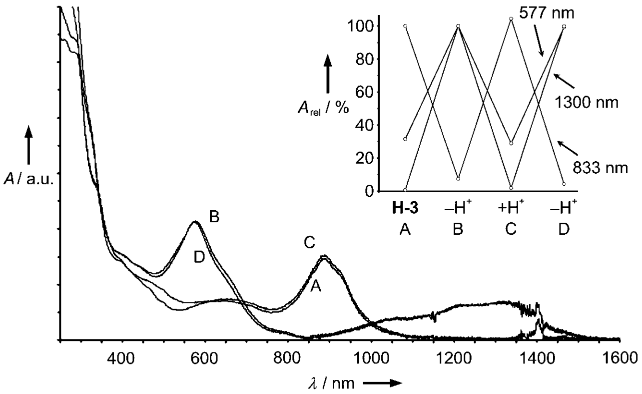


Figure 3. UV/Vis/NIR spectra of **H-3** (A), after deprotonation with P_1-*t*Bu (B), after re-protonation with TFA (C) and after repeated deprotation with P_1-*t*Bu (D) in CH_2Cl_2. The inset corroborates the reversibility by means of relative intensities of selected wavelengths.

Remarkably, the anionic complexes $\mathbf{1}^-$, $\mathbf{2}^-$ and $\mathbf{3}^-$ do emit at 512/528 nm, 503/518 nm and 514/533 nm (CH_2Cl_2/CH_3CN), respectively, when excited at a wavelength of 419 nm. The emission is slightly matrix-sensitive (positive solvatochromic). Figure 4 depicts the absorption spectrum, the emission spectrum and the excitation spectrum of $\mathbf{1}^-$ in CH_2Cl_2 (spectra of $\mathbf{2}^-$ and $\mathbf{3}^-$, as well as spectra in CH_3CN see Supporting Information). Maximum emission intensity is achieved using light with a wavelength of 416 (CH_2Cl_2) and 430 nm (CH_3CN). This is at significantly higher energy than required for the LLCT excitation. In addition the emission maximum occurs at higher energy than the LLCT absorption (Figure 4). The quantum yield amounts to about $\Phi = 2\times 10^{-4}$ and the lifetime lies at about $\tau_{av} = 3$ ns.[13]

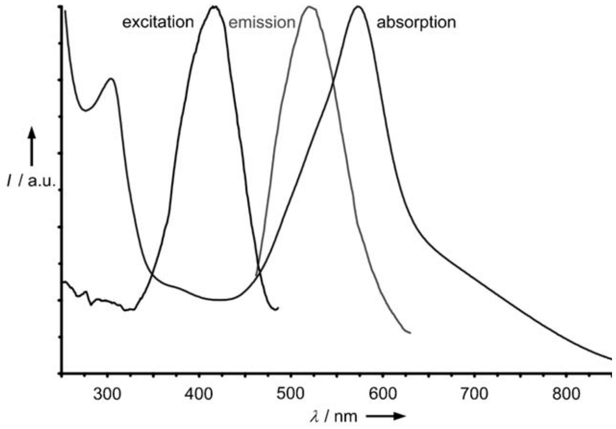
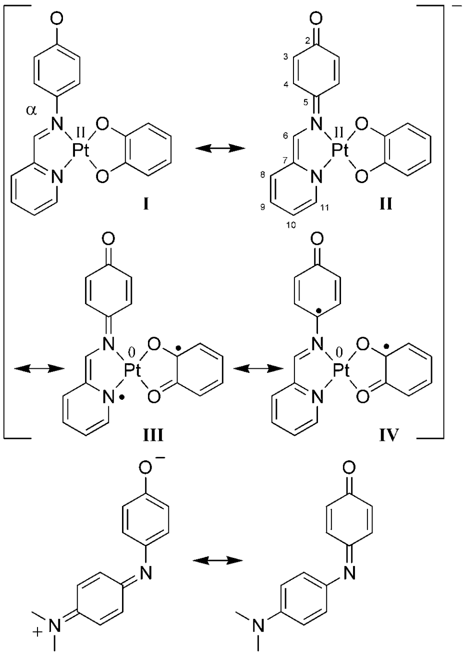


Figure 4. Normalised excitation ($\lambda_{obs} = 500$ nm), emission ($\lambda_{exc} = 419$ nm) and absorption spectra of $\mathbf{1}^-$ in CH_2Cl_2 at room temperature.

