

Metal–metal interactions of aqueous lead(II) and tin(II) ions with the ground and excited states of tetrakis(μ -diphosphito)diplatinatate(II)

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Abstract

The interactions of the metal–metal bonded compound tetrakis(μ -diphosphito)diplatinatate(II), $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$, in its ground state (Pt_2 ; $\lambda_{\text{abs}}=368$ nm) and lowest energy triplet excited state ($^*\text{Pt}_2$; $\lambda_{\text{lum}}=514$ nm) with the metal ions Pb^{2+} and Sn^{2+} in aqueous solution are investigated by electronic absorption and photoluminescence spectroscopies. New bands in the visible region of the absorption spectrum are assigned to charge transfer transitions from Pt_2 to Pb^{2+} and Sn^{2+} . These transitions are proposed to result from ground state metal–metal interactions of Pb^{2+} and Sn^{2+} with Pt at the axial sites of Pt_2 , interactions which also appear to be responsible for the observed static quenching of $^*\text{Pt}_2$ by these ions. In the case of Pb^{2+} in aqueous acid solutions ionic strength-dependent diffusional quenching of $^*\text{Pt}_2$ occurs ($k \approx 10^9$ – 10^{10} l mol $^{-1}$ s $^{-1}$), and no evidence for ground state interactions was found. The quenching process is proposed to be due to an excited state electron transfer reaction from $^*\text{Pt}_2$ to Pb^{2+} yielding Pt_2^+ and Pb^+ . These results are consistent with recent estimates of the reduction potentials of the $\text{Pt}_2^+/^*\text{Pt}_2$ and $\text{Pb}^{2+}/\text{Pb}^+$ redox couples and enable an estimate of $E^\circ > -1.6$ V versus NHE for the aqueous $\text{Sn}^{2+}/\text{Sn}^+$ couple to be made. The sharply contrasting behavior between the isoelectronic Pb^{2+} and Tl^+ ions towards Pt_2 and $^*\text{Pt}_2$ is discussed in the context of these results.

Keywords: Metal–metal interactions; Platinum complexes; Diphosphito complexes; Dinuclear complexes; Lead ions; Tin ions

1. Introduction

The metal–metal bonded compound $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ (Pt_2) has been the focus of much recent interest [1]. One of its most notable features is its intense green phosphorescence in aqueous solution upon excitation at 368 nm. We have recently demonstrated that Tl^+ ions interact with this excited state ($^*\text{Pt}_2$) to form luminescent exciplexes [2] in which Tl^+ ions appear to interact with the luminescent Pt–Pt moiety at the vacant axial sites in $^*\text{Pt}_2$. Ground state interactions between Tl^+ and Pt in square planar Pt(II) compounds have been structurally characterized in $\text{Tl}_2\text{Pt}(\text{CN})_4$ [3], $\text{Tl}(\text{crown-P}_2)\text{Pt}(\text{CN})_2^+$ (crown- P_2 is $\text{Ph}_2\text{PCH}_2\text{N}(\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4)_2\text{NCH}_2\text{PPH}_2$) [4] and *cis*- $[(\text{NH}_3)_2\text{Pt}(\text{1-MeT})_2\text{Tl}(\text{1-MeT})_2\text{Pt}(\text{NH}_3)_2]\text{NO}_3 \cdot 7\text{H}_2\text{O}$ (1-MeT is

1-methylthyminato) [5]. The bonding between Tl^+ and Pt in $\text{Tl}_2\text{Pt}(\text{CN})_4$ has been shown to involve the filled 6s and empty 6p $_z$ frontier orbitals of Tl^+ overlapping with the filled σ^* (5d $_{z^2}$) and empty $\sigma(6p_z)$ frontier orbitals of Pt, for which relativistic effects are important [6]. Several other examples of such ground state metal–metal bonding involving a variety of s 2 metal ions and square planar metallomacrocycles of Ir(I) have also been reported [7].

