

Radical anions of Pt(II) thiolates: Raman (spectro)electrochemical and isotopic substitution study

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Introduction

This contribution describes facility development of Raman (spectro)electrochemistry at the LSF, and the application of this technique, coupled with isotopic substitution, to identify diimine-localised vibrations in the radical-anions of Pt(II) diimine chloride and thiolate complexes.

Results and Discussion

I. A system for Raman (spectro)electrochemical studies has been constructed, consisting of a Sycopel Potentiostat, a standard flow system, a 2mm quartz tube as the Raman cell, and a 2-compartment /3-electrode cell for the electrogeneration of samples at controlled potentials. Samples were prepared under anoxic conditions and the flow system was deoxygenated prior to use with an Ar purge. The chromophores as DMF solution containing 0.2M ($t\text{Bu}_4\text{N}$)(BF_4) were first generated in the electrochemical cell then circulated through the flow system during the Raman data acquisition. In cases of extremely air-sensitive radicals, continuous electrolysis was performed during data acquisition.

II. Charge-separated excited states are key intermediate species in many natural (photosynthesis) and human-made (information processing, photocatalysis) applications. We have been developing a route to control charge separation in such excited states by generating a transient three-electron sulfur-sulfur bond, $\text{S} \cdot \cdot \text{S}$, which would act as a reservoir for the absorbed light quanta. $\text{Pt}(\text{NN})(\text{RS})_2$ ($\text{NN} = \text{diimine}$), possessing charge-separated lowest excited state, in which the formation of $\text{S} \cdot \cdot \text{S}$ can be anticipated, are explored as model compounds for this approach.^[1] Previous time-resolved resonance Raman studies^[2] provided vibrational signatures of their excited states, and suggested a presence of the $\nu(\text{SS})$ band in Raman spectra. However, the stringent assignment of the vibrations in the low frequency region, and the identification of $\nu(\text{SS})$, remains rather difficult, as many other vibrations (intra-ligand, $\nu(\text{Pt-N})$, $\nu(\text{Pt-S})$) are possible in this spectral region.^[3,4]

The charge separated excited state in model chromophores can be envisaged as a combination of $\text{NN}^{\cdot -}$ and three-electron bonded $\text{S} \cdot \cdot \text{S}$ moiety formed on a metal template, $^3[(\text{NN}^{\cdot -})\text{Pt}(\text{RS} \cdot \cdot \text{SR})]^*$. The present work is aimed at resonance Raman investigation of *in situ* generated radical anions of the model compounds, made possible due to the facile nature of their first reduction process.^[3] In these radical anions, the negative charge is localised mainly on the diimine moiety, such that the electronic structure may be envisaged as $[\text{Pt}(\text{NN}^{\cdot -})(\text{RS})_2]$.^[1]

Raman spectra of electrochemically generated (at -1.7 V vs. Fc^+/Fc) radical anions $[\text{Pt}(\text{NN}^{\cdot -})(4\text{-MeO-PhS})_2]$ ($\text{NN} = 4,4'$ -dimethyl-2,2'-bipyridine, or its d_{12} -perdeuterated analogue) were recorded. The corresponding $[\text{Pt}(\text{NN}^{\cdot -})\text{Cl}_2]$ were investigated for comparison. The probing wavelength was the 514 nm line of a cw Ar ion laser, to achieve resonance with the bpy-anion localised electronic transition.

As a background, the spectra of the chromophores prior to electrochemical reduction, acquired under identical experimental conditions, were used. The ground state of these chromophores was not in resonance with the probing wavelength.

The Raman data obtained by scaled subtraction of the spectra of the neutral species from the spectra of the fully reduced species, and the shift of individual vibrations upon deuteration, are summarized in Table 1, Fig. 1-3.

The following observations have been made.

