# The nature of the [Pt(bipy)$_2$]$^{2+}$ ion in aqueous alkaline solution: a new look at an old problem †

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It has been known since 1973 that addition of NaOH (aq) to an aqueous solution of [Pt(bipy)$_2$](NO$_3$)$_2$·H$_2$O gives rise to changes in both the solution UV/Vis and solution $^1$H and $^{13}$C NMR spectra of the complex. These spectral changes have been variously interpreted as arising either from attack of OH$^-$ at C-6 of a bipyridine ligand to form a covalent hydrate, or coordination of OH$^-$ to the Pt ion to form a higher coordinate complex. In this paper, we utilise $^{195}$Pt NMR spectroscopy for the first time to study this system. The broad $^{195}$Pt NMR peak due to [Pt(bipy)$_2$]$^{2+}$ at −2273 ppm decreases in intensity on sequential addition of less than stoichiometric amounts of NaOH (aq) and a significantly narrower peak appears at −2094 ppm in proportion to the amount of NaOH (aq) added. Only the latter peak is observed after addition of one mol equivalent of NaOH (aq). Neither NaCl (aq) nor Na$_2$SO$_4$ (aq) affect the $^{195}$Pt NMR spectrum of [Pt(bipy)$_2$]$^{2+}$ but addition of half a mol equivalent of Na$_2$S$_2$O$_3$ (aq) gives a peak ~430 ppm upfield of that due to [Pt(bipy)$_2$]$^{2+}$. The $^{195}$Pt chemical shift of the structurally characterised pseudo-five-coordinate complex [Pt(phen)$_2$(CN)]$^+$ is −2726 ppm. Our results rule out deprotonation of a water molecule weakly coordinated to [Pt(bipy)$_2$]$^{2+}$ by the added NaOH (aq) and are consistent with formation of a conformationally mobile pseudo-five-coordinate complex.

## Introduction

The nature of the products formed on dissolution of homoleptic Pt(II) complexes of 2,2′-bipyridine (bipy) and its derivatives in aqueous alkaline solution has been the subject of intense controversy since the first study by Gillard and Lyons in 1973.[1] These authors contended that UV/vis and $^1$H NMR data obtained from aqueous alkaline solutions of [Pt(bipy)$_2$]$^{2+}$ and [Pt(5,5′-Me$_2$bipy)$_2$]$^{2+}$ were consistent with reversible attack of OH$^-$ at the 6-position of the bipy ligand to give a covalent hydrate (Scheme 1, pathway I). The alternative possibility, attack of OH$^-$ at the metal ion to give a five-coordinate complex (Scheme 1, pathway II), was discounted on the basis that addition of Cl$^-$ to the complexes gave no spectral changes.
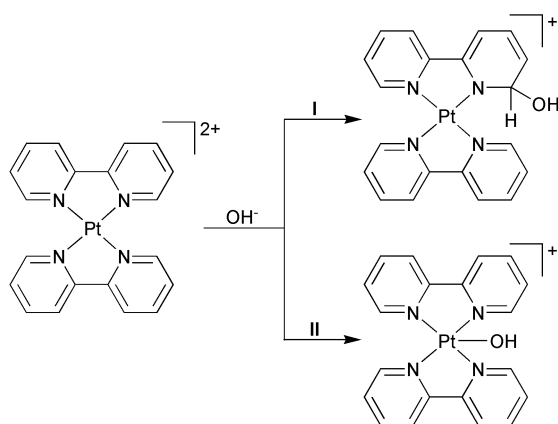


Scheme 1 Possible products from the reaction of [Pt(bipy)$_2$]$^{2+}$ with OH$^-$. Pathway I gives OH$^-$ attack at the ligand while Pathway II gives a five-coordinate complex.