Since the isoelectronic Pb^{2+} ion is also known to bond to Pt in square planar Pt(II) compounds, including $[(\text{CH}_3\text{CO}_2)\text{Pb}(\text{crown-P}_2)\text{Pt}(\text{CN})_2](\text{O}_2\text{CCH}_3)$ [4], we have undertaken a study of its interactions with Pt_2 and $^*\text{Pt}_2$ using electronic absorption and photoluminescence spectroscopies in order to compare its behavior to the Tl^+ ion. The results of that work as well as studies of the interactions of the related s 2 metal ion Sn^{2+} with Pt_2 are reported herein.

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2. Experimental

2.1. Potassium tetrakis- μ -diphosphito(P, P')diplatinate(II) dihydrate

Samples were prepared according to established procedures [8] and were stored in the dark under nitrogen to prevent decomposition.

2.2. Other materials

Aesar lead(II) nitrate (99.999% metal purity), Fluka tin(II) trifluoromethanesulfonate (>97% purity), Burdick and Jackson HPLC grade water, and Baker ACS reagent grade HClO_4 , HNO_3 , H_2SO_4 and KNO_3 were used as received.

2.3. Physical measurements

An NSG Type 71 FL-H quartz luminescence cell designed for convenient degassing was used to purge aqueous solutions of oxygen with a stream of high purity nitrogen gas passed through an Alltech Associates oxygen trap and connected to the cell via a teflon tube inserted directly into its glass arm. The concentration of Pt_2 in aqueous solution was determined by absorbance measurements at 368 nm ($\epsilon = 3.45 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$). Glassware was carefully cleaned with aqua regia or concentrated nitric acid followed by thorough rinsing with water to remove traces of metal ions and other impurities. All spectroscopic measurements were made within 3 h after preparation of the solutions to minimize problems due to sample decomposition.

Absorption spectra were recorded with a Shimadzu UV-240 spectrophotometer (1 nm slit widths) interfaced to an IBM-PC computer and controlled with Shimadzu PC-265 Spectroscopy Interface software. Luminescence and luminescence excitation spectra were recorded with a SPEX 1680 0.22 m double monochromator luminescence spectrophotometer interfaced to an IBM-PC computer. A 450-W xenon lamp, slit widths of 1 or 2 nm, and an integration time of 1 s were used in all cases. Both luminescence and luminescence excitation spectra were corrected for instrumental response variations. All spectral data files were imported into the Spectra Calc (Galactic Industries) computer program and converted from wavelengths to wavenumbers for analysis.

3. Results

Absorption spectra of aqueous solutions of $5 \times 10^{-6} \text{ mol l}^{-1} \text{ Pt}_2$ with and without added Pb^{2+} (from $\text{Pb}(\text{NO}_3)_2$) are shown in Fig. 1. In the presence of Pb^{2+} the 368 nm band of Pt_2 is seen to disappear and

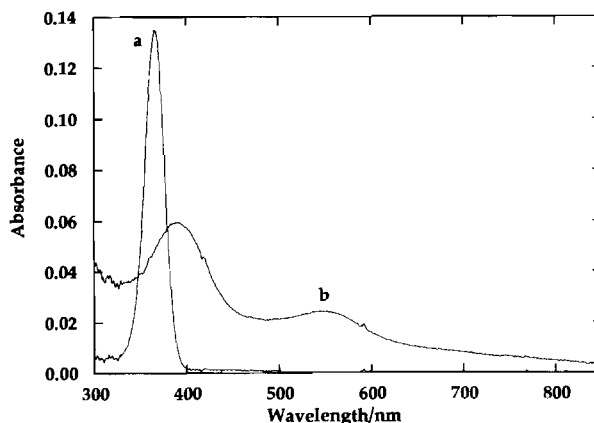


Fig. 1. Absorption spectra of $5 \times 10^{-6} \text{ mol l}^{-1}$ aqueous Pt_2 in the absence (a) and presence (b) of $8 \times 10^{-5} \text{ mol l}^{-1} \text{ Pb}^{2+}$.