1. Raman spectra of $[\text{Pt}(\text{NN}^{\cdot -})(4\text{-MeO-PhS})_2]$ and $[\text{Pt}(\text{NN}^{\cdot -})\text{Cl}_2]$ are virtually identical (Fig. 1), both by the band positions and the relative intensities. This fact is consistent with the LUMO being predominantly localised on the π^* orbital of the NN-unit^[1] (i.e., no resonances were expected from the RS part of the molecule). This also indicates that there is very little influence of the co-ligands on the vibrations of the diimine ligand. Therefore it is likely that all the vibrations registered for $[\text{Pt}(\text{NN}^{\cdot -})\text{Cl}_2]$ and $[\text{Pt}(\text{NN}^{\cdot -})(4\text{-MeOPhS})_2]$ will be present in the Raman spectra of the excited state (albeit subject to the degree of charge separation in the latter).

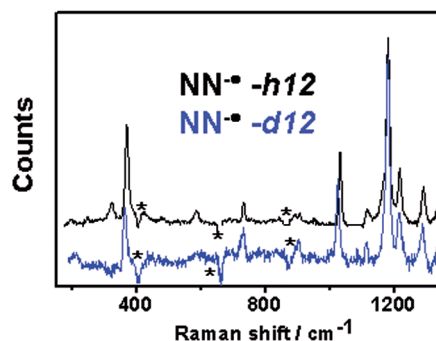


Figure 1. Raman spectra (DMF, RT, 514 nm) of $[\text{Pt}(4,4'\text{-diMe-bpy}^{\cdot -})(4\text{-MeO-PhS})_2]$ anion (blue line) and $[\text{Pt}(4,4'\text{-diMe-bpy}^{\cdot -})\text{Cl}_2]$ anion (black line). "*" - not fully compensated solvent bands.

The spectra are dominated by a band at 1524 cm⁻¹, which is attributed to a ν(CN) vibration, and accordingly displays rather moderate, -19 cm⁻¹, shift upon deuteration (Fig. 3).

An additional band at 585 cm⁻¹ was detected for [Pt(NN^{•-})Cl₂], which was not present in the spectrum of its thiolate counterpart. Nevertheless, it could be attributed to a bpy-localised vibration, as it shifts to 534 cm⁻¹ upon deuteration, and occurs at higher energies than one could expect for ν(Pt-Cl).

2. The data obtained for Pt(bpy)Cl₂, as a solid sample, under 457.8 nm pre-resonance with the MLCT absorption band, are given for comparison (Table 1). The vibrations which exhibit considerable shift upon formation of a radical anion, 386.9, 546, 769.4 and 1500/1563.6 cm⁻¹, indicate localisation of the LUMO.

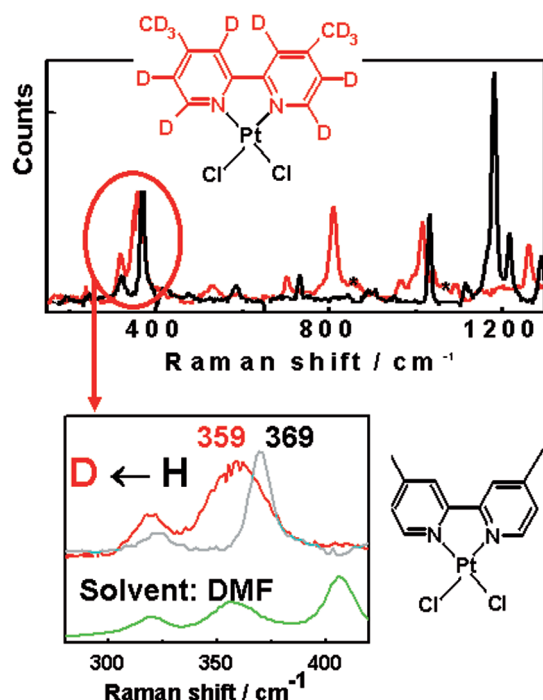


Figure 2. Raman (spectro)-electrochemical data for Pt(4,4'-diMe-bpy)Cl₂ (black lines) and its per-deuterated analog (red lines). DMF, RT, 514 nm.

3. *Isotopic substitution* (Fig. 2 and 3). All bands observed in the Raman spectra of the radical anions of the complexes show considerable negative isotopic shift (from -12 to -220 cm⁻¹) upon deuteration.^[3] This observation indicates that all the bands detected are due to bpy-localised vibrations and not due to Pt-S, Pt-N, or Pt-Cl vibrations.