This interpretation has since been the subject of considerable debate.[2–5] While both H$_2$O and OH$^-$ attack at a ring carbon of a number of free base, protonated and alkylated nitrogen heterocycles has been well documented, these heterocycles are, without exception, very electron deficient, usually containing two or more heteroatoms and/or electron-withdrawing substituents.[6–9] Crucially, neither bipy nor the $N$-methyl-2,2′-bipyridinium ion have been reported to undergo attack by OH$^-$ at a ring carbon, and Gillard and Lyons' interpretation thus requires Pt$^{2+}$ to have a remarkable and hitherto unrecognised Lewis acidity. Nord and coworkers proposed, on the basis of kinetic and $^1$H and $^{13}$C NMR studies, that OH$^-$ attacked [Pt(bipy)$_2$]$^{2+}$ at the metal ion to form a higher-coordinate complex, and noted that their NMR data were in fact inconsistent with attack of OH$^-$ at the ligand unless an extraordinarily rapid exchange of OH between the bipy ligands was occurring.[10,11] Although reports of analogous behaviour in *trans*-[Pt(py)$_4$Cl$_2$]$^{2+}$ [12] and *cis*-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ [13] have been effectively refuted,[14,15] debate as to the exact nature of the species present in aqueous alkaline solutions of [Pt(bipy)$_2$]$^{2+}$ continues.[16,17] Recent work has shown that OH$^-$ is not unique in modifying the UV/Vis spectrum of [Pt(bipy)$_2$]$^{2+}$ and other oxyanions (SO$_4$$^{2-}$, SO$_3$$^{2-}$, S$_2$O$_3$$^{2-}$, SeO$_3$$^{2-}$ and TeO$_3$$^{2-}$) also induce large spectral changes.[18] Of the many techniques used to study the [Pt(bipy)$_2$]$^{2+}$ system, $^{195}$Pt NMR spectroscopy is curiously absent, and surprisingly, as far as we can ascertain, the $^{195}$Pt chemical shift of the [Pt(bipy)$_2$]$^{2+}$ ion has not been reported in the literature.[19] This may be due, at least in part, to the difficulty in obtaining signals from PtN$_4$ systems, where both coupling of the Pt nucleus to four quadrupolar $^{14}$N nuclei and chemical shift anisotropy (CSA) effects at high magnetic field strengths result in very broad peaks.[20–22] In this paper, we detail results of our $^{195}$Pt NMR studies of [Pt(bipy)$_2$]$^{2+}$ and [Pt(phen)$_2$]$^{2+}$ on addition of a number of nucleophiles.

## Experimental

Elemental analyses were carried out at the Campbell Microanalytical Laboratory in the Department of Chemistry at the University of Otago.

[Pt(bipy)Cl$_2$] was prepared by the method of Osa *et al.*[23] (Found: C, 28.5; H, 1.9; N 6.5; Cl, 17.3. Calc. for C$_{10}$H$_8$Cl$_2$N$_2$Pt: C, 28.4; H, 1.9; N, 6.6; Cl, 16.8%).

[Pt(bipy)$_2$](ClO$_4$)$_2$ was prepared from [Pt(bipy)Cl$_2$] as described.[24] (Found: C, 34.2; H, 2.1; N 8.1; Cl, 10.0. Calc. for C$_{20}$H$_{16}$Cl$_2$N$_4$O$_8$Pt: C, 34.0; H, 2.3; N, 7.9; Cl, 10.0%). This was converted to the more soluble nitrate salt [Pt(bipy)$_2$](NO$_3$)$_2$·H$_2$O by treatment of a hot aqueous solution with Ph$_4$AsCl, removal of the precipitated Ph$_4$AsClO$_4$, and passage of the resulting solution through a column of Amberlite IR-45 anion exchange resin in the NO$_3^-$ form. The eluate was taken to dryness and the resulting yellow solid was recrystallised from hot water (Found: C, 36.8; H, 2.7; N 12.9. Calc. for C$_{20}$H$_{16}$N$_6$O$_6$Pt·H$_2$O: C, 37.0; H, 2.8; N, 12.9%).