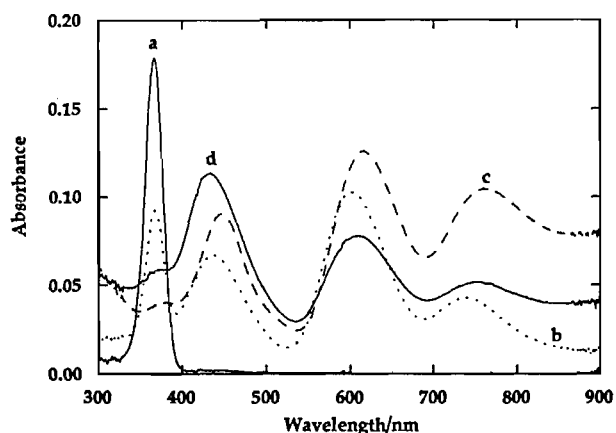


Fig. 2. Absorption spectra of $5 \times 10^{-6} \text{ mol l}^{-1}$ aqueous Pt_2 in the absence (a) and presence of (b) $8 \times 10^{-5} \text{ mol l}^{-1} \text{ Sn}^{2+}$, (c) $2.4 \times 10^{-4} \text{ mol l}^{-1} \text{ Sn}^{2+}$, and (d) $1.0 \times 10^{-4} \text{ mol l}^{-1} \text{ Sn}^{2+}$ and $0.01 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$.

is replaced by broad bands located at about 393 and 550 nm. At high concentrations of Pb^{2+} a blue-brown color results, accompanied by the formation of a brownish precipitate. In contrast, in solutions of $0.01 \text{ mol l}^{-1} \text{ HClO}_4 \text{ Pb}^{2+}$ has no effect on the Pt_2 absorption spectrum, and no color changes or precipitation at high Pb^{2+} concentrations were observed.

Absorption spectra of aqueous solutions of $5 \times 10^{-6} \text{ mol l}^{-1} \text{ Pt}_2$ with and without added Sn^{2+} (from $\text{Sn}(\text{CF}_3\text{SO}_3)_2$) are shown in Fig. 2. In the presence of Sn^{2+} the color of the solution becomes bright green as the 368 nm band of Pt_2 disappears and is replaced by broad bands located at 430–450, 600–620 and 735–765 nm. At high concentrations of Sn^{2+} a bright green precipitate forms. In contrast to the situation for Pb^{2+} , acid has little effect on the observed absorption spectrum changes with Sn^{2+} , the most notable difference being the reversal of the magnitude of the relative absorbances of the bands located at about 440 and 610 nm (Fig. 2).

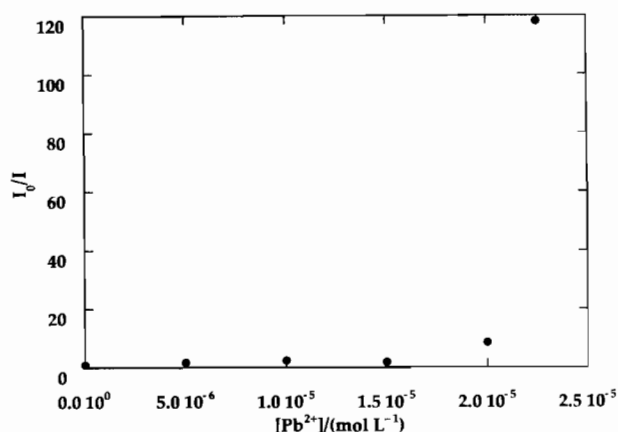


Fig. 3. Stern–Volmer plot of the phosphorescence quenching of *Pt_2 ($[Pt_2]=6 \times 10^{-6} \text{ mol l}^{-1}$) by Pb^{2+} in aqueous solution where I_0 represents the integrated intensity of the 514 nm phosphorescence in the absence of Pb^{2+} and I represents the intensity in the presence of varying amounts of Pb^{2+} .