In frozen solution (77 K) the complex [Pt(dbbpy)(O_2phen)Pt(dbcat)] displays a weak low-energy ^{3}LLCT emission band at 700 nm.[6] These data do not support an emitting ^{3}LLCT state for $\mathbf{1}^-$, $\mathbf{2}^-$ and $\mathbf{3}^-$. However, the large Stokes shifts of 4510 ($\mathbf{1}^-$), 3870 ($\mathbf{2}^-$) and 4820 cm^{-1} ($\mathbf{3}^-$) in CH_2Cl_2 suggest triplets as the emitting states. Possibly, the $^3\pi$–π^* excited states of the platinum coordinated phenolatediimine ligand can be invoked as the emissive states.[14,15] However, the deprotonated ligand itself and the anionic dichloro complex $\mathbf{4}^-$ are non-emissive under these conditions. Thus the particular geometric and electronic structure of $\mathbf{1}^-$, $\mathbf{2}^-$ and $\mathbf{3}^-$ should be responsible for the observed room-temperature luminescence.

To this end the geometries of compounds **H-1**, **H-2**, **H-3** and **H-4** and of their conjugates bases $\mathbf{1}^-$, $\mathbf{2}^-$, $\mathbf{3}^-$ and $\mathbf{4}^-$ were optimised with DFT methods[9] (B3LYP/LANL2DZ, for details see Supporting Information). In the complex anions $\mathbf{1}^-$, $\mathbf{2}^-$ and $\mathbf{3}^-$ the phenolate ring is oriented almost coplanar to the PtN_2O_2 coordination plane (C4-C5-N-C6 torsion angle $\alpha \approx 0°$, Scheme 2, top). On the other hand, all other complexes **H-1**, **H-2**, **H-3**, **H-4** and $\mathbf{4}^-$ as well as the diimine ligand HO-N∩N′ and its conjugate base [O-N∩N′]$^-$ display torsion angles α significantly distinct from zero. The rotational profiles for the torsion angle α of **H-5** and $\mathbf{5}^-$ (Scheme 2; as simplified models of **H-1**, **H-2** and **H-3** and $\mathbf{1}^-$, $\mathbf{2}^-$ and $\mathbf{3}^-$) as well as of the dichloro derivatives **H-4** and $\mathbf{4}^-$ show several minima with low activation barriers for compounds **H-4**, **H-5** and $\mathbf{4}^-$, but only a single energy minimum at $\alpha = 0°$ with a higher barrier at $\alpha = 90°$ (80 kJ mol^{-1}) for $\mathbf{5}^-$ (see Supporting Information).



Scheme 2. Resonance formulae of $\mathbf{5}^-$ (top) and of phenol blue (bottom).

Evidently, combining phenolate and catecholato ligands results in planarisation and rigidification of the diiminephenolate ligand system in the anionic complex $\mathbf{5}^-$. At the same time the phenolate substituent acquires some *para*-iminoquinoid character (shortened C–O and C–N bond lengths and significantly distinct C–C bond lengths within the ring (see Supporting Information).

Assuming that the calculated barrier for $\mathbf{5}^-$ in its ground state is also almost valid for the emissive excited states of $\mathbf{1}^-$, $\mathbf{2}^-$ and $\mathbf{3}^-$, radiationless deactivation of the excited states through this torsional mode should be reduced and the observed luminescence of $\mathbf{1}^-$, $\mathbf{2}^-$ and $\mathbf{3}^-$ would result from planarisation and rigidification of the molecules caused by valence isomerisation (RIR = restriction of intramolecular rotations[16b]). A new chromophore with (semi-)iminoquinone character is thus formed (Scheme 2) and radiationless relaxation processes are diminished.[16] Formulating the diimine-phenolate ligand with iminoquinone character is experimentally supported by ^{1}H NMR spectroscopy. Deprotonation of **H-2** to give $\mathbf{2}^-$ shifts the signal of proton H3 (Scheme 2, top) by $\Delta\delta = 0.92$ ppm to lower frequencies. A shift with similar order of magnitude is observed for the corresponding signal of 4-ferrocenylazophenol [Fc-N=N-C_6H_4-OH] under alkaline conditions and a quinoid description has been invoked accordingly.[17] On the other hand the phenol/phenolate acid/base pair displays only a marginal shift of $\Delta\delta < 0.2$ ppm for the respective proton signal.