4. The bands attributed to ring stretches of bpy, 1025 – 1216 cm⁻¹, exhibit an unusually large isotopic shift (Fig. 3).

5. A small but distinct isotopic shift of -10/-13 cm⁻¹ for the 363/9 cm⁻¹ band, and a presence of a 389 cm⁻¹ in the Raman spectrum of the neutral Pt(bpy)Cl₂, suggests that this band is also due to an intra-bpy vibration (Fig. 2 and 3, bottom). Previously, the vibration at 370 cm⁻¹ was assigned to an intra-bpy mode^[5] in [Fe^{II}(bpy)₃]²⁺ and

[Fe^{II}(bpy)₂(bpy⁻)]⁺. Interestingly, no shift in the vibrational frequency upon reduction has been reported, which may indicate a considerable charge delocalisation in the latter.

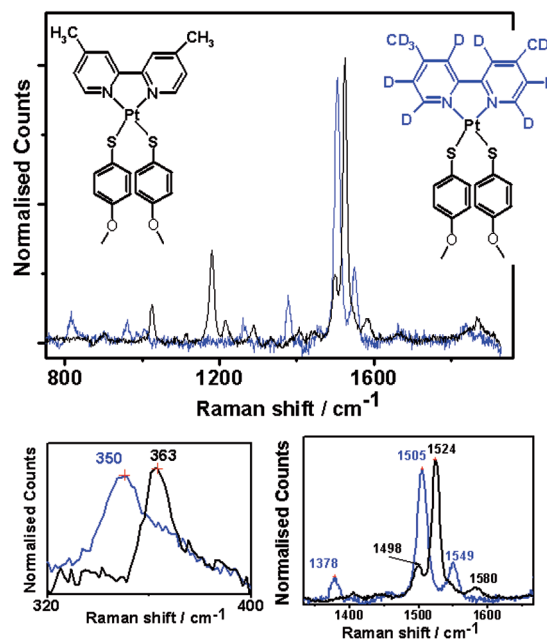


Figure 3. Raman (spectro)-electrochemical data for Pt(4,4'-diMe-bpy)(4-MeO-PhS)₂ (black) and its analog with perdeuterated dimethylbipyridine (blue lines). DMF, RT, 514 nm.

Table 1. Effect of deuteration of the NN=4,4'-diMe-bpy on the Raman frequencies of the electrochemically generated radical anions, 514 nm probing, DMF at RT.

[Pt(NN)(MeOPhS) ₂] ⁻			PtbpyCl ₂	[Pt(NN)Cl ₂]		
<i>h</i> ₁₂	<i>d</i> ₁₂	-Δ	neutral	<i>h</i> ₁₂	<i>d</i> ₁₂	-Δ
363 ^a	350	13	386.9 ^c	369	359	10
			546 ^c	585	534	51
731	701	30	769.4 ^c	732	704	28
1025 ^b	817	208	1027	1032	810	222
1112 ^b	962	150	1115	1116	964	152
1180 ^b	984	176	1176.7	1180	1017	163
1216 ^b	1006	210		1218	1041	177
1289	1261	28	1286	1292	1262	30
1498	1378	120				
1524	1505	19	1500 ^c			
1580	1549	31	1563.6 ^c			
1865	1838	27				

a – in cm⁻¹; ± 2 cm⁻¹; b – the correlation between the modes yet to be established; c – exhibit large shift upon reduction

Conclusions

A (spectro)electrochemical Raman set-up in LSF has been constructed. We have proved that electrochemical generation of the radical anion at potentials as negative as -1.7 V vs. Fc⁺/Fc is feasible in the system designed.

The bpy-localised vibrations were identified for $[\text{Pt}(\text{NN}^{\ominus})(\text{R})_2]$, (NN=4,4'-diMe-2,2'-bpy) by comparison between R=Cl and R = -S-Ph-OMe, and by means of isotopic substitution. No Pt-S, Pt-N, Pt-Cl or intra RS-ligand vibrations have been detected, consistent with the bpy-localised nature of the LUMO. The co-ligands do not affect the energies of the Raman active vibrations of the diimine anion. These data will be explored to assign the vibrations of $[\text{Pt}(\text{NN})(\text{R})_2]^*$ charge-transfer excited state, obtained by psTR³ in RAL.

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