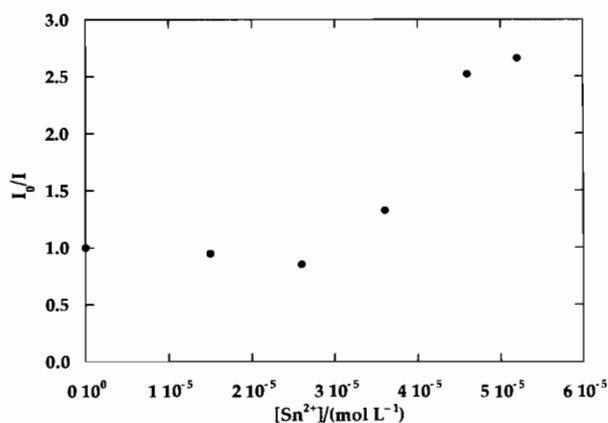


Fig. 4. Stern–Volmer plot of the phosphorescence quenching of *Pt_2 ($[Pt_2]=6 \times 10^{-6} \text{ mol l}^{-1}$) by Sn^{2+} in aqueous solution where I_0 represents the integrated intensity of the 514 nm phosphorescence in the absence of Sn^{2+} and I represents the intensity in the presence of varying amounts of Sn^{2+} .

Both Pb^{2+} (Fig. 3) and Sn^{2+} (Fig. 4) readily quench the 514 nm phosphorescence of *Pt_2 in strongly non-Stern–Volmer fashion in aqueous solution at room temperature (similar quenching of the 401 nm fluorescence of *Pt_2 was observed but no detailed results have been obtained). In each case little or no quenching was observed at metal ion concentrations less than about $2 \times 10^{-5} \text{ mol l}^{-1}$, while above this value very efficient quenching was found to take place. Although substantial changes in the absorption spectrum of Pt_2 were observed, no attempt was made to correct for the decrease in absorbance at 368 nm due to ground state interactions. No shifts in either band shape or position of the 514 nm phosphorescence of *Pt_2 were observed under these conditions.

In contrast, Pb^{2+} was found to quench the 514 nm phosphorescence of *Pt_2 in aqueous perchloric acid solutions in a more conventional manner (the 400 nm

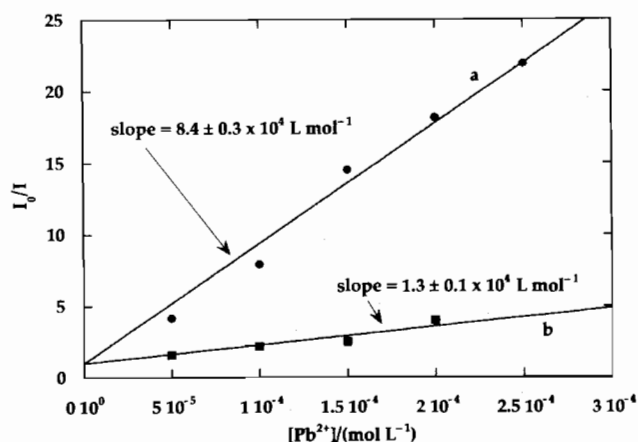


Fig. 5. Stern–Volmer plot of the phosphorescence quenching of *Pt_2 ($[Pt_2]=6 \times 10^{-6} \text{ mol l}^{-1}$) by Pb^{2+} in aqueous solutions of (a) 0.01 mol l^{-1} and (b) 1.0 mol l^{-1} perchloric acid where I_0 represents the integrated intensity of the 514 nm phosphorescence in the absence of Pb^{2+} and I represents the intensity in the presence of varying amounts of Pb^{2+} .

fluorescence of *Pt_2 was not affected by Pb^{2+} under these conditions). Fig. 5 shows the linear Stern–Volmer plots obtained for Pt_2 solutions of 0.01 and 1.0 mol l^{-1} perchloric acid. The slopes of the lines, determined by least-squares analysis according to the Stern–Volmer equation $I_0/I = 1 + K_{sv}[Pb^{2+}]$ [9], were determined to be $8.4 \pm 0.3 \times 10^4$ and $1.3 \pm 0.1 \times 10^4 \text{ l mol}^{-1}$ at 0.01 and 1.0 mol l^{-1} $HClO_4$, respectively. The presence of acid was found to have no effect on the quenching of either the phosphorescence or fluorescence of *Pt_2 by Sn^{2+} .