According to NBO analyses of $\mathbf{5}^-$, the negative charge of the anion is distributed on the diimine ligand (76 %), the cat/sq ligand (19 %) and platinum ion (5 %). The model complex $\mathbf{5}^-$, and thus complexes $\mathbf{1}^-$, $\mathbf{2}^-$ and $\mathbf{3}^-$, has to be described by several resonance formulae (Scheme 2, **I–IV**). Diradicaloid resonance formulae **III** and **IV**, which strengthen the *para*-iminoquinoid character, can only be drawn when both non-innocent ligands and the platinum atom cooperate (Scheme 2). Such formulations are impossible with simple innocent co-ligands such as chlorides in $\mathbf{4}^-$.

Resonance Raman spectra of $\mathbf{1}^-$, $\mathbf{2}^-$ and $\mathbf{3}^-$ (excitation at 514 nm, see Supporting Information) in CH_2Cl_2 reveal signals at 1610, 1584 and 1564 cm^{-1}, similar to signals observed for anilino radical *ortho*-benzosemiquinonatoruthenium(II) complexes (1611 and 1552 cm^{-1}),[2d] which additionally supports the (singlet-) diradical formulation[2j] **III** and **IV**. With respect to $\mathbf{4}^-$ the resonance formulae **III** and **IV** possible in $\mathbf{5}^-$ suggest an analogy of $\mathbf{5}^-$ to phenol blue dyes (Scheme 2, bottom; *N*-(4-dimethylaminophenyl)-*para*-benzoquinoneimine). A recent ab initio study for phenol blue (Scheme 2, bottom) has shown that ultrafast relaxation of the first excited singlet state S_1 to the ground state S_0 occurs in the vicinity of an S_1/S_0 conical intersection, which is characterised by an orthogonal arrangement of the *para*-iminoquinone and the *N*-substituent ($\alpha = 90°$).[18] In the anionic complexes $\mathbf{1}^-$, $\mathbf{2}^-$ and $\mathbf{3}^-$ an analogous radiationless relaxation pathway might be blocked as $\alpha = 90°$ corresponds to a transition state (in contrast to $\mathbf{4}^-$ and $[\text{O-N}\cap\text{N}']^-$) allowing for phosphorescence after intersystem crossing.

Novel complexes bearing different potentially non-innocent ligands (3,6-di-*tert*-butyl-catecholato; 1,10-phenanthroline-5,6-diolato; phenol-substituted α-diimine) coordinated to platinum(II) (**H-1**, **H-3**, **Me-1**) are oxidised to the corresponding radical cations **H-1**$^{\cdot+}$, **H-3**$^{\cdot+}$ and **Me-1**$^{\cdot+}$ with *ortho*-benzosemiquinonate character. Deprotonation of the phenol substituent of the α-diimine ligand in **H-1**, **H-2** and **H-3** yields the corresponding conjugate bases $\mathbf{1}^-$, $\mathbf{2}^-$ and $\mathbf{3}^-$, which are best described by invoking several resonance descriptions. The unique geometric and electronic structure of the anions $\mathbf{1}^-$, $\mathbf{2}^-$ and $\mathbf{3}^-$ allows for room-temperature luminescence in fluid solution in contrast to the neutral complexes or complexes with innocent chloro ligands in place to the cat/sq ligands. Compounds $\mathbf{1}^-$, $\mathbf{2}^-$ and $\mathbf{3}^-$ are thus members of a family of relatively rare platinum(II) complexes with co-ligands different from acetylide or thiolate that are emissive at room temperature in fluid solution[19] and which show proton-dependent luminescence quenching.[20]

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Keywords: dioxolene ligands · luminescence · platinum · radicals · solid-phase synthesis

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