[Pt(phen)$_2$]Cl$_2$·3H$_2$O was prepared from *cis*-[Pt(NH$_3$)$_2$Cl$_2$] by treatment with excess 1,10-phenanthroline[25] (Found: C, 41.9; H, 3.0; N 8.1; Cl, 10.2. Calc. for C$_{24}$H$_{16}$N$_4$Cl$_2$Pt.3H$_2$O: C, 42.4; H, 3.3; N, 8.2; Cl, 10.4%). Aqueous solutions of this complex at ambient pH slowly develop a slight green tinge and the crystalline solid obtained from such solutions gives a poor elemental analysis. The analytically pure product can only be obtained from slightly acidic solutions, which retain their bright yellow colour. The pure solid also appears to be slightly light-sensitive, slowly changing from bright yellow to green–yellow on exposure to ambient light.

$^{195}$Pt NMR spectra were obtained at 25.0 °C using a Varian VXR 300 MHz or Varian INOVA 500 MHz spectrometer at 64.325 and 107.132 MHz, respectively. Chemical shift values are reported relative to H$_2$PtCl$_6$ at 0 ppm by use of an external reference of K$_2$PtCl$_4$ in D$_2$O–DCl (−1620 ppm relative to H$_2$PtCl$_6$). Samples were dissolved in D$_2$O to give near-saturated solutions of the complexes, and stoichiometric amounts of aqueous solutions of NaOH, Na$_2$S$_2$O$_3$, NaCl, NaCN and Na$_2$SO$_4$ were added as appropriate. Data were collected over times ranging from 5 to 10 h and typical data collection parameters are given in Fig. 1. Reported chemical shifts were reproducible to ±5 ppm.
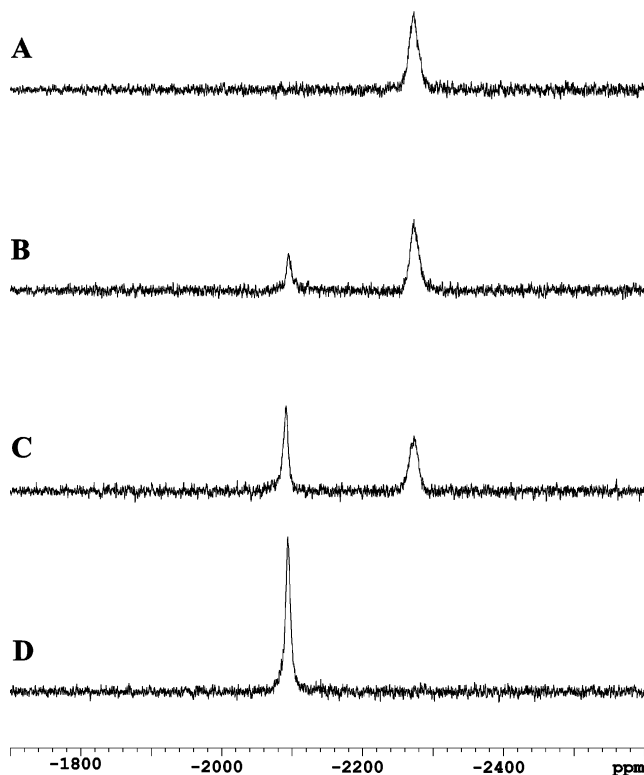


**Fig. 1** $^{195}$Pt NMR spectra (64.325 MHz, D$_2$O solution) at 25.0 °C of (A) [Pt(bipy)$_2$]$^{2+}$; (B) [Pt(bipy)$_2$]$^{2+}$ plus 0.2 mol equivalents of NaOH (aq); (C) [Pt(bipy)$_2$]$^{2+}$ plus 0.5 mol equivalents of NaOH (aq); (D) [Pt(bipy)$_2$]$^{2+}$ plus 1.0 mol equivalent of NaOH (aq). Data collection parameters: 21792 transients, sweep width 100000 Hz, line broadening 24 Hz, pulse width 15.0 μs, acquisition time 0.320 s, delay time 0.500 s. [Pt]$_{total}$ = 0.032 M in all spectra.