4. Discussion

The drastic changes in the absorption spectrum of aqueous Pt_2 in the presence of Pb^{2+} (Fig. 1) and Sn^{2+} (Fig. 2) indicate that there are substantial ground state interactions between these ions and Pt_2 . The broadness and large molar absorption coefficients of these new bands are indicative of charge transfer transitions, most plausibly from Pt_2 to Pb^{2+} and Sn^{2+} , i.e. metal to metal charge transfer (MMCT). In view of the tendency of s^2 metal ions to form direct but weak interactions with the metal centers of such square planar d^8 metal compounds [2–7], it is proposed that ground state interactions between Pb^{2+} and Sn^{2+} ions and the ‘exposed’ Pt atoms in the axial sites of Pt_2 are likely to occur. Such interactions can facilitate charge transfer transitions as a result of direct frontier orbital overlaps. In these cases it is likely that van der Waals-type interactions among the filled s and empty p valence orbitals of Pb^{2+} and Sn^{2+} and the filled σ^* ($5d_{z^2}$) and empty $\sigma(6p_z)$ orbitals, respectively, of Pt_2 result in some degree of electron donation from the Pt–Pt center of Pt_2 to the Pb^{2+} and Sn^{2+} ions.

The presence of at least two low energy transitions with Pb^{2+} (Fig. 1) and three with Sn^{2+} (Fig. 2) is not easily explainable and must await a more detailed study. Certainly the possibility of the formation of different types of aggregates such as Pt-Pt-M , M-Pt-Pt-M , Pt-Pt-M-Pt-Pt etc. ($\text{M} = \text{Pb}^{2+}$, Sn^{2+}), each yielding a different energy MMCT transition, must be considered, as must interactions between the metal ions and Pt_2 at sites other than the axial ones.

The luminescence quenching results in aqueous solution can also be understood in terms of such ground state interactions. It is known that these interactions often lead to 'static quenching' whereby non-linear Stern–Volmer plots are obtained. However, in the case of static quenching a simple curvature of the plots is usually found [9], unlike the behavior seen here where little or no quenching below a threshold concentration of quencher ($\approx 2 \times 10^{-5} \text{ mol l}^{-1}$ in the present cases), and strong quenching above this value, occur.

Such unusual behavior has been observed with other metal ions (Hg^{2+} [10] and certain trivalent lanthanoids [11]) and could be due to interactions at other sites in Pt_2 , such as the negatively charged oxygen atoms of the diphosphito ligands. If electrostatic interactions between the divalent and trivalent metal ions at these sites occur in preference to axial interactions with the Pt atoms, and if such non-axial interactions do not lead to significant quenching of $^*\text{Pt}_2$, then the unusual luminescence quenching behavior is understandable. For example, if each Pt_2 has about four non-axial sites possessing a much greater affinity for multiply-charged metal ions than the axial sites, then a metal ion concentration greater than about $2 \times 10^{-5} \text{ mol l}^{-1}$ (for $[\text{Pt}_2] = 6 \times 10^{-6} \text{ mol l}^{-1}$) might be necessary for extensive covalent interactions to take place at the axial sites.

The possibility that divalent and trivalent metal ions preferentially bond to non-axial sites in Pt_2 is in accord with the difference in behavior of isoelectronic Tl^+ and Pb^{2+} in their interactions with $\text{Pt}(\text{CN})_4^{2-}$. While Tl^+ is known to bond directly to Pt in crystalline $\text{Tl}_2\text{Pt}(\text{CN})_4$ [3], in all other compounds of $\text{Pt}(\text{CN})_4^{2-}$, including $\text{K}_2\text{Pb}[\text{Pt}(\text{CN})_4]_2 \cdot 6\text{H}_2\text{O}$ [4], the metal ions are bonded to the uncoordinated nitrogen atoms of the CN^- ligands.

The observations that in aqueous perchloric acid solutions containing Pb^{2+} the absorption spectrum of Pt_2 is unaffected, that no static quenching of the 514 nm phosphorescence $^*\text{Pt}_2$ is observed, that the 400 nm fluorescence of $^*\text{Pt}_2$ is not quenched, and that no brown precipitate of Pt_2 is formed, suggest that perchloric acid prevents ground state axial interactions between Pt_2 and Pb^{2+} . It is likely that protonation of the oxygen atoms on Pt_2 is responsible for these effects, although further work is needed to clarify these results.

In contrast to Pb^{2+} , the effects of Sn^{2+} on the absorption spectrum of Pt_2 and on the phosphorescence

and fluorescence intensities of $^*\text{Pt}_2$ are relatively insensitive to the presence of sulfuric acid. This suggests that the smaller Sn^{2+} ion interacts more strongly with the Pt and O atoms at the axial sites of Pt_2 than does Pb^{2+} . It also suggests that the hydrolysis of Sn^{2+} does not play a significant role in the interactions between Sn^{2+} and Pt_2 .

As in the case of the isoelectronic Tl^+ ion, Pb^{2+} appears to interact more strongly with $^*\text{Pt}_2$ than Pt_2 . Thus, while there is no spectroscopic evidence for ground state interactions between Pt_2 and Pb^{2+} in aqueous perchloric acid solutions, Pb^{2+} readily quenches the phosphorescence of $^*\text{Pt}_2$ with diffusion limited rate constants [12] in 0.01 and 1.0 mol l^{-1} HClO_4 of $8.4 \pm 0.3 \times 10^9$ and $1.3 \pm 0.1 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, respectively. As expected for such a reaction between oppositely charged ions, the rate constant decreases with increasing ionic strength.

An obvious question is why Pb^{2+} quenches the phosphorescence of $^*\text{Pt}_2$ so efficiently while the isoelectronic Tl^+ ion forms luminescent exciplexes [2]. A possible explanation lies in the relative reduction potentials for the aqueous Tl^+/Tl^0 and $\text{Pb}^{2+}/\text{Pb}^+$ redox couples. The value for Tl^+/Tl^0 has been determined to be $-1.94 \pm 0.05 \text{ V}$ versus NHE [13], nearly 1 V more negative than the estimate of $-1.0 \pm 0.1 \text{ V}$ versus NHE for the $\text{Pb}^{2+}/\text{Pb}^+$ couple [14]. Since the $\text{Pt}_2^+/^*\text{Pt}_2$ excited state redox potential has been estimated to be $-1.6 \pm 0.2 \text{ V}$ [15], oxidative quenching by Pb^{2+} is expected to be exoergic by about 60 kJ mol^{-1} while for Tl^+ it is expected to be endoergic by about 30 kJ mol^{-1} . The present results lend support to these redox potential estimates and suggest that the reduction potential for the $\text{Sn}^{2+}/\text{Sn}^+$ redox couple is greater than $-1.6 \pm 0.2 \text{ V}$ versus NHE since Sn^{2+} , like Pb^{2+} , readily quenches the phosphorescence of $^*\text{Pt}_2$.

These differences in reduction potentials are also likely to be responsible for the fact that both Pb^{2+} and Sn^{2+} , but not Tl^+ [2], form strong ground state interactions with Pt_2 resulting in low energy MMCT transitions.

5. Conclusions

The contrasting behavior observed between the interactions of Tl^+ on the one hand and Pb^{2+} and Sn^{2+} on the other can be interpreted in terms of the relative redox potentials for the reduction of these ions by $^*\text{Pt}_2$. Whereas in aqueous solution Tl^+ forms luminescent exciplexes with $^*\text{Pt}_2$ and interacts only weakly with Pt_2 [2], both Pb^{2+} and Sn^{2+} show appreciable ground state interactions with Pt_2 resulting in charge transfer transitions from Pt_2 to Pb^{2+} and Sn^{2+} and static quenching of $^*\text{Pt}_2$. In acidic aqueous solutions of perchloric acid

Pb²⁺ quenches *Pt₂ by a diffusion-limited excited state electron transfer reaction yielding Pb⁺ and Pt₂⁺.

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