## Results and discussion

Fig. 1 shows $^{195}$Pt NMR spectra obtained from D$_2$O solutions of [Pt(bipy)$_2$](NO$_3$)$_2$·H$_2$O containing varying amounts of added NaOH (aq).

The $^{195}$Pt NMR (64.325 MHz) spectrum of [Pt(bipy)$_2$]$^{2+}$ in D$_2$O consists of a single broad ($w_{1/2}$ = 987 Hz) peak at −2273 ppm.[26] Such broad peaks have been observed previously in PtN$_4$ complexes,[27] the broadness being due to interactions of the $^{195}$Pt nucleus with the quadrupolar $^{14}$N nuclei.[20–22] The peak position is only slightly solvent dependent; the chemical shift of [Pt(bipy)$_2$]$^{2+}$ in D$_2$O and H$_2$O is the same within experimental error, while in d$_6$-DMSO the peak is observed at −2255 ppm. On addition of less than stoichiometric amounts of NaOH (aq) to a D$_2$O solution of [Pt(bipy)$_2$]$^{2+}$, the peak due to starting material at −2273 ppm loses intensity in proportion to the amount of NaOH (aq) added, and a significantly narrower ($w_{1/2}$ = 490 Hz) peak is observed at −2094 ppm. After addition of one mol equivalent of NaOH (aq), only the peak at −2094 ppm is observed. Addition of one mol equivalent of HNO$_3$ (aq) to this solution results in a spectrum identical to that of [Pt(bipy)$_2$]$^{2+}$, consistent with a reversible process. A solution of [Pt(bipy)$_2$]$^{2+}$ to which one mol equivalent of NaOH (aq) has been added shows no change in its $^{195}$Pt NMR spectrum over a period of three weeks at ambient temperature, showing that the reaction product is stable over a significant time period and that loss of a bipy ligand from the product does not occur to any observable extent. The $^{195}$Pt NMR spectrum of a D$_2$O solution of [Pt(bipy)$_2$]$^{2+}$ containing two added mol equivalents of NaOH (aq) shows only a single peak at −2094 ppm.

The effect of addition of other nucleophiles to solutions of [Pt(bipy)$_2$]$^{2+}$ was also investigated by $^{195}$Pt NMR. Addition of one mol equivalent of NaCl (aq) to a D$_2$O solution of [Pt(bipy)$_2$]$^{2+}$ resulted in a spectrum showing only a single peak at −2273 ppm, due to starting material. This agrees with previous work, where Cl$^-$ was reported to have no effect on the UV/vis spectrum of [Pt(bipy)$_2$]$^{2+}$.[1] However, while both SO$_4^{2-}$ and S$_2$O$_3^{2-}$ have been reported to induce large changes in the UV/vis spectrum of [Pt(bipy)$_2$]$^{2+}$ [18] only S$_2$O$_3^{2-}$ affects the $^{195}$Pt NMR spectrum. Addition of half a mol equivalent of Na$_2$S$_2$O$_3$ (aq) results in observation of two peaks in the $^{195}$Pt NMR spectrum, one at −2273 ppm due to starting material and the other at −2704 ppm. As also seen on addition of NaOH (aq), the product peak is significantly less broad ($w_{1/2}$ = 474 Hz) than that of the starting material. Attempts to record spectra in the presence of NaCN (aq) were thwarted by rapid precipitation of the product. The $^{195}$Pt NMR spectrum of [Pt(phen)$_2$]$^{2+}$ in D$_2$O shows a single broad peak at −2254 ppm. Addition of less than stoichiometric amounts of NaOH (aq) resulted in rapid precipitation of a dark green solid. However, addition of half a mol equivalent of NaCN (aq) resulted in a $^{195}$Pt spectrum containing two peaks, one at −2264 ppm due to starting material, and the other at −2726 ppm, due to the pseudo-five-coordinate complex [Pt(phen)$_2$(CN)]$^+$.[28]

The above observations show that the reaction of [Pt(bipy)$_2$]$^{2+}$ with OH$^-$ proceeds to completion on the addition of one mol equivalent of NaOH (aq) to give a stable product, which may then be converted back to [Pt(bipy)$_2$]$^{2+}$ on addition of HNO$_3$ (aq). Such observations are in agreement with those made using spectrophotometry by previous workers.[1] The observation of individual peaks for [Pt(bipy)$_2$]$^{2+}$ and the product in the $^{195}$Pt NMR spectrum confirms that these two species do not equilibrate rapidly (NMR timescale) and this rules out Nord's original proposal that the added OH$^-$ deprotonates a water molecule loosely bound to [Pt(bipy)$_2$]$^{2+}$;[10] if this were the case, only one $^{195}$Pt NMR peak would be seen under all conditions of [OH$^-$] studied. The small difference observed in the chemical shift of [Pt(bipy)$_2$]$^{2+}$ on changing the solvent from D$_2$O to d$_6$-DMSO also argues against the presence of a coordinated water molecule [29] and the change in the $^{195}$Pt chemical
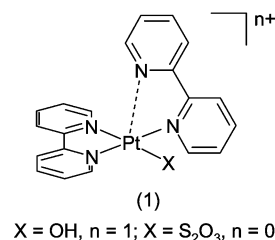
**Table 1** $^{195}$Pt NMR chemical shifts of selected platinum complexes

| Complex | $\delta$/ppm | Reference |
|---|---|---|
| $[Pt(bipy)_2]^{2+}$ | $-2273$ | This work |
| $[Pt(bipy)_2]^{2+}$ + 1 equiv. NaOH (aq) | $-2094$ | This work |
| $[Pt(bipy)_2]^{2+}$ + 1/2 equiv. Na$_2$S$_2$O$_3$(aq) | $-2273, -2704$ | This work |
| $[Pt(bipy)_2]^{2+}$ + 1 equiv. Na$_2$SO$_4$(aq) | $-2273$ | This work |
| $[Pt(bipy)_2]^{2+}$ + 1 equiv. NaCl(aq) | $-2273$ | This work |
| $[Pt(phen)_2]^{2+}$ | $-2254$ | This work |
| $[Pt(phen)_2(CN)]^+$ | $-2726$ | This work |
| $[Pt(bipy)(OH)_2]$ | $-1776$ | 32 |
| $[Pt(NH_3)_2(H_2O)_2]^{2+}$ | $-1593$ | 31 |
| $[Pt(NH_3)_2(OH)(H_2O)]^+$ | $-1601$ | 31 |
| $[Pt(NH_3)_2(OH)_2]$ | $-1572$ | 31 |
| $[Pt(NH_3)_2Cl(H_2O)]^+$ | $-1841$ | 31 |
| $[Pt(NH_3)_2Cl(OH)]$ | $-1826$ | 31 |



(1)

$X = OH$, $n = 1$; $X = S_2O_3$, $n = 0$

shifts observed in both $[Pt(NH_3)_2(H_2O)_2]^{2+}$ and $[Pt(NH_3)_2Cl(H_2O)]^+$ on deprotonation of a coordinated water molecule is much smaller than that observed in this system (see Table 1). The magnitude (~180 ppm) and direction (downfield) of the $^{195}$Pt chemical shift change on addition of OH$^-$ to solutions of $[Pt(bipy)_2]^{2+}$ are consistent with the formation of a pseudo-five-coordinate complex. Direct attack of OH$^-$ at the Pt centre should result in a significant change in chemical shift, the magnitude of which is difficult to predict given the paucity of directly comparable species in the literature. However, it is informative to note that the chemical shift of $[Pt(bipy)(OH)_2]$ lies 497 ppm downfield of $[Pt(bipy)_2]^{2+}$ (Table 1) and it might be expected that the chemical shift of a species such as $[Pt(\eta^2\text{-bipy})(\eta^1\text{-bipy})(OH)]^+$ would lie between these values, as is indeed observed. A downfield shift is consistent with a hard ligand entering the coordination sphere of the metal and displacing a softer ligand and would thus be expected on coordination of OH$^-$ at the expense of an aromatic N-donor.[20–22,30] The decreased linewidth of the products obtained on addition of NaOH(aq) and Na$_2$S$_2$O$_3$(aq) to $[Pt(bipy)_2]^{2+}$ are consistent with replacement of a quadrupolar N atom by an $I = 0$ S or O atom. Attack of a nucleophile at the bipy ligand would not disrupt the PtN$_4$ coordination sphere and $^{195}$Pt NMR linewidths comparable to those of the starting material should thus result.

While all of our observations appear to be consistent with the formation of a complex in which an N donor atom has been replaced by an O or S atom, the lack of similar systems for comparison renders these conclusions somewhat equivocal. However, it is known that $[Pt(phen)_2]^{2+}$ reacts with CN$^-$ to give a pseudo-five-coordinate complex in which CN$^-$ occupies a coordination site in the square plane.[28] Our attempts to observe analogous behaviour in $[Pt(bipy)_2]^{2+}$ were thwarted by essentially instantaneous precipitation of the product in the NMR tube on addition of NaCN(aq). However, we were able to record the $^{195}$Pt NMR spectrum of a D$_2$O solution of the pseudo-five-coordinate complex $[Pt(phen)_2(CN)]^+$, the peak at $-2726$ ppm being ~ 470 ppm upfield of that due to starting material. Similar behaviour was observed on addition of Na$_2$S$_2$O$_3$(aq) to a solution of $[Pt(bipy)_2]^{2+}$, with a peak due to the product ~ 430 ppm upfield of the starting material. By analogy with $[Pt(phen)_2]^{2+}$, we believe this product to be $[Pt(bipy)_2(S_2O_3)]$, a pseudo-five-coordinate complex containing an S-bound thiosulfate ligand. The upfield shifts observed in both systems are as expected for coordination of a soft donor atom to the Pt ion.

Our results are consistent with a conformationally mobile structure such as **1**, in which one pyridine nitrogen atom has been displaced by an entering OH$^-$ or S$_2$O$_3^{2-}$ ligand. The displaced pyridine nitrogen atom may occupy an apical position, but any interaction of this atom with the Pt centre will be very weak. Wernberg and Hazell have shown that such a structure is consistent with the $^1$H and $^{13}$C NMR spectra of $[Pt(phen)_2(CN)]^+$[28] and we believe the same arguments apply to both $[Pt(bipy)_2(OH)]^+$ and $[Pt(bipy)(S_2O_3)]$. Indeed, the $^1$H NMR spectrum of $[Pt(bipy)(S_2O_3)]$ consists of two broad, unresolved peaks at 7.99 ($w_{1/2} = 24$ Hz) and 7.42 ($w_{1/2} = 36$ Hz) ppm, consistent with a structure having conformational mobility.

In conclusion, we have shown that, contrary to previous reports,[17] $^{195}$Pt NMR spectroscopy is a viable tool for solution studies of homoleptic Pt(II) complexes of 2,2′-bipyridine and 1,10-phenanthroline. Our observations are consistent with attack of OH$^-$ at the metal centre of these complexes and there is no need to invoke unprecedented reactivity of metal-coordinated bipyridine and phenanthroline ligands to explain the obtained data.

## Acknowledgements

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